Saving Time by Reducing Calibrations for the Quantification of VOCs in Paints and Coatings using the Polyarc® System

Application Note

Paints and Coatings

Authors

Nemi Jain and Evelyn Rouge
Sherwin-Williams Co.
4440 Warrensville Center Rd.
Warrensville Hts., OH 44128
ncjain@sherwin.com

Charlie Spanjers
Activated Research Company
7561 Corporate Way
Eden Prairie, MN 55344
charlie.spanjers@activatedresearch.com

Abstract

The analysis of volatile organic compounds (VOCs) in solvent-borne as well as waterborne paints and coatings by GC/FID typically requires calibrations to determine the responses of each individual analyte before quantitative information can be obtained. In this application note, the analysis of a commercial coating with the Polyarc System is demonstrated. Because the Polyarc converts all organic molecules to methane before detection in the FID, calibration is not required. Instead, the peak area of one internal standard is used to accurately quantify every component in the mixture (17 analytes in this example).

Introduction

Many coatings necessarily contain high concentrations of volatile organic compounds (VOCs), which determine the coating characteristics and dry time. Household paints, on the other hand, must have very low levels of VOCs to prevent contamination of indoor air. In both cases, however, the concentration of VOCs must be accurately determined before a product can be sold. The technique that is most often used for identification and quantification of VOCs is gas chromatography (GC) with a flame ionization detector (FID).

The number of VOCs in a single sample can range from a few to hundreds of mostly oxygen-containing molecules. This complexity makes obtaining quantitative data both time consuming and challenging, as the FID response must first be calibrated for each individual VOC. This is because the response of the FID for each VOC is variable, based on the number of heteroatoms (O, N, etc.) and its chemical structure.

Figure 1. Polyarc System installed in the back detector position next to an FID on an Agilent 7890 GC.

In this application note, it is shown how the Polyarc System (Figure 1) can be used to save time by reducing calibrations for the GC/FID analysis of VOCs. The Polyarc is a catalytic microreactor that is an intermediate step after the column and before detection in the FID, in which all organic compounds are converted to methane through a two-step catalytic reaction:

Carbon-Containing Compounds + Air + H_2 → Methane (CH_4) + Non-Carbonaceous Byproducts

The response-per-carbon atom in the FID becomes equivalent for all carbon containing molecules because the FID only sees methane. Thus, a single internal standard (or an external standard) can be used to quantify all other components in the mixture, without the need to first calibrate. This means that quantitative information can be obtained in a single injection (compared to time-consuming analyses of calibration standards).

The quantitative analysis of a commercial coating with the Polyarc is described in this application note. A single internal standard (1-propanol) was used to quantify 17 analytes in a single injection without the need to calibrate each individual component.

Experimental

An Agilent 7890A GC equipped with a split/splitless inlet (Agilent G3454-64000), capillary-optimized FID, mass spectrometer (Agilent 5973), and Polyarc® reactor (ARC PA-RRC-A02) were used for the analysis. Helium (99.999%, Praxair) was used for carrier and FID makeup. Air (zero grade, Praxair) and H_2 (99.999%, Praxair) were supplied to the ARC electronic flow control module (PA-MFC-A09) and to the FID. The effluent of the GC column was connected to an Agilent 3-way CFT splitter (G3183-60500). The MS was connected to the splitter via a retention gap column (Agilent, 160-2635-5, 0.61 m, 0.1 mm ID). The inlet capillary to the Polyarc® was connected directly to the splitter. The splitter was controlled by an EPC (with restrictor frit removed) set to 4 psig.

Samples were prepared for GC analysis by adding a known concentration of pure 1-propanol as the internal standard (IS).

GC conditions

Front inlet	Split/splitless
Inlet temperature	250 °C
Inlet linter	Agilent 18740-80190
Carrier gas	He; 3 sccm constant flow
Septum purge flow	3 sccm
Oven	40 °C (hold 5 min) to 275 °C at 15 °C/min (hold 30 min)
Column	DB-5 UI (30 m × 0.25 mm × 1 µm film)
Syringe	10 µL
Injection volume	0.5 µL

FID conditions

Temperature	300 °C
H_2	1.5 sccm
Air	350 sccm
Makeup	20 sccm (He)

Polyarc® System conditions

Setpoint	293 (450 °C actual temp.)
H_2	35 sccm
Air	2.5 sccm

Results and Discussion

A commercial coating was analyzed with the Polyarc System using the experimental information shown above. The sample was first screened to ensure 1-propanol was not present. Then, 0.0956 g of pure 1-propanol was added to 0.9976 g of sample and injected into the system (see chromatogram in Figure 2). Each of the peaks in the chromatogram were identified using simultaneous data collection from a mass spectrometer (MS) (see Table 1 for identification). The 1-propanol peak area was then used to calibrate for every other peak in the chromatogram. Thus, the Polyarc System allowed for quantification of the 17 primary analytes in this sample with a single injection, without the need to calibrate each individual component.

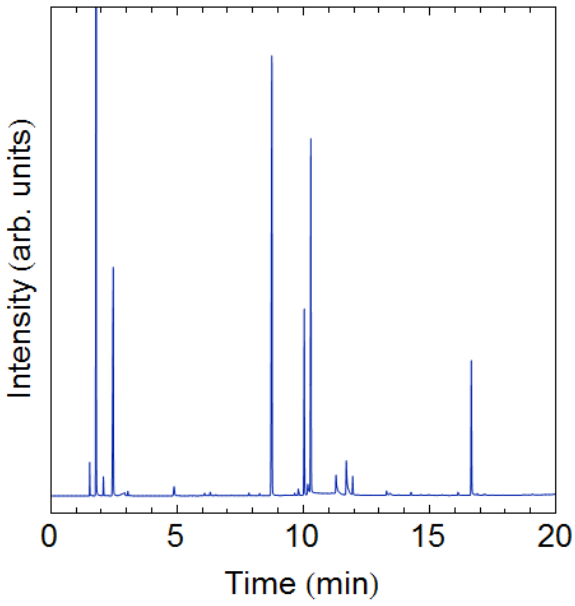

Figure 2. Chromatogram of a commercial coating using the Polyarc System.

Table 1. Quantitative analysis of a commercial coating using the Polyarc System.

Analyte	Mw (g/mol)	#C	Ret time (min)	Area	Polyarc Conc. (wt.%)	FID With Calibration (wt.%)	Theoretical Amount (wt.%)
Ethanol (wash solvent)	46	2	1.538	19399609	0.78		
Acetone	58	3	1.789	667510685	22.44	22.45	22.78
2-Methyl-2-Propanol	74	4	2.081	15571039	0.50	ND	
1-Propanol (IS)	60	3	2.47	275527557	N/A	N/A	
Acetic Acid	60	2	2.933	14986621	0.78	ND	0.92
2-Butanone	74	4	3.051	4693250	0.15	0.15	
1-Butanol	74	4	4.881	16838800	0.54	0.53	
Toluene	92	7	7.847	2949039	0.07	0.07	
3-Methylene-Heptane	112	8	8.27	2639491	0.06	NQ	
n-Butyl Acetate	116	6	8.754	542803684	18.25	18.93	21.29
p-Xylene	106	8	9.802	8549377	0.20	0.24	
Methyl n-Amyl Ketone	114	7	10.038	181595465	5.14	5.51	4.87
Styrene	104	8	10.177	9982979	0.23	NQ	
n-Butyl Propionate	130	7	10.299	349664679	11.29	11.54	10.76
2-ButylMethacrylate	142	8	11.295	40847080	1.26	NQ	
2-HydroxyEthyl Methacrylate	130	6	11.704	70244561	2.65	NQ	
2-Oxypanone	114	6	13.445	4337845	0.14	ND	
Isobornyl Methacrylate	222	14	16.656	141508531	3.90	NQ	

[N/A]Not applicable as 1-propanol was added as internal standard for Polyarc measurements.
[ND]Not detected.
[NQ]Not quantified.

Analysis Procedure

The area-per-mol of carbon is equivalent for all carbon-containing analytes because every molecule is completely converted to methane. This property allows for the determination of the concentration of any analyte using a single internal standard. For the data above, 1-propanol was used as the internal standard. The concentrations of all analytes were then calculated using the governing equation for the Polyarc:

$$C_A = C_S \left(\frac{Area_A}{Area_S}\right)\left(\frac{Mw_A}{Mw_S}\right)\left(\frac{\#C_S}{\#C_A}\right)^*$$

where:

C_A = Mass concentration of the analyte
C_S = Mass concentration of the standard
$Area_A$ = Integrated peak area of the analyte
$Area_S$ = Integrated peak area of the standard
Mw_A = Molecular weight of the analyte
Mw_S = Molecular weight of the standard
$\#C_S$ = Number of carbon atoms in standard
$\#C_A$ = Number of carbon atoms in analyte

*See "Quantification with the Polyarc.pdf" at https://www.activatedresearch.com/documents/ for more information.

Conclusions

The Polyarc System is a useful tool for the analysis of paints and coatings because of the complexity associated with these samples. Traditional methods for quantification of analytes in a complex mixture includes time-consuming calibrations of each individual components. With the Polyarc System, this process is greatly simplified because every molecule gives a uniform (equimolar) response in the FID. Further work will continue to explore the wide range of paints and coatings that this method is applicable to.

Contact Us

For more information or to purchase a Polyarc® system, please contact us at 612-787-2721 or contact@activatedresearch.com.

Please visit our website for details and additional technical literature.

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