Quarterly Progress Report on

Standard Agreement No. 04-329

For the Period

March 1, 2006 through July 31, 2006

Development of an Improved VOC Analysis Method for Architectural Coatings

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

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Disclaimer-

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I. Work This Reporting Period

This report summarizes work performed on the project from March 31, 2006 through July 31, 2006.

A. Task 1 Activities and Additional Activities from Task 2

During this time period, work was completed on all Task 1 activities

- Sources of error in current methods
- Comparison of existing methods
- Develop confidence limits calculation methods
- Determine confidence limits for coatings in ARB 2001 survey
- Purchase, install and test GC/MS/FID system

We have also begun a number of the activities listed under Task 2 of this project. Since the last reporting period, we have contacted all of the coatings manufacturers listed on the Samples List provided us by CARB and requested all 86 samples on the list. To date we have received approximately twenty of these samples.

We have significantly advanced our experimental research on new VOC analysis techniques to be included in the final method. The work is described under the following headings:

- Static headspace analysis for HAPs in various coatings
- Analysis of two-component architectural coatings
- Analysis of coatings containing semivolatile components by direct GC, static headspace, and extraction of paint films after total volatile analysis by ASTM D2369

B. Sources of error in current methods and confidence limits for coatings in ARB 2001 survey

In earlier work, an analysis was made of 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. We examined the status of any revisions, and the types of coatings for which Method 24 has limitations. We specifically examined the sources of error in and precision values for Method 24 and the pertinent ASTM methods referenced in Method 24. We compared Method 24 with existing ASTM VOC methods, the California Air Resources Board (CARB) Method 310, South Coast Air Quality Management Districts (SCAQMD) VOC methods, and the San Francisco Bay Area Air Quality Management District VOC methods.

Since this project most directly impacts EPA Method 24 (the indirect method) and ASTM D6886 (the direct method), we performed a systematic propagation of error analysis on these two methods to determine the expected error for each based on the published uncertainties of the various experimentally determined quantities.

We have continued this work and 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 D6886, 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. Initial propagation of error equations were determined using advanced mathematics software (Maple 9 – Maplesoft). All calculations of uncertainties in VOC were done using Excel. Copies of the Maple and Excel worksheets are available. We will have a version of the Excel VOC uncertainty calculation available similar to the CARB Excel "VOCCalculator" currently available on the CARB website.

The equation used to determine regulatory VOC for the indirect method (Method 24) is shown below:

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

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

f_{ex} = weight fraction exempt solvents

D_P = density of paint

D_W = density of water

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_{eac}, f_{ema}, f_{eba} and f_{etf}, respectively. This method could be modified to include any combination of exempt solvents for which uncertainty values are known.

The result for the uncertainty in the indirect VOC, sVOCid, based on the propagation of error analysis in terms of the quantities given above and their uncertainties (prefaced by an s, such as sDp, for the density of paint) is shown below.

Uncertainty in VOC for indirect method (Method 24) including exempts:

$$sVOCd := \left(\frac{Dp^2\, sfv^2}{\left(1 - \frac{fw\, Dp}{Dw}\right)^2} + \frac{Dp^2\, sfeac^2}{\left(1 - \frac{fw\, Dp}{Dw}\right)^2} + \frac{Dp^2\, sfema^2}{\left(1 - \frac{fw\, Dp}{Dw}\right)^2} + \frac{Dp^2\, sfeba^2}{\left(1 - \frac{fw\, Dp}{Dw}\right)^2} + \frac{Dp^2\, sfetf^2}{\left(1 - \frac{fw\, Dp}{Dw}\right)^2} \right.$$

$$+ \left(- \frac{Dp}{1 - \frac{fw\, Dp}{Dw}} + \frac{(fv - feac - fema - feba - fetf - fw)\, Dp^2}{\left(1 - \frac{fw\, Dp}{Dw}\right)^2 Dw} \right)^2 sfw^2$$

$$+ \left(\frac{fv - feac - fema - feba - fetf - fw}{1 - \frac{fw\, Dp}{Dw}} + \frac{(fv - feac - fema - feba - fetf - fw)\, Dp\, fw}{\left(1 - \frac{fw\, Dp}{Dw}\right)^2 Dw} \right)^2 sDp^2$$

$$\left. + \frac{(fv - feac - fema - feba - fetf - fw)^2\, Dp^4\, fw^2\, sDw^2}{\left(1 - \frac{fw\, Dp}{Dw}\right)^4 Dw^4} \right) ^{\wedge} 0.5$$

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 given by:

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

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

The result for the uncertainty in the direct VOC, sVOCd, based on the propagation of error analysis in terms of the quantities given above and their uncertainties is shown below.

Uncertainty in VOC for direct method (ASTM 6886) including exempts:

$$
\begin{aligned}
sVOCd := \Bigg(& \frac{fvoc^2\, Dp^4\, sfv^2}{\left(1 - \frac{(fv - feac - fema - feba - fetf - fvoc)\, Dp}{Dw}\right)^4 Dw^2} + \frac{fvoc^2\, Dp^4\, sfeac^2}{\left(1 - \frac{(fv - feac - fema - feba - fetf - fvoc)\, Dp}{Dw}\right)^4 Dw^2} \\
& + \frac{fvoc^2\, Dp^4\, sfeba^2}{\left(1 - \frac{(fv - feac - fema - feba - fetf - fvoc)\, Dp}{Dw}\right)^4 Dw^2} + \frac{fvoc^2\, Dp^4\, sfema^2}{\left(1 - \frac{(fv - feac - fema - feba - fetf - fvoc)\, Dp}{Dw}\right)^4 Dw^2} \\
& + \frac{fvoc^2\, Dp^4\, sfetf^2}{\left(1 - \frac{(fv - feac - fema - feba - fetf - fvoc)\, Dp}{Dw}\right)^4 Dw^2} + \left(\frac{Dp}{1 - \frac{(fv - feac - fema - feba - fetf - fvoc)\, Dp}{Dw}} \right. \\
& \left. - \frac{fvoc\, Dp^2}{\left(1 - \frac{(fv - feac - fema - feba - fetf - fvoc)\, Dp}{Dw}\right)^2 Dw} \right)^{\wedge 2} sfvoc^2 + \left(\frac{fvoc}{1 - \frac{(fv - feac - fema - feba - fetf - fvoc)\, Dp}{Dw}} \right. \\
& \left. + \frac{fvoc\, Dp\, (fv - feac - fema - feba - fetf - fvoc)}{\left(1 - \frac{(fv - feac - fema - feba - fetf - fvoc)\, Dp}{Dw}\right)^2 Dw} \right)^{\wedge 2} sDp^2 \\
& + \frac{fvoc^2\, Dp^4\, (fv - feac - fema - feba - fetf - fvoc)^2\, sDw^2}{\left(1 - \frac{(fv - feac - fema - feba - fetf - fvoc)\, Dp}{Dw}\right)^4 Dw^4} \Bigg)^{\wedge 0.5}
\end{aligned}
$$

We have calculated the expected uncertainties associated with the VOC levels of the water-borne coatings reported in the 2001 CARB 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 both indirect analysis (EPA Method 24) and direct analysis (ASTM 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 D3792). The uncertainty values used are shown below 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.

Table 1 Repeatability and Reproducibility Values

quantity	reproducibility (interlab)	repeatability (intralab)	ASTM reference method
fv	0.047	0.015	ASTM D2369-04
fw	0.055	0.035	ASTM D4017-02
voc	0.162	0.075	ASTM D6886-03
Dp	0.018	0.006	ASTM D1475-98
acetone	0.245	0.05	ASTM D6133-02
parachlorobenzotrifluoride	0.124	0.027	ASTM D6133-02
methyl acetate	0.293	0.046	ASTM D6133-02
t-butyl acetate	0.156	0.038	ASTM D6133-02
acetone	0.0194	0.0118	ASTM D6438-99
parachlorobenzotrifluoride	0.0147	0.0097	ASTM D6438-99
methyl acetate	0.007	0.0046	ASTM D6438-99
dichloromethane	0.179	0.03	ASTM D4457-02
1,1,1-trichloroethane	0.081	0.03	ASTM D4457-02

The VOC results for water-borne coatings derived from the 2001 survey with their respective expected uncertainties are given below in Table 2.

Table 2 VOC Values for Water-borne Coatings Derived from the 2001 ARB Coatings Survey with Expected Uncertainties

VOC results derived from 2001 ARB Coatings Survey						Uncertainties/(g/L)			
						Method 24		Direct Method	
coating class	fv	fw	fvoc	Dp	VOCreg (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	42	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	0	140	74	0	0
Pre-treatment 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 Unc	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

These results confirm our limited results from our previous report: 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 D6886) for all types of water-borne architectural coatings. For many classes, the uncertainties associated with Method 24 are larger than the actual VOC. 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 water-borne architectural coatings.

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

Table 3. Primary exempt compounds in solvent-borne coatings from 2001 Architectural Coatings Survey

Exempt Compound	lbs	fraction
acetone	1423625	0.834
4-chlorobenzotrifluoride	142645	0.084
methylene chloride	97078	0.057
tetrachloroethylene	13140	0.008
octamethylcyclotetrasiloxane	11636	0.007
total		0.988

Of these five, acetone is present in by far the largest quantity. 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 solvent-borne 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 one percent 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 fraction 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 assuming 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 below in Table 4.

Table 4 Effect of Uncertainties of Exempt Compounds on VOC Determinations for Solvent-borne Coatings

class	method	fv	feac	Dp (g/L)	VOC	sVOC		
						no ex	D6133	D6438
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 nalysis, 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
D6133: exempt uncertainty from ASTM D6133
D6438: exempt uncertainty from ASTM D6438

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 D6886, a direct method, is not the preferred method for analysis of traditional solvent-borne

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 D6438 has much smaller uncertainties and provides more precise results than method D6133. However, for the coatings in Table 3, 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 3, 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 solvent-borne coatings should generally be small and much less of a problem than those for water-borne coatings.

C. Comparison of Existing Methods

We have compared methods used by the principle regulatory agencies in California with those of the U.S. Environmental Protection Agency and applicable ASTM methods. A summary of the methods investigated is shown in Table 4 below.

Table 5 VOC Analysis Methods used by California Regulatory Agencies

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

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

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

method essentially uses relative response factors to determine amounts of each exempt. No uncertainties are reported for either Method 313 or Method 303.

The BAAQMD Methods 21 and 22 are essentially indirect methods similar to EPA Method 24. Exempt compounds are determined using gas chromatography with internal standards and measured response factors. BAAQMD Method 41 allows determination of parachlorobenzotrifluoride directly using gas chromatography with internal standard. BAAQMD Method 43 allows determination of volatile methylsiloxanes directly using gas chromatography with n-octane as internal standard in carbon disulfide solutions with measured response factors. None of the methods report any uncertainties or other precision factors.

Recently the SCAQMD has begun using ASTM 6886 for analysis of water-borne coatings.

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

We have been in direct contact with CARB, SCAQMD and BAAQMD concerning the goals of this project. We have also asked all three agencies to join us in testing the methods developed in the project to verify the methods and assist in determining precision values for the methods. All agencies are eager to participate. As preliminary work for this project, we have cooperated with SCAQMD in testing ASTM 6886 on thirteen water-borne coatings, including flats, primers, urethanes, water sealants, and coatings requiring addition of a catalyst. These preliminary studies showed very good agreement between VOC values obtained from both labs using ASTM 6886. SCAQMD also performed a Method 24-type indirect analysis on these coatings and found the Method 24 results generally differed substantially from the direct results.

D. Testing of Agilent 6890 gas chromatography/mass spectrometry system

A major part of this project is the acquisition of a new GC/MS/FID system to use in developing and testing the new methods and for training analysts in how to perform the new methods. The choice of system was based on overall performance, reputation and familiarity in the VOC analysis community, and versatility. Based on these criteria, the following system was chosen:

Agilent MS with Chemstation/turbopump	
GC with s/s inlet	
Second s/s inlet for FID	
Ion gauge	
NIST library	
FID detector	
Headspace attachment with autosampler	

The new Agilent 6890 GC/MS system is now completely installed and is fully operational in both the GC/FID mode and the GC/MS mode using both direct injection and headspace injection using the autosampler. We are extremely pleased with this system and it is performing beyond our expectations. We are especially pleased with the ease of use and versatility of the headspace system. Much more will be said about its capabilities and use in methods developing in following sections.

All parts of Task 1 have now been completed. The rest of this report will discuss work on Task II.

E. Samples Chosen for Analysis

After consultation between Cal Poly and CARB, CARB chose eighty-six coatings from the 2005 ARB Survey to be included in the initial list of possible samples to be analyzed as part of this project. Coatings were chosen to enable testing on the widest possible variety of coatings types. The list of coatings chosen is given below in Table 6.

We have contacted manufacturers of all coatings listed in Table 6 and requested samples. We also requested formulation data, including density, solids, water content, and amounts and identities of VOCs used. To date have received approximately twenty samples.

Table 6 Coatings from 2005 ARB Survey chosen for possible analysis

		WATERBORNE				SOLVENTBORNE			
	Coating Category	Low VOC	High VOC	High Multi	Low Solids	High Multi	Low Solids	High Solids	High Exempt
1	Fire Resistive	X							
2	Recycled	X							
3	Industrial Maintenance					X			
4	Bituminous Roof	X							
5	Bituminous Roof		X						
6	Driveway Sealer	X							
7	Metallic Pigmented	X							
8	Faux Finishing		X						
9	Stains - Clear/Semitransparent				X				
10	Stains - Opaque	X							
11	Dry Fog	X							
12	Specialty Primer, Sealer, and Undercoater	X							
13	Varnishes - Clear		X	X					
14	High Temperature								X
15	Industrial Maintenance					X			
16	Bond Breakers				X				
17	Form Release Compounds							X	
18	Form Release Compounds				X				
19	Floor	X							
20	Mastic Texture		X						
21	Stains - Clear/Semitransparent				X				
22	Bond Breakers				X				
23	Concrete Curing Compounds				X				
24	High Temperature								X
25	Swimming Pool					X			
26	Swimming Pool			X					
27	Waterproofing Sealers	X							
28	Low Solids	X			X				
29	Varnishes - Clear		X						
30	Varnishes - Semitransparent		X						
31	Varnishes - Semitransparent				X				
32	Lacquers	X							
33	Roof	X							
34	Dry Fog	X							
35	Dry Fog	X							
36	Faux Finishing	X							
37	Roof	X							
38	Waterproofing Concrete/Masonry Sealers	X							
39	Bituminous Roof	X							
40	Driveway Sealer	X							
41	Driveway Sealer	X							
42	Metallic Pigmented	X							
43	Roof	X							
44	Magnesite Cement								X
45	Varnishes - Clear			X					

Table 6 (con't.) Coatings from 2005 ARB Survey chosen for possible analysis

		WATERBORNE				SOLVENTBORNE			
	Coating Category	Low VOC	High VOC	High Multi	Low Solids	High Multi	Low Solids	High Solids	High Exempt
46	Concrete Curing Compounds				X				
47	Wood Preservatives	X			X				
48	Wood Preservatives				X				
49	Swimming Pool					X			
50	Mastic Texture	X							
51	Waterproofing Concrete/Masonry Sealers	X							
52	Bond Breakers				X				
53	Form Release Compounds							X	
54	Fire Resistive					X			
55	Rust Preventative		X						
56	Low Solids	X			X				
57	Lacquers						X		X
58	Concrete Curing Compounds				X				
59	Floor							X	
60	Metallic Pigmented		X						
61	Varnishes - Clear		X						
62	Stains - Clear/Semitransparent								X
63	Floor		X						
64	Waterproofing Sealers				X				
65	Waterproofing Sealers	X			X				
66	Multi-Color	X			X				
67	Multi-Color	X							
68	Multi-Color	X							
69	Mastic Texture	X							
70	Driveway Sealer	X							
71	Traffic Marking								X
72	Traffic Marking								X
73	Traffic Marking	X							
74	Industrial Maintenance					X			
75	Bituminous Roof	X							
76	Faux Finishing		X		X				
77	Lacquers								X
78	Lacquers						X		X
79	Sanding Sealers				X				
80	Stains - Opaque	X			X				
81	Concrete Curing Compounds	X			X				
82	Waterproofing Concrete/Masonry Sealers	X			X				
83	Quick Dry Primer, Sealer, and Undercoater	X							
84	Shellacs - Clear						X		
85	Shellacs - Clear						X		
86	Wood Preservatives	X			X				

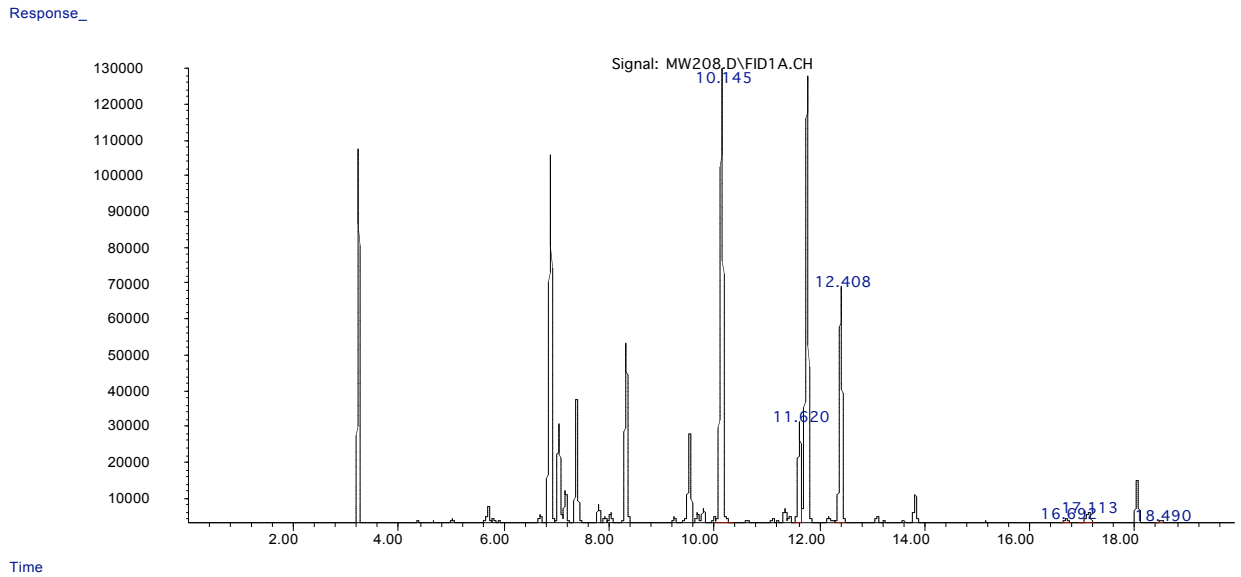
1. "Low VOC": <=3% VOCs by weight. "High VOC": >=10% VOCs by weight. "High Exempt": >=10% Exempt Compounds by weight.
2. "High Multi": Categories that have more than 10% multi-component products, by sales volume.
3. "Low Solids": 0-20% solids by volume. "High Solids": 80-100% solids by volume.
4. "Low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

F. Static Headspace Analysis

One of the goals of this project is to develop methodology for analyzing coating HAP and exempt compound content. The method of static headspace analysis described by us in our previous report appears to work particularly well and may represent a replacement method for the current EPA Method 311. We have analyzed the same solvent-borne coatings analyzed in an NPCA Method 311 round robin conducted in 2003. The coatings analyzed consisted of a nitrocellulose lacquer, a melamine-cure automotive primer, a melamine-cure automotive topcoat, and a UV-cure sealer. While these coatings do not represent architectural coatings, the study was conducted to evaluate the new method since Method 311 round robin data was available to compare results with. The methodology developed should be applicable to any type of coating and it is our intent to apply it to the architectural coatings being evaluated in this project. The headspace method has also been employed to measure the VOC content of one powder coating and one two-component waterborne polyurethane architectural coating.

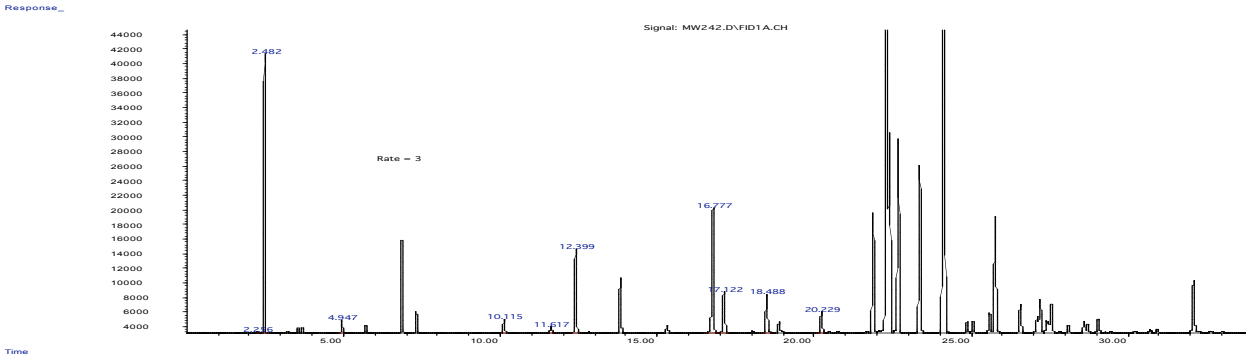
To prepare samples for static headspace analysis, a known amount of the neat liquid coating was placed in a 40mL vial containing ceramic beads. A known amount of internal standard was added and the contents were then mixed to obtain homogeneity. The internal standard used in this study was p-fluorotoluene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

1. Nitrocellulose Lacquer



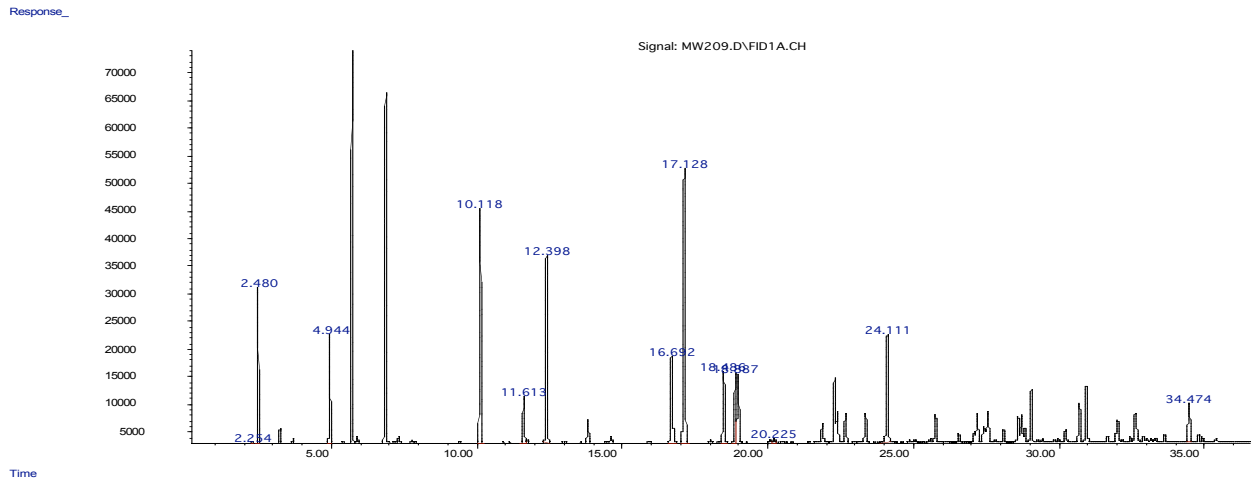
	Head Space, 150C	Method 311, Cal Poly	Method 311, All labs
Cpd	%	%	%
MIBK	14.52	14.09	14.57
Toluene	2.15	2.10	2.17
EtBz	0.10	0.10	0.09
m,p-Xy	0.37	0.34	
o-Xy	0.07	0.08	
Xylenes	0.44	0.42	0.35
5µL Akzo Lac - 9.6885g/pFTol - 0.5652g			

2. Melamine-Cure Automotive Topcoat



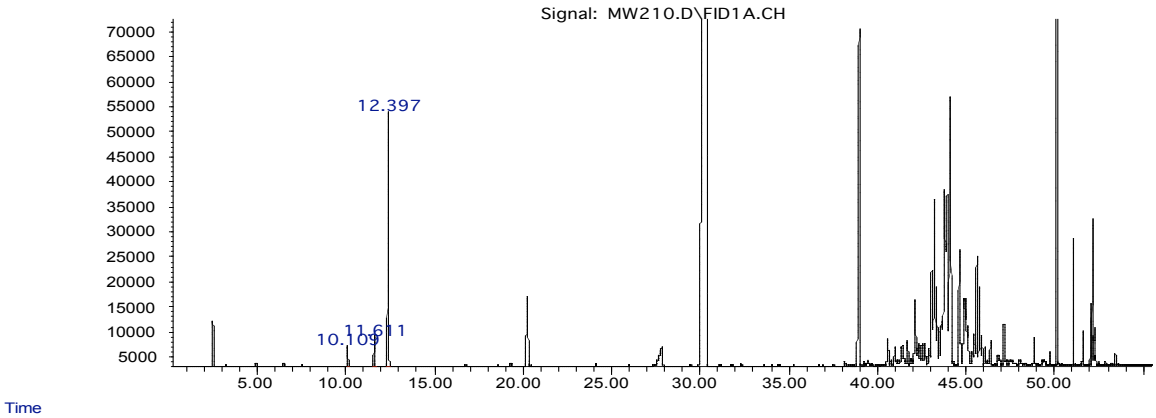
	Head Space, 150C	Head Space, 150C	Method 311, Cal Poly	Method 311, All labs
Cpd	%, slow ramp	%,fast ramp	%	%
HCHO	0.023	0.027		
MeOH	4.52	5.29		
MEK	0.09	0.09	0.09	0.10
MIBK	0.13	0.13	0.11	0.25
Toluene	0.04	0.04	0.03	0.03
EtBz	NR	0.10	0.08	0.19
m,p-Xy	0.33	0.32	0.28	
o-Xy	0.28	NR	0.24	
xylenes	0.60			0.52
EB	0.15	NR	0.22	0.19
Cumene	0.17	0.17	0.14	0.12
1,2,4-TMB	5.20	5.16		
5µL PPG Gray-17.416g/113.9mg pFT				

3. Melamine-Cure Automotive Primer



	Head Space, 150C	Method 311, Cal Poly	Method 311, All labs
Cpd	%	%	%
HCHO	0.025		
MeOH	4.02		
MEK	1.65	1.50	1.76
MIBK	3.47	3.42	3.51
Toluene	0.49	0.46	0.48
EtBz	1.21	1.10	0.99
m,p-Xy	3.49	3.51	
o-Xy	0.81	0.84	
xylenes	4.30	4.35	4.46
EB	1.47	1.68	1.81
Cumene	0.05	0.05	0.06
Napth	0.45	0.56	0.53
5µLDuPontPrimr13.4621pnt/321.5mgpFT			

4. UV-Cure Sealer



	Head Space, 150C	Method 311, Cal Poly	Method 311, All labs
Cpd	%	%	%
MIBK	0.06	0.06	0.06
Toluene	0.07	0.06	0.06
20mg_17.97g pnt/119.8mg pFT			

The static headspace method is relatively simple to run. Conditions for running the method are easily changed to give acceptable results. These method changes include chromatographic heating rates and column types. Advantages of static headspace are that the coating sample need not be dispersed in a solvent and the coating is not subjected to high inlet temperatures as is the case for the direct injection method that must be used in carrying out a Method 311 determination. The automotive coatings described above illustrate these advantages. By the direct Method 311, the sample is typically subjected to GC inlet temperatures exceeding 200°C to give vaporization of the volatile components. Under these conditions, the coating cures under very high temperature and cure volatiles (such as methanol) are released in varying amounts. Using the static headspace conditions, the coating sample is subjected to the same "cure" conditions (temperature and time) normally used in the actual application process.

G. Analysis of two-component architectural coatings

We have investigated the use of the static headspace method for addition of two component (2-K) architectural coatings. In addition to the 28 single component architectural coatings submitted to Cal Poly by the SCAQMD for their Rule 1113 assessment, six 2K architectural coating were also submitted. These consisted of two waterborne polyurethane coatings, two non-water containing epoxies, and two waterborne zinc rich primers. One of the 2K polyurethane coatings 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 procedures are summarized below in Table 7.

Table 7 Results for two component polyurethane by EPA Method 24, EPA Method 24 with internal standard, and direct static headspace analysis

2-Component WB Polyurethane - Method 24 Analysis

Formulation				
	grams	Density, lbs/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		

2-Component WB Polyurethane with 6% EGDE in part B - Method 24 Analysis

Formulation				
	grams	Density, lbs/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		

2-Component WB Polyurethane - Static Headspace Direct Analysis at 110C

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

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 hours prior to heating at 110°C for one hour. The use of a dilution solvent (or water) would inhibit the cure of the coating. 2K systems cure by chemical reaction of the components rather than by simple solvent evaporation. Use of a dilution solvent would slow or impede the required chemical cure reaction. The 24 hour 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 hours. 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 minutes. 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 two-component coating are in excellent agreement with the indirect results obtained using EPA Method 24.

H. Analysis of coatings containing semivolatile components by direct GC, static headspace GC and extraction of paint films after total volatile analysis by ASTM D 2369

In the course of analyzing the 28 samples provided by South Coast'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 US definition of VOC content is defined as the amount of VOC that evaporates from a sample during a specified heat/time cycle (Method D 2369). There

often exists, therefore, a disconnect between the amount of semivolatile component which evaporates during a D 2369 determination and a D 6886 determination with the former giving lower numbers by an amount related to the nature of the semivolatile component and the matrix that it is in. We have addressed this problem by analyzing the paint film after a D 2369 determination for residual 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. The ISO define VOC based on boiling point and a GC retention time marker and have thus avoided this complication. For waterborne coatings, the marker used in ISO standards is diethyl adipate with a boiling point of 250°C. Use of such a boiling point marker greatly simplifies the definition of VOC and would be very useful in simplifying the laboratory VOC determination by gas chromatography in this country. Additionally, a boiling point marker would allow us to integrate the static headspace method into the arsenal of new VOC methods with ease in that the equilibration temperature used in the static headspace method could be increased and give nearly complete evaporation of all the volatile and semivolatile components in a coating. This concept is illustrated in Table 8 in which three paints are described containing the Texanol and two other semi-volatiles.

Table 8. Comparison of Semivolatile Evaporation Using ASTM D 6886, Static Headspace at 110°C and 150^{0}C, and ASTM D 2369

Sample	coalescent	Direct Injection, D6886	Static Headspace, 110°C	Static Headspace, 150°C	Left in film after D2369 determination	% left in film
1	Texanol	1.29	1.06	1.13	0.07	5.3
2	Semivolatile 1	1.07	0.38	1.14	0.6	55.8
3	Semivolatile 2	0.76	0.15	0.84	0.62	80.8

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

II. Future work

We will continue work on Task 2 during the next reporting period

III. Overall progress of project.

Project is on time and on budget.