

Quarterly Progress Report on
Standard Agreement No. 04-329
For the Period
June 1, 2005 through October 31, 2005

***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-

The statements and conclusions in this report are those of the University and not necessarily those of the California Air Resources Board. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products.

Acknowledgements

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I. Work This Reporting Period

This report summarizes work performed on the project from June 1 through October 31, 2005. Due to the delay in formal signing of the contract and the delay in having the new GC/MS system shipped to Cal Poly, this report covers the first five months of the project, instead of the period from June 1 to August 31, 2005.

A. Task I Activities

During this time period, work began on 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
- Consult on development of methods manual
- Purchase and begin installation and testing of GC/MS/FID system

Progress was made on all activities and work is continuing toward completion of Task 1. In addition we have begun experimental research on new VOC analysis techniques to be included in the final method. The work is described under the following headings: sources of error in current methods, testing of Agilent 6890 gas chromatography/mass spectrometry system, determination of VOCs in dried paint films and review of existing test methods.

B. Sources of error in current methods

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 began a comparison of 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.

When a computation involves one or more variables each with an associated uncertainty, the result will likewise be uncertain. The manner in which this random error is *propagated* into the final result depends upon the functional form of the computation. For example, suppose we wanted to determine the uncertainty in the area of a rectangle having sides of length 4.00 ± 0.05 cm and 5.00 ± 0.05 cm. Determining the answer requires the use of calculus. (Incidentally, the area would be 20.00 ± 0.07 cm.)

Suppose one wishes to determine the uncertainty in the quantity Z , which is a calculated quantity from the variables x , y and w : $Z=Z(x,y,w)$. The uncertainties in the variables are σ_x , σ_y and σ_w . The uncertainty in the calculated result Z may be found from:

$$\sigma_z = \sqrt{\left(\frac{\partial Z}{\partial x}\right)^2 \sigma_x^2 + \left(\frac{\partial Z}{\partial y}\right)^2 \sigma_y^2 + \left(\frac{\partial Z}{\partial w}\right)^2 \sigma_w^2}$$

We have used this approach to determine the uncertainty in the VOC level based on published uncertainties in the quantities used to determine VOC. Both the indirect method (based on EPA Method 24) and the direct method described in ASTM Method D-6886 were examined.

The equation used for the indirect method (Method 24) is shown below:

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

Where,

$$f_V - f_W = f_{VOC}$$

$$f_{VOC} = \text{weight fraction of VOC}$$

$$f_V = \text{weight fraction of total volatile content}$$

$$f_W = \text{weight fraction of water content}$$

$$D_P = \text{density of paint}$$

$$D_W = \text{density of water}$$

The result for the uncertainty in the VOC, sVOC, 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):

$$sVOC = \sqrt{\frac{D_p^2 s f_V^2}{\left(1 - \frac{f_W D_p}{D_w}\right)^2} + \left(-\frac{D_p}{1 - \frac{f_W D_p}{D_w}} + \frac{(f_V - f_W) D_p^2}{\left(1 - \frac{f_W D_p}{D_w}\right)^2 D_w}\right)^2 s f_W^2 + \left(\frac{f_V - f_W}{1 - \frac{f_W D_p}{D_w}} + \frac{(f_V - f_W) D_p f_W}{\left(1 - \frac{f_W D_p}{D_w}\right)^2 D_w}\right)^2 s D_p^2 + \frac{(f_V - f_W)^2 D_p^4 f_W^2 s D_w^2}{\left(1 - \frac{f_W D_p}{D_w}\right)^4 D_w^4}}$$

The equation use for the direct method based on fraction of VOC content (ASTM D-6886) is given by:

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

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

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

$$sVOC := \sqrt{\frac{f_{voc}^2 D_P^4 s_{f_V}^2}{\left(1 - \frac{(f_V - f_{voc}) D_P}{D_W}\right)^4 D_W^2} + \left(\frac{D_P}{1 - \frac{(f_V - f_{voc}) D_P}{D_W}} - \frac{f_{voc} D_P^2}{\left(1 - \frac{(f_V - f_{voc}) D_P}{D_W}\right)^2 D_W}\right)^2 s_{f_{VOC}}^2 + \left(\frac{f_{voc}}{1 - \frac{(f_V - f_{voc}) D_P}{D_W}} + \frac{f_{voc} D_P (f_V - f_{voc})}{\left(1 - \frac{(f_V - f_{voc}) D_P}{D_W}\right)^2 D_W}\right)^2 s_{D_P}^2 + \frac{f_{voc}^2 D_P^4 (f_V - f_{voc})^2 s_{D_W}^2}{\left(1 - \frac{(f_V - f_{voc}) D_P}{D_W}\right)^4 D_W^4}}$$

Sample results based on the above equations are shown below:

Table 1 Calculated VOC uncertainties (sVOC) based on indirect and direct analysis methods

fv	sfv	fw	sfw	fvoc	sfvoc	Dp (g/L)	sDp	VOC g/L	sVOC uncertainties g/L	
intralaboratory									indirect	direct
0.53	0.008	0.5	0.0135	0.03	0.0023	1200	7.2	90	44	7
0.51	0.0077	0.5	0.0135	0.01	0.0008	1200	7.2	30	45	3
0.85	0.0128	0.8	0.0216	0.05	0.0038	1000	6	250	103	28
interlaboratory									indirect	direct
0.53	0.0249	0.5	0.0375	0.03	0.0049	1200	21.6	90	127	16
0.51	0.024	0.5	0.0375	0.01	0.0016	1200	21.6	30	131	5
0.85	0.04	0.8	0.06	0.05	0.0081	1000	18	250	302	48

These results compare theoretical paints with coatings VOCs of 30, 90 and 250 g/L. The fraction volatile and fraction water values are typical for these coatings. The uncertainties are from the relevant ASTM methods. These data clearly show the advantage of the direct method over the indirect method. The unreliability of the indirect method, especially for low VOC waterborne coatings, has been studied before and estimated uncertainties for the indirect method have been published based on information provided in Method 24. However, to our knowledge, this is the first comparison of the direct and indirect methods based on an impartial, statistical propagation of error analysis of the methods.

C. 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

The new Agilent 6890 GC/MS system is partially installed and is operational in the GC/FID mode and the GC/MS mode. A few trial samples have been analyzed and results compared with those obtained with our older HP 5890 system. The associated headspace analyzer for the new system has been delivered and is scheduled for installation in late November. In general, the new system gives excellent chromatographic results. Volatile organic compounds not detectable on our older system are now clearly detectable and sensitivity appears to be markedly improved. Triethyl amine which gave broad peaks on our old system gives sharp, clearly resolved peaks on the new system. Aminomethylpropanol (AMP-95), present in many waterborne coatings systems, sometimes in concentrations of 0.5% or less, is clearly measurable with the new system. Chromatograms for a masonry sealer with a reported 0.35 weight percent AMP-95 are shown below in Figures 1 and 2. The AMP-95 cannot be accurately identified using the old system, however, the AMP-95 is clearly evident using the new system and can be easily quantified.

Figure 1 Masonry sealer as analyzed on old GC/FID system (HP 5890)

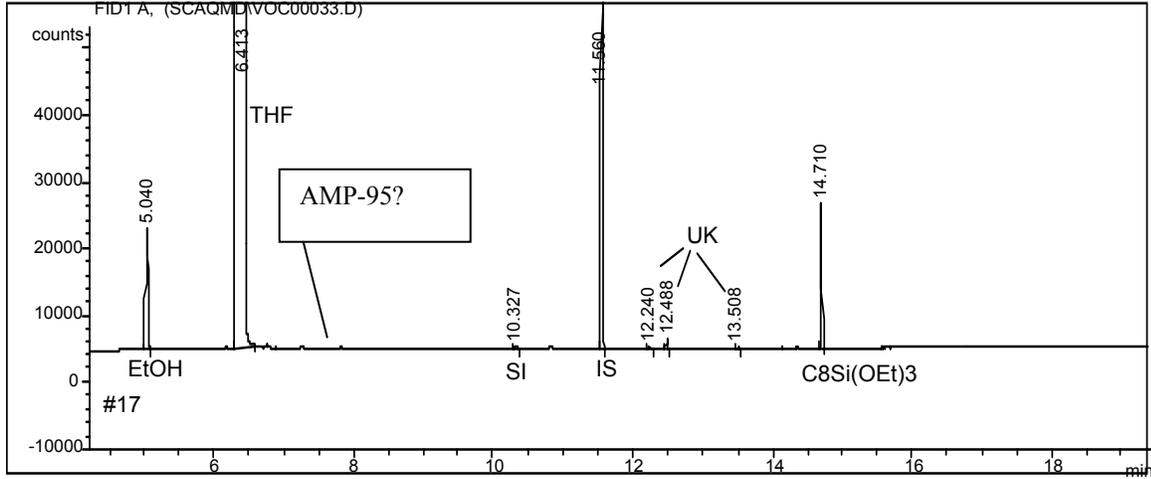
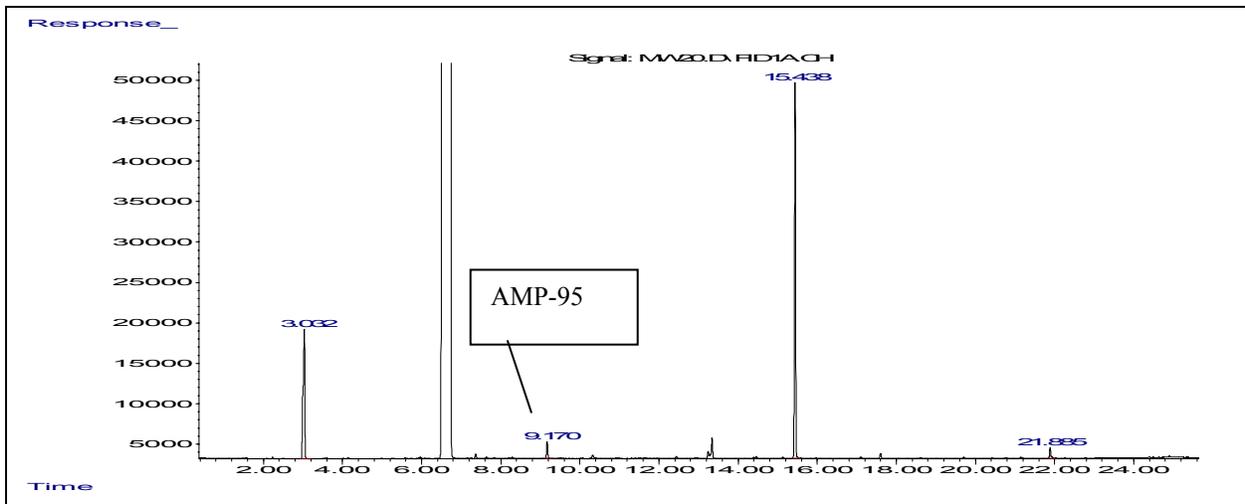


Figure 2 Masonry sealer as analyzed on new GC/FID system (HP 6890)



We are beginning a series of quantitative evaluation tests on the new system. We plan to test several paints of known composition (we will prepare these paint in our laboratory). Initially, two flat paints containing differing known amounts of propylene glycol (PG), aminomethylpropanol (AMP-95), and Texanol (TX) were prepared and analyzed using ASTM Method D6886 with the new system. Results for these two paints are given below in Tables 2 and 3.

Table 2. Flat Paint A

	Trial 1	Trial 2	
	%	%	Formulation value
PG	0.48	0.45	0.49
AMP95	0.33	0.27	0.45
TX	0.39	0.37	0.51
Total paint VOC wt fraction	0.0120	0.0110	0.0145
Calculated water wt fraction	0.4955	0.4965	0.4930
Material VOC, g/L	14	13	17
Coating VOC, g/L	36	33	43

Table 3 Flat Paint B

	Trial 1	Trial 2	
	%	%	Formulation value
PG	0.96	0.93	0.9970
AMP95	0.32	0.30	0.4500
TX	0.80	0.74	1.0700
Total paint VOC wt fraction	0.0207	0.0196	0.0252
Calculated water wt fraction	0.4868	0.4879	0.4823
Material VOC, g/L	25	24	30
Coating VOC, g/L	60	57	72

We plan to prepare these paints a second time under more stringent conditions to insure accuracy of the formulation. In particular, we will analyze the raw materials to determine their purity (we used materials donated to our program). We will also prepare and analyze both satin and semi-gloss coatings.

D. Determination of VOCs in dried paint films

Certain high boiling organic compounds present in some paints may not be totally volatilized when films are analyzed using indirect methods. These compounds may contribute only partially to the VOC value for a paint as predicated on volatile weight loss when a sample of paint is subjected to experimental total volatile content determination. One of these VOCs widely used in architectural coatings is 2,2,4-trimethylpentane-1,3-diol, monoisobutyrate (Texanol), boiling point = 244°C. Studies currently underway by the manufacturer of Texanol (Eastman Chemical) have shown that the amount of Texanol retained in some paint films after heating liquid paint for 1 hour at 110°C may be as high as 50%, thus affecting both the material and coating VOC levels. Gas chromatographic determination of VOC content (ASTM Method D6886) measures *all* of a volatile organic compound present in a coating, whether or not it is fully volatilized from films when heated for one hour at 110°C.

We are currently working on developing a method to measure the amounts of residual volatile organic compounds in paint films. This method would be used following a D2369 total volatile content determination. We would subtract the amount remaining in the film from the total amount found by direct chromatographic analysis (ASTM D6886). Initial efforts have involved extraction of paint films with either THF or MEK by simple stirring of the solvent/dried paint film mixture at room temperature. We are also evaluating the efficacy of refluxing the paint films with either THF or MEK. The amount of organic compound remaining in the paint film is measured by the same GC technique used to measure the total organic compound content of the liquid paint. This work is ongoing and we will present our results in a future report.

In addition to developing an extraction procedure for residual solvents in dried paint films, we are investigating experiments in which the amount of Texanol emitted from a paint during D2369 cure conditions is captured and measured directly. Using this technique we hope to verify Texanol mass balance by measuring emitted Texanol and adding this to the amount of Texanol retained in dried paint films. The method being used to make direct emission measurements is a draft method developed at Cal Poly for determining VOC content of cure volatile emissions from thermosetting coatings and is attached as Appendix A. We will present results of these experiments in a future report.

E. Review of Existing Test Methods

We are currently examining the various methods used for measuring the total volatile content of architectural coatings. This procedure is described in the following existing methods:

- ASTM Method D 2369-04 - Standard Test Method for Volatile Content of Coatings
- EPA Method 24 – Determination of Volatile Matter Content, Water Content, Density, Volume Solids, and Weight Solids of Surface Coatings
- SCAQMD Method 304-91 – Determination of Volatile Organic Compounds (VOC) in Various Materials
- BAAQMD Method 21 – Determination of Compliance of Volatile Organic Compounds for Water Reducible Coatings

- BAAQMD Method 22 – Determination of Compliance of Volatile Organic Compounds for Solvent Based Coatings, Inks and other Related Products

The common feature for determining the volatile content of all coatings is that a specified amount of sample is heated for 1 hour at 110°C. Differences between the methods and our recommendations are described below.

Multi-component Coatings: Both EPA Method 24 and ASTM D 2369 specify that the sample be diluted with a solvent prior to heating. D 2369 specifies an induction period prior to heating the sample of 1 hour. Method 24 specifies an induction period of no less than 1 hour and not more than 24 hours. Method 304 specifies an induction period of 1 hour but does not clearly indicate if the sample should or should not be diluted with solvent during sample preparation. Both Methods 21 and 22 specify that the sample should not be diluted with solvent and specifies an induction period of 30 minutes prior to heating.

Recommendation: Multi-component coatings cure by chemical reaction of the individual components followed by loss of any solvent that may or may not be present in the individual components. Single component coatings cure (or dry) by simple physical loss of the dilution solvent. Since the rate of chemical reactions is dependent on concentration, dilution of a multi-component coating system could slow or completely impede the desired chemical reaction (cure) if solvent is added. We recommend that all of the methods specify that no dilution solvent be added to the test specimen when carrying out a volatile content determination.

Silane containing Coatings: Waterborne masonry water repellent treatments or coatings containing silanes, siloxanes and silane-siloxane blends cure when they come in contact with the masonry substrate and release low molecular weight alcohols (generally ethanol). The substrate functions as a catalyst for the cure reaction. These coatings cannot be analyzed by D 2369, Method 24, Method 304, or Methods 21/22 and must be analyzed for volatile content by ASTM Method 5095, “Determination of the Nonvolatile Content in Silanes, Siloxanes and Silane-Siloxane Blends Used in Masonry Water Repellent Treatments” .

Recommendation: Method D2369 contains a statement that silane containing coatings be analyzed by ASTM D 5095. District methods and EPA 24 should have similar statements.

II. Future work

We will continue work on Phase I as well as preliminary work on methods development during the next period.

III. Overall progress of project.

Project is on time and on budget.

Standard Test Method for Determination of Cure Volatiles Emitted from Heat-Cure Coatings by Gas Chromatography¹

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

1. Scope

1.1 This test method is for the quantitative laboratory determination of the individual and total volatile organic compounds emitted from heat-cure coatings. The method has been studied with melamine-crosslinkable automotive coatings and with various types of powder coatings. The method is applicable for the measurement of total cure emissions in the range of zero to ten weight percent.

1.2 Components that are present at the 0.01 mass % level or greater can be determined.

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

2. Referenced Documents

2.1 *ASTM Standards:*

To be added

3. Terminology

3.1 *Definitions:*

To be added

¹ This test method is under the jurisdiction of ASTM Committee and is the direct responsibility of Subcommittee

Current edition approved XXX. XX, XXXX. Published XX XXXX.

4. Summary of Test Method

4.1 Sufficient coating to give a final film thickness of 2 to 3 mils, are placed in a new 1-quart paint can. Five to ten mL of a suitable solvent are added to disperse the coating uniformly over the bottom of the can and is then allowed to evaporate. A 150 mm by 15 mm open test tube containing a known amount of a suitable internal standard is placed in the can.

4.2 The can containing the solvent-free coating sample and internal standard is sealed with a lid fitted with nitrogen inlet and outlet ports and is placed in a suitable oven where it is brought to the coating cure temperature and is then held at that temperature for one hour.

4.3 Ultra-pure pure nitrogen is flushed through the can at 400 mL per minute. The nitrogen outlet tube exiting from the can is split into two streams inside the oven. One of the two outlet streams, a 25 to 50 mL per minute split, is allowed to pass through a cooled sorbent tube outside the oven where the volatiles are collected. When measuring cure methanol, the split stream is passed through an impinger containing cold water. This nitrogen split stream is controlled by a precision mass-flow controller.

4.4 Cure volatiles collected in the sorbent tube are extracted with a solvent and the resulting solution containing the cure volatiles and internal standard is analyzed by gas chromatography. Summing of the individual components gives the total cure volatile content. When methanol is a cure volatile, the amount is determined by GC/MS.

5. Significance and Use

5.1

To be added

6. Interferences

6.1

To be added

7. Apparatus

Emission Chamber Design

7.1 To collect the VOC emissions associated with the curing of a selected coating, a sampling chamber was constructed. The chamber was fabricated from a 1 quart, friction-top metal paint can, housed in a modified forced draft oven, (an obsolete Varian Model 3700 gas chromatograph was used as an oven). The can top was equipped with quarter inch stainless steel fittings which allowed the released VOC emissions to be swept from the chamber by a stream of ultra-high purity nitrogen into a manifold leading to single or multiple sorbent tubes containing a multisorbent or to an impinger containing water. A septum adapter, which may be used for introducing liquid coatings, was also located in the container top. A schematic diagram of the chamber sampling system is shown in Figure 1. Details of the sampling chamber are shown schematically in Figure 2. Photographs of the actual components are shown in Figures 3 and 4. The use of Teflon-seated stainless steel quick-connect fittings, (Swagelok QT series, double-ended shut off) in the oven interior allowed the sampling chamber to be easily positioned. In its final configuration, the sorbent tubes (and mass flow controllers) were the only components outside of the oven. The downstream-end of the sorbent tubes were directly attached to bulkhead fittings through the roof of the oven. This design allowed for complete transfer of emissions to the sorbent tubes or impinger. The purged emissions were pulled through the sorbent tube/impinger manifold by a Teflon-faced diaphragm vacuum pump (KNF Neuberger, model N05) placed upstream of the sorbent tubes/impinger. Teflon tubing (0.25 inch) was used to

connect the vacuum pump to the upper sorbent tube/impinger manifold and for all other necessary connections. Flow through each of the sorbent tubes/impinger was regulated by separate mass flow controllers (Tylan model FC-260).

7.2 During operation, ultra pure nitrogen gas, delivered from an aluminum cylinder (Scott Marin Co.), was metered into the chamber at the rate of 0.4 liter per minute. The effluent from the can entered the lower stainless steel manifold. Three mass flow controllers, operated in the range of 10 to 50 mL per minute were used to direct a portion of the flow to separate sorbent tubes or an impinger, where the VOCs emitted from the coating were retained. Collection time for cure-volatile emissions was normally one hour at the manufacturer's recommended cure temperature. To minimize the possibility of breakthrough, the sorbent tube(s) were cooled with ice/water contained in a plastic funnel attached to the sorbent tube by means of a septum cap (Figure 4).

7.3 When cure volatiles were collected in water by means of an impinger (methanol is not retained by most sorbents), the volatiles were transferred to the impinger by means of a 12 inch length of 0.25 inch stainless steel tubing wrapped with heating tape and was maintained at the manufacturer's recommended cure temperature. The impinger was cooled in an ice bath.

7.4 The balance of the effluent stream not led to sorbent tubes/impinger was vented through a tee located on the can top. By venting most of the effluent, overloading the sorbent was avoided. The total mass of VOCs applied to the sorbent was easily controlled by this method. The sorbent tube analyzed by GC-MS must contain a lower concentration than if it were analyzed using GC-FID, due to the requirements of the analytical instrumentation systems used. The final sampling system allowed for much versatility in terms of replicates, and sample splits.

7.5 With the sampling system fully assembled, a dummy run was performed, using ultrapure nitrogen as sweep gas through a modified 1 quart paint can. The pressure in the can was monitored by a Magnehelic gauge (0-10" H₂O). At the nominal flow rate of 1000 mL/min, the pressure drop across the can was only 0.1" H₂O. Thus, the emissions from coating samples in the can were evolved at essentially atmospheric pressure. During this run, the temperature INSIDE the can was monitored by a thermocouple suspended in the middle of the can. Just before the start of the run, the can was placed inside the oven, which was at ambient temperature, and the sweep flow of nitrogen was established. When the oven was commanded to 110°C, it required about 2 minutes to reach and stabilize at the set point. During the heating, the temperature of the can lagged behind. At t = 1.00 minute, the oven was at 86 °C, while the can interior was at 64°C. At t= 2.00 minutes, the oven had reached 100°C, while the can interior was at 94°C. At t= 5 minutes, the can interior was at 109°C. By t = 6 minutes, the can had reached 110°C. During the entire 1 hour run, the temperature inside the can was within 0.2 degrees of the oven temperature. As a result of this test, plans to pre-heat the nitrogen before leading it into the can were abandoned. The surface of the paint can appears to efficiently heat the nitrogen as it flows into the can, at least at the flow rates used for our investigation.

8. Reagents and Materials

8.1 The VOCs emitted from paint and coating samples cover a wide range of boiling points and polarities. A single sorbent cannot effectively absorb and retain both low- and high boiling compounds. For this reason, a multi-sorbent was selected for this study. Pre-packed 0.25 inch

stainless steel sorbent tubes containing Carbotrap 300 are commercially available. (Supelco, ORBO tube #100). The following information on the nature of the sorbents used in the tubes is provided by the tube manufacturer.

The Carbotrap C and Carbopack C adsorbents used in Carbotrap adsorbent tubes differ in mesh size only (20/40 mesh and 60/80 mesh respectively) and have a surface area of approximately 10m²/gram. Researchers at Supelco have found that, relative to other adsorbents, Carbotrap C and Carbopack C have superior trapping ability for a wide variety of C12 and above (depending on molecular size and shape) organic contaminants for both air sampling and purge and trap applications.

Carbotrap B and Carbopack B adsorbents used in Carbotrap adsorbent tubes differ in mesh size only (20/40 mesh and 60/80 mesh respectively) and have a surface area of approximately 100 m²/gram. Researchers at Supelco have also found that relative to other adsorbents, Carbotrap and Carbopack B have superior trapping ability for a wide variety of C5 and above (depending on molecular size and shape) organic contaminants for both air sampling and purge and trap applications. Studies of thermal desorption are an ongoing effort at Supelco.

Carbosieve S-III spherical carbon molecular sieve has a large surface area (about 800 m²/gram) and 15 to 40 angstrom pores. This structure makes Carbosieve S-III adsorbent very useful for trapping small molecules such as vinyl chloride. The pure carbon framework allows thermal desorption of small analytes without loss.

8.2 Compounds with carbon numbers ranging from C2 to over C12 are effectively sorbed by the combination of three sorbents used in the Carbotrap 300 tubes. These tubes were designed for thermal desorption into a chromatographic inlet system. In this study we investigated the possibility of using solvent desorption of the powder coating emissions followed by GC/FID analysis.

8.3 For use with a solvent desorption system, a glass sorbent tube (Supelco, ORBO Tube #100) was selected for evaluation. This tube contains two separate beds of Carbotrap (graphitized carbon black). The main portion contains 350 mg of 20/40 mesh Carbotrap, while the backup section contains 175 mg of the same sorbent. The stock ORBO tube has physical dimensions similar, but not identical, to the steel thermal desorption units. The outer diameter of the glass ORBO tube is 7 mm (vs. 0.25” for the stainless steel tube). This size difference required some modifications in the sampling system. The final configuration involved drilling out 0.25”

Swagelock nuts with a 0.281” drill. Matching Teflon ferrules were similarly drilled out. This configuration provided a reliable connection to the stainless steel sampling manifold and mass flow controllers. The tube manufacturer (Supelco) can supply custom glass tubes, in 0.25” diameter, allowing for better integration into the steel sampling system with standard sized ferrules.

9. Hazards

9.1

To be added

10. Sampling, Test Specimens, and Test Units

10.1

To be added

11. Calibration and Standardization

11.1

To be added

12. Conditioning

12.1 A new one quart metal paint can was use for each run. The empty can is heated for 2 hours at the cure temperature and then cooled prior to making a run.

13. Procedure

13.1 Add sufficient solid (powder) coating to a tared, conditioned one-quart paint can to give the desired cured film thickness. Weigh the coating to the nearest 0.1 mg. For liquid coatings, add a sufficient quantity of the well mixed coating to a conditioned one-quart can using a disposable syringe and determine the coating weight to the nearest 0.1 mg by weighing the syringe before and after adding the liquid coating to the can. Add 5 to 10 mL of a suitable solvent (dichloromethane or toluene work well for powders and tetrahydrofuran works well for liquid coatings). Swirl the contents to dissolve or disperse the coating evenly over the bottom of the can and place in a hood to allow solvents to evaporate. The can must stay level while solvent is evaporating. Place the can and uncured coating in a vacuum oven and reduce the pressure to approximately 100 mm Hg and maintain at 40⁰C for one hour.

13.2 Weigh 5 to 10 mg, weighed to the nearest 0.01 mg, of a suitable internal standard into a 150 x 15 mm screw cap test tube and seal with a Teflon-faced cap (suitable internal standards include nonane for coatings cured near 150⁰C and undecane for coatings cured near 200⁰C. When measuring methanol as a cure volatile and GC/MS is used for analysis the internal standard is methanol-*d*-3 or methanol-*d*-4. If methanol is measured by GC/FID, the internal standard should be dioxane or methyl ethyl ketone. In both instances, when measuring methanol as a cure volatile the internal standard is added to the test tube as a 10 % solution in water).

13.3 A custom Orbo 100 tube, surrounded by a plastic funnel, or impinger containing 20 mL of water is attached to the emissions system. Immediately prior to making a run, the cap is removed from the test tube containing the internal standard and is placed in the can containing the uncured coating. The can and contents are placed in the oven and closed with the lid containing the nitrogen inlet and outlet fittings. (Note: The lid was attached using finger pressure only. It is desirable to have the system relatively leak free but small leaks do not interfere with

the determination since the ratio of internal standard and coating emissions going to the sorbent tube or impinger is constant and is only a fraction of the total emissions from the can.

13.4 Nitrogen flow is established through the can at 400mL/min and through the Orbo tube at 25 to 50 mL/min. A mixture of ice and water is placed in the funnel and maintained for the duration of the run. The bottom of the cooling funnel should be even with the bottom of the lower sorbent section in the Orbo tube. When using the impinger, cooling is carried out with an ice/water bath. The oven temperature is increased from ambient to the desired cure temperature at a rate of 30 to 40 degrees per minute (about 5 to 7 minutes) and is then maintained at the cure temperature for one hour.

13.5 At the end of the run, the system is allowed to cool to room temperature. The upper bed of sorbent in the Orbo tube is transferred to a clean 10mL screw-cap test tube with a Teflon-lined cap. The lower sorbent bed, including the retaining spring and cotton plug, are transferred to a second 10mL screw-cap test tube. The empty Orbo tube is rinsed with small portions of methylene chloride (total of about 5mL) and the rinsings are added to the test tube containing the lower (main) sorbent bed. Five mL of methylene chloride is added to the test tube containing the upper sorbent bed. Both test tubes are then sonicated for 10 minutes and let stand until sorbent has settled.

13.6 The methylene chloride solution containing the upper bed is chromatographed by injecting 1 μ L into the GC. The GC trace should not show the presence of any materials other than those which might be present in the methylene chloride used to extract the sorbent. (A blank GC run of the pure solvent should be carried out). If peaks other than those present in the blank are present, "breakthrough" of emissions from the main (lower) sorbent bed into the secondary sorbent bed may be occurring. The methylene chloride solution containing the main sorbent bed

is chromatographed by GC/MS to identify the emissions. One μL of the methylene chloride solution containing emissions from the main sorbent bed is then chromatographed by GC/FID. After identification of the individual emissions they are quantified using Equation 1. Summing the various X's obtained gives the weight percent of total VOC's emitted from the coating.

13.7 When measuring cure methanol, the emissions are collected in 20 mL of cold water in an impinger. Analyze the aqueous solution by GC/MS in the SIM mode and measure the ions of mass 31(methanol, CH_2OH) and 33(deuterated methanol, CD_2OH). When analyzing by GC/FID, use the procedure given below.

$$13.8 \quad \%X = \frac{(AA)(MI)(100)}{(AI)(RF)(MC)}$$

Equation 1

where

- X = One of several possible emissions from the coating
- RF = Relative response factor of emission X
- AA = Peak area of emission X
- MI = Mass of internal standard
- AI = Peak area of internal standard
- MC = Mass of coating

13.9 After identifying the emissions of the coating prepare a dilute solution of known concentration of each of the components, from known pure materials, and the internal standard in methylene chloride. The concentration of this solution should be near 0.1mg/mL of each component and internal standard.

13.10 Chromatograph the solution in 14.8 by injecting 1 μL into the GC/FID using the same GC conditions used to analyze the coatings emissions in 14.6. Calculate the relative response factors for each of the emissions relative to the internal standard using Equation 2:

$$RF = \frac{AA * MI}{AI * MA} \quad \text{Equation 2}$$

where RF = Relative response factor
AA = Area of individual component
MI = Mass of internal standard
AI = Peak area of internal standard
MA = Mass of individual component

13.11 Standard GC/FID Instrument Conditions:

Detector: Flame ionization
Column: 30 m x 0.25 mm 5% phenyl/95% methyl siloxane, 1.0 µm film
 thickness.
Carrier Gas: Helium
Flow Rate: 1.0 mL per minute, constant flow
 Split Ratio: Variable
Temperatures, °C:
Inlet 270^o
Detector 290^o
Initial 40^o for 4 minutes
Rate 20^o per minute to 270^o, hold 15 minutes

Note: The designated column is commercially available from several vendors as the following: DB-5, SPB-5, HP-5, AT-5, CP Sil 8CB, RTx-5, BP-5. As this method becomes further refined, capillary columns with a thinner film thickness (stationary phase) may prove to be more effective for detecting high boiling emissions.

14. Calculation or Interpretation of Results

14.1

To be added

15. Precision and Bias

15.1

To be added

16. Keywords

16.1

To be added

APPENDIX

Figure 1 - Schematic of Chamber Sampling System

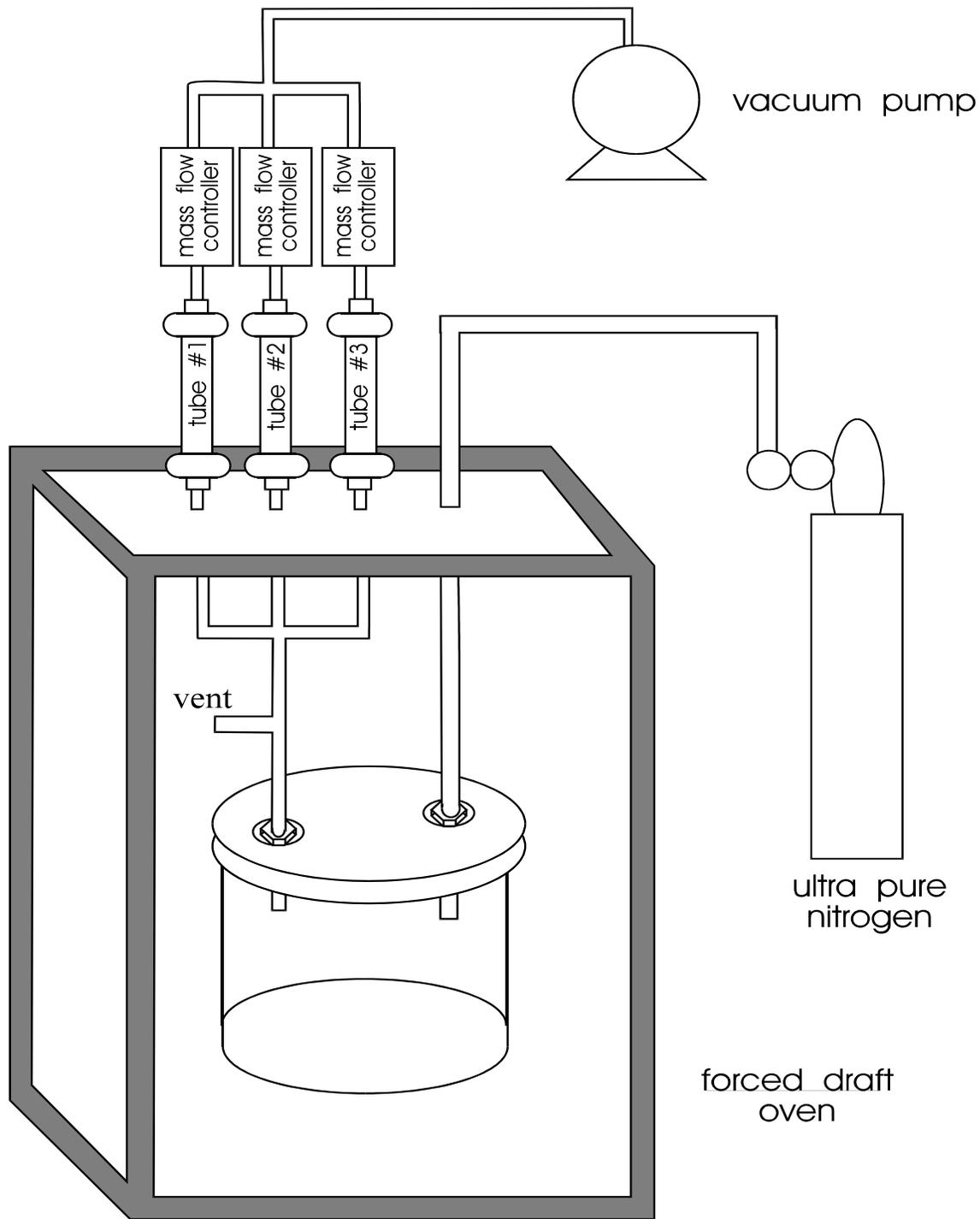


Figure 2 – Details of Chamber Sampling System

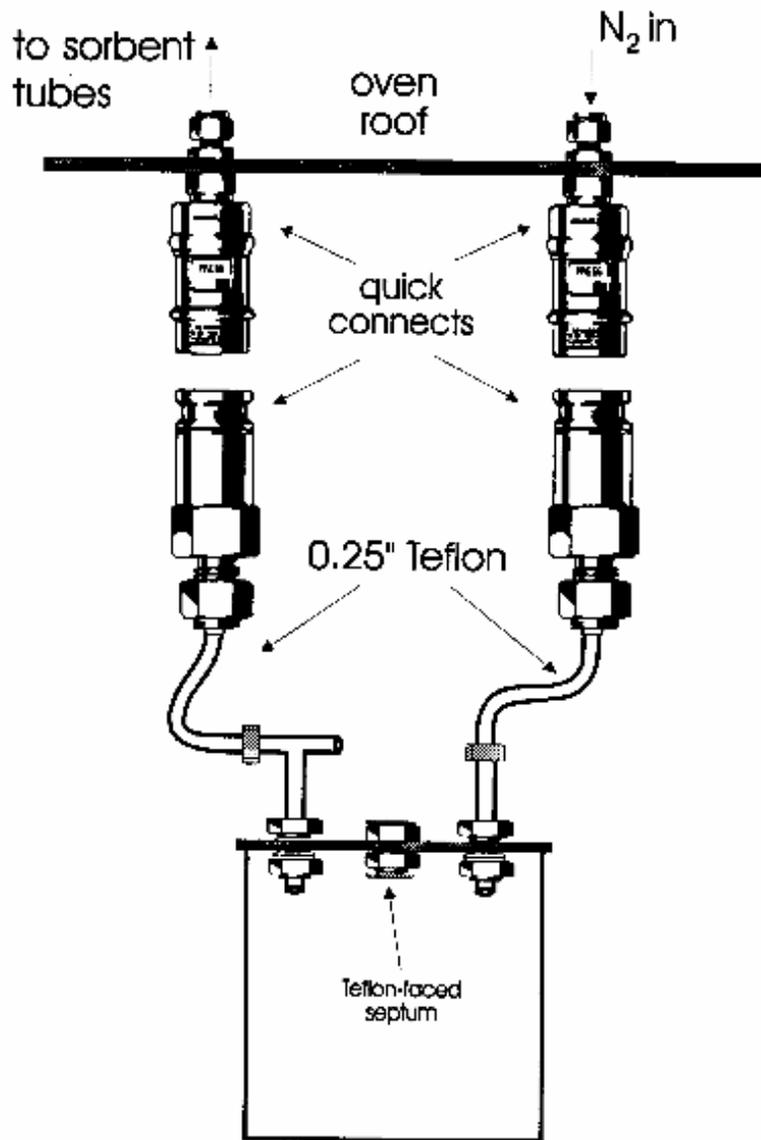
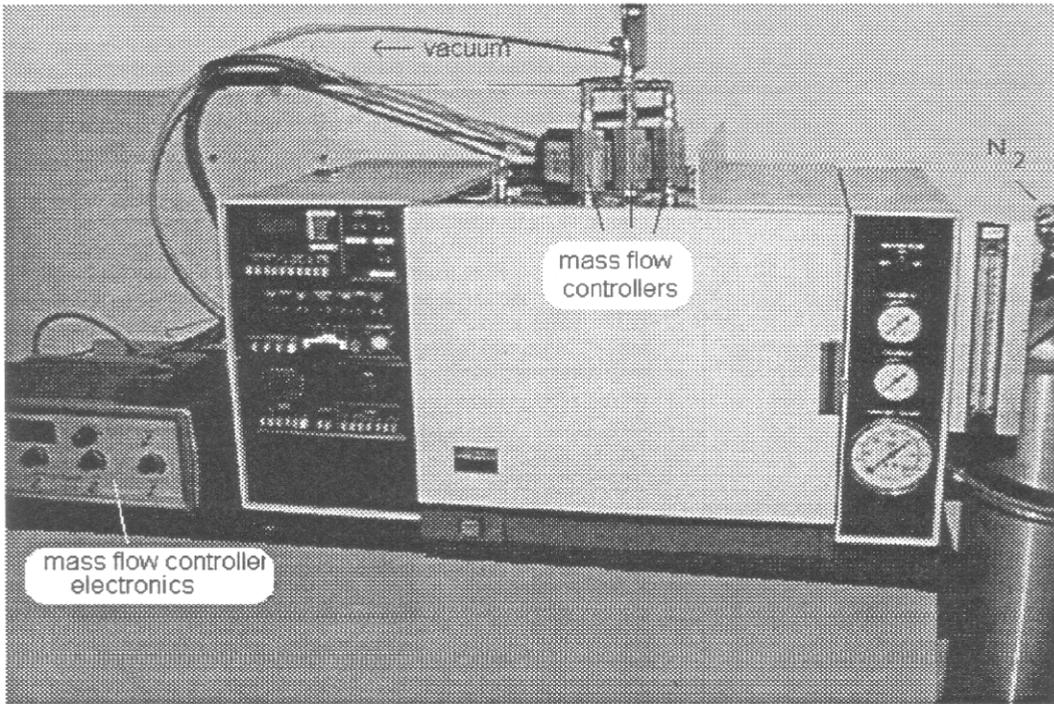


Figure 3 – Photograph of Chamber Sampling System

Exterior View of Emission Chamber



Interior View of Emission Chamber

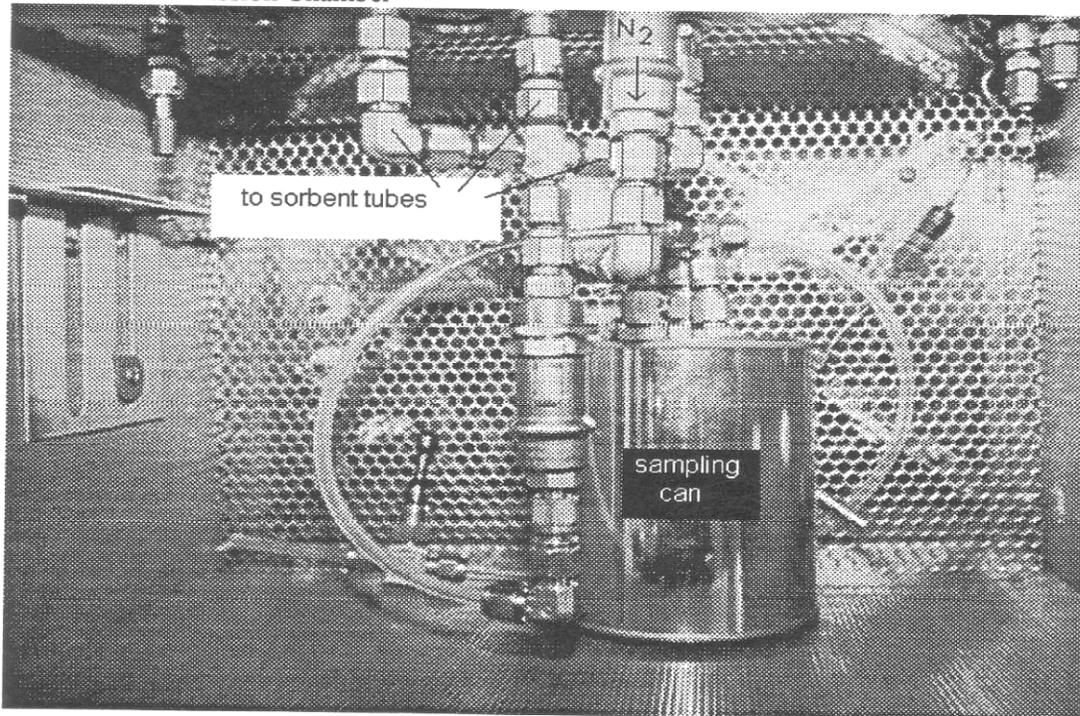


Figure 4. Sorbent Collection Tube with Cooling Funnel

