Comprehensive VOC Analysis Method for Architectural Coatings

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Specific regulatory volatile organic compound (VOC) limits have been set for architectural coatings to ensure that 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 (U.S. 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 waterborne coatings. Method 24 is also not suitable for determining the VOC content of solventborne 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.

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

We have developed direct methods for determining the VOC content in architectural coatings based on direct injection, headspace analysis, and solid phase microextraction (SPME) using gas chromatography with both flame ionization and mass spectral detection. These methods are suitable for direct determination of VOCs for all waterborne architectural coatings, even those with very low VOC levels. The methods are also suitable for direct determination of HAPs and exempt compounds in solventborne coatings. These methods can be used with confidence to determine whether or not a given coating meets the appropriate regulatory VOC level.

INTRODUCTION

In the United States the volatile organic compound (VOC) content of coatings is most commonly measured using EPA Method 24. The VOC content is determined indirectly by subtraction of the water and exempt

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compound content from the total volatile content of the coating. The equation used to determine regulatory VOC for the indirect method (Method 24) is shown in equation (1):

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

where,

$f_V - f_W - f_{ex} = f_{VOC}$
f_{VOC} = weight fraction of VOC
f_V = weight fraction of total volatile content
f_W = weight fraction of water content
f_{ex} = weight fraction exempt solvents
D_P = density of paint
D_W = density of water

Total volatile content is determined by heating a coating sample for one hour at 110°C and measuring weight loss (ASTM Method D 2369). This technique works well for coatings that do not contain water (or exempt solvents) but gives poor precision for low VOC content coatings, particularly waterborne coatings.

Newer methods for coating VOC analysis involve direct gas chromatographic determination. ASTM Method D 6886 is such a direct method and was published in 2003. The equation used to determine regulatory VOC for the direct method based on direct analysis of the fraction of VOC content (ASTM D 6886) is shown in equation (2):

$$VOC = \frac{f_{VOC}(D_P)}{1-[(f_V - f_{VOC} - f_{ex})(D_P/D_W)]} \qquad (2)$$

where,

f_V = weight fraction of total volatile content
f_{VOC} = weight fraction of VOC content
f_{ex} = weight fraction exempt solvents
D_P = density of paint
D_W = density of water

ASTM D 6886 is currently being used by many companies to verify the composition of the volatile components of many different types of coatings and was recently used collaboratively by California Polytechnic State University and California's South Coast Air Quality Management District (SCAQMD) to determine the VOC content of various architectural coatings. The ISO community uses a VOC measurement similar to Method 24 but only for coatings containing more than 15 wt% VOC. For coatings with a VOC content between 0.1 and 15%, a direct GC method similar to ASTM D 6886 is used. In the ISO GC method, a boiling point marker is used to define what constitutes a VOC. For waterborne coatings that boiling point marker is diethyl adipate (bp = 250°C) and compounds eluting after this marker on a specified capillary column are not considered to be VOCs (ISO 17895:2005).

We have applied the propagation of error approach to a full analysis of uncertainties in VOC determinations by the indirect method (based on EPA Method 24) and the direct method described in ASTM Method D 6886, including determination of exempt compounds. Although we have included the ability to calculate contributions from specific exempt solvents in both our indirect and direct methods, no indirect method exists for determining amounts of exempt solvents in coatings.

We performed an analysis assuming up to four different exempt solvents were used in a coating (although this is highly unlikely, we wanted to preserve the flexibility of the equation to deal with any coating). The four exempts included in this analysis are acetone, methyl acetate, *tert*-butyl acetate, and parachlorobenzotrifluoride. We choose these four exempt solvents because published uncertainty values (for both interlaboratory and intralaboratory analyses) are available. Their fractions are given by f_{ace}, f_{emac}, f_{tbac} *and* f_{pcbtf}, respectively. This method could be modified to include any combination of exempt solvents for which uncertainty values are known.

We have calculated the expected uncertainties associated with the VOC levels of the waterborne coatings reported in the 2001 California Air Resources Board Architectural Coatings Survey. These VOC calculations are only to be used as estimates for the different classes and do not represent real VOC numbers for any particular coating. We calculated both repeatability (intralab) and reproducibility (interlab) uncertainties based on

Table 1—Repeatability and Reproducibility Values

Quantity	Reproducibility (Interlab)	Repeatability (Intralab)	ASTM Reference Method
fv	0.047	0.015	ASTM D 2369-04
fw	0.055	0.035	ASTM D 4017-02
VOC	0.162	0.075	ASTM D 6886-03
Dp	0.018	0.006	ASTM D 1475-98
Acetone	0.245	0.05	ASTM D 6133-02
Parachlorobenzotrifluoride	0.124	0.027	ASTM D 6133-02
Methyl acetate	0.293	0.046	ASTM D 6133-02
t-Butyl acetate	0.156	0.038	ASTM D 6133-02
Acetone	0.0194	0.0118	ASTM D 6438-99
Parachlorobenzotrifluoride	0.0147	0.0097	ASTM D 6438-99
Methyl acetate	0.007	0.0046	ASTM D 6438-99
Dichloromethane	0.179	0.03	ASTM D 4457-02
1,1,1-Trichloroethane	0.081	0.03	ASTM D 4457-02

Table 2—VOC Values for Waterborne Coatings Derived from the 2001 ARB Coatings Survey with Expected Uncertainties

						Uncertainties/(g/L)			
	VOC Results Derived from 2001 ARB Coatings Survey					Method 24		Direct Method	
Coating Class	fv	fw	fvoc	Dp	VOC Reg (g/L)	Inter-Laboratory	Intra-Laboratory	Inter-Laboratory	Intra-Laboratory
Antenna	0.48	0.37	0.11	1221.96	245	61	27	31	14
Bituminous Roof	0.49	0.49	0.000	1054.24	0	77	41	0	0
Bituminous Roof Primer	0.45	0.41	0.040	1018.3	70	52	26	11	5
Bond Breakers	0.86	0.80	0.060	982.36	275	237	111	40	17
Concrete Curing Compounds	0.78	0.74	0.040	1018.3	165	207	102	25	11
Dry Fog	0.43	0.36	0.070	1389.68	195	72	34	26	12
Faux Finishing	0.64	0.56	0.080	1138.1	251	120	55	33	15
Fire Resistive	0.40	0.38	0.020	1245.92	47	65	33	7	3
Fire Retardant-Clear	0.55	0.54	0.010	1186.02	33	127	66	5	2
Fire Retardant-Opaque	0.43	0.40	0.030	1365.72	90	86	43	14	6
Flat	0.47	0.44	0.030	1365.72	103	106	53	16	7
Floor	0.36	0.29	0.070	1221.96	132	47	20	19	9
Flow	0.55	0.36	0.190	1245.92	429	65	25	42	19
Form Release Compounds	0.82	0.81	0.010	982.36	48	276	143	9	4
Graphic Arts	0.48	0.44	0.040	1305.82	123	95	47	18	8
High Temperature	0.55	0.45	0.100	1233.94	277	88	39	34	15
Industrial Maintenance	0.45	0.37	0.080	1329.78	209	70	32	28	13
Lacquers	0.68	0.56	0.120	1030.28	292	95	42	36	16
Low Solids	0.91	0.85	0.060	1006.32	417	357	154	65	25
Mastic Texture	0.39	0.35	0.040	1281.86	93	59	29	14	6
Metallic Pigmented	0.61	0.57	0.040	1114.14	122	121	60	18	8
Multi-Color	0.66	0.58	0.080	1054.24	217	109	51	29	13
Nonflat–High Gloss	0.54	0.46	0.080	1209.98	218	88	41	29	13
Nonflat–Low Gloss	0.51	0.47	0.040	1281.86	129	106	52	19	9
Nonflat–Medium Gloss	0.56	0.50	0.060	1209.98	184	106	51	26	12
Other	0.55	0.55	0.000	1198.00	0	140	74	0	0
Pretreatment Wash Primer	0.63	0.54	0.090	1126.12	259	107	49	33	15
Primer, Sealer, and Undercoater	0.51	0.47	0.040	1269.88	126	104	51	19	8
Quik Dry Enamel	0.58	0.48	0.100	1126.12	245	83	38	31	14
Quick Dry Primer, Sealer, and Undercoater	0.51	0.45	0.060	1281.86	182	95	45	25	11
Recycled	0.51	0.42	0.090	1269.88	245	81	37	31	14
Roof	0.43	0.41	0.020	1269.88	53	78	40	8	4
Rust Preventative	0.57	0.52	0.050	1293.84	198	140	67	28	12
Sanding Sealers	0.73	0.65	0.080	1030.28	250	137	63	33	15
Specialty Primer, Sealer, and Undercoater	0.42	0.38	0.040	1305.82	104	71	35	16	7
Stains–Clear/Semitransparent	0.73	0.66	0.070	1078.2	262	164	76	35	15
Stains–Opaque	0.57	0.53	0.040	1209.98	135	124	61	20	9
Swimming Pool	0.49	0.43	0.060	1353.74	194	97	46	27	12
Traffic Marking	0.25	0.20	0.050	1629.28	121	37	17	18	8
Varnishes–Clear	0.69	0.58	0.110	1042.26	290	105	47	36	16
Varnishes–Semitransparent	0.71	0.61	0.100	1030.28	277	115	52	35	16
Waterproofing Concrete/ Masonry Sealers	0.48	0.44	0.040	1305.82	123	95	47	18	8
Waterproofing Sealers	0.74	0.70	0.040	1126.12	213	246	119	33	14
Wood Preservatives	0.86	0.82	0.040	1018.3	247	327	156	40	17

both indirect analysis (EPA Method 24) and direct analysis (ASTM D 6886). None of these coatings contained statistically significant amounts of exempt solvents. All uncertainty values are based on precision values published in relevant ASTM methods (we assumed water was determined by Karl-Fisher titration, results would be similar for determining water by gas chromatography [ASTM D 3792]).The uncertainty values used are shown in *Table* 1. All compounds listed in *Table* 1 are classified as exempt compounds for VOC calculations. Several of these exempt compounds have alternate names; for example, dichloromethane is also called methylene chloride and parachlorobenzotrifluoride is also referred to as 4-chlorobenzotrifluoride or the trade name Oxol 100. We have only included those exempt solvents in *Table* 1 for which published uncertainties are available.

The VOC results for waterborne coatings derived from the 2001 survey with their respective expected uncertainties are given in *Table* 2.

These results confirm our limited results from our previous studies: uncertainties associated with VOC analysis using the indirect method (EPA Method 24) are substantially larger than those associated with VOC analysis using the direct method (ASTM D 6886) for all types of waterborne architectural coatings. For many classes, the uncertainties associated with Method 24 are larger than the actual VOCs. This is true both for high- and low-VOC coating types. The major source of error in Method 24 involves the determination of the fraction water in the coating. These results strongly support the use of a direct method of VOC analysis for waterborne architectural coatings.

We have also examined the effect of including uncertainties in exempt compound levels on VOC calculations for solventborne coatings. In examining the 2001 survey, five exempt solvents were found to make up nearly 99% of the total mass of exempts, as shown in *Table* 3.

Of these five, acetone is present in the largest quantity by far. In order to correct for uncertainties in exempt compound measurement, published values for uncertainties in these compounds must be available. We have been unable to find published uncertainty values for tetrachloethylene and octamethylcyclotetrasiloxane.

The 2001 survey listed nine categories of solventborne coatings containing exempt compounds. Of these, four are primarily used on concrete or are classed as concrete cements. Flat and non-flat high gloss each had only 1% exempts. We have calculated the effect of including exempt solvent uncertainties for the flat, high temperature (high T), traffic marking (traffic), and lacquer categories. These categories range in exempt fractions from 0.01 to 0.09. We have used average volatile fractions and paint densities from the survey. In order to calculate an uncertainty for an exempt, we need to know which exempt was used. Since this data is not available, we have based all our calculations on the assumption that acetone was the only exempt solvent used. This should at least give us an idea of how significant uncertainties in exempt solvents are for these classes of coatings. The results are given in *Table* 4.

Several comments are in order in reference to *Table* 4. First, these results are based on average data and do not represent any particular coating. Second, as noted earlier, it was assumed acetone was the exempt solvent in each case (more will be said in reference to this later). The first column under sVOC, labeled "no ex," gives the expected uncertainty based solely on the uncertainties in the quantities other than the amount of exempt solvent. The other two columns under sVOC include uncertainties from exempts along with all other uncertainties based on the two ASTM exempt methods. In this way, the effect of uncertainty in exempt solvent can be seen more clearly. In all cases, the overall uncertainties are relatively small compared to the total VOC. Also, the VOC uncertainties are greater for interlaboratory results than for intralaboratory results, as expected. In most cases, the uncertainties based on the direct method of analysis are greater than those based on the indirect (Method 24) analysis. This is also as expected. ASTM D 6886, a direct method, is not the preferred method for analysis of traditional solventborne coatings. These coatings can be best analyzed using a combination of indirect analysis, based on Method 24, to determine total volatiles and an appropriate direct method for analysis of any exempt solvents present. Of the two ASTM methods for acetone analysis, Method D 6438 has much smaller uncertainties and provides more precise results than Method D 6133. However, for the coatings in *Table* 4, either method gives acceptable results. In general, the changes in VOC uncertainty due to uncertainties in exempt solvents are small. For those coatings types listed in *Table* 4, calculations of VOC uncertainties do not generally need to include uncertainties in exempt solvents. These results would have been the same regardless of which exempt solvent or solvents were used in calculating the uncertainties. Based on these results, the uncertainties in the VOC values reported in the 2001 survey for solventborne coatings should generally be small and much less of a problem than those for waterborne coatings.

With the incorporation of ASTM D6886, low-VOC waterborne coatings can now be analyzed accurately. However, using ASTM D 6886, all of the volatile compounds in a sample are analyzed, whether they come off a sample when baked in an oven at 110°C (ASTM

Table 3—Primary Exempt Compounds in Solventborne Coatings from 2001 Architectural Coatings Survey

Exempt Compound	lbs	Fraction
Acetone	1,423,625	0.834
4-chlorobenzotrifluoride	142,645	0.084
Methylene chloride	97,078	0.057
Tetrachloroethylene	13,140	0.008
Octamethylcyclotetrasiloxane	11,636	0.007
Total		0.988

Table 4—Effect of Uncertainties of Exempt Compounds on VOC Determination for Solventborne Coatings

						sVOC		
Class	Method	fv	feac	Dp (g/L)	VOC	No Ex	D 6133	D 6438
Flat	in/inter	0.26	0.01	1431	358	19	19	19
	in/intra				358	17	18	17
	d/inter				358	38	38	38
	d/intra				358	17	17	17
High T	in/inter	0.36	0.04	1171	375	21	21	21
	in/intra				375	7	7	7
	d/inter				375	39	39	39
	d/intra				375	18	18	18
Traffic	in/inter	0.14	0.09	1668	83	12	12	12
	in/intra				83	4	8	4
	d/inter				83	12	12	12
	d/intra				83	6	6	6
Lacquer	in/inter	0.65	0.09	1019	570	33	33	33
	in/intra				570	11	11	11
	d/inter				570	41	43	41
	d/intra				570	19	19	19

Methods:
in/inter = indirect analysis, interlaboratory uncertainty
in/intra = indirect analysis, intralaboratory uncertainty
d/inter = direct analysis, interlaboratory uncertainty
d/intra = direct analysis, intralaboratory uncertainty

fv: Fraction volatiles
feac: Fraction acetone
Dp: Paint density in g/L
VOC: Regulatory VOC
sVOC: Uncertainty in total VOC
No Ex: No uncertainty in exempt included
D 6133: Exempt uncertainty from ASTM D 6133
D 6438: Exempt uncertainty from ASTM D 6438

D 2369) or not. We have investigated the possibility of some high boiling solvents remaining in the paint film of samples when analyzed using ASTM D 2369 and we will discuss our findings later in this article.

Although ASTM D 6886 is highly suitable for analysis of low-VOC waterborne coatings, several classes of coatings exist for which ASTM D 6886 is problematic. These include 2K coatings, UV cure coatings, and powder coatings. These coatings all require either a reaction between two components or the application of light or heat to properly cure the coating. Recent investigations sponsored by the Emulsion Polymers Council and the Adhesive and Sealant Council (EPC/ASC) involve the development of an improved static headspace/gas chromatographic method for VOC measurement. These investigations are largely the result of recent advancements and availability of precision headspace instrumentation. We have investigated the applicability of static headspace methodology to a wide variety of coatings types including architectural, OEM, 2K, UV-cure, and powder coatings. The method works especially well for the determination of nearly all volatile compounds including HAPs and exempt solvents. We will discuss details of our headspace experiments later in this article. We anticipate that a single universal method can be created for measuring VOCs, HAPs, and exempt solvents and will be applicable to virtually any coating now being manufactured.

METHOD DEVELOPMENT AT CAL POLY, SAN LUIS OBISPO

ASTM D 6886 Modification

When this method was first conceived, it was postulated that the majority of high-sales volume waterborne architectural coatings (flat, eggshell, semi-gloss) would contain less than 5% by weight of VOC and that the number of specific solvents would be both small and consist of relatively common materials, i.e., ethylene glycol, propylene glycol, butoxyethanol, butoxyethoxyethanol, and Texanol®. In a round robin involving eight laboratories and five commercial coatings (a flat, an eggshell, a semi-gloss, a gloss, and a primer) this was indeed the case. In carrying out the method, a sample of coating is dispersed in tetrahydrofuran (THF) containing an internal standard (p-cymene, cyclohexanol, and p-fluorotoluene have been used). An aliquot of this dispersion is then chromatographed and the amount of each volatile component is determined from peak areas. The sum of the components represents the total VOC content of the coating.

More recently, we have changed the solvent system from THF to water containing diethoxyethane as internal standard. Water is less hazardous than THF and does not give a GC peak in the FID detection mode. The improvement in precision using D 6886 instead of

Table 5—Coating VOC of Various Architectural Coatings, EPA Method 24, and ASTM Method D 6686 Comparison (g/L-water)

Sample Description	Formulation Value	SCAQMD Method 24	SCAQMD D 6886	Cal Poly D 6886
Nonflat, medium gloss	0	10	0.4	0
Nonflat, low gloss	150	81	116	111
Nonflat, low gloss	49	232	154	141
Primer	142	160	126	139
Primer	63	77	57	48
Exterior stain	0	31	21	22
Clear wood coating	57	183	143	173
Clear wood coating	50	122	167	146
Rust preventative	<50	151	150	145
Rust preventative	0	32	6	1
Masonry sealer	86	152	127	129
Masonry sealer	<65	203	132	233

Method 24 is approximately ten-fold and improves further as the VOC content approaches zero. Negative VOC values are not obtained as is sometimes the case for low VOC coatings using Method 24.

As a test of this new modification of ASTM D 6886, we have analyzed 13 widely different paint samples. The South Coast Air Quality Management District also carried out both Method 24 and D 6886 analyses on these samples. A comparison of the results is presented in *Table* 5. It is clear the results from direct analysis (ASTM D 6886) from the two laboratories are in good agreement.

Static Headspace Analysis

In static headspace analysis, a relatively small sample of coating, generally 20 mg or less, is placed in a 20 mL vial and sealed with an aluminum crimp cap. Any volatile materials present in the sample are confined within this sealed vial. To analyze the sample, the vial is transferred to a precision oven where it is heated to a predetermined temperature for a specified length of time, generally 110°C to 150°C for 10 to 20 min. Other temperatures and time intervals may also be used. During the heating period virtually all of the volatile components evaporate into the headspace because the sample amount is relatively small compared to the available headspace volume. At the end of the heating period a portion of the headspace is transferred via a heated transfer line to a gas chromatograph where the components are separated on a suitable capillary column and measured by either flame ionization or mass spectral detection. After sample preparation, the entire method is computer controlled using static headspace/GC instrumentation available from various commercial vendors.

We have used this methodology successfully on various coatings we previously analyzed using ASTM D 6886 and have found that the results are essentially the same using either method. The static headspace method is particularly useful for coatings systems that cure by chemical reaction. These include powder coatings, melamine-cure automotive coatings, various two-component coatings, and radiation-cure coatings. An example of a melamine-cure automotive primer that was analyzed for HAP content by static headspace and also in a recent NPCA sponsored Method 311 round robin is given in *Table* 6. In headspace analysis, the sample is heated at the same temperature as the actual application cure temperature for this particular coating, making it possible to determine both the cure HAP methanol as well as the HAP solvents which are actually added during manufacture of the coating. A particular advantage to the headspace method is that the coating does not need to be dissolved in a solvent such as THF prior to analysis, as is the case in a Method 311 determination. We have also analyzed melamine-cure automotive topcoats, a UV-cure primer, and a nitrocellulose lacquer, with similar results. Static headspace analysis may represent a replacement method for the current EPA Method 311.

We have investigated the use of the static headspace method for analysis of 2K architectural coatings. A 2K polyurethane coating was analyzed using the normal EPA Method 24 procedure, an EPA Method 24 procedure using an internal standard, and a static headspace procedure using an internal standard. Prudent changes in the methodology were incorporated and are explained below. This coating consists of a Part A containing a waterborne polyester and a Part B containing an isocyanate and no water. The results of these analyses are summarized in *Table* 7.

The reported VOC content of this coating is: Coating VOC, Part A = 23 g/L; Part B = 139 g/L. Material VOC, Part A = 11 g/L; Part B = 139 g/L.

Table 6—HAP Content in a Melamine-Cured Automotive Primer Using Static Headspace Analysis and Direct Injection Analysis

Compound	Head Space 150°C, %	Method 311 Cal Poly, %	Method 311 All Labs, %
Methanol	4.02	—[a]	—[a]
MIBK	3.47	3.42	3.51
Toluene	0.49	0.46	0.48
Xylene	4.30	4.35	4.46
Cumene	0.05	0.05	0.06
Naphthalene	0.45	0.56	0.53

(a) Methanol cannot be determined by a Method 311 determination.

Table 7—Results for Two-Component Polyurethane by EPA Method 24, EPA Method 24 with Internal Standard, and Direct Static Headspace Analysis

2K WB Polyurethane—Method 24 Analysis

Formulation	Grams	Density, lb/gal	Density g/L	Volume, L
Part A (aqueous polyester)	92.1	11.42	1368	0.0673
Part B (isocyanate)	25.0	9.30	1114	0.0224
Water	9.0	8.35	1000	0.0090
TOTAL	126.1		1277	0.0988
	Trial 1	Trial 2		
Water fraction by KF, Part A	0.3771	0.3811		
Solids fraction, TOTAL	0.6190	0.6190		
Water fraction, TOTAL, calculated	0.3468	0.3497		
VOC fraction, TOTAL, calculated	0.0342	0.0313		
g VOC in Total, indirect	4.31	3.94		
Material VOC g/L	44	40		
Coating VOC g/L	78	72		

2K WB Polyurethane with 6% EGDE in part B—Method 24 Analysis

Formulation	Grams	Density, lb/gal	Density g/L	Volume, L
Part A (aqueous polyester)	92.1	11.42	1368	0.0673
Part B (isocyanate)	25.0	9.3	1114	0.0224
EGDE	1.596		842	0.0019
Water	9.0	8.35	1000	0.0090
TOTAL	127.7		1269	0.1007
	Trial 1	Trial 2		
Water fraction by KF, Part A	0.3771	0.3811		
Solids fraction, TOTAL	0.6116	0.6116		
Water fraction, TOTAL, calculated	0.3425	0.3453		
VOC fraction, TOTAL, calculated	0.0460	0.0431		
EGDE fraction	0.0125	0.0125		
Corrected VOC fraction	0.0335	0.0306		
g VOC in TOTAL, indirect	4.27	3.91		
Material VOC g/L	42	39		
Coating VOC g/L	78	71		

2K WB Polyurethane—Static Headspace Direct Analysis at 110°C

g VOC in TOTAL	4.05
Material VOC g/L	40
Coating VOC g/L	74

Summary

Method	VOC TOTAL Grams	Material VOC g/L	Coating VOC g/L
EPA 24	4.31, 3.94	44, 40	78, 72
EPA 24 with Internal Standard	4.27, 3.91	42, 39	78, 71
Headspace GC with Internal Standard	4.05	40	74

The top section of *Table 7* pertains to analysis by Method 24 with no internal standard. Only Part A was analyzed for water content by Karl Fischer titration (ASTM Method D 4017). After water determination on Part A, the individual components were weighed into a one-pint can and mixed according to the manufacturer's directions. The water content of the mixture was then determined by calculation and appears in the table as "TOTAL." Immediately after mixing, a portion of the TOTAL was transferred to tared aluminum dishes and spread with the aid of a paper clip stirrer for ASTM D 2369 solids determination. No solvent or water was added to the sample. The sample was allowed to stand at room temperature for 24 hr prior to heating at 110°C for one hour. 2K systems cure by chemical reaction of the components rather than by simple solvent evaporation. Use of a dilution solvent (or water) would slow or impede the required chemical cure reaction. The 24-hr induction period prior to heating allowed the components to react. If the sample were heated prior to cure, reactive components could evaporate prior to the intended chemical cure reaction. The material and coating VOC were then calculated for this coating.

The second section of *Table 7* pertains to analysis of sample with internal standard. The Part B component was diluted with 6% of the internal standard ethylene glycol diethyl ether (EGDE). The paint was then prepared, as described above, by mixing the components in a one-pint can. The water content of the TOTAL mixture was then determined by calculation. The solids content was again determined for this new paint as described above and the material and coating VOC content was determined using the EPA Method 24 criteria. In carrying out this calculation, the added EGDE was treated as an exempt solvent.

Immediately after mixing the components of this paint, a small quantity of the TOTAL was transferred to a headspace vial, capped with an aluminum crimp cap, and allowed to cure at room temperature for 24 hr. The results of the headspace analysis are shown in the third region of *Table 7*. After curing in the headspace vial, the

VOC content was determined by static headspace gas chromatography using an equilibration temperature of 110°C for 20 min. This headspace procedure represents a direct method of analysis while both EPA 24 methods represent indirect methods of analysis. As shown in the summary at the bottom of *Table* 7, the direct analysis headspace results for this 2K coating are in excellent agreement with the indirect results obtained using EPA Method 24.

Table 8—Comparison of Semi-volatile Evaporation Using ASTM D 6886, Static Headspace at 110 and 150°C, and ASTM D 2369

Sample	Coalescent	Direct Injection D 6886 % by wt	Static Headspace 100°C % by wt	Static Headspace 150°C % by wt	Left in Film After D 2369 Determination, % by wt	% of Total Coalescent Remaining in Film
1	Texanol	1.29	1.06	1.13	0.07	5.3
2	A	1.07	0.38	1.14	0.60	56
3	B	0.76	0.15	0.84	0.62	81

To analyze a powder coating, a sample of the powder is placed in a headspace vial along with an internal standard, sealed with a crimp cap, then heated to its recommended cure temperature. Analysis of a glycidyl methacrylate powder showed that it emits methyl methacrylate, butyl methacrylate, glycidyl methacrylate, benzoin, and several other components.

Two-component coatings are analyzed by first mixing the components and then placing a small sample of the mixture along with an internal standard into a headspace vial. The vial is sealed with a crimp cap and is then allowed to cure in the vial at the recommended cure temperature for 24 hr. After cure, the volatiles retained in the vial are analyzed using static headspace/GC at an appropriate temperature. In one experiment with a waterborne polyurethane 2K coating, the Method 24 result was identical to the headspace result. An advantage of the headspace result is that the actual amounts of the individual components emitted may be determined.

VOC ANALYSIS OF SEMIVOLATILE COMPONENTS

In the course of analyzing the samples provided by SCAQMD's Rule 1113 VOC assessment, it was found that some coatings contain semivolatiles with boiling points higher than that of Texanol, which is itself considered a semivolatile compound. These included dibutyl phthalate and benzyl butyl phthalate. In carrying out an ASTM Method D 6886 direct determination of the VOC content of a coating containing semivolatile components, the semivolatile component is measured in its entirety. The current U.S. 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 often exists a disconnect between the amount of semivolatile component which evaporates during a D 2369 determination and the amount measured by a D 6886 determination, with the former giving lower numbers by an amount related to the nature of the semivolatile component and the matrix in which it is present. We have addressed this problem by analyzing the paint film after a D 2369 determination for residual semivolatiles 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. As mentioned earlier, the ISO define VOC based on boiling point and a GC retention time marker and have thus avoided this complication. 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 to insure nearly complete evaporation of all the volatile and semivolatile components in a coating. This concept is illustrated in *Table* 8 in which results on three paints containing Texanol and two higher boiling coalescents are described.

The results in *Table* 8 show that the use of headspace analysis with suitably high equilibration temperature allows determination of all of the semivolatile coalescent contained in the paint. Headspace analysis at 110°C results in only partial analysis of semivolatiles.

CONCLUSIONS

Methods are currently under development to provide accurate VOC analysis of all types of architectural coatings. Direct analysis of coatings using gas chromatography and static headspace/gas chromatography provides accurate results on a wide variety of samples including low-to-zero VOC waterborne coatings, 2K coatings, HAP and exempt compound-containing solventborne or waterborne coatings, powder coatings, and reactive coatings. These methods can also be used to determine the amounts of semivolatile compounds remaining in coating films after heating for one hour at 110°C. ■