Development of an Improved VOC Analysis Method for Architectural Coatings

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A Proposal Prepared for the

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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.

The recent 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.

Abstract

Task 1:The contractor will analyze the United States Environmental Protection Agency (US EPA) Method 24, the method most widely used to test the VOC content of coatings, to determine its applicability for the analysis of architectural coatings sold in California. The contractor will examine the status of any revisions, and the types of coatings for which Method 24 has limitations. The contractor will specifically examine the sources of error in and precision values for Method 24. The contractor will compare Method 24 with existing ASTM VOC methods, the California Air Resources Board (CARB) Method 310, South Coast Air Quality Management Districts (SCAQMD) VOC methods, the San Francisco Bay Area Air Quality Management District VOC methods and any other relevant methods and propose unification of these methods for coating VOC analysis. The contractor will develop a procedure for calculating expected upper and lower 95% confidence limits from method precision values for all major classes of architectural coatings. The categories of architectural coatings will include all of the coatings types identified in the 2001 ARB Architectural Coatings Survey.

Task 2:The contractor will analyze coatings representing all water-borne coatings categories listed in ARB's 2001 Architectural Coatings Survey using a recently developed ASTM direct VOC analysis method (ASTM Method D6886) to determine its applicability to all the different coatings categories. In addition, some of the same water-borne architectural coatings will be analyzed by a new headspace method, also a direct method, currently under development by the Emulsion Polymers Council/Adhesive and Sealant Council. Coatings samples will be obtained directly from manufacturers and to the extent possible, formulation data will be obtained. This approach will enable us to compare results from two different direct VOC methods with each other and also with formulation VOC values. Because sales of water-borne architectural coatings in California made up 83% of total sales of all architectural coatings in 2000 and contributed 41% of total VOC emissions from all architectural coatings, and because EPA Method 24 lacks sufficient precision for measuring their VOC content, we believe that establishment of direct VOC measurement methods for them is of paramount importance. The contractor will develop a qualitative SPME/GC method for identifying exempt compounds and HAPs in all categories of water-borne and solvent-borne architectural coatings. The contractor will convene a meeting or conference of all parties responsible for testing and regulating architectural coating VOC content (EPA, ARB, SCAQMD, BAAQMD, ASTM, NPCA, etc.) for the purpose of information sharing on new VOC test method development. The contractor will create/write a separate and unifying architectural coatings VOC testing manual for use by California Air Districts. The contractor will establish direct VOC test method training sessions at Cal Poly at the conclusion of this project.

Project 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 below 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 below 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%. Values of selected **r** and **R** values are given in Table1.

Table 1. Precision Values used in 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 KF	D4017-02	2.7%	7.5%

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. To determine the regulatory VOC content of waterborne coatings, Method 24 uses D1475 (density), D2369 (volatile content) and D4017 (water content by Karl Fisher) or D3792 (water content by GC). The equation used in doing the calculation is:

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

Where,

$f_V - f_W$ = f_{VOC}

f_{VOC} = weight fraction of VOC

f_V = weight fraction of total volatile content

f_W = weight fraction of water content

D_P = density of paint

D_W = density of water

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, measured as upper and lower 95% confidence limits, will be poor. This is illustrated in Figure 1 for a waterborne coating with a density of 1000 g/L, a constant VOC of 2.0 weight percent, and variable solids/water ratios.

All of the coating VOC methods currently being used by the various regulatory agencies rely on obtaining an **INDIRECT** VOC value by subtracting the water fraction from the total volatile fraction. Cal Poly has developed a gas chromatographic method, published by ASTM in 2003 as D6886-03, Standard Test Method for Speciation (**Note 1**) of the

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

Volatile Organic Compounds (VOCs) in Low VOC Content Waterborne Air-Dry Coatings by Gas Chromatograpy, which measures the VOC fraction directly. The method has a reproducibility value of 16.2% which is significantly larger than any of the reproducibility 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. This improvement in overall precision is illustrated in Table 2 and Figure 2 by calculating upper and lower 95% reproducibility limits for the same coating illustrated in Table 2 and Figure 1 in which Method 24 was used. When the VOC content of a waterborne coating is measured directly, water can be calculated by subtracting the VOC fraction from the total volatile fraction, thus eliminating the need for a water determination. The equation used for calculating regulatory VOC when the VOC fraction is determined directly becomes:

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

Where,

f_V = weight fraction of total volatile content

f_{VOC} = weight fraction of VOC content

D_P = density of paint

D_W = density of water

Table 2. Upper and Lower Precision Confidence Limits of Regulatory VOC for Method 24 and ASTM D6886 (Direct Method) of a Low VOC/High Water-Content Coating.

VOC Fraction	Solids Fraction	Water Fraction	Direct Method, Lower Conf. Limit	Method 24, Lower Conf. Limit	Mean Value of Regulatory VOC	Method 24, Upper Conf. Limit	Direct Method, Upper Conf. Limit
0.02	0.75	0.23	21	-12	**26**	64	31
0.02	0.65	0.33	24	-32	**30**	90	36
0.02	0.55	0.43	28	-60	**35**	126	43
0.02	0.45	0.53	33	-102	**43**	174	54
0.02	0.35	0.63	40	-169	**54**	245	72
0.02	0.25	0.73	52	-300	**74**	358	105
0.02	0.15	0.83	74	-652	**118**	570	201

Figure 1. Upper and Lower Precision Confidence Limits of Regulatory VOC for Method 24 of a Low VOC/High Water-Content Coating.

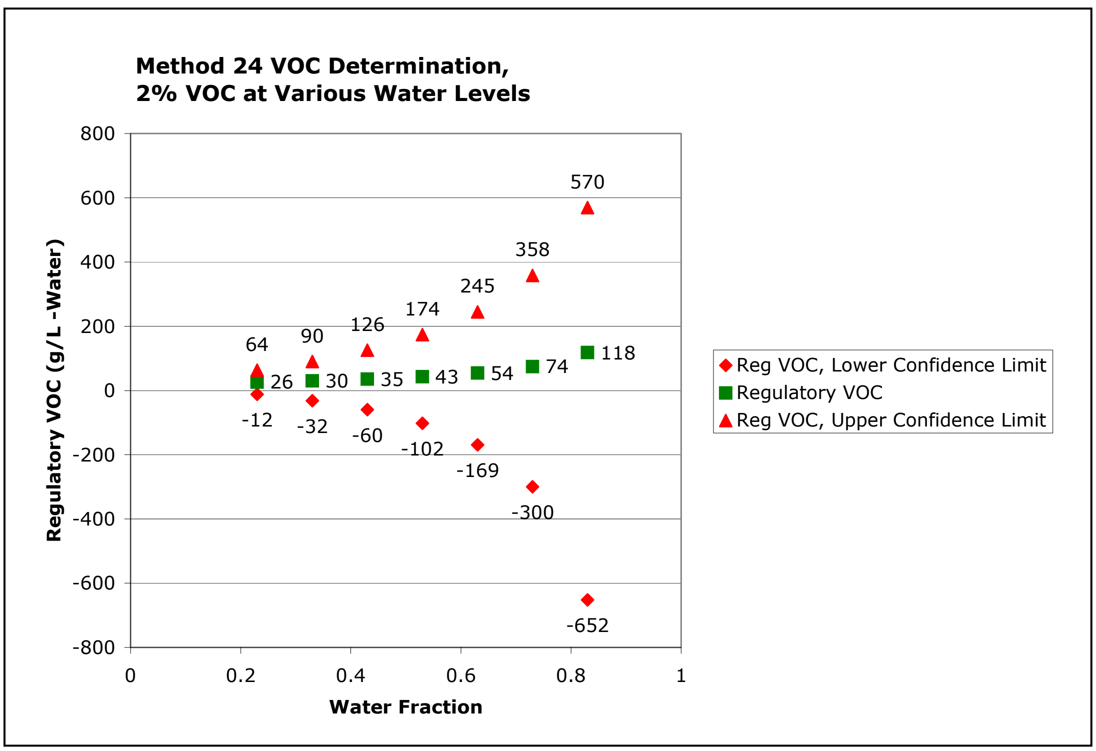
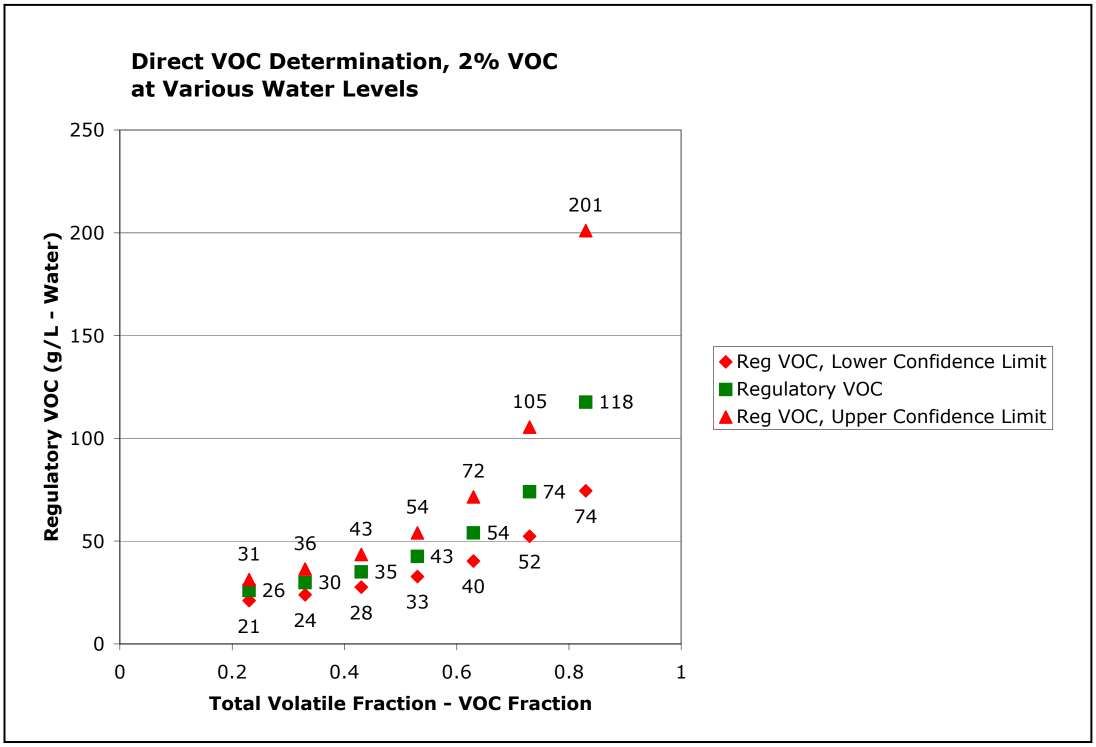


Figure 2. Upper and Lower Precision Confidence Limits of Regulatory VOC for ASTM D6886 (Direct Method) of a Low VOC/High Water-Content Coating.



The same arguments made above for waterborne coatings can be made for solventborne coatings which contain exempt VOC compounds. If the VOC fraction is relatively low and the exempt VOC content is relatively high, using Method 24 would give very poor precision for regulatory VOC, again because the VOC fraction is determined **indirectly**. The published ASTM Method, D6133-02 (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) reproducibility is 24.5% for acetone. The upper and lower precision limits for a hypothetical coating with a density of 800 g/L and containing 5 weight percent VOC and varying acetone/solids ratios is shown in Table 3 and Figure 3. At the present time there are no methods for determining the VOC fraction **directly** in solventborne coatings containing exempt VOCs. If such a method existed, and even if this direct method had a reproducibility value as high as 50%, the overall method precision would improve. Figure 4 shows the same coating, with the same composition as in Figure 3, using a hypothetical **R** value for direct VOC weight fraction determination of 50%. Again, it should be pointed out, that if a direct measurement of VOC content were made, the acetone fraction could be determined indirectly by simply subtracting the determined VOC fraction from the total volatile fraction.

Table 3. Upper and Lower Precision Confidence Limits of Regulatory VOC for Method 24 and a Hypothetical Direct Method (R = 50%) Measurements of VOC of a Low VOC/High Exempt Compound-Content Solventborne Coating.

VOC Fraction	Solids Fraction	Acetone Fraction	Direct VOC Analysis, Lower Conf Limit	Method 24 VOC Analysis, Lower Conf Limit	Mean Value of Regulatory VOC	Method 24 VOC Analysis , Upper Conf Limit	Direct VOC Analysis, Upper Conf Limit
0.05	0.8	0.15	24	4	**47**	89	71
0.05	0.7	0.25	27	-29	**54**	127	81
0.05	0.6	0.35	30	-76	**62**	173	95
0.05	0.5	0.45	36	-148	**73**	230	113
0.05	0.4	0.55	43	-277	**90**	303	142
0.05	0.3	0.65	54	-569	**117**	399	189

Figure 3. Upper and Lower Precision Confidence Limits of Regulatory VOC for a Method 24 Measurement of VOC of a Low VOC/High Exempt Compound-Content Solventborne Coating.

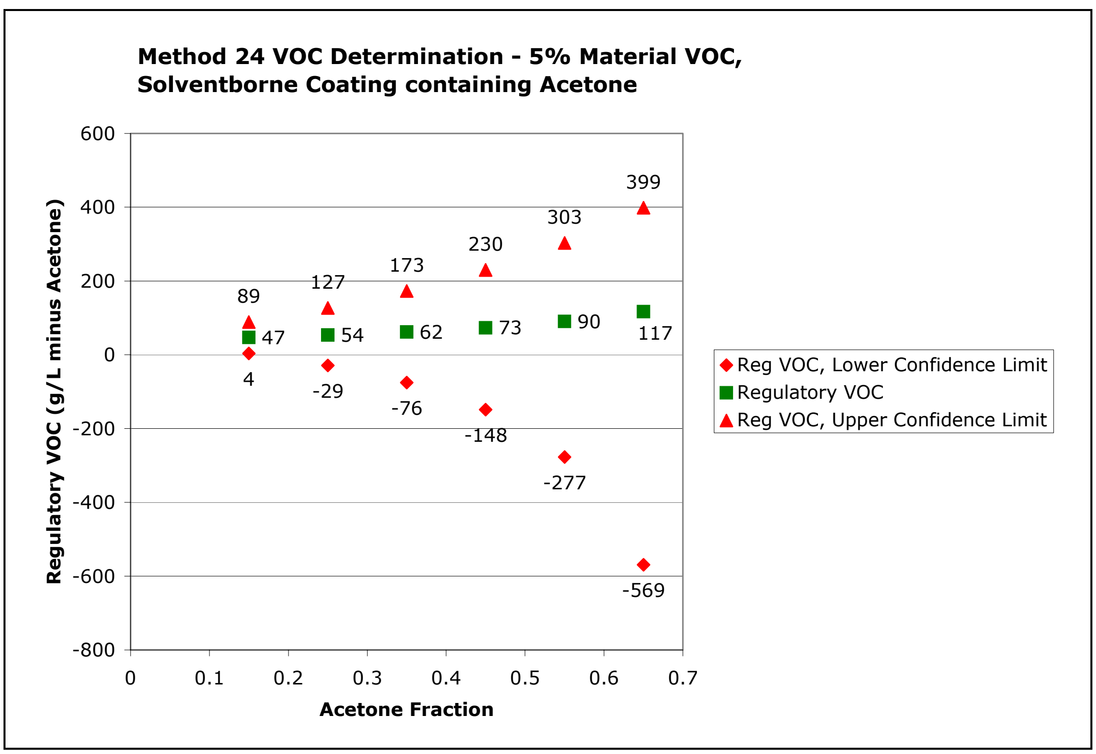
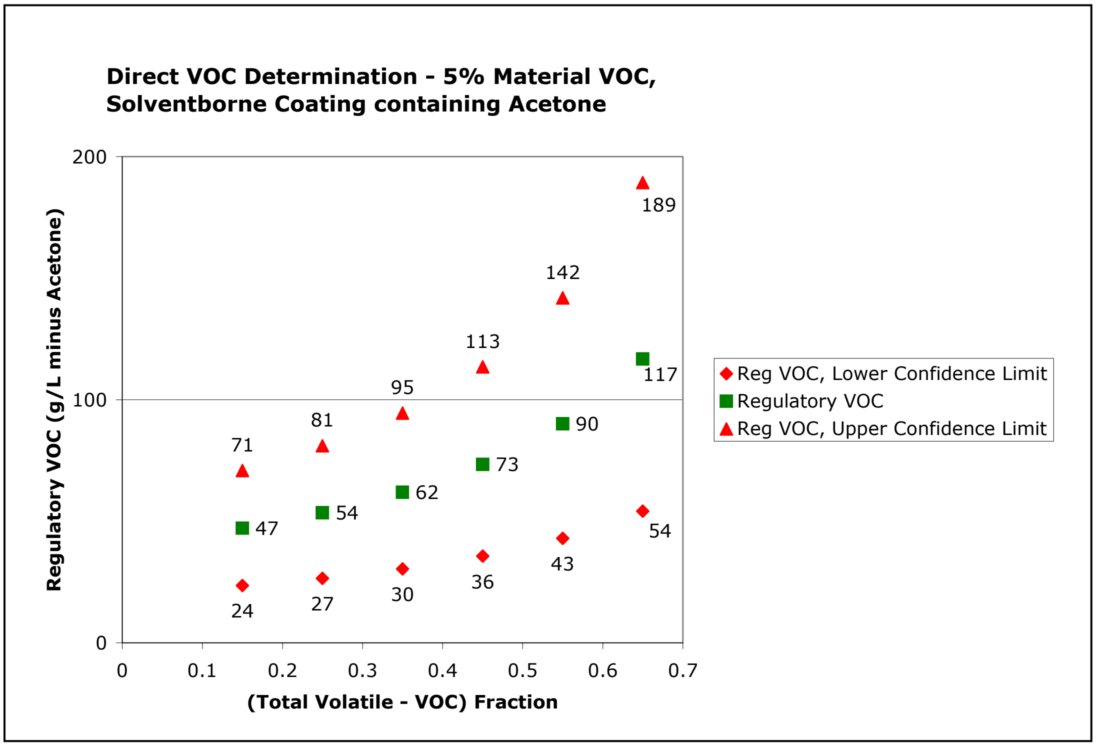


Figure 4. Upper and Lower Precision Confidence Limits of Regulatory VOC for a Direct Method (R = 50%) Meaurement of VOC of a Low VOC/High Exempt Compound-Content Solventborne Coating.



A preliminary examination of the methods used by different agencies reveals the following:

1. US EPA METHOD 24: The method was last posted February, 2000. For architectural coatings Method 24 incorporates, by reference, ASTM methods D14475 (Density), D2369 (Volatile Content), D3792 (Water by GC), D4017 (Water by KF), and D4457 (Exempt VOCs dichloromethane and 1,1,1-trichloroethane). Method 24 is an indirect method and gives rise to large uncertainties for high water content coatings. Listed precision values, **r** and **R**, do not correspond to lower values in later ASTM method revisions. Method 24 has no provisions for dealing with the exempt VOCs acetone, p-chlorobenzotrifluoride, the volatile siloxanes and methyl acetate. D4457 is rarely used because modern architectural coatings normally do not contain large quantities of dichloromethane or 1,1,1-trichloroethane..

2. SOUTH COAST AQMD LABORATORY METHODS OF ANALYSIS FOR ENFORCEMENT SAMPLES: SCAQMD Method 304-96, Determination of Volatile Organic Compounds (VOC) in Various Materials, uses the same ASTM reference methods as EPA Method 24 with the exception of D4457. SCAQMD Method 304 specifies that " the procedure in the most recent version" of the specific ASTM method be used. SCAQMD has developed its own method for exempt compounds, Method 303-96. The method is not specific for all of the exempt compounds normally found in architectural coatings nor does the method have a precision statement.

3. CALIFORNIA ARB METHOD 310: Some of the methods related to the analysis of architectural coatings are based on existing ASTM methods but have been changed significantly without developing precision statements. In fact, none of the methods appear to have been validated in an ILS.

Two California ARB publications have been examined and relevant information in them, as it pertains to the present proposal, are summarized below. The two publications are:

1. " Coatings Operations Test Method and Method Development Survey", Contract No. 93-344, Final Report, February 1998, http://www.arb.ca.gov/research/abstracts/93-344.htm and will be referred to in this proposal as the "ARB Method Survey"

2. "Final Report of the 2001 Architectural Coatings Survey", http://www.arb.ca.gov/coatings/arch/survey/2001/survey.htm, and will be referred to in this proposal as the "2001 ARB Coatings Survey".

ARB Coatings Operations Test Method and Method Development Survey

Language from this survey includes:
"The laboratory methods, such as EPA Method 24, have served extremely well in the applications for which they were developed – determining the VOC content of traditional solvent-based, high-VOC coatings. As a result of these methods, and the federal, and state and local regulations based on them, VOC emissions from paints and other coatings have been dramatically reduced over the past 25 years (Kirschner, 1994).

However, 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. Basically, Method 24 defines VOC content as:

$$VOC = \frac{\text{(Total Volatile Content) - (Water Content) - (Exempt Compound Content)}}{\text{(1 – (Water Fraction) - (Exempt Compound Fraction)) x 100\%}}$$

It is obvious from this equation that as VOC content gets smaller and water content and exempt compound content get larger (which is true for many new coatings), then the calculated VOC concentration becomes extremely unreliable, primarily due to the subtraction terms in the denominator [and the numerator]. It is even possible to calculate negative VOC concentration of low solvent-high water content coatings. These problems exist even if the individual measurements used to calculate VOC content are done with very high precision (**Note 2**). For VOC concentrations below 100 g/L, the experimental error is often larger than the calculated value [of VOC content] (Brezinski, 1993).

> **Note 2**. Over the past several years, the "Cal Poly Water Method" has frequently been quoted as a means of improving the VOC measurement

precision for water-borne coatings. This method was developed by us in 1993-94 and was published in the Journal of Coatings Technology (JCT, February 1995, 67:53-59). The method involves Karl Fischer titration of water in coatings by first removing the water from a coating by azeotropic distillation with 1-methoxy-2-propanol. The method was not adopted by ASTM even though the precision for water determination was markedly improved. ASTM argued that the method added undesirable complexity to the experimental procedure. ARB (Michael Poore) incorporated the "Cal Poly Water Method"into its Method 310 SOPs as SAS03, Standard Operating Procedure for the Karl Fischer (KF) Determination of Water with a KF Drying Oven in Consumer Products.

It would be much better for this category of coatings (low-VOC, high water-content) to obtain a direct measurement of VOC content rather than continue to calculate it as the difference between total volatile and water content (and exempt compounds).

There is also the need for a method to measure hazardous air pollutants (HAPs) in paints and other coatings. The US EPA has recently proposed a new method (Method 311, Analysis of HAP Compounds in Paint and other Coatings by Direct Injection into a GC). Several ASTM subcommittees are currently investigating the use of GC and GC-MS for analysis of VOCs and HAPs in paints and other coatings (Fujimoto, 1995). SCAQMD uses their method 304 for HAPs and VOCs of materials that contain < 50 g/L VOC. It would appear that collaboration with the ASTM groups currently engaged in this research would be the most effective approach to developing new test methods for low-VOC, high water-content coatings.

In addition to recommending cooperation and collaboration with ASTM, a related issue should be mentioned: the necessity to update the methods cited in district regulations are outdated, sometimes by more than a decade, while EPA method updates are published haphazardly in the Federal Register, with current versions and proposed changes also made available on the EMTIC (Emission Measurement Technical Information Center) bulletin board. The continuous revision process makes it possible for different versions to be available on the EMTIC bulletin board, current annual CFR books, and in the Federal Register. Some form of coordination between ASTM, EPA, and perhaps the ARB should be initiated in order to establish a single, official location (such as the EMTIC bulletin board) where the latest approved methods would be collected and made available to everyone, including the districts, laboratories, etc. It follows that district regulations should be written to specify the latest approved version of a test method, rather than a specific version which may be 15 years out of date in current regulations."

The ARB Test Method Survey held a telephone conference (October 17, 1995) on test method problems. Participants in this conference included five air districts (Bay Area AQMD, Sacramento Metropolitan AQMD, San Diego County APCD, San Joaquin Valley Unified APCD, and the South Coast AQMD) and represent areas comprising more than 80% of the population of California, and encompassing all of the regulatory categories for VOC emissions from coatings and coatings operations identified by the

ARB Test Method Survey. The participants in the telephone conference were virtually unanimous in their agreement on the number one problem with current test methods for VOC emissions from coatings and coatings operations: **the inability of EPA Method 24 (and related ASTM and district methods) to provide accurate results for coatings containing low VOC and high water content. The current methods cannot be used with confidence for water-borne coatings containing VOC < 100 g/L. The problem is not primarily with the analytical techniques involved, but with the method of calculating the VOC concentration. The problems with EPA Method 24 and related methods are not amenable to improvements in the various analytical techniques involved [for low VOC, high water content coatings]. Therefore, it appears necessary to develop a new, direct method for determining the VOC content of coatings that can be used for low VOC, high water-content coatings.** The use of a direct method would address a number of problems in addition to the problem with low VOC coatings, including the proliferation of exempt compounds, the need to measure hazardous air pollutants (HAPs), and the proposals to base ozone control strategies on the atmospheric reactivity of individual VOCs, rather than the total VOC content (Russell, et al., 1995; Bergin, et al., 1995)".

The ARB Method Survey ranked various test method problems in order of priority. EPA Method 24 was considered the most important problem method. The ARB Method Survey wrote the following:

Test Method: EPA Method 24 and ASTM [Practice] D 3960: Determination of Volatile Matter Content, Density, Volume Solids, and Weight Solids of Surface Coatings (**Note 3**).

> **Note 3.** ASTM Standards take several forms. These include test methods, practices and guides, and classifications. A standard test method typically includes a concise description of an orderly procedure for determining a property or constituent of a material, an assembly of materials, or a product. The directions for performing the test should include all of the essential details as to apparatus, test specimen, procedure, and calculations needed to achieve satisfactory precision and bias. A standard practice, on the other hand, is an accepted procedure for the performance of one or more operations or functions. In certain cases a practice may include one or more test methods necessary for full use of the practice. ASTM Practice D3960, for example, is a procedure for calculating regulatory VOC values from a collection of various individual ASTM Test Methods

Problem:
Calculation of VOC for low-VOC, high water-content coatings using the "minus water equation" gives extremely poor precision and accuracy, regardless of the precision and accuracy of the individual test methods used to provide the data for calculation.

Importance of Problem:

Relative importance: Affect all low-VOC, high water-content coatings
Magnitude of errors: Very large

Cost of current method: Increasing with complexity of test method
Importance assigned by districts: very high
Other considerations: Other problems associated with Method 24
Overall importance: Very high

Resolution effort:
Develop new method using direct determination of VOC. Collaborate with ASTM in testing and validation of method
Estimated cost of resolution effort: $150,000-200,000

ARB 2001 Architectural Coatings Survey

Several aspects of the ARB's 2001 Architectural Coatings Survey provide important information that may be used to help in adopting effective protocols and test methods for use in the experimental determination of the VOC content of architectural coatings. Pertinent pieces of information taken from the survey include the following:

- 98.5 million gallons of architectural coatings were sold in California in 2000
- 83% of total sales were water-borne coatings; 17% of total sales were solvent-borne coatings.
- 41% of total VOC emissions were from water-borne coatings; 59% of emissions were from solvent-borne coatings
- Exempt solvents were reported for solvent-borne coatings; only very minor amounts of exempt solvents were reported for water-borne coatings; 862.1 tons/year of exempt compound emissions were reported for the year 2000 which represents 3.7% of total emissions from solvent-borne coatings (excluding cleanup and thinning).
- Average levels of exempt compounds were reported for 9 of the 43 classes of solventborne coatings.
- 9.36% of total sales of solvent-borne coatings were multi-component coatings; 1.50% of total sales of water-borne coatings were multi-component coatings; 2.85% of all coatings sold were multi-component coatings.

Direct Methods for Coating VOC Analysis

The following methods are either currently in use or are in developmental stages:

- 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. A 1990 ASTM interlaboratory study involving 14 participating laboratories showed that the reproducibility precision (R) was 2.9%. 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. The

2001 ARB Coatings survey reports that 9.36% of the 2000 California sales of solvent-borne coatings consisted of multi-component coatings. Water-borne multi-component coatings make up only 1.50% of the 2000 sales for water-borne coatings. We are not aware of any significant problems in applying Method 24 to the VOC analysis of solvent-borne multi-component coatings but some specific issues related to these coatings may need to be addressed. At the present time we are treating “reactive diluent” solvent-borne coatings as multi-component coatings. Even though the sales of water-borne multi-component coatings is quite small, VOC measurement precision issues for these are the same as they are for single-component water-borne coatings.

- ASTM Method D 6886: This method, “Speciation of the Volatile Organic Compounds (VOCs) in Low VOC Content Waterborne Air-Dry Coatings by Gas Chromatograpy”, 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 (See Figures 1 and 2 and Table 2 of this proposal). The method measures the VOC fraction in water-borne coatings directly. “Speciation” in the title could just as easily read “ Direct Analysis”. This title name change proposal will be submitted to ASTM (Max Wills, subcommittee chair of ASTM D01.21.52) at the January, 2005 ASTM D01 meeting in Fort Lauderdale, Florida. 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 prmer/sealer/undercoater. These five classes of coatings comprise 82.15% of the sales of the entire ARB list of 44 classes of water-borne coatings. ARB’s 2001 coatings survey indicates that the VOC levels in the 44 classes range from 0 to 19%. The range of VOC is 0 to 5% by weight in 71.78% of the sales, 0 to 6% in 93.92% of the sales, and 0 to 10% in 99.43% of the sales. This information is presented in tabular form in Table 4.1 (water-borne coatings classes sorted by sales) and Table 4.2 (water-borne coatings classes sorted by VOC weight fraction). 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 Task 2 of this proposal should include the analysis of additional coatings from the 44 ARB classes with VOC contents ranging from 0 to 10% and additional coatings from the 5 classes already studied but with VOC content above 5% if such coatings exist at all (most, if not all, water-borne flats sold in California have a weight percent VOC content below 5%).

Table 4.1, Water-borne Coatings Classes Sorted by Sales (Derived from ARB's 2001 Coatings Survey)

					a	b	c	(b-c)	(a)(c)/1000	(a)(b-c)	(a)(b-c)/(1-((a)(c)/1000))
	2000 Sales of WB Coatings(gallons including small containers)	Percent of 2000 Sales	Cummulative % of Sales	Density, lbs/gal	Density, g/L	Total Volatile Weight Fraction	Water Weight Fraction	VOC Weight Fraction	Water Volume Fraction	Actual VOC, g/L	Regulatory VOC
Flat	34,798,306	42.67	42.67	11.4	1366	0.47	0.44	0.03	0.60	41	103
Nonflat - Medium Gloss	17,539,565	21.51	64.18	10.1	1210	0.56	0.50	0.06	0.60	73	184
Primer, Sealer, and Undercoater	6,755,899	8.28	72.46	10.6	1270	0.51	0.47	0.04	0.60	51	126
Nonflat - Low Gloss	6,570,365	8.06	80.52	10.7	1282	0.51	0.47	0.04	0.60	51	129
Traffic Marking	2,539,241	3.11	83.63	13.6	1629	0.25	0.20	0.05	0.33	81	121
Bituminous Roof	1,637,364	2.01	85.64	8.8	1054	0.49	0.49	0	0.52	0	0
Other	1,494,345	1.83	87.48	10.0	1198	0.55	0.55	0	0.66	0	0
Nonflat - High Gloss	1,329,648	1.63	89.11	10.1	1210	0.54	0.46	0.08	0.56	97	218
Floor	1,275,125	1.56	90.67	10.2	1222	0.36	0.29	0.07	0.35	86	132
Roof	1,047,906	1.29	91.95	10.6	1270	0.43	0.41	0.02	0.52	25	53
Stains - Opaque	862,448	1.06	93.01	10.1	1210	0.57	0.53	0.04	0.64	48	135
Concrete Curing Compounds	660,024	0.81	93.82	8.5	1018	0.78	0.74	0.04	0.75	41	165
Industrial Maintenance	613,964	0.75	94.57	11.1	1330	0.45	0.37	0.08	0.49	106	209
Waterproofing Sealers	574,622	0.70	95.28	9.4	1126	0.74	0.70	0.04	0.79	45	213
Waterproofing Concrete/Masonry Sealers	482,690	0.59	95.87	10.9	1306	0.48	0.44	0.04	0.57	52	123
Stains - Clear/Semitransparent	481,082	0.59	96.46	9.0	1078	0.73	0.66	0.07	0.71	75	262
Mastic Texture	418,417	0.51	96.97	10.7	1282	0.39	0.35	0.04	0.45	51	93
Quick Dry Primer, Sealer, and Undercoater	400,703	0.49	97.47	10.7	1282	0.51	0.45	0.06	0.58	77	182
Varnishes - Clear	372,743	0.46	97.92	8.7	1042	0.69	0.58	0.11	0.60	115	290
Specialty Primer, Sealer, and Undercoater	355,060	0.44	98.36	10.9	1306	0.42	0.38	0.04	0.50	52	104
Recycled	323,216	0.40	98.75	10.6	1270	0.51	0.42	0.09	0.53	114	245
Dry Fog	216,709	0.27	99.02	11.6	1390	0.43	0.36	0.07	0.50	97	195
Faux Finishing	166,709	0.20	99.22	9.5	1138	0.64	0.56	0.08	0.64	91	251
Metallic Pigmented	112,412	0.14	99.36	9.3	1114	0.61	0.57	0.04	0.64	45	122
Bituminous Roof Primer	100,527	0.12	99.49	8.5	1018	0.45	0.41	0.04	0.42	41	70
Bond Breakers	93,896	0.12	99.60	8.2	982	0.86	0.80	0.06	0.79	59	275
Lacquers	72,849	0.09	99.69	8.6	1030	0.68	0.56	0.12	0.58	124	292
Pre-treatment Wash Primer	71,154	0.09	99.78	9.4	1126	0.63	0.54	0.09	0.61	101	259
Rust Preventative	43,151	0.05	99.83	10.8	1294	0.57	0.52	0.05	0.67	65	198
Form Release Compounds	32,090	0.04	99.87	8.2	982	0.82	0.81	0.01	0.80	10	48
Fire Retardant - Opaque	26,690	0.03	99.90	11.4	1366	0.43	0.40	0.03	0.55	41	90
Low Solids	13,413	0.02	99.92	8.4	1006	0.91	0.85	0.06	0.86	60	417
Graphic Arts	12,722	0.02	99.93	10.9	1306	0.48	0.44	0.04	0.57	52	123
Wood Preservatives	10,462	0.01	99.95	8.5	1018	0.86	0.82	0.04	0.84	41	247
Swimming Pool	9,687	0.01	99.96	11.3	1354	0.49	0.43	0.06	0.58	81	194
Sanding Sealers	7,816	0.01	99.97	8.6	1030	0.73	0.65	0.08	0.67	82	250
Multi-Color	7,517	0.01	99.98	8.8	1054	0.66	0.58	0.08	0.61	84	217
Varnishes - Semitransparent	3,205	0.00	99.98	8.6	1030	0.71	0.61	0.10	0.63	103	277
Fire Resistive	PD			10.4	1246	0.40	0.38	0.02	0.47	25	47
Fire Retardant - Clear	PD			9.9	1186	0.55	0.54	0.01	0.64	12	33
Flow	PD			10.4	1246	0.55	0.36	0.19	0.45	237	429
High Temperature	PD			10.3	1234	0.55	0.45	0.10	0.56	123	277
Quik Dry Enamel	PD			9.4	1126	0.58	0.48	0.10	0.54	113	245
Antenna	PD			10.2	1222	0.48	0.37	0.11	0.45	134	245
TOTAL	**81,533,742**	**99.98**									

"PD": *Protected data (fewer than three companies reported sales)*

Table 4.2, Water-Borne Coatings Classes Sorted by VOC Weight Fraction (Derived from ARB's 2001 Coatings Survey)

				a	b	c	(b-c)	(a)(c)/1000	(a)(b-c)	((a)(b-c))/(1-((a)(c)/1000))
	2000 Sales of WB Coatings(gal including small containers)	Percent of 2000 Sales	Density, lbs/gal	Density, g/L	Total Volatile Weight Fraction	Water Weight Fraction	**VOC Weight Fraction**	Water Volume Fraction	Actual VOC, g/L	Regulatory VOC
Bituminous Roof	1,637,364	2.01	8.8	1054	0.49	0.49	0	0.52	0	0
Other	1,494,345	1.83	10.0	1198	0.55	0.55	0	0.66	0	0
Form Release Compounds	32,090	0.04	8.2	982	0.82	0.81	0.01	0.80	10	48
Fire Retardant - Clear	PD		9.9	1186	0.55	0.54	0.01	0.64	12	33
Roof	1,047,906	1.29	10.6	1270	0.43	0.41	0.02	0.52	25	53
Fire Resistive	PD		10.4	1246	0.4	0.38	0.02	0.47	25	47
Flat	34,798,306	42.67	11.4	1366	0.47	0.44	0.03	0.60	41	103
Fire Retardant - Opaque	26,690	0.03	11.4	1366	0.43	0.40	0.03	0.55	41	90
Stains - Opaque	862,448	1.06	10.1	1210	0.57	0.53	0.04	0.64	48	135
Primer, Sealer, and Undercoater	6,755,899	8.28	10.6	1270	0.51	0.47	0.04	0.60	51	126
Nonflat - Low Gloss	6,570,365	8.06	10.7	1282	0.51	0.47	0.04	0.60	51	129
Concrete Curing Compounds	660,024	0.81	8.5	1018	0.78	0.74	0.04	0.75	41	165
Waterproofing Sealers	574,622	0.70	9.4	1126	0.74	0.70	0.04	0.79	45	213
Waterproofing Concrete/Masonry Sealers	482,690	0.59	10.9	1306	0.48	0.44	0.04	0.57	52	123
Mastic Texture	418,417	0.51	10.7	1282	0.39	0.35	0.04	0.45	51	93
Specialty Primer, Sealer, and Undercoater	355,060	0.44	10.9	1306	0.42	0.38	0.04	0.50	52	104
Metallic Pigmented	112,412	0.14	9.3	1114	0.61	0.57	0.04	0.64	45	122
Bituminous Roof Primer	100,527	0.12	8.5	1018	0.45	0.41	0.04	0.42	41	70
Graphic Arts	12,722	0.02	10.9	1306	0.48	0.44	0.04	0.57	52	123
Wood Preservatives	10,462	0.01	8.5	1018	0.86	0.82	0.04	0.84	41	247
Rust Preventative	43,151	0.05	10.8	1294	0.57	0.52	0.05	0.67	65	198
Traffic Marking	2,539,241	3.11	13.6	1629	0.25	0.20	0.05	0.33	81	121
SUBTOTAL, 5% OR LESS VOC		**71.78**								
Bond Breakers	93,896	0.12	8.2	982	0.86	0.8	0.06	0.79	59	275
Quick Dry Primer, Sealer, and Undercoater	400,703	0.49	10.7	1282	0.51	0.45	0.06	0.58	77	182
Swimming Pool	9,687	0.01	11.3	1354	0.49	0.43	0.06	0.58	81	194
Nonflat - Medium Gloss	17,539,565	21.51	10.1	1210	0.56	0.50	0.06	0.60	73	184
Low Solids	13,413	0.02	8.4	1006	0.91	0.85	0.06	0.86	60	417
SUBTOTAL, 6% OR LESS VOC		**93.92**								
Stains - Clear/Semitransparent	481,082	0.59	9.0	1078	0.73	0.66	0.07	0.71	75	262
Floor	1,275,125	1.56	10.2	1222	0.36	0.29	0.07	0.35	86	132
Dry Fog	216,709	0.27	11.6	1390	0.43	0.36	0.07	0.50	97	195
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Industrial Maintenance	613,964	0.75	11.1	1330	0.45	0.37	0.08	0.49	106	209
Faux Finishing	166,709	0.20	9.5	1138	0.64	0.56	0.08	0.64	91	251
Sanding Sealers	7,816	0.01	8.6	1030	0.73	0.65	0.08	0.67	82	250
Multi-Color	7,517	0.01	8.8	1054	0.66	0.58	0.08	0.61	84	217
Recycled	323,216	0.40	10.6	1270	0.51	0.42	0.09	0.53	114	245
Pre-treatment Wash Primer	71,154	0.09	9.4	1126	0.63	0.54	0.09	0.61	101	259
Varnishes - Semitransparent	3,205	0.00	8.6	1030	0.71	0.61	0.10	0.63	103	277
High Temperature	PD		10.3	1234	0.55	0.45	0.10	0.56	123	277
Quik Dry Enamel	PD		9.4	1126	0.58	0.48	0.10	0.54	113	245
SUBTOTAL, 10% OR LESS VOC		**99.43**								
Varnishes - Clear	372,743	0.46	8.7	1042	0.69	0.58	0.11	0.60	115	290
Antenna	PD		10.2	1222	0.48	0.37	0.11	0.45	134	245
Lacquers	72,849	0.09	8.6	1030	0.68	0.56	0.12	0.58	124	292
Flow	PD		10.4	1246	0.55	0.36	0.19	0.45	237	429
TOTAL	81,533,742	**99.98**								

"PD": *Protected data (fewer than three companies reported sales)*

- The “Battelle” Method: In the mid-1990s 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 110^0C 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 325^0C and transferred to a capillary GC column with flame ionization detection. 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 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.
- 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. Other participants included PPG Industries, BASF Corporation, Akzo Nobel Coatings Inc., US EPA, The Sherwin-Williams Company, DuPont Performance Coatings, and the Rohm and Haas Company. Samples analyzed included the following: a DuPont Solvent-Borne Automotive Primer, a DuPont White Waterborne Automotive Base Coat, a Valspar Door Skin Primer, an Akzo Nobel solvent-borne lacquer, a PPG Solvent -Borne Automotive Topcoat, and a PPG UV Cure Coating. The participants agreed in advance to use a specific gas chromatic analysis method based on information given in EPA Method 311. The HAPs which were determined included:

  Butyl Cellosolve,
  Cumene
  Ethyl Benzene

2-Hexyloxyethanol
Methyl Ethyl Ketone (MEK)
Methyl Isobutyl Ketone (MIBK)
Naphthalene
Toluene
Xylenes

Cal Poly is currently preparing this study for publication as a standard ASTM method. 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.

- 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.This method was originally written by Joseph Benga at PPG Industries. The method is now part of ASTM task group D01.21.52 (Max Wills, Cal Poly, task group chairperson). 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.
- 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. When a coating is suitably internally standardized, the SPME methodology can be used to quantify the exempt compounds (or any other VOC compounds) present in a coating. To our knowledge, ASTM D6438 is the first ASTM method to utilize SPME technology. The initial cost of setting up SPME capability is about $500. The SPME fibers may be used hundreds of times and cost about $20 per fiber to replace. One of the most effective uses of SPME is for qualitative screening of individual VOCs and exempt compounds present in a coating. The coated SPME fiber captures volatile compounds as they are emitted from a coating. An advantage in using SPME is that only coating emissions, rather than the entire coating, are introduced into an analytical system thus preserving the integrity of the analytical system. Injection of whole coatings samples into a hot GC inlet can give polymer decomposition products, as well as the normally emitted volatiles. GC peaks observed from polymer decomposition are confirmed when an SPME screen of the same sample does not show them. 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. In the 2001 ARB Coatings Survey the identities of exempt compounds (solvents) were reported. This information is of value in order to choose a method that may be used for the laboratory analysis of specific exempt compounds. The ARB Survey reported average values of weight percent exempt compounds in 9 of the 43 classes of solvent-borne coatings (Table 5). While these average values were generally low, a range of values would be helpful in deciding if Method 24 is applicable for VOC determination. 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.

Table 5. Exempt Compound Emissions (Derived from ARB's 2001 Coatings Survey)

		a	b	c	(a*b)	(a*b*c)/(100*2000)
ARB 2001 Solvent-Borne Classes Containing Exempt Compounds		Density, lbs/gal	2000 Sales of SB (gallons including small containers)	% Exempt from 2001 ARB Survey	solvent-borne sales (lbs)	tons of exempt per year
Concrete Curing Compounds		8.3	32,395	4	268879	5.4
Flat		12.1	11,952	1	144619	0.7
High Temperature		9.9	18,621	4	184348	3.7
Lacquers		8.5	374,503	9	3183276	143.2
Magnesite Cement (PD)		8.9	0	24	0	0.0
Nonflat - High Gloss		10	596,788	1	5967880	29.8
Traffic Marking		14.1	799,677	9	11275446	507.4
Waterproofing Concrete/Masonry Sealers		10	225,227	7	2252270	78.8
Waterproofing Sealers		8.4	442,989	5	3721108	93.0
Total Exempt (tons/year)						**862.1**
Total VOC Emissions from Solvent-Borne (tons/year)						**23,444.2**
Exempt as a % of Total SB Emissions						**3.68 percent**

ARB provided the initial matrix (Table 6) to aid in development of a more specific matrix for this project. The resultant matrix is shown in Table 7:

Table 6. VOC Test Method Matrix (ARB version)

				Single-component	Multi-component	Reactive diluent	Exempt-containing
Air dried Architectural Coatings	Water-borne	Higher water content (≤ 100 g/l)	Higher solids	D 6886	?	?	?
			Lower solids	Part of proposal	?	?	?
		Lower water content (> 100 g/l)	Higher solids	Part of proposal	?	?	?
			Lower solids	Part of proposal	?	?	?
	Solvent-borne	Higher exempt content	Higher solids	Part of proposal	?	?	Part of proposal
			Lower solids	Part of proposal	?	?	Part of proposal
		Lower exempt content	Higher solids	Method 24	?	?	Method 24?
			Lower solids	Method 24?	?	?	Method 24?

Notes: Some of these cells may be NA. For example, there may be no such thing as a SB, lower exempt, lower solids, multi-component coating; or any relevant reactive diluent coatings; or all reactive diluent coatings may be multi-component

Table 7. VOC Test Method Matrix (Cal Poly Version)

				Single-component	Multi-component and Reactive Diluent
Air dried Architectural Coatings	1. Qualitative Determination of Exempt Compounds by SPME (part of proposal) 2. Quantitative Determination of Exempt Compound Content by D4457, D6133, and/or D6438	1. Qualitative Determination of HAPs (TACs) by SPME (part of proposal) 2. Quantitative Determination of HAPs (TACs) by D6886 and part of proposal	Waterborne, Material VOC Less than 5%	D 6886 and proposal (Note 1)	D 6886 and proposal (Note 1)
			Waterborne, Material VOC More than than 5%	Part of proposal	Part of proposal
			Solventborne, Low Exempt Compound Content	Method 24	Method 24 and part of proposal
			Solventborne, High Exempt Compound Content	Method 24 and part of proposal (Note 2)	Method 24 and part of proposal (Note 2)

Notes:

1. For waterborne coatings the precision in using Method 24 is poor at low VOC and high water levels. This is not the case using ASTM Method D6886. For example, a coating with a density of 1000g/L, a water content of 80%, and material VOC content of 5% would have a regulatory VOC content of 250g/L. For such a coating D6886 gives good precision and Method 24 gives poor precision. If one assumes that D6886 may be used for waterborne coatings with material VOC content as high as 10%, virtually all waterborne coatings could be analyzed by D6886.
2. The ARB 2001 Coatings Survey indicates that exempt compounds are present in 9 of 43 solvent-borne categories and generally at relatively low levels.

Technical Plan

All tasks will be performed in laboratories and offices of the Department of Chemistry and Biochemistry at Cal Poly, San Luis Obispo. Although GC/MS and GC/FID instruments are available in these laboratories, these instruments are 10-15 years old and are not representative of instrumentation currently available nor are they capable of performing all the required analyses. Consequently, purchase of a new GC/MS/FID system capable of performing all of the analyses described in this technical plan is critical to the success of this project. Not only will the use of current instrumentation make the development of successful methods more likely, it will also insure methods developed will be repeatable at other laboratories. This instrumentation should be kept at Cal Poly for use in upgrading of methods and training of others in the application of methods developed as part of this project.

Task 1

- The contractor will describe the sources of error in using the US EPA Method 24 to determine the VOC content of coatings, the status of any revisions of Method 24, and the types of coatings for which Method 24 has limitations. The same analysis will be carried out for CARB Method 310 , South Coast AQMD VOC methods and the Bay Area AQMD VOC methods as they apply to architectural coatings.
- The contractor will compare Method 24 with existing ASTM VOC methods, CARB Method 310, South Coast AQMD VOC methods and the Bay Area AQMD VOC methods and propose unification of these methods for architectural coating VOC analysis. Many, but not all of these methods are based on existing ASTM methods. All of the ASTM methods dealing with the measurement of VOC content of solvent-borne, waterborne, and related coatings are required to be re-approved every five years. In many instances, when significant changes are made in the methods requiring a new ILS for precision, the methods are re-approved more frequently. Most importantly, all ASTM methods must provide a precision statement making it possible to assess the reliability of the method. All of the ASTM methods involved in determining the VOC content of paints and related coatings are contained in an ASTM Standard Practice (For an explanation of a standard practice see Note 3, page 13). An ASTM Practice is updated annually. A document summary of the 2004 ASTM Practice D3960, Standard Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings, is attached as Appendix A. If CARB Method 310 and the SCAQMD and BAAQMD methods were to specify, by reference, the methods contained in the most recent version of ASTM Practice 3960, a number of advantages would be realized. These advantages include method unification, access to precision statements, access to newly developed VOC methods, and access to annual method updates. Participants in ASTM include individuals from industry, universities, the regulatory community from the United States (including the US EPA), and the International Standards Organization (ISO). Cal Poly San Luis Obispo has been involved with ASTM Committee D-01, Paint - Tests for Chemical, Physical, and Optical Properties; Appearance, for the past 10 years and has contributed gas chromatographic methods (D6133, D6438, and D6886) which have been published by ASTM. Cal Poly is currently developing ASTM VOC test methods for

speciation of aerosol paints, cure volatiles from powder coatings, direct analysis of solvent-borne paints, HAPs, and cure volatiles from automotive coatings.

- The contractor will create a method for calculating expected upper and lower 95% confidence limits from method precision values for all major categories of architectural coatings listed in the 2001 ARB Coatings Survey. One of the possible forms of this calculation could be an Excel spreadsheet where the user simply enters values for a coating's density, total volatile content, water content, exempt compound content, and VOC fraction if measured either directly (ASTM Method D6886) or indirectly (Method 24 for coatings containing water or exempt compounds). This calculation would give upper and lower 95% confidence limits and provide the user information on the relative precision of direct VOC analysis (Method D6886 and new methods yet to be developed) versus indirect VOC analysis (Method 24).
- The contractor will prepare graphical and/or tabular data showing 95% confidence limits comparing direct (ASTM D6886) and indirect (Method 24) analysis for all the architectural coatings categories in the ARB 2001 Architectural Coatings Survey for those coatings that contain water or exempt compounds.
- The contractor will consult with selected California Air Districts, including CARB, and initiate creation of a separate methods manual (this could be called a "California Method 24" manual) specifically for architectural coatings which would be uniform for all Air Districts and which could be easily revised on a regular basis to incorporate new methods and to update changes in existing methods. This manual would not replace any of the existing district methods manuals but would be in addition to these. Consultation could be by mail (survey), conference call, or face-to-face meetings.
- The contractor will purchase and begin installation of new GC/MS/FID system.

Task 2

- The contractor will finish testing of new GC/MS/FID system.
- Obtain paint samples from manufacturers including VOC data. Estimated number of samples to be tested is 50-60. Exact number and composition of samples to be determined in consultation with ARB Research Division staff.
- ASTM Method D6886-03, Standard Test Method for Speciation of the Volatile Organic Compounds (VOCs) in Low VOC Content Waterborne Air-Dry Coatings by Gas Chromatograpy, was developed by Cal Poly San Luis Obispo and published by ASTM in 2003. The method was validated in an ILS which included 5 architectural coatings, a primer, a flat, an eggshell, a semigloss, and a gloss latex paint, all having water fractions of about 50% and regulatory VOC contents ranging from 10 to 100 g/L – water. We propose that this method be used to measure the VOC content of additional waterborne coatings for which formulation VOC values are available. Additional coatings could be chosen from the 2001 ARB Architectural Coatings Survey category of water-borne coatings. We propose that two or more coatings be chosen from each of those categories making up 95% of the cumulative sales, which would cover a minimum of 14 of the 44 categories (See Table 4.1). This would result in at least 28 samples. We further propose that at least one coating be chosen from each of the remaining 30 categories. This would comprise a minimum of 58 samples for analysis. At least duplicate analysis of all

samples will be made. Analysis of these coatings would show the extent to which ASTM Method D6886 is applicable to the different coatings types listed in the ARB survey.

- We believe that the EPC/ASC headspace method (described earlier in this proposal) represents a potentially very good alternate direct VOC analysis method despite what appear to be cost and technical challenges. A second direct method would provide additional validation for results obtained by ASTM Method D6886 and serve as a backup to D6886 in possible instances where D6886 might fail as a VOC measurement method. The contractor will study the EPC/ASC headspace method with waterborne coatings, chosen from the 2001 ARB Survey, and of known composition and selected from those samples obtained as described earlier. These coatings will have been analyzed using ASTM Method D6886 in the previous task. Specific samples will be chosen in consultation with ARB staff. This will increase the number of analyses by approximately ten samples. Information obtained in this study will enable us to determine the suitability and validity of the headspace method for measuring VOC directly.
- In the event neither Method D6886 nor the EPC/ASC headspace method proves capable of analyzing a particular coating or coatings, an attempt will be made to modify these methods to provide a workable method. We do not expect major difficulties in applying these methods but our proven expertise in methods development should give us an excellent chance of insuring a successful method can be found. Results from the initial ILS conducted in the development of D6886 indicates that the precision of this method, depending on water, solids and VOC levels, is 5 to 10 times better than that obtained with Method 24 for calculating regulatory VOC. The ILS also indicated that the accuracy of the method, as measured by comparison of measured VOC values with theoretical formulation VOC values, is extremely good. Once the precision values of both direct methods have been determined, it will be possible to compare the two methods numerically and also with Method 24.
- The contractor will develop and validate an ASTM method for the qualitative analysis of architectural coatings to determine what exempt compounds and hazardous air pollutants, commonly found in architectural coatings, are present in a specific coating. The methodology will be solid phase microextraction (SPME) and gas chromatography with FID and, alternately, MS detection. This new method will be based on a method we have developed previously, ASTM D6438, and should serve as a simple exempt compound/HAPs screening method for any architectural coating . If exempt compounds are identified, one of the existing ASTM methods can then be used to quantify the exempt compound. This method will be tested on those paint samples mentioned earlier. Specific samples will be chosen in consultation with ARB staff.
- A meeting will be convened between parties responsible for regulating VOCs and parties involved in testing and test method development of VOCs for the purpose exchanging information Representatives should include the various government regulatory agencies (EPA, ARB, SCAQMD, BAAQMD, etc) and other groups such as ASTM, NPCA, testing laboratories, universities, and industry. A possible way of holding such a meeting would be to have it coincide with one of the semi-annual meetings of the ASTM Committee D01.21.
- The contractor will consult with selected California Air Districts, including CARB, and create a separate methods manual (this could be called a “California Method 24” manual) specifically for architectural coatings which would be uniform for all Air

Districts and which could be easily revised on a regular basis to incorporate new methods and to update changes in existing methods. This manual would not replace any of the existing district methods manuals but would be in addition to these.

- At the conclusion of Task 2 the contractor is considering the possibility of holding day-long training sessions on direct VOC measurement methods at Cal Poly for anyone interested in becoming more familiar with the test methods.

Task 3 - Final Report

A final report will be prepared which describes in detail the results of the analysis of current methods in Task 1 and the methods developed in Task 2. The results will be presented in a format suitable to ARB. Copies will be prepared in accordance with ARB guidelines.

Detailed Workplan

Anticipated Personnel Work Plan													
Personnel		months											
	task	1-3	4-6	9-12	13-15	16-18	19-21	22-25	26-28	29-31	32-34	35-36	Total hours by task
D. Jones	1	50	50	75									170
Principal Investigator	2				85	85	80	80	80				425
	3								20	60		20	100
subtotal													680
M. Wills	1	50	50	70									170
Research Associate	2				80	80	80	80	80				400
	3								20	20		10	50
subtotal													620
Graduate Student Assistant	1	25	25	50									100
	2				75	75	75	75	50				350
Student Assistant	1	25	25	50									100
	2				75	75	75	75	50				350
subtotal													900
TOTAL													**2200**

Principal investigator: Dr. Dane R. Jones, Professor of Chemistry, Department of Chemistry and Biochemistry, California Polytechnic State University, San Luis Obispo, CA 93407

Research associate: Dr. Max T. Wills, Professor of Chemistry, Department of Chemistry and Biochemistry, California Polytechnic State University, San Luis Obispo, CA 93407

Graduate student: to be identified as soon as the project is funded. The person will be a full time student in the Polymers and Coatings Science MS program at Cal Poly.

Undergraduate student: to be identified as soon as the project is funded. The person will be a full time student in the Polymers and Coatings Concentration in the Chemistry and Biochemistry Department at Cal Poly.

Project Schedule

We have attempted to estimate for each major task the percent of effort devoted to specific subtasks. These are only estimates and final subdivision of effort will depend on results of consultation with ARB staff and situations as they arise in the course of the project.

Task 1

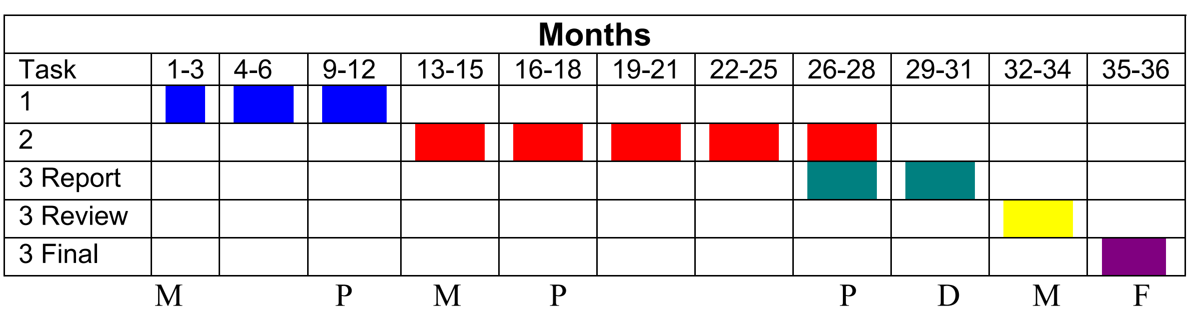
- Sources of error in current methods .. 10%
- Comparison of existing methods .. 10%
- Develop confidence limits calculation methods .. 20%
- Determine confidence limits for coatings in ARB 2001 survey .. 20%
- Consult on development of methods manual .. 20%
- Purchase and begin installation of GC/MS/FID system .. 20%

Task 2

- Finish testing of GC/MS/FID system .. 10%
- Obtain paint samples and VOC data .. 10%
- Perform VOC analysis (duplicate, minimum) on at least 58 samples using ASTM Method D6886-03 .. 25%
- Perform VOC analysis (duplicate, minimum) on at least 10 samples using method to be based on EPC/ASC headspace method .. 15%
- If necessary, modify available methods .. 5%
- Develop and validate method for exempt/HAPs screening, test on all samples (minimum 58) obtained for earlier tests .. 15%
- Convene meeting to exchange information .. 5%
- Consult and create methods manual .. 10%
- Hold training sessions on new method at Cal Poly .. 5%

Task 3

- Prepare draft final report .. 70%
- Prepare final report .. 30%



P = progress report
D = deliver draft final report
F = deliver final report
M = meeting with ARB staff

Related Research

As is shown in the curriculum vitae of the investigators (See Appendix B), a number of research efforts are in areas that are related to the proposed research topic. Those not sponsored by CARB are summarized below.

Max T. Wills

A. *Sampling, Testing, and Evaluation of Recyclable and Recycled Latex Paint*.
•Sponsored by California Integrated Waste Management Board and California EPA, Department of Toxic Substances Control, $98,000.
•Secondary sponsors include the Los Angeles Society for Coatings Technology, the Southern California Paint & Coatings Association, EL RAP, the Golden Gate Society for Coatings Technology, the Golden Gate Paint & Coatings Association, PARLE, the California Paint Council, and the National Paint & Coatings Association, $50,000.
•Project completed in September, 1995.

B. *New Method Development for VOC Analysis of Coatings*.
Sponsored by the Rohm and Haas Company, $5,000.
Project is on-going.

C. *ASTM D01.21 Committee*
Task group chairman for gas chromatographic coatings VOC methods. Developed several new ASTMVOC analysis methods.Activity is on-going.

Dane R. Jones

A. *Effect of Opaque Polymers on Color of Latex Coatings*. Sponsored by the Rohm and Haas Co., $47,000; 1994.

B. *Studies in the Mechanism of Blue Fade in Exterior Architectural Coatings.* Sponsored by the Dunn-Edwards Corporation, $3,000, 1999.

C. *Investigation of Photoinitiator Fragmentation and Through-drying of UV-Cured Wood Coatings*. Sponsored by the Rohm and Haas Co., $25,000, 1998.

Both Wills and Jones have been research associates on three major CARB funded projects related to VOC analysis within the past six years.

Management Plan

The ultimate fiscal responsibilities associated with this project will be assumed by the Cal Poly Foundation, following the issuance of a State Standard Agreement. The Principal Investigator will submit requests for purchases, travel funds, and payroll in accordance with the methods established by the Foundation.

The Principal Investigator will oversee all technical aspects of the project, and will be responsible for final preparation of periodic progress reports, as well as the Interim and Final Reports. Throughout the project, weekly meetings of the principal investigator, research associate and student research assistants will be held, to review information and timetables, and to discuss potential difficulties and their resolution. The Principal Investigator and Research Associate will share primary responsibility for analysis of current practices and development and testing of new proposed methods and will participate in analyzing errors in current methods, testing of coatings, and validation of procedures . Student research assistants will assist in analyzing errors in current methods, testing of coatings, and validation of procedures. All project workers will contribute to the preparation of reports.

Dane Jones is the principal investigator and project director. He has worked for nearly thirty years in analysis of polymers and coatings. He has participated as a research associate on three major CARB funded projects related to coatings VOCs. He will oversee all aspects of the project, direct research, research existing methods, develop new methods, test coatings, perform computer analysis of data, write reports, make presentations and handle all budgetary items.

Max Wills is the primary research associate and is recognized as the leading developer of new VOC methods in the U.S. He has worked for over fifteen years on VOC development and is active in ASTM. He has published several new VOC methods and has developed several new methods for ASTM. He will research existing methods, develop new methods, develop methods to predict reliability of methods, test coatings, assist in writing reports, and assist with presentations.

The graduate student will be identified as soon as the project is funded. The person will be a full time student in the Polymers and Coatings Science MS program at Cal Poly. The student will have a broad background in polymers and coatings and will be experienced in VOC analysis including use of GC and GC/MS. The graduate student will assist in researching existing methods, testing of coatings, writing reports and computer analysis of data.

The undergraduate student will be identified as soon as the project is funded. The person will be a full time student in the Polymers and Coatings Concentration in the Chemistry and Biochemistry Department at Cal Poly. The student will have a background in polymers and coatings and will be experienced in VOC analysis including use of GC and GC/MS. The student will assist in researching existing methods, testing of coatings, writing reports and computer analysis of data.

Both students will be working under both Jones and Wills. Both Jones and Wills will train, advise and supervise the students.

Curriculum vitae for Jones and Wills are included in Appendix B.

Appendix A (See Note 3 for discussion of ASTM Standards)

Document Summary

D3960-04 Standard Practice for Determining Volatile Organic Compound (VOC) Content of Paints and Related Coatings

Developed by Subcommittee: D01.21
See Related Work by this Subcommittee
Adoptions: DOD Adopted; Building Codes;
Book of Standards Volume: 06.01

1. Scope

1.1 This practice measures the volatile organic compound (VOC) content of solventborne and waterborne paints and related coatings as determined from the quantity of material released from a sample under specified bake conditions and subtracting exempt volatile compounds and water if present.

Note 1—The regulatory definition, under the control of the U.S. EPA, can change. To ensure currency, contact the local air pollution control agency.

1.2 This practice provides a guide to the selection of appropriate ASTM test methods for the determination of VOC content.

1.3 Certain organic compounds that may be released under the specified bake conditions are not classified as VOC, as they do not participate in atmospheric photochemical reactions. Such nonphotochemically reactive compounds are referred to as exempt volatile compounds in this practice.

Note 2—A list of the current US EPA approved exempt volatile compounds is found in , paragraph .

1.4 VOC content is calculated as a function of (*1*) the volume of coating less water and exempt volatile compounds, and (*2*) the volume of coating solids, and (*3*) the weight of coating solids.

2. Referenced Documents

D1475 Test Method for Density of Liquid Coatings, Inks, and Related Products
D2369 Test Method for Volatile Content of Coatings
D2697 Test Method for Volume Nonvolatile Matter in Clear or Pigmented Coatings
D2832 Guide for Determining Volatile and Nonvolatile Content of Paint and Related

Coatings
D3792 Test Method for Water Content of Coatings by Direct Injection into a Gas Chromatograph
D3925 Practice for Sampling Liquid Paints and Related Pigmented Coatings
D4017 Test Method for Water in Paints and Paint Materials by Karl Fischer Method
D4457 Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph
D5095 Test Method for Determination of the Nonvolatile Content in Silanes, Siloxanes and Silane-Siloxane Blends Used in Masonry Water Repellent Treatments
D5201 Practice for Calculating Formulation Physical Constants of Paints and Coatings
D5403 Test Methods for Volatile Content of Radiation Curable Materials
D6093 Test Method for Percent Volume Nonvolatile Matter in Clear or Pigmented Coatings Using a Helium Gas Pycnometer
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
D6419 Test Method for Volatile Content of Non-Heatset Web Offset Printing Inks
D6438 Test Method for Acetone, Methyl Acetate, and Parachlorobenzotrifluoride Content of Paints and Coatings by Solid Phase Microextraction-Gas Chromatography
D6886 Test Method for Speciation of the Volatile Organic Compounds (VOCs) in Low VOC Content Waterborne Air-Dry Coatings by Gas Chromatography
E180 Practice for Determining the Precision of ASTM Methods for Analysis and Testing of Industrial and Specialty Chemicals
EPA Federal Reference Method24-Determination of Volatile Matter Content, Density, Volume Solids, and Weight Solids of Surface Coatings
EPA 450/3-84-019, U.S. Environmental Protection Agency Procedures for Certifying Quantity of Organic Compound Emitted by Paint, Ink, and Other Coatings
EPA 450/3-83-013R, U.S. Environmental Protection Agency Glossary for Air Pollution Control of Industrial Coatings Operations

Index Terms

test precision; VOC; VOC calculations; VOC content; VOC content of paint

Appendix B - Curriculum Vitae of Personnel

DANE R. JONES

Department of Chemistry and Biochemistry, California Polytechnic State University
San Luis Obispo, CA 93407
Telephone (805) 756-2528 E-mail: djones@ calpoly.edu

EDUCATION

Stanford University, Stanford, California, 1969-1974. Graduate student in physical chemistry. Ph.D. March 1974.

University of Utah, Salt Lake City, Utah, 1966-1969. Chemistry major, B.A. magna cum laude 1969.

RESEARCH AND WORK EXPERIENCE

California Polytechnic State University: professor. Teaching responsibilities in physical chemistry, polymer chemistry, general chemistry, and specialty courses. Developed concentration in Polymers and Coatings (certified as B.S. in Polymer Chemistry by American Chemical Society) and focused MS program in Polymers and Coatings Science. Research on laser Raman analysis of diamond-like films, thermal and spectroscopic analyses of polyimide composites, color spectroscopy of coatings, and NMR studies of weak molecular complexes and polymer systems, VOC analysis, UV-curing of coatings (1976-present).

Dunn-Edwards Corporation: visiting scientist. Research on acrylic and vinyl coatings (1997).

University of California, San Diego: visiting associate professor of chemistry. Research on Fourier transform NMR and its applications to physical chemistry (1983).

IBM Research Laboratories, San Jose, CA: summer faculty research program, research on use of mass spectrometry in the study of electron beam sensitive compounds (1979).

University of Utah: instructor, research associate, working with Professor C. H .Wang. Research on Brillouin, Rayleigh and Raman laser light scattering from polymers and small heterocyclic ring compounds and simple fluids (1975-1976).

Institute for Physical Chemistry, Uppsala University, Uppsala, Sweden: research on depolarized Rayleigh laser light scattering from simple fluids and polymer solutions at high pressures using Fabry-Perot interferometry, under the direction of Professor Stig Claesson (1974-1975).

Stanford University: research on band shapes and correlation functions from infrared and Raman spectra of symmetric top liquids under the direction of Professor H. C. Andersen and Professor R. Pecora (1969-1974).

PROFESSIONAL, HONORARY SOCIETIES, AWARDS

Member American Chemical Society, Los Angeles Society for Coatings Technology, Phi Beta Kappa, Phi Kappa Phi; Woodrow Wilson Fellow (1969-70); Distinguished Teaching Award (1979) and Exceptional Merit Service Award (1984) - Cal Poly; Outstanding Faculty in College of Science and Mathematics -- awarded by College of Engineering, Cal Poly (1993).

RECENT DEPARTMENT AND UNIVERSITY ACTIVITIES

Related Funded Research and Development:

Characterization of Diamond-like Coatings on Magnetic Media Using Laser Raman Spectroscopy, sponsored by Seagate Technology, Inc (1987-1988), $25,000.

Characterization of Polyimide Materials for Printed Wiring Boards, sponsored by Digital Equipment Corporation, Inc. (1988-1989), $50,000.

The Polymers and Coatings Program at Cal Poly, funded by the Western Coatings/Cal Poly Foundation (1990-1995), $65,000.

Effect of Opaque Polymers on Color of Latex Coatings, funded by Rohm and Haas Co.(1992-1993), $47,000.

Dispersing Instrumentation for Coatings Laboratory, funded by the Coatings Industry Education Fund, Federation of Societies for Coatings Technology (1992-1993), $10,000.

Thermal Analysis in the Polymers and Coatings Laboratory, funded by National Science Foundation (1992-1994), $80,000.

Gel Permeation Chromatography and Pyrolysis Gas Chromatography in the Polymers and Coatings Laboratory, funded by Hewlett-Packard Co. (1993), $85,000.

Dynamic Viscometry in the Polymers and Coatings Laboratory, funded by the Coatings Industry Education Fund, Federation of Societies for Coatings Technology (1993), $20,000.

Improvement of Species Profiles for Architectural and Industrial Coating Operations, California Air Resources Board (1994-1996), $150,000.

Advances in Laser Raman Spectroscopy, Chevron Research Corporation, (1995-1996), $7,500.

Species Profiles for Aerosol Coatings, California Air Resources Board, (1996-1998), $150,000.

Investigation of Photoinitiator Fragmentation and Through-drying of UV-Cured Wood Coatings, Rohm and Haas Co. (1997-1998), $25,000.

Correlation Between Solids Content and Hiding as it Relates to Calculation of VOC Content in Architectural Coatings, California Air Resources Board, (2002-2004).

Polymers and Coatings Program at Cal Poly

Developed first undergraduate program in polymers and coatings in western U.S. with industry support and minimal state support. Raised $250,000 for instrumentation and equipment for polymers and coatings laboratory. Secured annual funding of $12,000 for scholarships. Secured industry support for student internships and normal operating costs of program. Program certified by American Chemical Society. Developed unique focused Masters program in Polymers and Coatings Science.

PUBLICATIONS

1. "Intermolecular Hydrogen Bonding of Azo Dyes in Aqueous Solutions", with W. Inskeep, W. Silvast, E. M. Eyring, Proc. Nat. Acad. Sci., 59, 1027 (1968).

2. "Graduate Study and College Teaching", J. Chem. Educ., 50, 57 (1973).

3. "Effect of a Finite Collection Aperture on Autocorrelation Light-scattering Spectros-copy", with K. Czworniak, J. Opt. Soc. Am., 64, 86 (1974).

4. "Infrared and Raman Studies of Rotational Correlation Functions in Liquids", with H. C. Anderson and R. Pecora, Chem. Phy., 9, 339 (1975).

5. "Depolarized Rayleigh Light Scattering and Molecular Reorientation under High Pressure", with S. Claesson, Chemica Scripta, 9, 103 (1976).

6. "Studies of Molecular Motion of Dibromoethane in the Liquid State by Depolarized Rayleigh and Raman Scattering", with C. H. Wang and D. H. Christensen, J. Chem. Phys., 64, 2820 (1976).

7. "Depolarized Rayleigh Scattering Studies of Molecular Motion of 1,3,4-(D_2) Thiadiazole", with C. H Wang and D. H. Christensen, Chem. Phys. Lett., 38, 557 (1976).

8. "Single Particle Reorientation and Pair Correlations of Methyl Iodide Solutions Studies by Depolarized Rayleigh and Raman Scattering", with C. H. Wang and C. K. Cheung, J. Chem. Phys., 64, 3567 (1976).

9. "Depolarized Raman and Rayleigh Scattering Studies of Liquid 1,2,5-Thiadiazole", with C. H. Wang and D. H. Christensen, J. Chem. Phys., 64, 4475 (1976).

10. "Depolarized Rayleigh Scattering and Backbone Motion of Polypropylene Glycol", with C. H. Wang, J. Chem. Phys., 65, 1835 (1976).

11. "Depolarized Rayleigh and Raman Scattering Studies of Molecular Motion in 1,2,5-Thiadiazole and Dibromomethane", with C. H. Wang and D. H. Christensen in Molecular Spectroscopy of Dense Phases (Elsevier Scientific Publishing Company, Amsterdam, 1976), pp. 673-681.

12. "A Comparison of the Rough Sphere Rotational Diffusion Model with Experimental Results for Liquid Methyl Iodide", J. Chem. Phys., 65, 2034 (1976).

13. "Depolarized Rayleigh Scattering and Orientation Motion of Polyethylene Glycol", with C. H. Wang, J. Chem. Phys., 66, 1659 (1977).

14. "Light Scattering from Orientational and Density Fluctuations in Liquid 1,2,5-Thiadiazole", with C. H. Wang, D. H. Christensen and P.-A. Lund, J. Chem. Phys., 67, 399 (1977).

15. "Brillouin Scattering and Segmental Motion of a Polymeric Liquid, II", with Y. -H. Lin and C. H. Wang, Mol. Phys., 37, 287 (1979).

16. "Depolarized Rayleigh Scattering Study of Pyridine in Cyclohexane", with S. L. Whittenburg, D. H. Christensen and C. H. Wang, J. Chem. Phys., 70, 2035 (1979).

17. "The Use of FTIR and Raman Spectroscopy for Corrosion Product Identification", with B. Borgard and R. Heidersbach, Paper No. 154, Corrosion/88, St. Louis Missouri, March 1988.

18. "Raman Analysis of Carbon Coatings on Rigid Magnetic Media", with J. Borgard and R. Heidersbach, Pacific Coast Conference on Chemistry and Spectroscopy, October 1988.

19. "Failure Analysis in Concrete Structures: A Correlation of Field Data with Results from Laboratory Exposures,," with B. Borgard, S. Somayaji, D. Keeling, and R. Heidersbach, Paper No. 390, Corrosion/89, New Orleans, LA, April 1989.

20. "Laboratory Simulation of Corrosion in Reinforced Concrete," with C. Ramirez.. B. Borgard, and R. Heidersbach, Materials Performance, December 1990, 33.

21. "Polymers and Coatings Program at Cal Poly San Luis Obispo," with M.T. Wills and J.D. Westover, Western Coatings Society Symposium, February, 1991.

22. "The Cal Poly Polymers and Coatings Program," with M.T. Wills and J.D. Westover, Polymer News, 16, 251 (1991).

23. "From Dream to Reality -- The Polymer and Coatings Program at Cal Poly", with M. T. Wills and J. D. Westover, Western Societies for Coatings Technology Symposium, March, 1993.

24. "Effect of Opaque Polymer on Color Acceptance of Latex Coatings", with E. Williams, Western Societies for Coatings Technology Symposium, February, 1995.

25. "A structural assignment for a stable acetaldehyde-lysine adduct", with K.P. Braun, R.B. Cody, and C.M. Peterson, J. Biol. Chem., 270, 1, 1995.

26. "VOC Analysis of Water-based Coatings by Gas Chromatography and Solid Phase Microextraction", with Albert Censullo and Max Wills, Journal of Coatings Technology, June, 1997.

Résumé

Max Thomas Wills
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California Polytechnic State University
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Telephone: 805-756-2746 (office)
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E-Mail : mwills@calpoly.edu

EDUCATION:

- American Chemical Society Short Course in Polymer Chemistry, Virginia Polytechnic Institute, December 1990.
- Ph.D. in Chemistry (Organic), University of Washington, Seattle, WA, 1965.
- B.S. in Chemistry, University of Puget Sound, Tacoma, WA, 1961.

PROFESSIONAL SOCIETIES:

- American Chemical Society.
- Federation of Societies for Coatings Technology.
- American Society for Testing Materials.

PROFESSIONAL EXPERIENCE:

- Professor of Chemistry; Cal Poly, San Luis Obispo, CA; 1967 - present.
- Polymers and Coatings faculty member, Cal Poly, San Luis Obispo, CA 1989 - present.
- Research Chemist (Plastics and Resins), Shell Development Company, Emeryville, CA, 1965 - 67.

RESEARCH GRANTS:

- “Analysis of Dioxane by Solid Phase Microextraction”, $3,000, Chemron Corporation, funded January 1998.
- “Development of New Analysis Methods for Total Petroleum Hydrocarbons”, $5,000, Cal Poly Environmental Biotechnology Institute, funded September 1997.
- “Photoinitiator Studies of UV Cured Wood Coatings”, $25,000, Rohm and Haas Company, funded January 1997.
- “Improvement of Species Profiles for Aerosol Coatings” research associate with Dr. Albert Censullo (principal investigator) and Dr. Dane Jones, $150,000, California Air Resources Board, funded January 1996.
- "Improvement of Species Profiles for Architectural and Industrial Coating Operations", research associate with Dr. Albert Censullo (principal investigator) and Dr. Dane Jones, $150, 000, California Air Resources Board, funded September 1994.
- "Testing and Evaluation of Recycled Latex Paints", $99,500, California Integrated Waste Management Board, funded June, 1992.
- "Testing and Evaluation of Recycled Latex Paints", $51,120, various paint industry associations, funded June, 1992.

- "Correlation Between Solids Content and Hiding as it Relates to Calculation of VOC Content in Architectural Coatings", $90,000, California Air Resources Board (2002-2004).

CONSULTING and OTHER PROFESSIONAL ACTIVITIES:

- Task Group Chairman, ASTM D01.21, Gas Chromatographic VOC Method Development of Coatings,
- Charter member of the California Polytechnic State University Environmental Biotechnology Institute
- Member of the California Paint Recycling Task Force. Sponsoring agencies include the California Integrated Waste Management Board, the California Department of Toxic Substances Control, and the California Paint Industry. 1990 - 95.
- Member of the California Department of Agriculture Pesticide Science Advisory Committee, 1990 - 92.
- Pacific Gas & Electric; Contract for PCB and other toxic chemical analysis of oil, sediment, and water samples using gas chromatography, atomic absorption, mass spectroscopy, NMR, IR, and HPLC; 1984 - 89.

PUBLICATIONS and PRESENTATIONS:

- Albert C. Censullo, Max T. Wills, and Dane R.Jones, "Improvement of Speciation Profiles for Aerosol Coatings", Final Report to the California Air Resources Board.
- Max T. Wills, "Analysis of Acetone, Toluene and Xylenes in Paint by Solid Phase Microextraction", presented at the Annual Meeting of the American Society for Testing Materials, San Diego, California, January, 1998.
- Max T. Wills, "The Cal Poly Paint Study: Latex Paint Collected at HHW Collection Facilities/Events is a Hazardous Waste", presented at the Hazardous Materials Management Conference of the Solid Waste Association of North America, San Diego, California, November, 1997.
- Max T.Wills, Albert C. Censullo, and Dane R. Jones, "Direct VOC Analysis of Water-Based Coatings by Gas Chromatography and Solid-Phase Microextraction", Journal of Coatings Technology, 69, pages 33-41, June, 1997.
- Dane R. Jones, Max T. Wills and Albert C. Censullo, "The Analysis of Aerosol Coatings by SPME and Gas Chromatography", presented at the Western Coatings Symposium, Anaheim, California, February, 1997.
- Albert C. Censullo, Max T. Wills, and Dane R.Jones, "Improvement of Speciation Profiles for Architectural and Industrial Maintenance Coating Operations", Final Report to the California Air Resources Board, June 1996.
- Max T.Wills, "Direct VOC Analysis of Water-Based Coatings by Gas Chromatography and Solid-Phase Microextraction", presented at the International Coatings Exposition, Chicago, October, 1996.
- Max T. Wills, Joseph C Reilly, Robert Sypowicz, and V.C. Bud Jenkins, "VOC Testing Comparison: EPA Method 24 Versus the Cal Poly Method", Journal of Coatings Technology, 67, pages 53-59, February, 1995.
- Max T. Wills, "Sampling, Testing, and Evaluation of Recyclable and Recycled Latex Paint", Final Report to the California Integrated Waste Management Board, December, 1995.

AWARDS:

- American Paint and Coatings Journal A.V. Voss Award for best paper and presentation, International Coatings Exposition, Chicago, Il, 1996.

American Paint and Coatings Journal A.V. Voss Award for best paper and presentation, National Paint and Coatings Conference, New Orleans, LA, 1994.