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Headspace Assay of Household Interior Paint with Teledyne Tekmar HT3™ Static Headspace Instrument

Application Note

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A Introduction

The reduction or removal of compounds that react in the atmosphere with sunlight to form ozone has become a priority effort to improve air quality worldwide. Air quality for both indoor and outdoor environments has been closely regulated in recent years. Volatile organic compounds (VOCs) are one group that have been linked to increase ozone levels. When VOCs are present in enclosed indoor spaces at high enough levels, they can have numerous symptoms that are classified as sick building syndrome.

One of the man-made materials that add VOCs to these environments is paint. Recently the EPA has lowered the allowable VOC in paint, requesting that paint manufacturers reduce the amount of VOC's effective January 1, 2009[1].

The paint manufactures have not only lowered the VOC present in their paint but also reduced or removed undesirable highly reactive VOCs such as xylenes that create more ozone than other VOCs when exposed to concentrations of NOx and sunlight. Ozone is one component of smog that is currently monitored in metropolitan areas around the country. High ozone levels have been shown to increase respiratory problems in people with asthma triggering ozone alerts in major metropolitan areas during the summer time.

One method referenced in the EPA final rule is the California Air Resources Board Method 310 – Determination of Volatile Organic Compounds in Consumer Products and reactive Organic Compounds in Aerosol Coatings[2]. This method allows the use of EPA Method 8260B3 which uses headspace for the determination of VOC's in sample matrixes.

This application note presents the analysis of water-based acrylic latex paint by static headspace. A Teledyne Tekmar HT3™ was used to analyze the paint with by headspace/GC/MS. The headspace method was used to demonstrate the reduction in sample preparation and its ability to show the differences in various commercially available paint samples.

Instrument Parameters:

The commercially available water-based acrylic latex paint samples were analyzed by headspace/GC/MS. The headspace/GC/MS consisted of a Teledyne Tekmar HT3™ connected to the Thermo Focus GC with DSQ II mass spectrometer.

The Teledyne Tekmar HT3™ headspace instrument conditions are presented in Table 1. The Thermo Focus GC with DSQ II mass spectrometer conditions are presented in Table 2.

Variable	Value
Valve Oven Temp	120°C
Transfer Line Temp	120°C
Platen/Sample Temp	105°C

Variable (Cont'd)	Value
Pressurize	15 PSIG
Pressurize Time	2.00 min
Pressurize Equil Time	0.20 min
Loop Fill Pressure	10 PSIG
Loop Fill Time	2.00 min
Inject Time	2.00 min

Table 1: Static HT3 Parameters (Loop)

Column	HP-5, 30m x 0.32m diameter, 0.25 m film thickness, Constant Pressure 14.5psi
Inlet	Split ratio 30:1, inlet temperature of 280°C

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Oven	35°C for 1 min, then 10°C/min to 200°C, 0 min hold, then 30°C/min to 300°C, 2 min final hold
MS	Start Time 0.5 min, 29.0 m/z to 350 m/z full scan, scan rate 806.30
Source	200^{o} C

Table 2: Thermo Focus GC with DSQ II Mass Spectrometer Conditions

Sample Preparation:

Six commercially available water-based acrylic latex paint samples were obtained for this comparison. Paint is available in various grades depending on the coating, its durability, and its impact on the environment.

Paint grade A was purchased prior to the EPA 2009 deadline. The same label-grade was again purchased after the EPA 2009 deadline. Paint grades B, C, and D were purchased after the EPA 2009 deadline. Paint grade D is a low odor No VOC paint. Paint D was sampled prior to and after the addition of the color additives. All of the paint grades also listed the paint as non-photochemically reactive, which indicates that they do not contain chemicals that react with other atmospheric contaminates in sunlight to produce smog-forming ozone. Table 3 is a list of the information found on the label of each paint sample.

Paint	Sample No	Label VOC (g/L)	Label Comments	Label Components
Paint A Pre 2009	1	145	Non-photochemically Reactive	Vinyl Polymer Ethylene Glycol 2(2-butoxyethoxy)ethanol
Paint A Post 2009	3	41	Non-photochemically Reactive	Vinyl Polymer Acrylic Polymer
Paint B	2	83	Non-photochemically Reactive	Ethylene Glycol
Paint C	4	40	Low Odor, Low VOC Non-photochemically Reactive	Acrylic Polymer Vinyl Chloride Polymer Ethylene Glycol
Paint D w/o Colorant	5	0[4]	Low Odor, No VOC Non-photochemically Reactive	Vinyl Polymer
Paint D w Colorant	6	0[4]	Low Odor, No VOC Non-photochemically Reactive	Vinyl Polymer

Table 3: Label Information from the Commercially Available PaintSample Analyzed by Headspace/GC/MS and Headspace/GC/FID

Approximately 1g of each paint sample was weighed into 22mL headspace vials which were sealed with an aluminum crimp seal and Teflon-lined silicone septa. These were analyzed with the HT3™ with the Thermo Focus GC with DSQ II mass spectrometer system at 105°C to provide data for comparison of the different paint formulations and to indicate a reduction in the VOCs present.

Data:

The peak areas detected with the headspace/GC/MS system for each of the six different paint samples were summed. The data for the headspace/GC/MS system is presented in Table 4. The data was normalized to an arbitrary value of 10 using the summed peak area of Paint D without colorant as the normalized value. The data is presented graphically in Figure 1.

Label VOC (g/L)	Sample No.	GC/MS Data		
		Normalized	Peak Area	Sample
145	1	42.74	21.61×10^{9}	A Pre 2009

83	2	39.72	20.08×10^9	B
41	3	39.27	19.85×10^9	A Post 2009
40	4	16.88	8.53×10^9	C
10	6	9.77	4.93×10^9	D w Color
10	5	10.00	5.06×10^9	D w/o Color

Table 4: Comparison of the Summed Peak Area Data for the Six Paint Formulations for the Headspace/GC/MS at a Sample temperature of 105°C

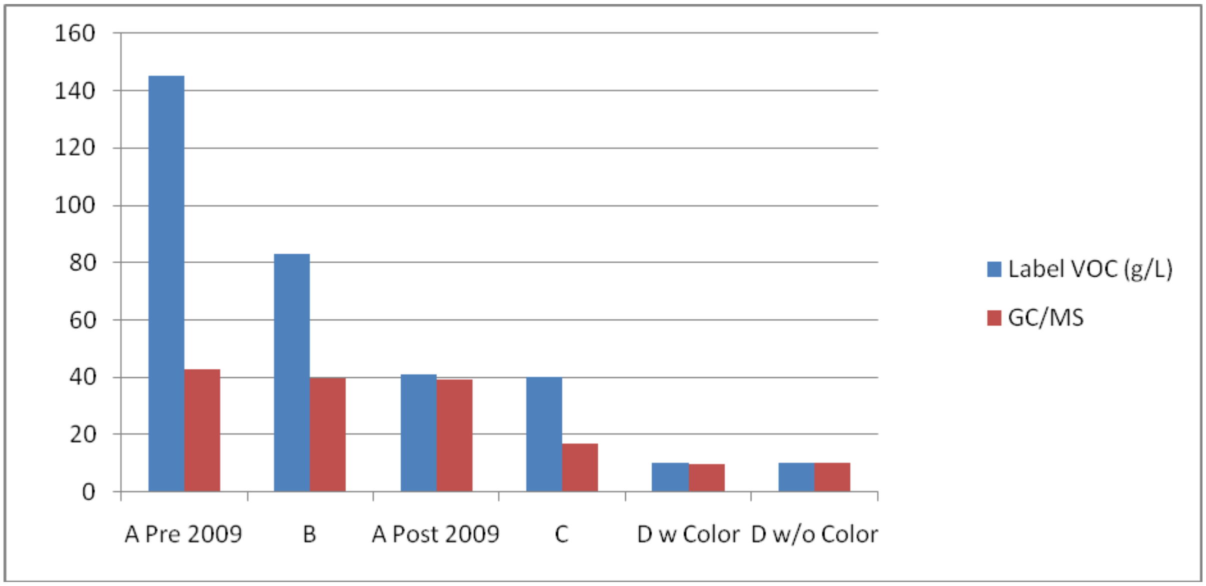
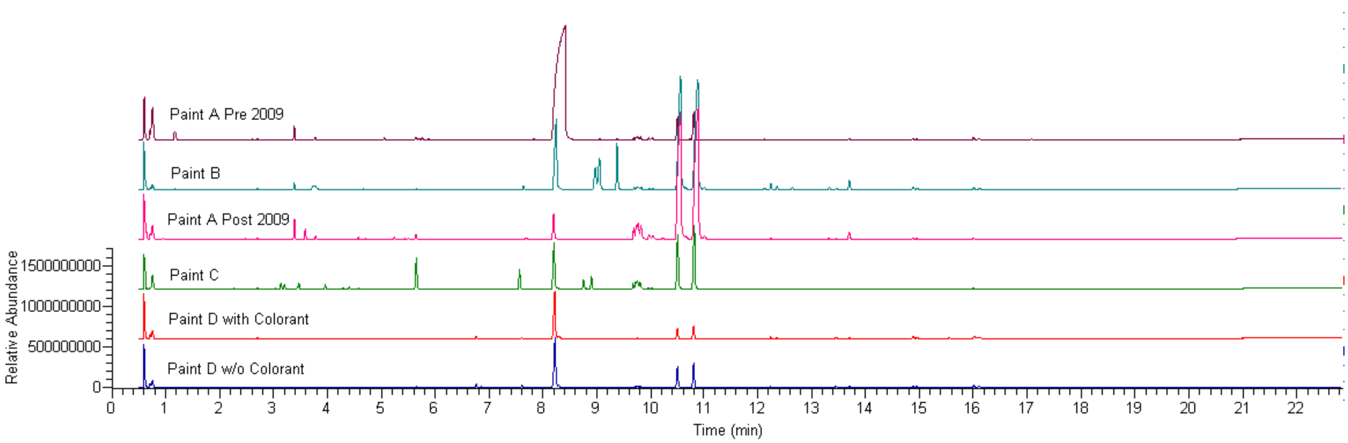


Figure 1: Graphical Comparison of the Summed Peak Area Data for the Six Paint Formulations for the Headspace/GC/MS and the Headspace/GC/FID at a Sample temperature of 105°C

The headspace/GC/MS chromatography data listed in Table 5 are displayed in Figure 2. The upper overlaid chromatogram is with the peaks on scale. The lower overlaid chromatogram is the same chromatogram with the major peaks off scale to display the difference in the paint formulations.



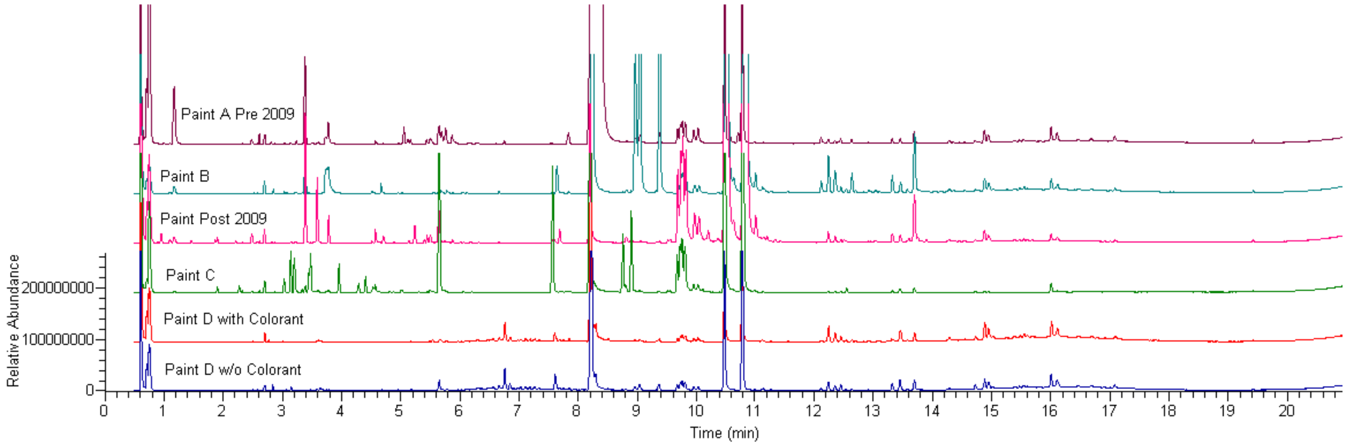


Figure 2: Overlay Comparison of the Headspace/GC/MS Chromatogram for the Six Paint Samples. The Upper Overlaid Chromatogram is with the Peaks On Scale. The Lower Overlaid Chromatogram is with the Minor Peaks On Scale to Exhibit the Difference between the Paint Formulations Detectable with the Headspace System.

The headspace/GC/MS data indicated that the peak at 8.2 minutes had the greatest decrease from paint A purchased prior to 2009 versus Paint A purchased after 2009. The headspace/GC/MS peak area data is presented in Table 5. The data is normalized to an arbitrary value of 10 using the peak area of paint D without colorant as the normalized value. The data is presented graphically in Figure 3.

Label VOC (g/L)	Sample No.	Normalized	Peak Area	Sample
145	1	121.00	17.63×10^9	A Pre 2009
83	2	17.65	2.57×10^9	B
41	3	4.76	0.69×10^9	A Post 2009
40	4	9.08	1.32×10^9	C
10	6	9.92	1.45×10^9	D w Color
10	5	10.00	1.46×10^9	D w/o Color

Table 5: Headspace/GC/MS Peak Area Data for Compound at 8.2 Minutes with Data Normalized to the Peak Area of Paint D without Colorant

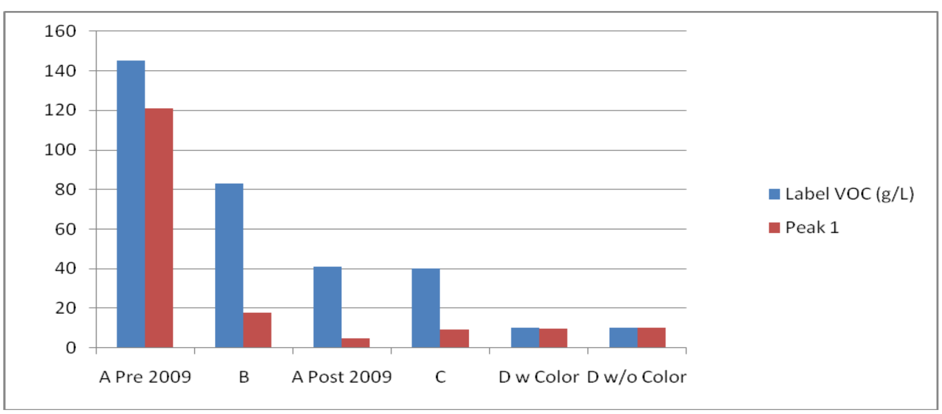


Figure 3: Graphical Comparison of the Headspace/GC/MS Peak Area Data for Compound at 8.2 Minutes with Data Normalized to the Peak Area of Paint D without Colorant

Conclusion:

Paint manufactured prior to the EPA deadline of January 1, 2009 had significantly more compounds detected by headspace/GC/ MS than the same paint grade manufactured after the deadline.
The headspace method was also able to detect the change in the formulation from the sample prior to and after the EPA deadline to maintain the paints' final dry finish requirements. The headspace analysis of these two samples also indicates the reduction of one compound from a normalized peak area of 121 to 5, a 24-fold decreases.

Headspace analysis was also able to differentiate paint formulations from the pattern of compound detected with the headspace/GC/MS method.

The Teledyne Tekmar HT3™ Static Headspace instrument provided a quick and easy method for the determination of VOCs and other components of paint samples. The sample preparation was minimal with the sample being weighed directly into the headspace vial and capped immediately.

References:

1 –National Volatile Organic Compound Emission Standards for Aerosol Coatings: Final Rule, March 24,2008, 40 CFR Parts 51 and 59, Environmental Protection Agency, Part III,.

2 – Method 310 Determination of Volatile Organic Compounds (VOC) in Consumer Products and Reactive Organic Compounds is Aerosol Coating Products, (Including Appendices A and B), Amended June 22, 2000, California Environmental Protection Agency, Air Resource Board

3 – Method 8260B Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry, Revision 2 December 1996, Environmental Protection Agency

4 – Low- and No-VOC paint are allowed to contain some VOCs. Theses paint will be assigned an arbitrary value of 10 g/L.