

Cryogen-free analysis of VOCs in car exhaust

Thermal desorption coupled to gas chromatography with dual flame ionization detectors

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Goal

The goal of the methodology described here was to demonstrate the suitability of a simplified, cryogen-free method for the analysis of VOCs in exhaust gases, using thermal desorption (TD) coupled to dual-column gas chromatography-flame ionization (GC-FID) detection.

Introduction

The presence of volatile organic compounds (VOCs) in the atmosphere is a concern for environmental protection agencies across the globe. Along with their hazardous chemical properties their potential for reacting with other



hazardous air pollutants to produce smog poses a risk to human and environmental health. VOC pollutants also play a large role in ozone depletion allowing increased amounts of harmful UV rays to reach Earth's surface adding to the potentially negative health impacts.

A subset of VOCs known as ozone precursors are monitored at photochemical assessment monitoring stations (PAMS) by the EPA. In the United States, most PAMS sites measure 56 target hydrocarbons, including alkane, alkene, and aromatic compounds ranging from C₂ to C₁₁.

For PAMS stations, thermal desorption (TD) coupled with gas chromatography (GC) dual flame ionization detectors

(FID) is the preferred technique, but for more complicated VOC lists, GC with mass spectrometry (MS) is used. Detector choice depends on several factors, mainly the type and range of VOCs to be detected and expected concentration levels.

Historically, TD systems used for the analysis of the very volatile organic compounds (VVOC) utilized liquid cryogen as a method for trapping and focusing the compounds for analysis. This was very cumbersome for field operations and was replaced with electrical cooling devices coupled with multi-sorbent bedded focusing traps to exceed the performance of the cryogen systems. The advantages of using the electrically cooled systems, not only means less cost and inconvenience, but also allows the use of superior water management techniques.

The following application note demonstrates an advanced, cryogen-free method for the analysis of VOCs in exhaust gases using thermal desorption coupled to a dual-column GC-FID.

Experimental conditions

Standards

A multicomponent standard (of varying concentrations ~42.5 ppb) as well as a propane standard (at 3000 ppb) were supplied in Tedlar™ bags from the California Air Resources Board and used to generate calibration curves. This was achieved by sampling differing volumes of the standards, removing the need for gas dilution. An additional 11-component standard at 25,000 ppb, for the assessment of carryover, and a Tedlar bag containing VOC exhaust compounds, sampled from a testing chamber, were also analyzed to test the performance of the analytical setup.

Instrument and method setup

A Markes™ CIA Advantage-xr™ on-line sampler with a Kori-xr™ water removal device and UNITY-xr™ thermal desorber (Figure 1) were coupled to a Thermo Scientific™ TRACE™ 1310 gas chromatograph in a dual-column, dual-flame ionization detector (FID) configuration utilizing a Thermo Scientific™ Deans Switch microfluidics kit, P/N 19005580, (Figure 2). The entire system is cryogen free.

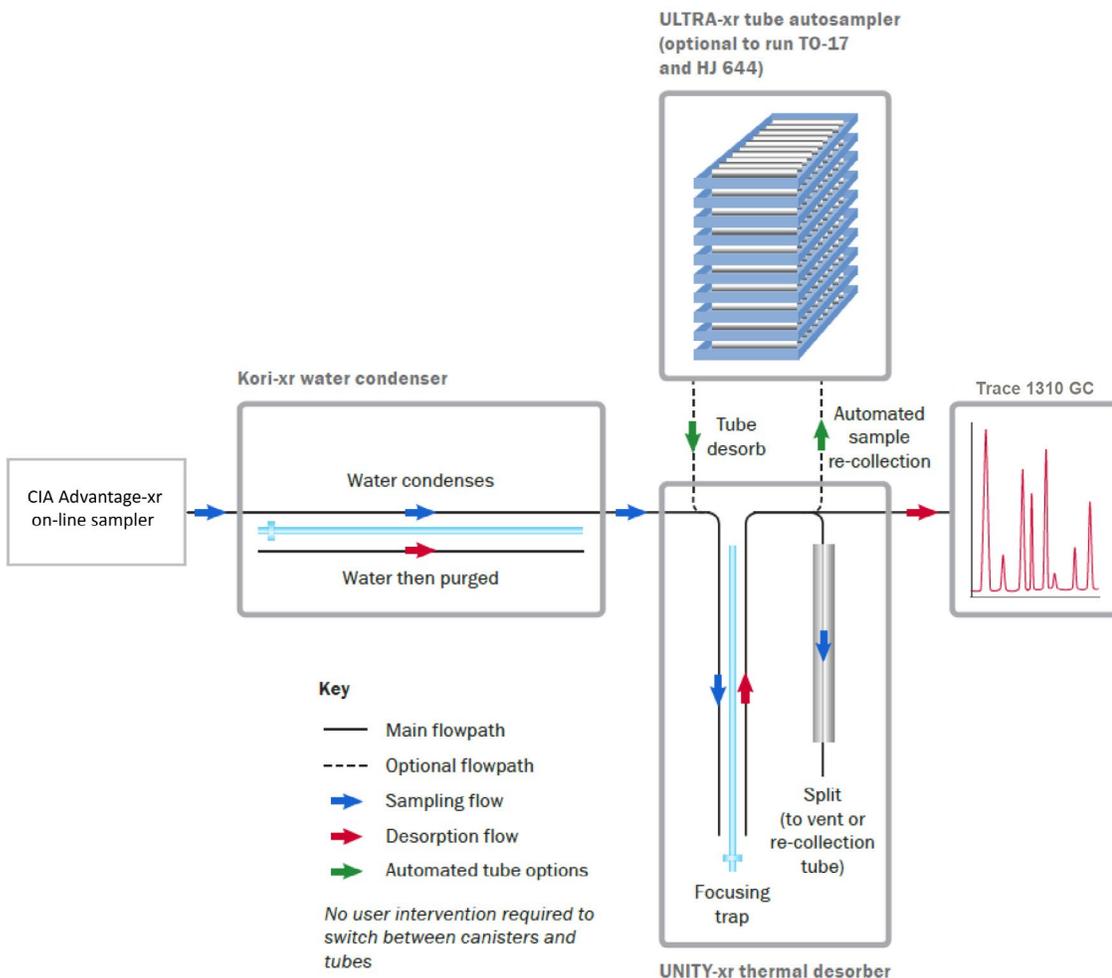


Figure 1. Overview of the analytical system used for this analysis showing the path of the sample from on-line sampler, to water condenser, to thermal desorber, to the GC-FID

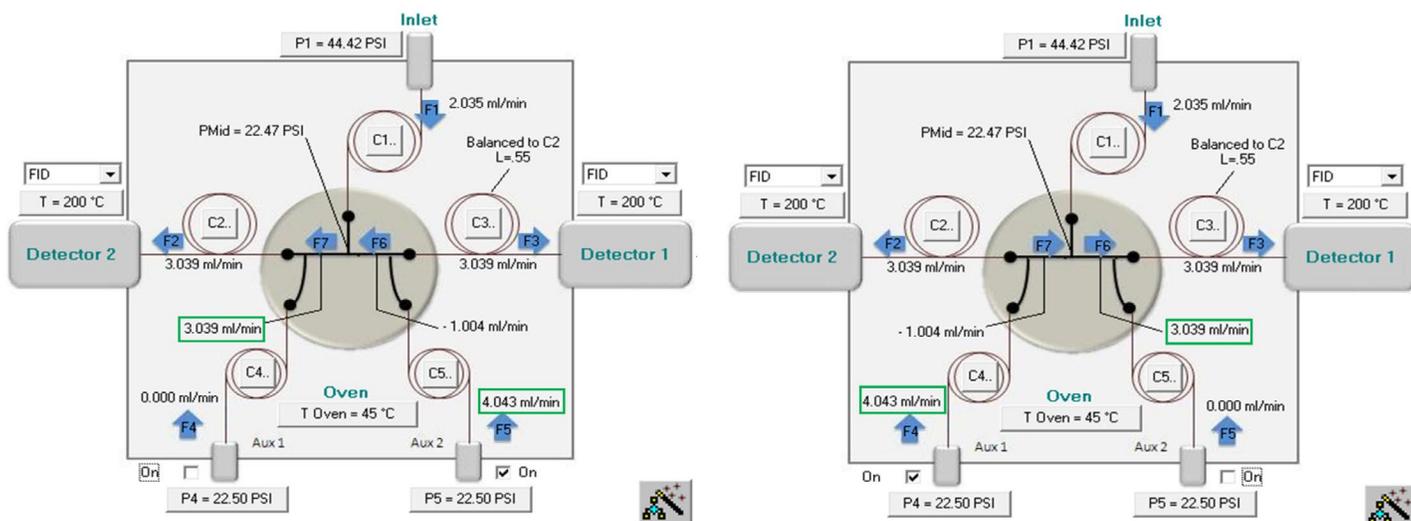


Figure 2. Dual-column dual-FID GC instrument operation shown in the Deans Switch wizard software with the flow through columns 1 and 2 on the left and through columns 1 and 3 on the right

The CIA *Advantage xr* instrument for on-line sampling allows air/gas to be sampled at a user controlled rate, with automatic interchange between four or fourteen sample channels allowing remote system calibration or validation.

Before entering the thermal desorber, samples pass through a Kori-*xr* device that efficiently removes humidity from the air stream. Water removal is vital in this application because retention of the ultra volatile C_2 compounds required the temperature of the focusing trap to be at $-30\text{ }^\circ\text{C}$. It has the added benefit of eliminating the risk of poor chromatography from water interference. The Kori-*xr* design means that oxygenates and monoterpenes can also be analyzed without loss. Note that the Kori-*xr* can be applied to bag, canister, and on-line samples as part of the Dry-Focus3™ approach, involving water removal, analyte focusing, and a trap dry-purge.

With excess water removed, samples pass into the UNITY-*xr* thermal desorber. This contains a narrow focusing trap, electrically cooled to $30\text{ }^\circ\text{C}$ for this application, and filled with separate beds of porous polymer and carbonized molecular sieve sorbents. This combination of sorbents of different strengths ensures that compounds over a wide volatility range are quantitatively trapped. Once the analytes are trapped, the flow of gas is reversed, and the trap is heated rapidly (up to $100\text{ }^\circ\text{C/s}$), to “backflush” the analytes onto the GC column.

Note that sampling through the entire CIA *Advantage*–Kori–UNITY-*xr* system is performed using an electronic mass flow controller and pump, located downstream of the focusing trap to avoid contamination. Once the trap has desorbed, the system re-equilibrates and begins collection of the next sample, while analysis of the previous sample continues allowing for a reduction in overall time between injections, this is termed overlap mode.

Separation was achieved using a Thermo Scientific™ TraceGOLD™ TG-1MS, $60\text{ m} \times 0.25\text{ mm} \times 1\text{ }\mu\text{m}$ film capillary column, P/N 26099-3080 (primary column) and an HP-PLOT AL/S, $50\text{ m} \times 0.32\text{ mm} \times 8\text{ }\mu\text{m}$ film capillary column (secondary column). A $0.55\text{ m} \times 0.1\text{ mm}$ deactivated fused silica column, included in the Deans Switch kit, is used as a restrictor. C_2 – C_6 compounds elute from the TraceGOLD TG-1MS column first and the Deans Switch directs them to column 2 for further separation, and the front FID detector (detector 2). Once 1-hexene has eluted from column 1, the Deans Switch directs the eluents via a fused silica restrictor (column 3) to the back FID detector (detector 1). Carrier gas continues to flow down column 2, so compounds continue to elute for the duration of the GC run, resulting in two chromatograms. The parameters are detailed in Tables 1, 2, 3, and 4. The optimization of the gas flows and the pressure settings during the method development was simplified by the use of the Deans Switch wizard software which represents a useful tool for simulating pressures and flows at different operating conditions, as shown in Figure 2.

Table 1. GC and FID parameters

TRACE 1310 parameters			
Column flow			
Primary column	2 mL/min		
Secondary column	3 mL/min		
Inlet module and mode	SSL, splitless mode		
Purge flow	5 mL/min		
Inlet pressure and mode	44.6 psi (constant pressure)		
Auxiliary flow program			
Auxiliary 1	Off at 0 min, 22.5 psi at 14.5 min		
Auxiliary 2	22.5 psi at 0 min, Off at 14.5 min		
Primary column (Column 1)	TraceGOLD TG-1MS, 60 m × 0.25 mm × 1 µm		
Secondary column (Column 2)	HP-AL/S PLOT, 50 m × 0.32 mm × 8 µm		
Restrictor (Column 3)	Fused deactivated silica (0.55 m × 0.1 µm)		
Oven temp. program	Rate (C/min)	Target temp. (C)	Hold time (min)
Temperature 1	-	45	13.00
Temperature 2	5	170	2.00
Temperature 3	10	200	10
Run time	53 min		
FID conditions			
Temperature	200 °C		
H ₂ flow	35 mL/min		
Air flow	350 mL/min		
Makeup	Off		
Acquisition rate	5 Hz		

Table 2. Canister sampling conditions

CIA Advantage-xr	
Sample purge flow	50 mL/min
Purge time	4 min
Sample flow	50 mL/min
Sample volume	50–600 mL
Post-sample purge flow	50 mL/min for 5 min

Table 3. Water removal conditions

Kori-xr	
Trap temperatures	-30 °C/300 °C

Table 4. Thermal desorption parameters

UNITY-xr	
Focusing trap	PAMS trap, Markes P/N U-T20PAM-2S
Flow path temperature	120 °C
Trap purge flow	50 mL/min
Trap purge time	1 min
Trap low temperature	-30 °C
Trap high temperature	280 °C
Trap hold time	6 min
Outlet split flow	10 mL/min

Data processing

Data were acquired and processed using the Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software. Integrated instrument control ensures full automation from instrument setup, to data acquisition, raw data processing, reporting, and storage. Simplified e-workflows deliver effective data management, ensuring ease of use and automated adherence to PAMS method requirements. Chromeleon CDS also offers the option to scale up the entire analytical process in the laboratory from a single workstation to an enterprise environment.

Results and discussion

Chromatography

Figure 3 shows an example chromatogram for the highest concentration multi-component standard (63.2 ppb benzene, 58.6 ppb propane). The use of a zero dead volume microfluidic connector and the precise pneumatic control preserved the column efficiency during Deans Switch operation. All 56 compounds show excellent peak shape and chromatographic resolution with asymmetry factors of between 0.99 and 1.1 for column 1, between 1.0 and 1.5 for column 2, and chromatographic peak resolution ≥ 1.4 for all peaks. Peak identification is reported in Tables 5 and 6. It is important to note that the sampling and analysis are achieved in a sample-to-sample cycle time of approximately 56 minutes, without the use of liquid cryogen, due to the excellent Trace 1310 chromatographic separation and the overlap capability of the Markes sampling system.

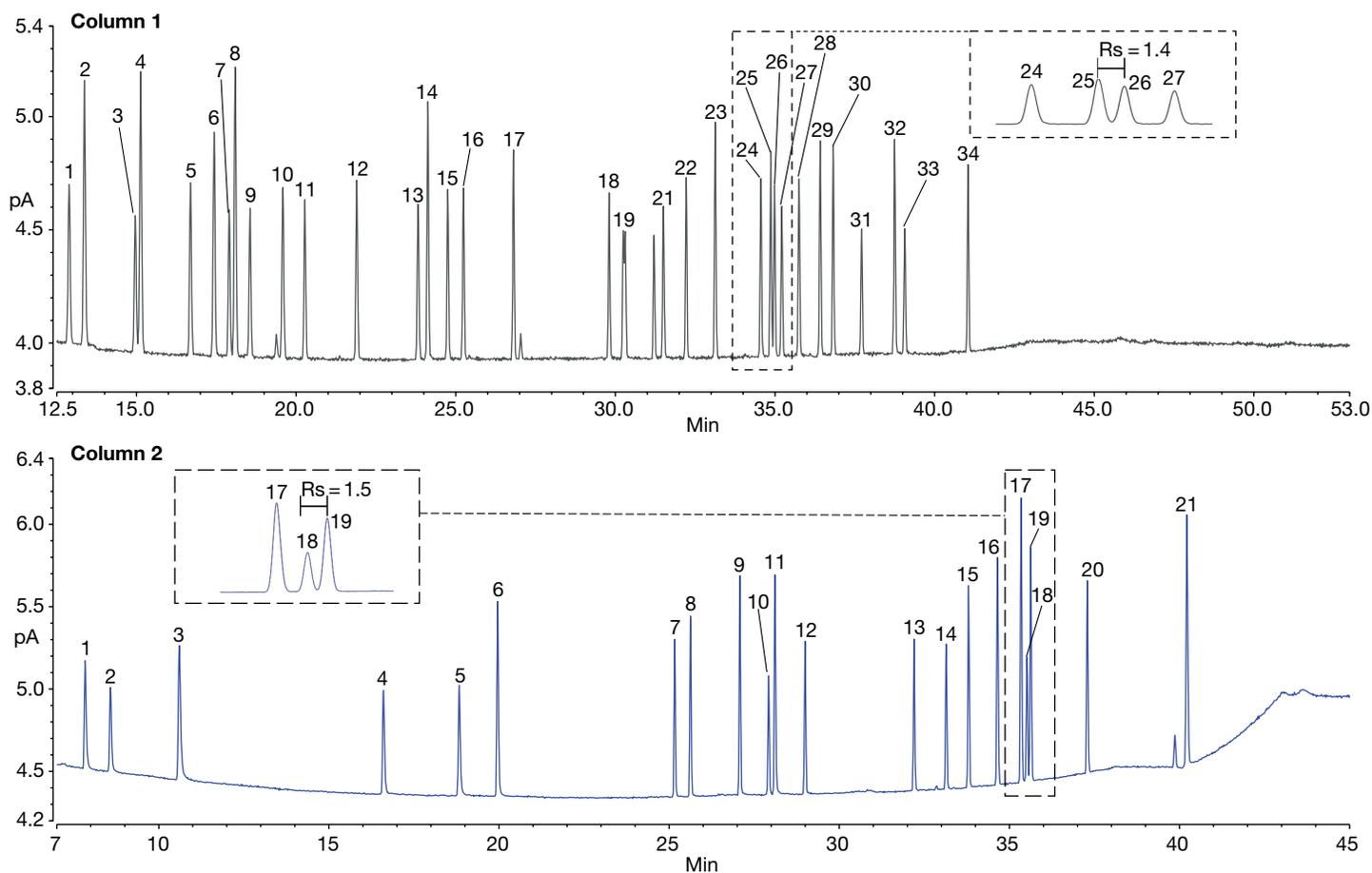


Figure 3. Overlay of the chromatograms obtained from column 1 (top) and column 2 (bottom) for the highest concentration multicomponent standard. For peak identification see Tables 5 and 6.

Table 5. Compound elution order on column 1 (TraceGOLD TG-1MS column, 60 m \times 0.25 mm \times 1 μ m)

Number	Compound	Number	Compound
1	<i>n</i> -hexane	18	Ethylbenzene
2	2-methyl-2-pentene	19	<i>m,p</i> -xylene
3	Methylcyclopentane	20	Styrene
4	2,4-dimethylpentane	21	<i>o</i> -xylene
5	Benzene	22	<i>n</i> -nonane
6	Cyclohexane	23	Isopropylbenzene
7	2-methylhexane	24	<i>n</i> -propylbenzene
8	2,3-dimethylpentane	25	<i>m</i> -ethyltoluene
9	3-methylhexane	26	<i>p</i> -ethyltoluene
10	2,2,4-trimethylpentane	27	1,3,5-trimethylbenzene
11	<i>n</i> -heptane	28	<i>o</i> -ethyltoluene
12	Methylcyclohexane	29	1,2,4-trimethylbenzene
13	2,3,4-trimethylpentane	30	<i>n</i> -decane
14	Toluene	31	1,2,3-trimethylbenzene
15	2-methylheptane	32	<i>m</i> -dimethylbenzene
16	3-methylheptane	33	<i>p</i> -diethylbenzene
17	<i>n</i> -octane	34	<i>n</i> -undecane

Table 6. Compound elution order on column 2 (HP-AL/S, 50 m \times 0.32 mm \times 8 μ m)

Number	Compound	Number	Compound
1	Ethane	12	<i>n</i> -pentane
2	Ethylene	13	<i>trans</i> -2-pentene
3	Propane	14	1-pentene
4	Propylene	15	<i>cis</i> -2-pentene
5	Isobutane	16	2,2-dimethylbutane
6	<i>n</i> -butane	17	2,3-dimethylbutane
7	<i>trans</i> -2-butene	18	2-methylpentane
8	1-butene	19	3-methylpentane
9	<i>cis</i> -2-butene	20	Isoprene
10	Cyclopentane	21	1-hexene
11	2-methylbutane		

Linearity

For accurate quantitation, linearity of the detector is essential. For this method, benzene was used to generate the calibration curve for the quantitation of the compounds eluting from column 1 (TraceGOLD TG-1MS), Figure 4a,

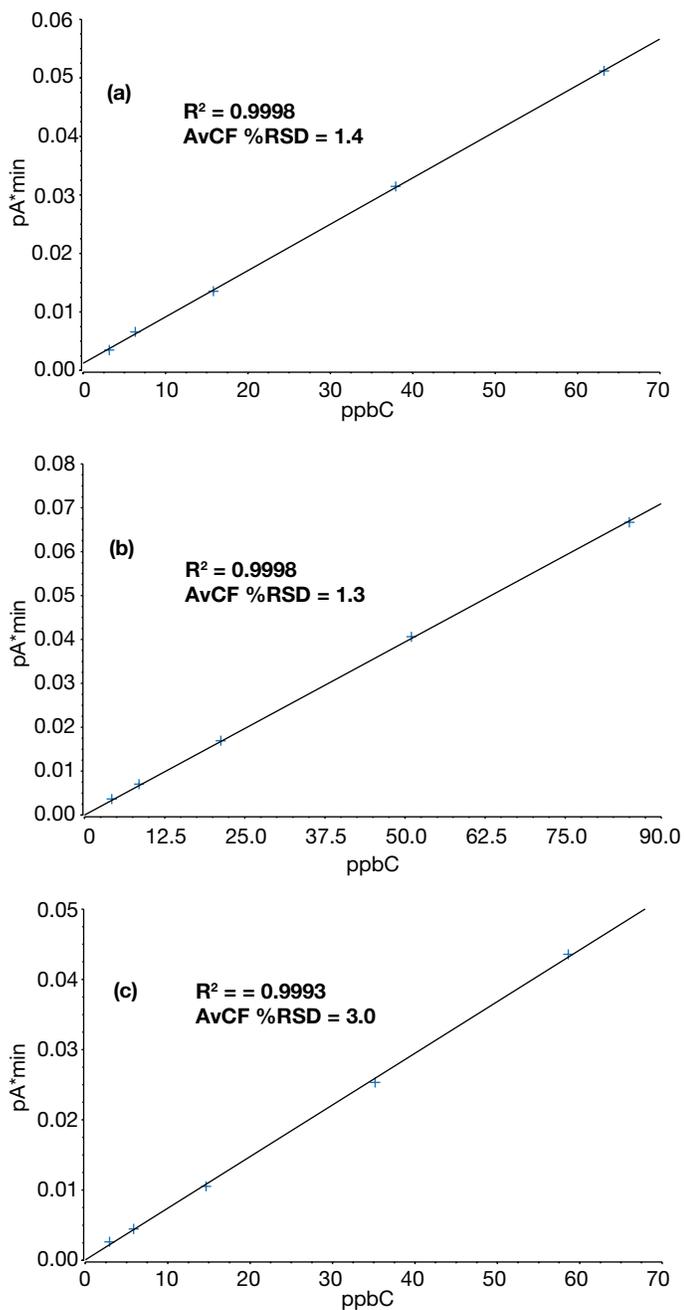


Figure 4. Linearity plots for benzene (a), propane (b), and undecane (c) showing R^2 values of 0.9998, 0.9998, and 0.9993 and AvCF %RSDs of 1.4, 1.3, and 3.0, respectively

and propane was used to generate the calibration curve for the quantitation of the compounds eluting from column 2 (PLOT) Figure 4b, as per the EPA PAMS recommendations⁷. The linearity of undecane, the heaviest standard in the mix, was also assessed to check for any bias or loss in the flow path or focusing trap, Figure 4c. The curves produced from taking 10 mL, 20 mL, 50 mL, 120 mL, and 200 mL of the multi-component standard all have excellent linearity with R^2 values >0.999 and average calibration factor (AvCF) %RSDs of <3 for all three compounds assessed.

By combining the multicomponent standard and the higher level 3000 ppb propane standard, an 8-point calibration curve ranging from 4.25 ppb to 6000 ppb was produced to verify consistency across the calibration range (Figure 5). An R^2 value of 0.9998, RSD of average calibration factor (AvCF) of 2.7%, and a relative response factor (RRF) RSD of 6.9% was obtained. The RRF RSD of the data was observed at $<30\%$, which is acceptable for most EPA air toxics methods. The Thermo Scientific™ Instant Connect FIDs provided excellent sensitivity over a wide dynamic range. Instant Connect injector and detector modules can be swapped out and installed in two minutes without the need for special training and tools. This unique capability can dramatically reduce downtime and allow unskilled technicians to easily service instrumentation with minimal guidance.

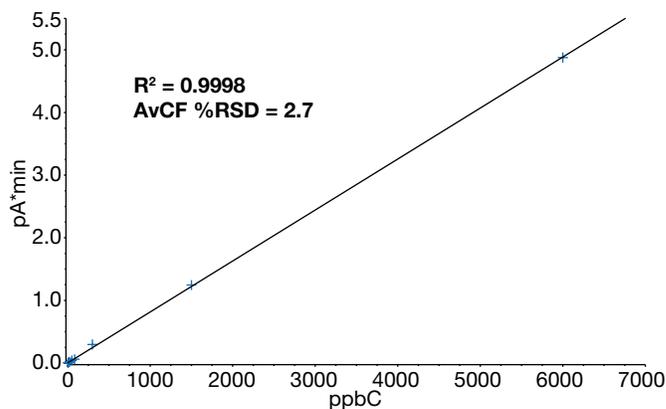


Figure 5. Propane calibration curve from 4.25 ppb to 6000 ppb showing an R^2 value of 0.9998 and an AvCF %RSD 2.7

Carryover testing

It is important that the instrumentation used for analyzing trace level samples has minimal carryover from previous samples. This is important especially when previous samples are at higher concentrations than those that follow. High levels of carryover affect recovery results and require additional blanks to be built into analytical sequences to prevent any compounds interfering with subsequent samples.

To assess the carryover of the system, 10 mL of a standard containing 11 components at 25,000 ppb was run followed by a system blank. Carryover in the system blank was assessed as a percentage of the area response of high level standard. No carryover was detected for the compounds eluting from column 1, TraceGOLD TG-1MS, while carryover of $\leq 0.3\%$ was obtained for all compounds eluting from column 2, HP-PLOT AL/S (Table 7).

Repeatability

A Tedlar bag containing VOC exhaust compounds sampled from a testing chamber was analyzed three times over two different days. The results can be seen in Figure 6 and Table 8. The results from both columns show good repeatability across the three injections with RSD of peak area $< 10\%$ for all compounds. The microfluidic Deans Switch dual-column configuration employed in this work

Table 7. Results of carryover testing demonstrating carryover of $\leq 0.26\%$ for all compounds

Compound	Peak area, 25,000 ppb standard (pA*min)	Peak area, system blank (pA*min)	Carryover
Ethylene	2.2844	0.0032	0.14%
Propane	2.5033	0.0066	0.26%
<i>n</i> -Butane	2.6608	0.0047	0.18%
2-methylpropene	2.5351	0.0041	0.16%
2-methylbutane	2.3648	0.0026	0.11%
<i>n</i> -hexane	2.5614	None detected	None detected
Benzene	2.425	None detected	None detected
Toluene	2.1522	None detected	None detected
<i>n</i> -Octane	2.184	None detected	None detected
<i>p</i> -Xylene	1.8562	None detected	None detected
<i>n</i> -Decane	2.0508	None detected	None detected

provides confident identification and quantitation by utilizing the optimum separation for the various compounds with reliable, leak-free switching between columns. The electronic carrier gas control between the CIA *Advantage-xr* and the GC, alongside the efficient water removal of the Kori-xr, helps to stabilize retention times on the PLOT column. This means that data processing can be fully automated with less time spent manually adjusting peak integrations and retention times.

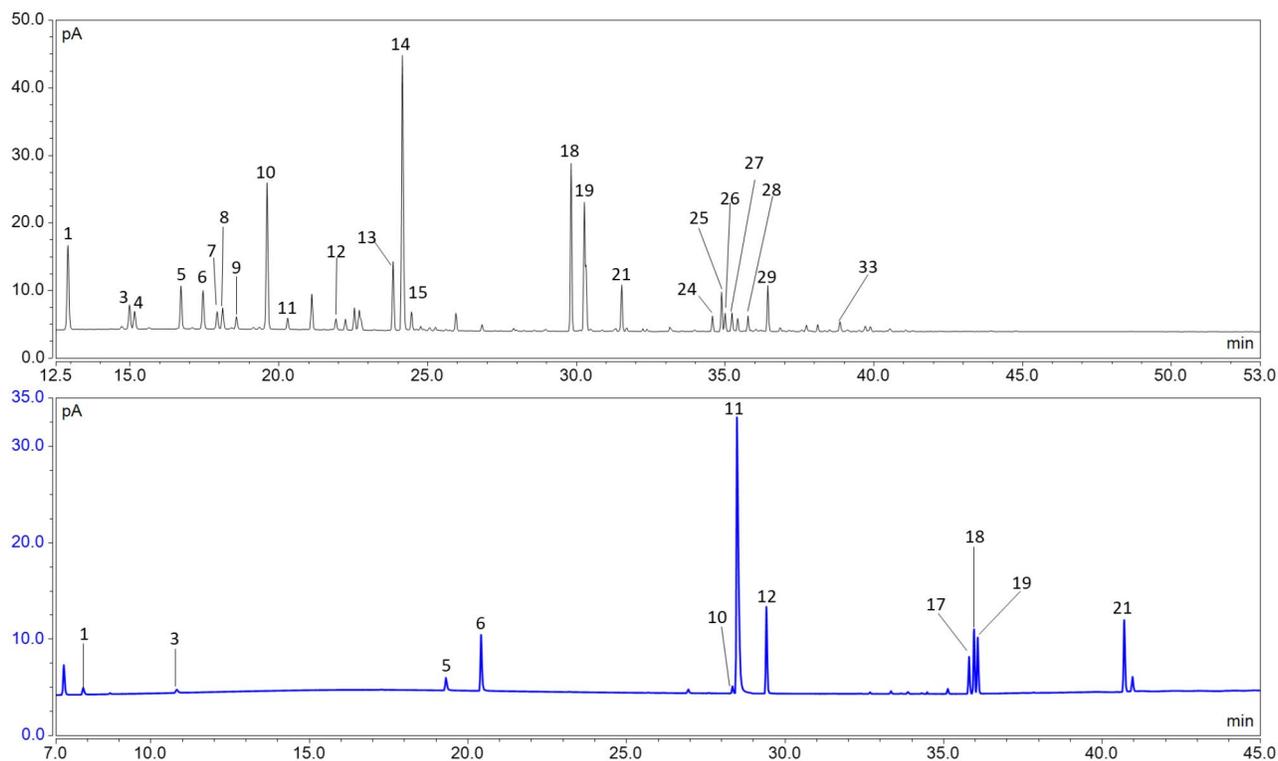


Figure 6. Example VOC exhaust sample FID chromatogram, column 1, TraceGOLD TG-1MS (top), column 2, PLOT (bottom). Peaks are labeled according to Tables 5 and 6.

Table 8. Repeatability of n=3 injections of VOC exhaust sample displaying compound name and %RSD area

Column 1			
Compound	%RSD	Compound	%RSD
<i>n</i> -hexane	0.7	Ethylbenzene	0.8
2-methyl-2-pentene	1.9	<i>m,p</i> -xylene	0.7
Methylcyclopentane	1.3	Styrene	1.8
2,4-dimethylpentane	0.6	<i>o</i> -xylene	5.1
Benzene	0.8	<i>n</i> -nonane	0.9
Cyclohexane	0.7	Isopropylbenzene	0.7
2-methylhexane	1.6	<i>n</i> -propylbenzene	0.5
2,3-dimethylpentane	1.2	<i>m</i> -ethyltoluene	0.8
3-methylhexane	1.3	<i>p</i> -ethyltoluene	1.5
2,2,4-trimethylpentane	0.4	1,3,5-trimethylbenzene	2.1
<i>n</i> -heptane	2.7	<i>o</i> -ethyltoluene	1.1
Methylcyclohexane	0.9	1,2,4-trimethylbenzene	0.8
2,3,4-trimethylpentane	0.3	<i>n</i> -decane	1.6
Toluene	0.5	1,2,3-trimethylbenzene	0.6
2-methylheptane	3.4	<i>m</i> -dimethylbenzene	0.5
3-methylheptane	5.8	<i>p</i> -diethylbenzene	4.0
<i>n</i> -octane	0.6	<i>n</i> -undecane	8.1

Column 2			
Compound	%RSD	Compound	%RSD
Ethane	0.6	<i>n</i> -pentane	0.5
Ethylene	2.8	<i>trans</i> -2-pentene	1.7
Propane	2.8	1-pentene	2.0
Propylene	6.5	<i>cis</i> -2-pentene	5.1
Isobutane	0.4	2,2-dimethylbutane	0.9
<i>n</i> -butane	0.9	2,3-dimethylbutane	0.9
<i>trans</i> -2-butene	5.5	2-methylpentane	3.9
1-butene	5.1	3-methylpentane	3.9
<i>cis</i> -2-butene	5.0	Isoprene	7.4
Cyclopentane	0.8	1-hexene	0.7
2-methylbutane	0.6		

Conclusion

Taken together, the results of this application demonstrate that the cryogen-free TD combined with a dual-column, dual-FID GC configuration offers an advanced solution that meets PAMS method requirements for routine monitoring of VOCs from vehicle exhaust at ppb concentrations. The combined Markes/Thermo Scientific TD GC-Dual FID system delivers outstanding results as demonstrated by:

- Excellent chromatographic separation obtained on the TraceGOLD TG-1MS column and the PLOT column in combination with the microfluidic Deans Switch device allow for a 53-minute GC runtime for full C₂-C₁₁ analysis.
- Overlapping capability of the Markes sampler and the fast oven cooling of the TRACE 1310 GC to give an approximately 56-minute cycle time between injections.
- Robust and proven electrical trap cooling that eliminates the requirement for liquid cryogen.
- Efficient water removal and precise pressure control throughout the system stabilize the VOC retention times on the PLOT column, meaning less time spent on manual data manipulation is required, saving time and speeding up analysis reports.
- Analysis of a wide range of VOCs with excellent linearities thanks to the linear dynamic range of the Instant Connect FID. (R² > 0.999, AvCF %RSD < 3) provides confidence in the measured results.
- A dedicated software tool to greatly simplify the Deans Switch method development for the optimal timing and pressure settings.
- Chromeleon CDS software that automates instrument setup and customizes data processing and reporting for PAMS site workflow requirements allowing technician level operation and control.

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