

VOC Analysis of Water-Based Coatings by Headspace-Gas Chromatography

Introduction

ASTM International publishes a number of different methods for the determination of volatile compounds in water-based coatings. Method D3960 is a gravimetric technique where a sample of known weight is baked under specific conditions; the % weight of volatile organic compounds (VOCs) is calculated from a series of measured masses. This method requires relatively simple equipment, but is labor intensive and its accuracy relies on the ability of the analyst to reproducibly follow the procedure. Method D6886 is a direct-injection gas chromatography (GC) technique. This method achieves adequate precision and accuracy. However, it is a liquid-injection method that requires dissolution of the coating. This reduces sensitivity and introduces non-volatile compounds into the GC injection port. Presented here is a headspace-gas chromatography (HS-GC) method to quantify and identify VOCs in water-based coatings with very limited sample preparation and no solvent use.

Headspace as a technique for analyzing VOCs in water-based coatings is often limited by the need to analyze for glycols. Within headspace, there are two common mechanisms for collecting a sample aliquot of known volume. The first, more common technique is to collect the sample in a loop of known volume. The loop-sampling technique, when used to analyze glycols, often results in carryover, poor precision and poor linearity of calibration curves. The technique utilized here is a pressure-balanced system. The basis of sample collection in this system is a calculation of sample volume, allowing gas at a known flow rate to enter the analytical column for a specific time. The advantage of a pressure-balanced system is that the sample never contacts metal loops, allowing for better recovery and essentially zero carryover of difficult compounds.

Presented in this study is the analysis of a short list of VOCs commonly found in coatings by total evaporation HS-GC. This list includes glycols and alcohols among others, representing the more difficult classes of VOCs. These compounds have typically limited the performance of headspace in this analysis. The data presented here will show a linear calibration from 0.04% through 4.00% for each of these compounds. Additionally, precision and carryover data at both low (0.4%) and high (4.00%) levels are presented.

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Experimental

The samples were prepared by adding 5 mg of an aqueous sample to a 22-mL headspace vial. This was accomplished with a 10- μ L syringe. The headspace conditions are summarized in Table 1. This method utilized total evaporation of the sample, with the headspace-vial oven temperature set to 150 °C. Each subsequent heated zone in the sample path between the headspace and the GC was heated 10 °C higher than the previous to keep the analytes from condensing at any point in the system.

Table 1. Instrumental Conditions for the TurboMatrix™ Headspace Sampler.

Headspace Unit:	PerkinElmer® TurboMatrix HS-Trap (HS mode)
Needle Temperature:	155 °C
Transfer Line Temperature:	160 °C
Oven Temperature:	150 °C
Column Pressure:	15 psig
Injection Pressure:	30 psig
High Pressure	ON
Transfer Line:	Deactivated Fused Silica 320 μ m ID
Withdraw Time:	0.2 min
Injection Time:	0.02 min
Thermostat Time:	10 min
GC Cycle Time:	25 min
Vial Pressurization Time:	1.0 min
Headspace Mode:	Constant
Vial Vent:	ON
Injection Mode:	Time

Although the analyte list in this study was short, the GC program was chosen because it will afford the necessary separation to resolve other similar compounds which would be found in a water-based coating.

Results

This analysis contained 6 compounds which represent each of the various classes of compounds often found in water-based coatings. Figure 1 demonstrates a chromatogram of a 0.4% aqueous standard. The study includes carryover checks, precision data and calibration curves, demonstrating that the analytical system utilized here can easily analyze a water-based matrix for these classes of compounds. The first step in the analysis of these types of analytes in a difficult matrix is to verify the sample-introduction technique's reliability and reproducibility.

Table 2. Instrumental Conditions for the Clarus® Gas Chromatograph.

Gas Chromatograph:	PerkinElmer® Clarus 500 w/FID		
Analytical Column:	RTX-200 (25 m x 0.320 mm x 1.0 μ m)		
Headspace Interface:	Injector Port (Headspace Control Enabled)		
Oven Program:	Temp: 40 °C 140 °C	Hold Time: 5 min End	Temp Rate: 10 °C/min
Carrier Pressure:	He @9 psi		
CAP Injector Temp:	250 °C		
FID Temperature:	300 °C		
FID Attenuation:	0		
FID Range:	1		

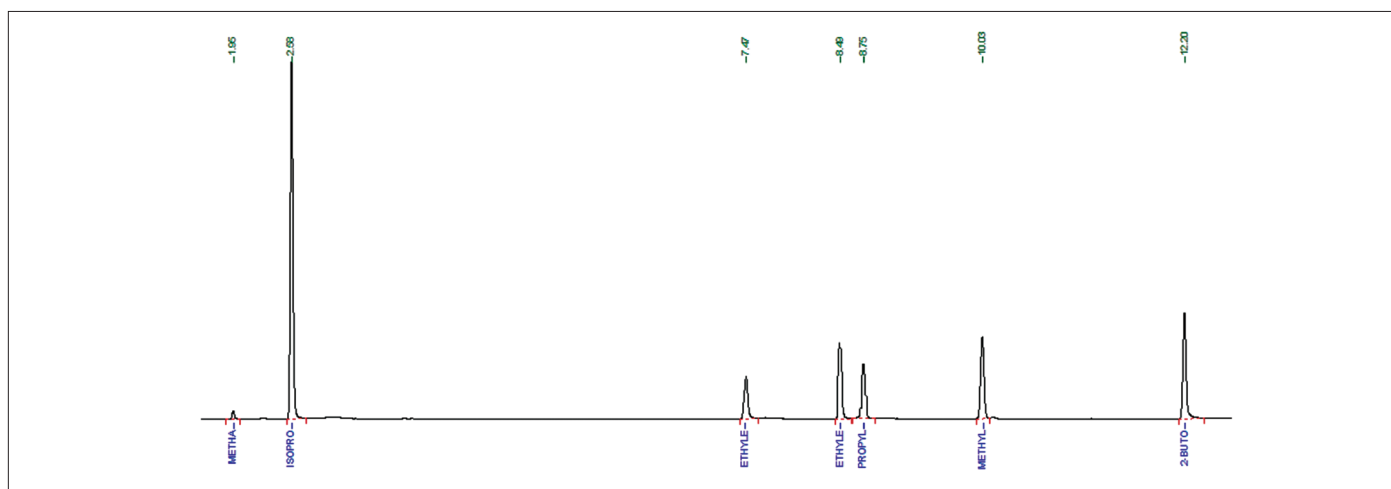


Figure 1. Chromatogram of a 0.4% aqueous VOC standard; the peaks in order of retention are methanol, isopropanol, ethylene glycol, ethylene glycol diethyl ether, propylene glycol, methyl isobutyl ketone, 2 butoxy ethanol.

The sample-introduction technique was proven to be effective through a carryover and precision study. The carryover study consisted of the analysis of blank samples closely following standards containing various levels of each analyte. Table 3 summarizes the carryover study performed here. Additionally, the chromatograms in Figure 2 (Page 4) confirm that no discernable peaks exist in the baseline of the blank analysis. The top chromatogram in Figure 2 is a magnified view of the 4% VOC solution in water. This is the upper end of the calibration range. The chromatogram in the center of Figure 2 is a blank water sample analyzed immediately following the 4% VOC run; no extra rinsing procedures were utilized at any point in this study. Lastly, in the bottom chromatogram of Figure 2, a 0.04% VOC standard is pictured at the same magnification to show a reference point for the actual concentration of zero carryover.

Following the confirmation that this technique will perform without carryover of analytes, a simple precision study verified that the introduction is reproducible. Table 4 demonstrates that the percent relative standard deviation of successive runs is acceptable – low %RSD further demonstrates that the system is not susceptible to analyte carryover.

Knowing that the introduction technique is viable, the next step is to calibrate the system. Calibration standards were made through dilution to cover a working range of 0.04% total VOC content to 4.00% total VOC content, in water. A summary of the calibration is presented in Table 5 (Page 4); as you can see, the calibration of all compounds was linear across this working range.

Table 3. Carryover Check – Summary of Sample Peak Areas in Blank and Standard Analyses.

	Isopropyl Alcohol	Ethylene Glycol	Ethylene Glycol Diethyl Ether	Propylene Glycol	Mehtyl Isobutyl Ketone	2-Butoxy Ethanol
Sample Name	Peak Area	Peak Area	Peak Area	Peak Area	Peak Area	Peak Area
Blank	0	0	0	0	0	0
Blank	0	0	0	0	0	0
0.4% Solution	14439	2506	4345	3007	5616	4949
0.4% Solution	14301	2557	4331	3154	5562	5062
Blank	0	0	0	0	0	0
Blank	0	0	0	0	0	0
4% Solution	134044	27121	35073	32125	39648	48904
4% Solution	130613	22573	34512	30471	38736	46665
Blank	0	0	0	0	0	0
Blank	0	0	0	0	0	0

Table 4. Precision Check of a 4% VOC.

	Isopropyl Alcohol	Ethylene Glycol	Ethylene Glycol Diethyl Ether	Propylene Glycol	Mehtyl Isobutyl Ketone	2-Butoxy Ethanol
	Peak Area	Peak Area	Peak Area	Peak Area	Peak Area	Peak Area
4% Solution	134165	25345	35287	30245	40233	46946
4% Solution	137927	26401	36216	31115	41192	48245
4% Solution	134241	24435	35078	29745	40065	46092
4% Solution	134757	25777	35604	30379	40358	47308
4% Solution	133133	25675	35266	30443	39884	47064
Average	134844.60	25526.60	35490.20	30385.40	40346.40	47131.00
StDev	1821.03	720.05	447.55	491.30	505.23	773.07
%RSD	1.35%	2.82%	1.26%	1.62%	1.25%	1.64%

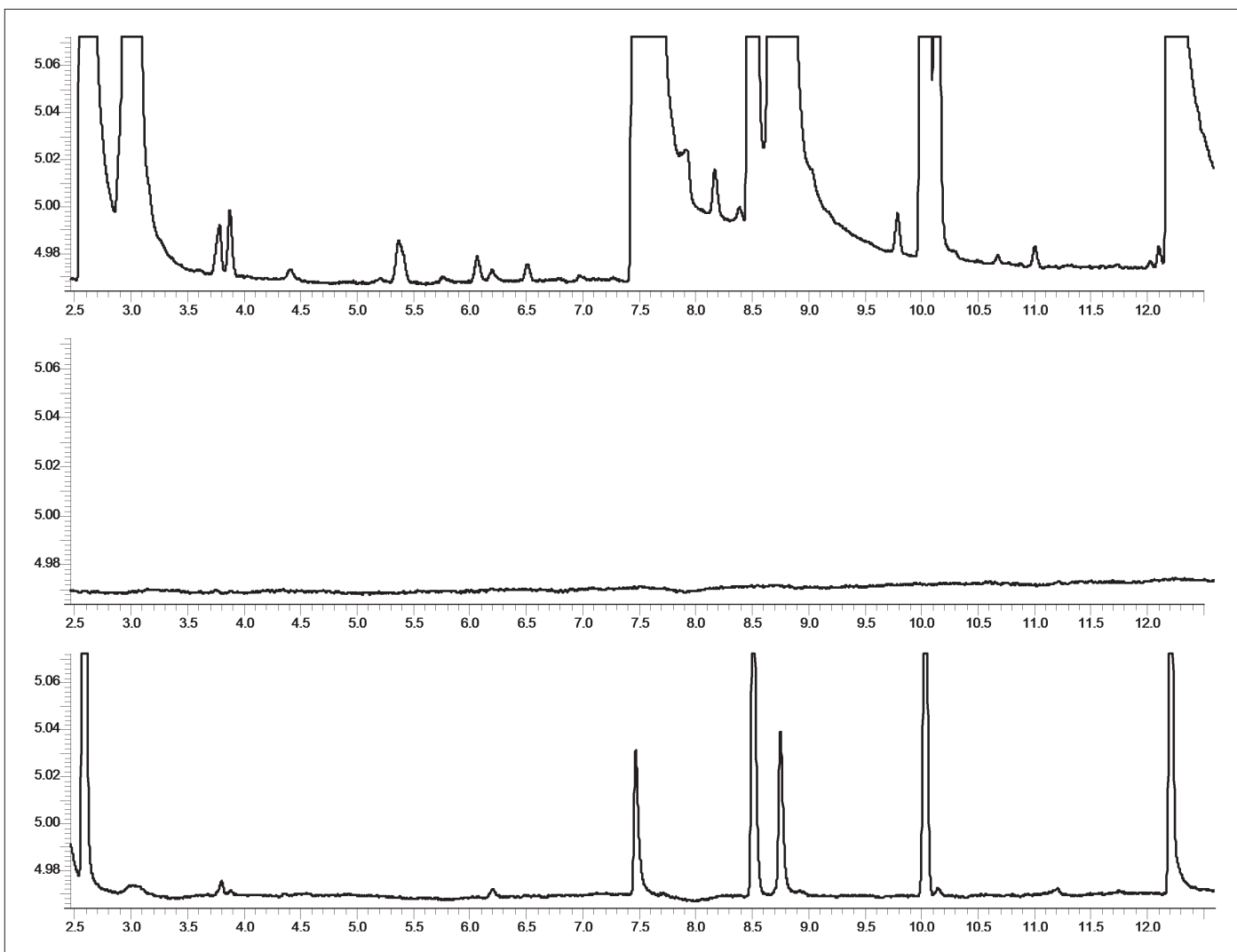


Figure 2. Chromatograms demonstrating a headspace system with zero carryover. From top to bottom the chromatograms are magnified views of: 4% VOC solution; blank immediately after the 4% run; 0.04% VOC standard.

Table 5. Calibration Summary Standards Prepared in Water Between 0.04% ad 4.00%.

	Isopropyl Alcohol	Ethylene Glycol	Ethylene Glycol Diethyl Ether	Propylene Glycol	Methyl Isobutyl Ketone	2-Butoxy Ethanol
Standard Concentration	Peak Area	Peak Area	Peak Area	Peak Area	Peak Area	Peak Area
0.04%	1441	167	400	192	432	452
0.10%	3903	558	1072	652	1161	1351
0.20%	7654	1238	2101	1502	2251	2789
0.40%	15490	2560	4179	3129	4571	5592
1.00%	37446	6423	10063	7693	11089	13840
2.00%	75244	13272	20273	16661	22444	28147
4.00%	141655	26998	37982	32158	42524	52679
R² value	0.9991	0.9999	0.9990	0.9996	0.9993	0.9989

Conclusion

Analyzing polar VOCs in complex, water-based matrices poses a challenge with analyte carryover and reproducibility. Additionally, standard ASTM methods are susceptible to a number of different errors. Headspace as a sample-introduction technique is well suited to address all of the issues associated with a matrix such as this. However, many headspace systems have difficulty analyzing glycols, as a result of their high boiling point and “stickiness”. The method that was presented here will reliably analyze difficult compounds in a difficult matrix with great precision, linearity, and without carryover.

Currently, Methods D3960, a gravimetric technique, and D6886, a liquid-injection GC technique, are the preferred methods to determine VOC content in water-based coatings. D3960 and D6886 both require extensive sample preparation; not only are these preparations slow, but they are also costly. The headspace technique presented here is fully automated, reducing cost, analyst time, and improving the precision and accuracy of the results.

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