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Analysis of Volatile Organic Compounds in Air by Online TD-GC

Introduction

Volatile Organic Compounds (VOCs) have been identified as a major source of air pollution, and as such, have been regulated as a cause of both primary and secondary pollution, such as photochemistry smog. The U.S. Environmental Protection Agency (U.S. EPA) regulates 189 hazardous air pollutants under the Clean Air Act (CAA) of 1990, 51% of which are VOCs. The CAA offers further regulation and guidance for the monitoring of VOCs and ozone pollution in ambient air with a list of 57 ozone-precursor target analytes monitored under U.S. EPA's *Technical Assistance Document for Sampling and Analysis of Ozone Precursors,* EPA/600-R-98/161 (1998)[1], as well as the requirement of states to establish Photochemical Assessment Monitoring Stations (PAMS).

In 2017, U.S. EPA released guidance[2] to all PAMS required sites strongly suggesting the collection of hourly speciated VOC measurements, with analysis of 27 primary and 37 optional compounds by gas chromatography.[3] In the same year, China also initiated regulations requiring monitoring of the 57 VOC compounds included in the original PAMS guidance, as well as 13 aldehydes and ketones, and 47 halohydrocarbons and oxygen containing VOCs.

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The PerkinElmer TurboMatrix™ 300 TD is an effective and efficient thermal desorber, developed for automated sampling and concentrating of hydrocarbons in the C2 – C12 range. When combined with a PerkinElmer Clarus® GC, ambient air samples can be analyzed with ease and accuracy for VOC contamination in accordance with regulatory requirements. The PerkinElmer system is the gold standard for ozone precursor analysis, with high repeatability and low quantitation limits.

This paper details an application for VOC monitoring with an extended target compound list utilizing a PerkinElmer TurboMatrix online 300 TD and PerkinElmer Clarus 580 GC. The application note demonstrates results with good repeatability, linearity and detection limits.

Experimental

Instrumentation

A PerkinElmer Clarus 580 dual GC/FID with a TurboMatrix online 300 TD was used to perform this experiment, with the conditions presented in Table 1. A BP-1 column (50 m x 0.22 mm x 1.0 µm) was used as the primary column, and was directly connected with the Thermal Desorption transfer line. A classic Alumina PLOT column was used for separation of the lighter components in the sample. Heavier components were separated by switching to an FID through a fused silica restrictor tubing and a D-Swafer™ with a heartcutting technique. A schematic diagram of the system is presented in Figure 1.

An enhanced air monitoring trap was used in this study to concentrate the target compounds. As discussed in a prior application note describing ambient air monitoring[4], a small guard zone with the weaker adsorbent is positioned ahead of the two stronger adsorbents to enhance precision and recovery of heavier compounds.

Gas Standards

Calibration gas mixtures, PAMS and TO-15, were purchased from Linde Gas and diluted by a dynamic diluter (Besser Technology).

Results and Discussion

The chromatograms of calibration standards for low and high carbon channels are shown in Figures 2 and 3, with good peak shapes and baseline resolution of the target compounds. The heartcut time was 9.8 minutes, thus the compounds that eluted earlier than cis-1,2-Dichloroethene were switched to the PLOT column for further separation, and other compounds went through the restrictor tubing for detection. Tables 2-5 summarize the results for retention time (RT), method dynamic range, and signal to noise (S/N) at the reporting limit. The determination coefficients (r^2) of all compounds were over 0.996, showing the reliability of the analysis in the range of 1-40 ppbc. The results for retention time stability, peak area precision and S/N were measured by analyzing six replicates at the concentration specified.

Table 1. Analytical parameters.

| Thermal Desorber Parameters		GC Parameters	
Sampling Time	40 min	Initial Oven Temp	45 °C
Pump Flow	15 mL/min	Oven Hold	15.0 min
Mode	Online	Ramp	5 °C/min
Concentrator Trap Low	-30 °C	2nd Oven Temp	170 °C
Concentrator Trap High	320 °C	Oven Hold	0 min
Concentrator Trap Hold	6 min	Ramp	15 °C/min
Concentrator Trap Heating Rate	40 °C/min	3rd Oven Temp	200 °C
Valve Temp	180 °C	Oven Hold	6.0 min
Transfer Line Temp	220 °C	FPD Temp	200 °C
Column Pressure	38.5 psi	Air Flow	400 mL/min
Inlet Split	OFF	H₂ Flow	40 mL/min
Outlet Split	4 mL/min	Heartcut Time	9.8 min
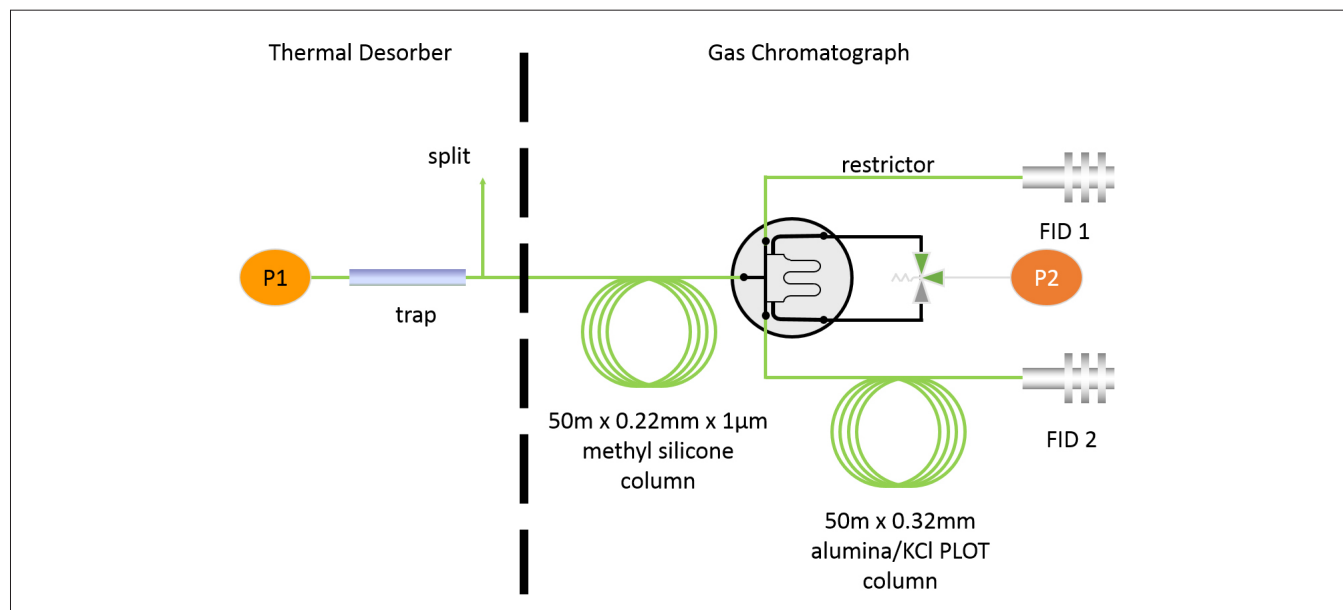
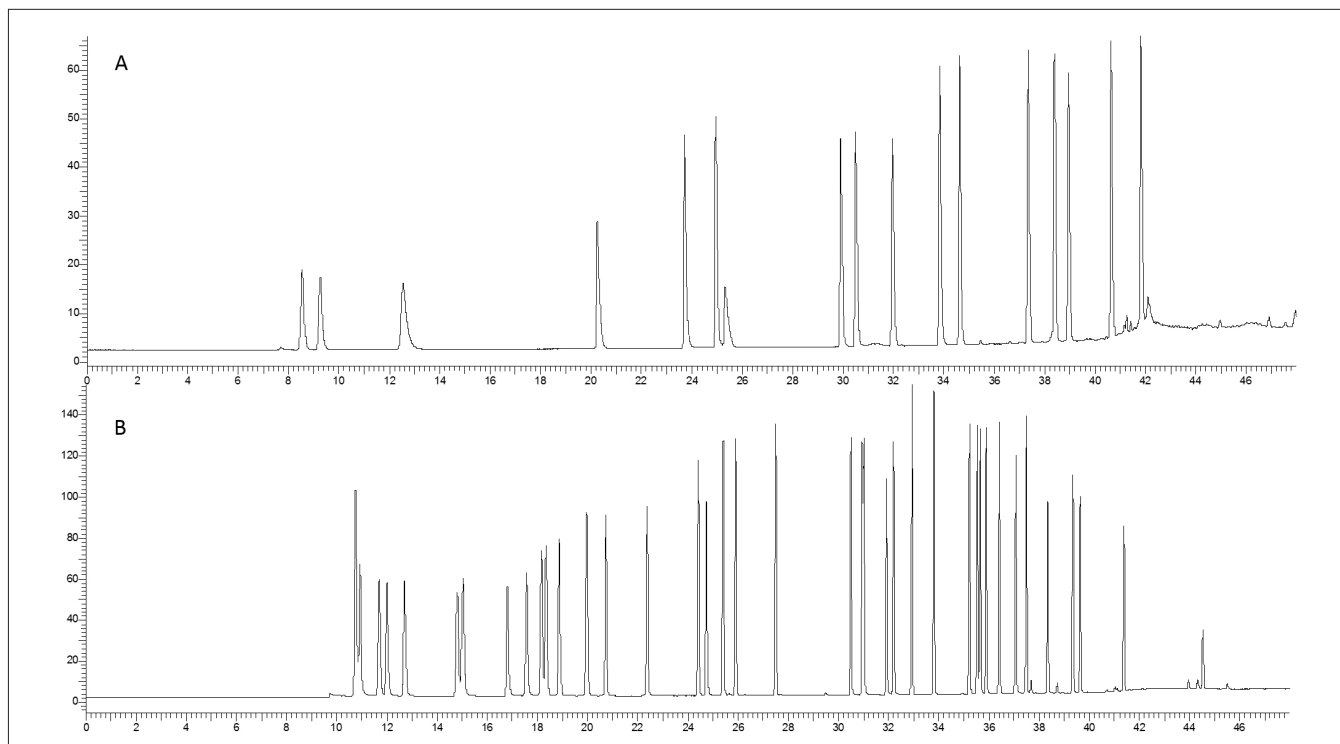*Figure 1.* Schematic diagram of the online TD-GC system.

Figure 2. The chromatograms of PAMS calibration standards for low (A) and high (B) carbon channels at 50 ppbc.

Table 2. Results for retention time (RT), method dynamic range and signal to noise (S/N) at the reporting limit for low carbon channel for AMS components.

RT	Compound Name	CAS	Channel	Linearity (1 – 40 ppbc)	Reporting Limit	Precision (RSD%) at 5 ppbc	
				r^2	SN at 0.5 ppbc	RT	Area
8.53	Ethane	74-84-0	Low	0.9998	7.25	0.19	2.83
9.26	Ethylene	74-85-1	Low	0.9962	6.53	0.91	1.93
12.55	Propane	74-98-6	Low	0.9987	2.01	1.17	3.07
20.25	Proplyene	115-07-1	Low	0.9983	4.91	2.23	2.44
23.71	Isobutane	75-28-5	Low	0.9993	8.86	1.48	3.73
24.96	Butane	106-97-8	Low	0.999	20.85	1.41	3.70
25.32	Acetylene	74-86-2	Low	0.9961	5.51	2.24	3.59
29.90	t-2-Butene	107-01-7	Low	0.9986	18.87	1.24	3.45
30.50	1-Butene	106-98-9	Low	0.9995	19.45	1.25	8.62
31.95	Cis-2-Butene	590-18-1	Low	0.9988	18.78	1.13	3.80
33.83	Cyclopentane	287-92-3	Low	0.9982	25.32	0.92	3.80
33.83	Iso-Pentane	78-78-4	Low	0.9982	25.32	0.92	3.80
34.62	n-Pentane	109-66-0	Low	0.9984	12.13	0.90	3.66
37.34	t-2-Pentene	646-04-8	Low	0.9983	26.52	0.89	3.74
38.39	1-Pentene	109-67-1	Low	0.9981	26.08	0.94	3.38
38.95	Cis-pentene	627-20-3	Low	0.9982	24.31	0.89	3.65
40.63	2,2-Dimethylbutane	75-83-2	Low	0.9981	26.78	0.78	3.92
41.81	Isoprene	78-79-5	Low	0.9992	26.82	0.75	3.89

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Table 3. Results for retention time (RT), method dynamic range and signal to noise (S/N) at the reporting limit for high carbon channel for PAMS components.

| RT	Compound Name	CAS	Channel	Linearity (1 – 40 ppbc)	Reporting Limit	Precision (RSD%) at 5 ppbc	
				r²	SN at 0.25 ppbc	RT	Area
10.75	2,3-Dimethylbutane	79-29-8	High	0.9993	23.68	0.04	1.89
10.93	2-Methylpentane	107-83-5	High	0.9998	16.24	0.04	4.55
11.69	3-Methylpentane	96-14-0	High	0.9995	14.27	0.05	1.06
12.00	1-Hexene	592-41-6	High	0.9994	12.85	0.04	1.73
12.71	n-Hexane	110-54-3	High	0.9992	12.50	0.04	0.69
14.80	Methylcyclopentane	96-37-7	High	0.9995	12.84	0.05	1.26
15.03	2,4-Dimethylpentane	108-08-7	High	0.9998	15.01	0.04	0.79
16.81	Benzene	71-43-2	High	0.9996	21.27	0.03	2.57
17.57	Cyclohexane	110-82-7	High	0.9996	16.45	0.03	1.37
18.16	2-Methylhexane	591-76-4	High	0.9998	18.85	0.03	0.69
18.35	2,3-Dimethylpentane	565-59-3	High	0.9996	18.43	0.03	0.81
18.87	3-Methylhexane	589-34-4	High	0.9996	21.78	0.03	0.53
19.97	2,2,4-Trimethylpentane	540-84-1	High	0.9995	22.61	0.02	0.96
20.73	n-Heptane	142-82-5	High	0.9994	24.43	0.02	0.54
22.37	Methylcyclohexane	108-87-2	High	0.9994	17.49	0.03	0.72
24.41	2,3,4-Trimethylpentane	565-75-3	High	0.9992	37.38	0.02	0.38
24.74	Toluene	108-88-3	High	0.9994	30.99	0.02	1.08
25.41	2-Methylheptane	592-27-8	High	0.9994	56.37	0.02	0.28
25.91	3-Methylheptane	589-81-1	High	0.9991	51.42	0.02	0.26
27.50	n-Octane	111-65-9	High	0.9992	28.05	0.02	0.65
30.50	Ethylbenzene	100-41-4	High	0.9996	43.13	0.02	0.25
30.95	p-Xylene	108-38-3	High	0.9993	34.00	0.02	0.65
31.01	m-Xylene	106-42-3	High	0.9998	32.11	0.01	0.52
31.92	Styrene	100-42-5	High	0.9998	14.77	0.01	1.02
32.20	o-Xylene	95-47-6	High	0.9999	33.24	0.01	1.76
32.93	Nonane	111-84-2	High	0.9993	49.85	0.02	0.41
33.81	Isopropylbenzene	98-82-8	High	0.9995	32.25	0.02	0.11
35.23	n-Propylbenzene	103-65-1	High	0.9994	32.38	0.02	0.51
35.54	m-Ethyltoluene	620-14-4	High	0.9993	28.46	0.01	0.47
35.66	p-Ethyltoluene	622-96-8	High	0.9995	25.78	0.01	0.36
35.89	1,3,5-Trimethylbenzene	108-67-8	High	0.9995	29.14	0.01	0.53
36.41	o-Ethyltoluene	611-14-3	High	0.9995	22.80	0.01	0.68
37.07	1,2,4-Trimethylbenzene	95-63-6	High	0.9993	14.81	0.01	1.99
37.49	n-Decane	124-18-5	High	0.9994	25.91	0.01	0.61
38.34	1,2,3-Trimethylbenzene	526-73-8	High	0.9997	12.88	0.01	0.74
39.35	m-Diethylbenzene	141-93-5	High	0.9993	20.38	0.01	1.12
39.64	p-Diethylbenzene	105-05-5	High	0.9992	16.77	0.00	1.50
41.38	n-Undecane	1120-21-4	High	0.9996	12.69	0.00	1.72
44.53	n-Dodecane	112-40-3	High	0.9995	7.70	0.01	2.56
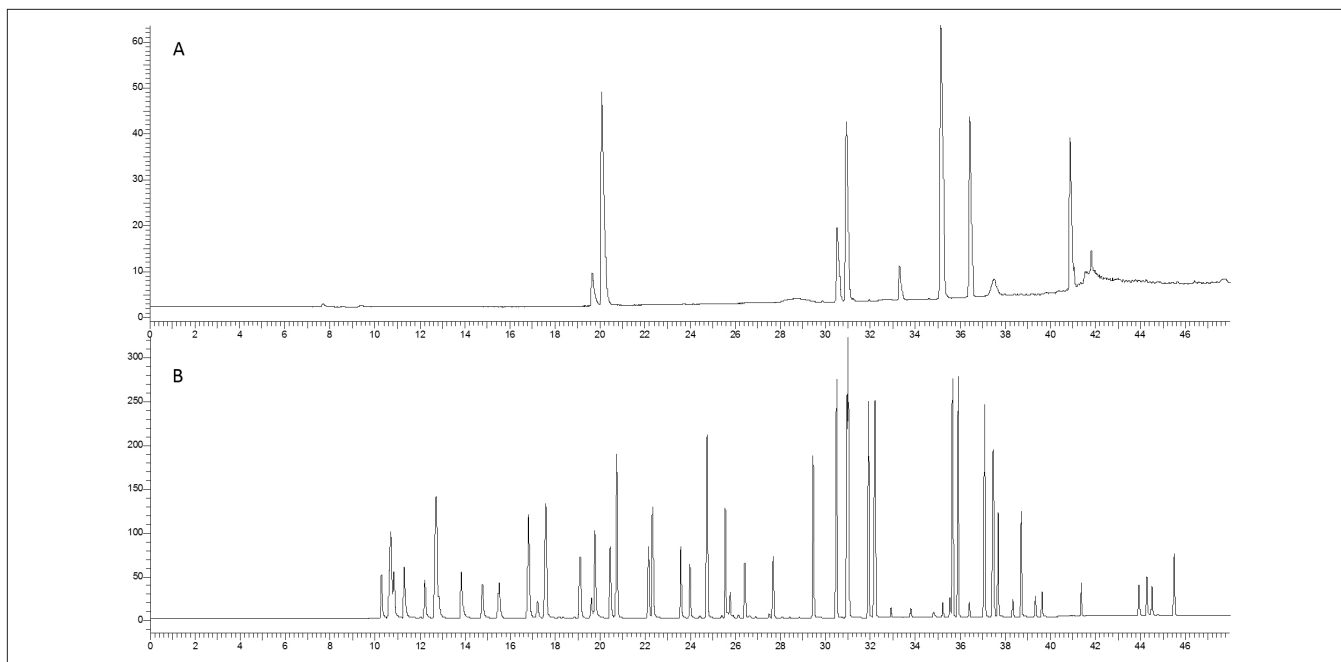
Figure 3. The chromatograms of TO-15 calibration standards for low (A) and high (B) carbon channels at 100 ppbc.

Summary

In this study, various VOCs were collected, concentrated and desorbed utilizing a TurboMatrix 300 TD with an online air sampling accessory, followed by analysis on a Clarus 580 GC equipped with a D-Swafer. The enhanced air monitoring trap provides outstanding precision and recovery of heavier compounds. The data presented shows the excellent results for both PAMS components and those in standard TO-15 target compound lists, thus demonstrating the expanded scope of applications for this system.

References

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