APPLICATION NOTE

Gas Chromatography

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HS-GC-FID: VOC Analysis of Commercial Paint

Introduction

When CASE chemicals like coatings and paints are formulated (even if water-based), pigments, binding agents, and additives are dissolved into a carrier solvent, often a volatile organic compound (VOC) or water. This solvent functions to lower the mixture's viscosity, enabling it to coat a surface easily and evenly. Once applied to a surface, VOCs evaporate, leaving behind a coating of the paint's nonvolatile fractions. A wide variety of VOCs are used in paint formulations including alcohols, ketones, and aromatic hydrocarbons, among others.

Many governments regulate the release of VOCs into the atmosphere due to negative health outcomes from VOC exposure.[1,2] For example, studies on the health effects of ambient VOCs showed cases of asthma and respiratory symptoms in children and higher cancer risk for occupational painters using ship and furniture coating.[3,4] For these reasons and others, many paint manufacturers have begun to utilize water as carrier solvent. However, for paints that rely on VOC solvents, robust quantitative analytical methods are an essential tool for calculating emissions, exposure, environmental risk, and regulatory compliance.

To address these potential risks, many countries and regions have established regulatory limits or industry standards for the VOC content of paints. For instance, the U.S. Environmental Protection Agency (USEPA) promulgated 40 CFR Part 59: National Volatile Organic Compound Emission Standards for Consumer and Commercial Products, which identifies standards for numerous VOC-containing products, including paints.[5] Also, in the European Union, the Directive 2004/42/CE defines the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain paints and varnishes and vehicle refinishing.[6]

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The ASTM International standard D268-22, "Standard Guide for Sampling and Testing Volatile Solvents and Chemical Intermediates for Use in Paint and Related Coatings and Material," is commonly used by manufacturers in their product quality control analyses.[7] The standard presents detailed procedures for the sampling and testing of VOCs used in the production of paints and related products.

This application note reports the quantitative analysis of VOC solvents in a commercial paint performed with the PerkinElmer™ GC 2400™ System equipped with a flame ionization detector (FID), and headspace autosampler (HS). The system provides full integration of the headspace autosampler in the overall GC workflow managed by the PerkinElmer SimplicityChrom™ Chromatography Data System (CDS) Software. The GC 2400 Platform features a detachable touchscreen that enables real-time data acquisition monitoring and provides an engaging software interface that can be used from any location within the company network.

Experimental

The consumable materials, hardware, and software used in the method are detailed in the following sections.

Materials and Reagents

The consumable materials used are listed in Table 1.

Table 1. Consumables.

Consumable	PerkinElmer Part No.
Elite 5 column; 30 m x 0.25 mm x 0.25 µm	N9316076
Advanced Green Inlet Septum	N9306218
1 mm Ultra Deactivated Quartz Liner	N6121006
Triple Filter (Hydrogen & Nitrogen)	N9306110
Moisture/Hydrocarbon Trap (Air)	N9306117
22 ml headspace vials, 100 pk	N9306079
PTFE/SIL liner, crimps, springs	B0104241

Hardware and Software

The analysis of solvents in paint was performed by the PerkinElmer GC 2400 System equipped with FID Detector and HS 2400 Headspace Sampler. A PerkinElmer Elite-5 column was conditioned according to the recommended protocol in the PerkinElmer Capillary Column Quick Care Guide. Instrument control and data analysis were completed with the SimplicityChrom CDS Software.

Methods

The instrument parameters, calibration standards, and blanks used in the method are described in the following sections.

Instrument Conditions

HS-GC-FID conditions used in the method are provided in Table 2.

Figure 1. PerkinElmer GC 2400 System with HS 2400 Headspace Sampler.

Table 2. Instrument Operating Conditions.

GC Parameters			
Instrument	PerkinElmer GC 2400 System and HS 2400 Headspace Sampler		
Column	Elite 5; 30 m x 0.25 mm x 0.25 µm		
GC Oven Parameters	Initial	Ramp	Final
	45° C (5 min hold)	40° C/min	200° C (1 min hold)
Gas Filters	Triple Filter (Hydrogen & Nitrogen) Moisture/Hydrocarbon Trap (Air)		
Carrier	Grade 5 Hydrogen, 12 psi		
Split	5 mL/min		
Injector	Capillary Split/Splitless (CAP)		
Headspace Parameters			
Oven Temperature	150° C		
Needle Temperature	155° C		
Transfer Line Temperature	160° C		
Pressure	Grade 5 Hydrogen Gas, 16 psi Pressure		
GC Cycle Time	35.0 min		
Timings	12 min Thermostat, 1 min Pressurizing, 0.04 min Injection, 0.3 min Withdraw		
Vent Time	5.0 sec		
Transfer Line	1.0 m 0.32 mm I.D. Fused Silica		
Options	Operative Mode: Constant Inject Mode: Time		
Injector Parameters			
Carrier/mode	Split, Split Flow = 5 ml/min		
Temperature	160° C		
Septum Flow	3 ml/min		
Detector Parameters			
Type	FID		
Temperature	250° C		
Hydrogen	Grade 5 Hydrogen, 30 ml/min		
Air	Grade 5 Air, 400 ml/min		
Make Up Gas	Grade 5 Nitrogen, 25 ml/min		
Data rate	10 Hz		

Calibration Standards

Pure standards of methanol, acetone, methylethyl ketone (MEK), butyl acetate, toluene, and parachlorobenzotrifluoride (PCBTF) were purchased from Millipore Sigma (Burlington, MA). 1,2-dichlorobenzene diluent was also purchased from this vendor. Stock standard 1 was prepared volumetrically: 10% by volume of each of the six solvents with the remaining 40% comprised of the diluent. Serial dilutions were performed at a 1:1 vol/vol ratio to construct the remaining stock standards until a total of 8 stocks were made. Lastly, volumetric concentrations were converted to µg/ml using each compound's standard density.

The calibration standards consisted of 5 µl of each stock placed into a 22 ml headspace vial with crimp top. A total evaporation technique was employed, heating each vial within the headspace oven to above the boiling point of each analyte. This allowed the use of small sample amount leading to savings in terms of sample and solvent used, while enabling required accuracy levels.

Commercial Sample and Blank Preparation

A commercial paint was purchased from a local vendor. This sample was diluted to 10% vol/vol in 1,2-dichlorobenzene for a total of n=3 samples. 5 µl aliquots of the resulting solutions were added to 22 mL crimp-top headspace vials. The samples were sequenced subsequent to the calibration curve with an instrument blank of 5 µl pure 1,2-dichlorobenzene employed between the final calibration standard (most concentrated) and the samples.

Results and Discussion

The calibration and sample results are presented in the following sections.

System Performance

Calibration results for all six solvents are presented in Figure 1. The GC 2400 System and HS 2400 Headspace Sampler achieved excellent linearity for all analytes, with coefficients of determination, R2, meeting or exceeding 0.999 for all regressions. Compound concentrations were calculated using each respective regression equation.

Sample Results

The commercial paint sample contained three target analytes: acetone, toluene, and butyl acetate. Table 3 presents the triplicate results for the sample. The method achieved high levels of precision as demonstrated by a relative standard deviation (RSD) of less than 2% for each analyte. From the vendor's product specification sheet, it was stated that toluene comprised 25–50% by weight and butyl acetate comprised 10% or less by weight. This method obtained values in agreement with the formulation. Expected acetone concentration was not listed by the vendor in their specification sheet.

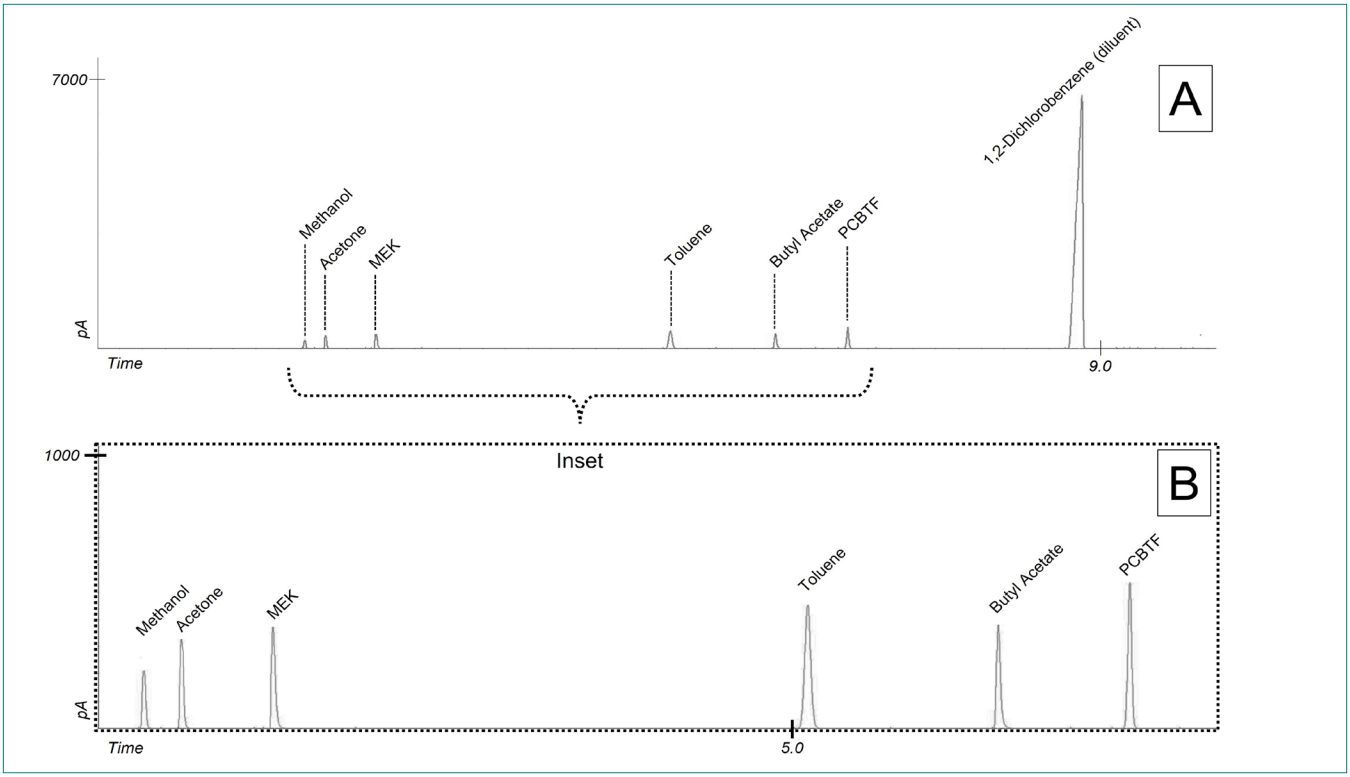

Figure 2. Separation of target compounds using HS 2400 Headspace Sampler and GC 2400 System.

Table 3. Triplicate Analysis Results For the Paint Sample Showing High Analytical Precision and Agreement with Vendor Specifications.

*Note: Average wt% composition calculated using paint density of 1.08 g/ml from material SDS.

Sample Run	Acetone	Toluene	Butyl Acetate
Sample 1, mg/ml	20.058	343.766	83.330
Sample 2, mg/ml	19.754	336.454	80.843
Sample 3, mg/ml	19.379	366.185	81.245
Average*, mg/ml	19.731 (18.3 wt%)	338.802 (31.4 wt%)	81.806 (7.57 wt%)
% RSD	1.72%	1.27%	1.63%
Formulation listed by vendor	Not Listed	25 – 50 wt%	≤ 10 wt%

The chromatogram of calibration standard #6 is shown in Figures 2A and 2B along with an inset of the target compounds. Excellent peak shape was obtained for all compounds on the Elite 5 column, including small, polar analytes. Figure 4 presents the chromatogram of the sample from Table 3, highlighting both target compounds and non-target peaks.

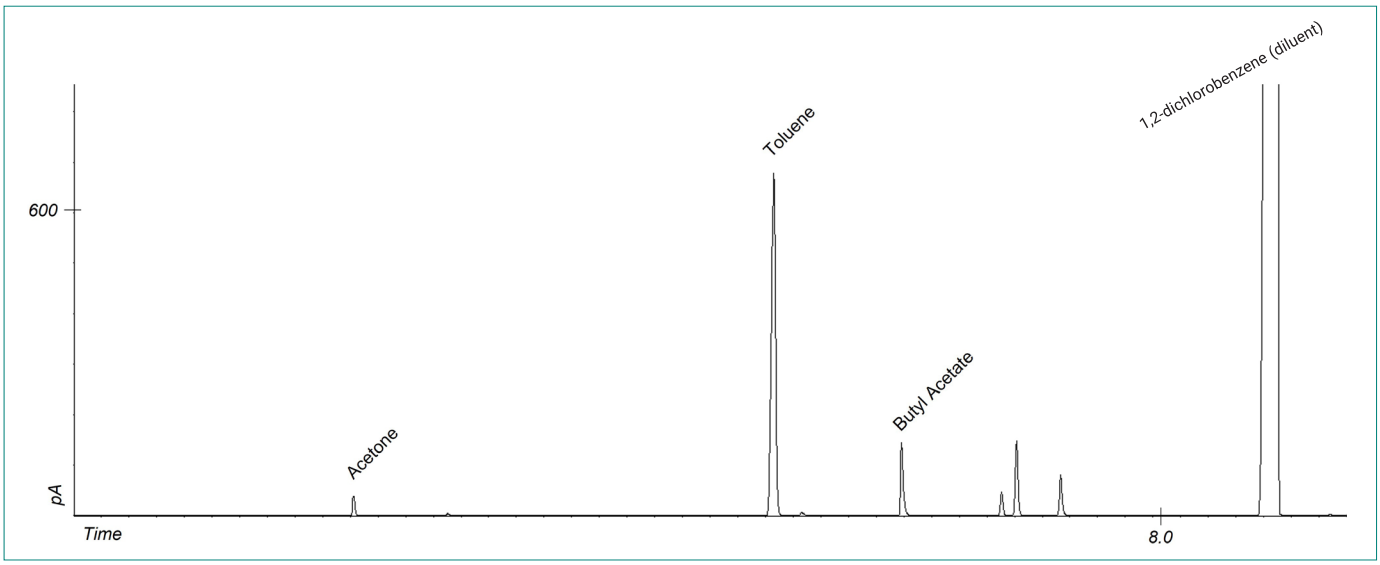

Figure 3. Chromatogram of a commercial paint sample.

Conclusion

VOCs in CASE chemicals, such as commercial paint were successfully characterized using the PerkinElmer GC 2400 System, using a PerkinElmer Elite 5 30 m X 0.25 mm ID X 0.25 µm column, with the HS 2400 Headspace Sampler. Target analytes were accurately quantified in the commercial sample. Triplicate sample results demonstrated the high level of precision achieved by the GC 2400 System. Thanks to the integrated workflow, the HS 2400 Headspace Sampler operates in constant communication with the GC 2400 System, allowing a continuous optimization of the pneumatic values based on the feedback received by the GC instrument. This provides ultimate precision in GC retention time. The high throughput of the GC-FID configuration coupled with headspace sampling is proven to be a robust, reliable, and precise method for analyzing solvents in paint. The HS 2400 Headspace Sampler, powered by pressure-balanced technology, allows to perform the total evaporation technique of a paint sample and is, therefore, highly robust over the linear range. The steep temperature ramp employed, 40° C/min, highlights the excellent repeatability of the GC 2400 System oven under the most demanding method conditions.

In addition, data acquisition and analysis by the SimplicityChrom CDS Software supports compliance with regulatory data requirements and provides a practical, customizable user experience with multifunctionality and accessibility options. Real time information is available on the detachable touchscreen that provides versatility/portability and ultimately improves laboratory productivity.

References

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