

Gas Chromatography

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Improvements to Ambient Air Monitoring (U.S. EPA PAMS) Using a Clarus 690 Gas Chromatograph

Introduction

In the United States, the Clean Air Act of 1970 gave the U.S. Environmental Protection Agency (EPA) responsibility for maintaining clean air for health and welfare. Six parameters are measured routinely in ambient air: SO_x, NO_x, PM₁₀ (particulate matter less than 10 microns), Pb, CO

and ozone. In the 1990 Clean Air Act Amendments, Title 1 expanded the measurements in air to include volatile organic compounds (VOCs) that contribute to the formation of ground-level ozone. These parameters are measured in urban areas that do not meet the attainment goals for ozone. These measurements are implemented through a program known as Photochemical Assessment Monitoring Stations (PAMS).

This program has been in place in the U.S. for a number of years, and in 2008 the National Ambient Air Quality Standards (NAAQS) for Ground-Level Ozone was reduced to 0.075 ppm for an 8-hour period. The U.S. EPA predicts that a large number of counties will violate the 2008 standard¹.

Similar recommendations have also been made in Europe. Following the 1992 Ozone Directive and United Nations Economic Commission for Europe's protocol on controlling VOC emissions, a European ozone precursor priority list was established by Kotzias et al, and subsequently modified by the EC 2002/3/CE directive².

The analysis of C2 to C12 volatile organic ozone-precursor compounds can present a technical challenge to the analytical chemist. These compounds are present in low concentrations in the atmosphere meaning that a pre-concentration step of the sample is required before analysis by gas chromatography (GC). While the samples can be collected in the field and returned to the laboratory, on-line analysis in the field allows reduced data turnaround time, minimizes sample collection hardware and permits the presence or absence of VOCs to be correlated with meteorological data. In the field, low-molecular-weight C₂ VOCs can be trapped on solid adsorbents if those adsorbents are cryogenically cooled.

The focus of this discussion is to present enhancements to the chromatographic separation, to the recoveries of target components and to the ease of use of Dean Switching.

Why These Enhancements?

A few years ago, the U.S. EPA became increasingly concerned with a significant number of real world non-target compounds that were co-eluting with target compounds thus reporting ozone precursor compounds at erroneously higher levels. At a recent U.S. EPA evaluation, GC systems were challenged with the more demanding Texas Commission of Environmental Quality (TCEQ) standard with 102 analytes. This was indeed challenging for the classic BP-1 column and as such alternative columns needed to be investigated. The TCEQ mix was used to identify a column with better separation ability and the reduced number of co-elutions for real world samples. This application note is focused on using a PerkinElmer Elite-624Sil MS column as a replacement for the current BP-1 methyl silicone primary column. The 624 column has a larger ID than the BP-1 (0.25 vs 0.22) and is also longer (60m vs 50m). Both columns use very

similar parameters making the column swap relatively straight forward. The use of a 624 vs BP-1 was acceptable and successful as the primary column, using the classic Alumina PLOT column for the lighter components, at a multi-month field evaluation monitored by the EPA in 2015. The classic Dean Switch is constructed of glass-lined Tee and fitting and while reliable, it does require skill in assembling. Several years ago, PerkinElmer introduced the Swafer™ system (Figures 1 and 2) that has proven itself reliable over the years as a modern replacement for the classic Dean Switch. The Swafer is a compact inert disk that provides Dean Switch functionality such as bleed restrictor, column and gas connections without the need for additional fittings and their associated potential leaks. To minimize leaks even further, the Swafer utilizes soft metal ferrules that securely attaches to the column and will not leak, even with repeated aggressive temperature ramps.

This system was tested using both the classic Air Monitoring trap (part number M0412836) and a newly developed Enhanced Air Monitoring trap. The classic Air Monitoring trap worked well up to the highest target, dodecane, but if higher molecular weight compounds are present in the sample this can appear as broad ghost peaks in future chromatograms. The investigative Enhanced Air Monitoring trap was designed using PerkinElmer's patented technologies and proven through field use in a related air monitoring analysis. This new trap was specifically designed to virtually eliminate higher molecular compounds from contaminating the trap, and to enhance recoveries of higher boiling compounds.



Figure 1. Swafer Micro-channel Flow Technology.

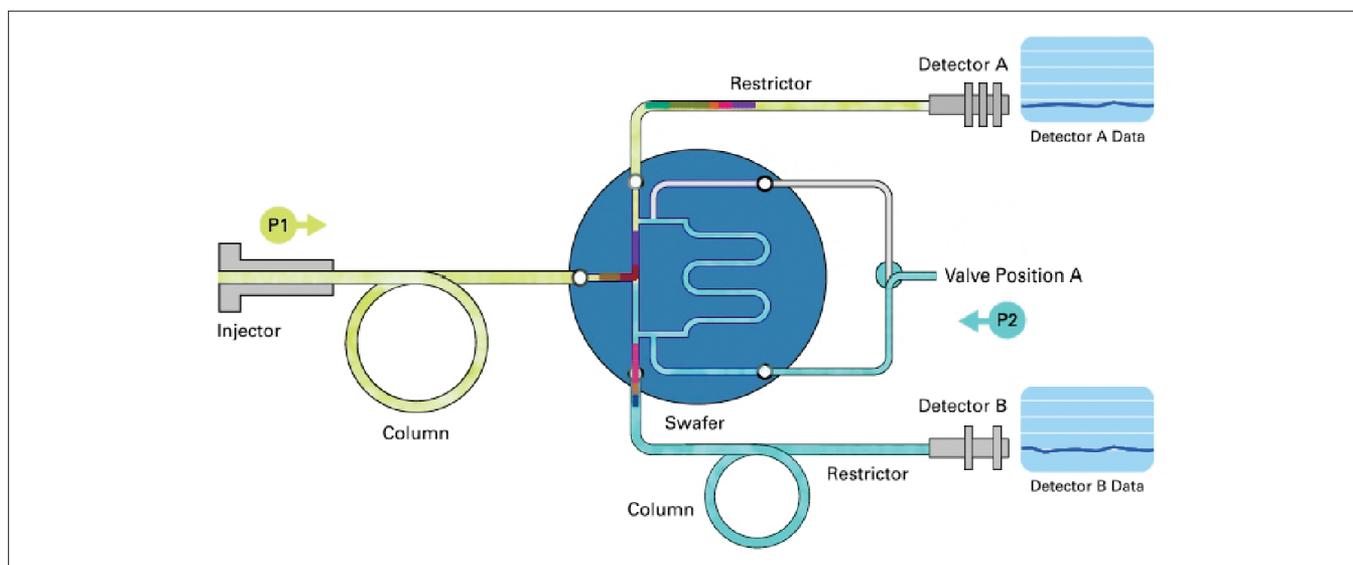


Figure 2. D-Swafer in a Dean Switch configuration.

System Requirements

Table 1 lists the ozone-precursor target analytes specified in the U.S. EPA "Technical Assistance Document for Sampling and Analysis of Ozone Precursors," EPA/600-R-98/161, September 1998, issued by National Exposure Research Laboratory, Research Triangle Park, NC 27711, USA.

This document is available from the U.S. EPA web site at³:

<http://www.epa.gov/ttn/amt/cfiles/ambient/pams/newtad.pdf>.

These target compounds vary tremendously in their volatilities and therefore place demands on their collection and subsequent gas chromatography. Furthermore, the method requires that each sample must be collected over a period of time not less than 40 minutes in each hour and be analyzed at hourly intervals. For unsupervised operation, this means that each analysis must take less than one hour in total. The European Union measures a smaller number of compounds. These are listed in Table 2. Although the European Union list is smaller than the U.S. EPA list, it also includes the requirement to measure 1,3-butadiene which is not in the U.S. list of analytes.

In 2017, the U.S. EPA revised the original PAMS components to 27 priority compounds and 37 additional optional compounds as found in Table 3⁴.

Table 1. Original U.S. EPA ozone precursor target analytes.

Ethylene	2,3-Dimethylbutane	n-Octane
Acetylene	2-Methylpentane	Ethylbenzene
Ethane	3-Methylpentane	m&p-Xylene
Propylene	n-Hexane	Styrene
Propane	Methylcyclopentane	o-Xylene
Isobutane	2,4-Dimethylpentane	Nonane
1-Butene	Benzene	Isopropylbenzene
n-Butane	Cyclohexane	n-Propylbenzene
Trans-2-Butene	2-Methylhexane	m-Ethyltoluene
Cis-2-Butene	2,3-Dimethylpentane	p-Ethyltoluene
Isopentane	3-Methylhexane	1,3,5-Trimethylbenzene
1-Pentene	2,2,4-Trimethylpentane	o-Ethyltoluene
n-Pentane	n-Heptane	1,2,4-Trimethylbenzene
Isoprene	Methylcyclohexane	n-Decane
Trans-2-Pentene	2,3,4-Trimethylpentane	1,2,3-Trimethylbenzene
Cis-2-Pentene	Toluene	m-Diethylbenzene
2-2-Dimethylbutane	2-Methylheptane	p-Diethylbenzene
Cyclopentane	3-Methylheptane	n-Undecane

Table 2. European Union Ozone precursor analytes.

Ethylene	Isopentane	n-Heptane
Acetylene	1-Pentene	Toluene
Ethane	n-Pentane	n-Octane
Propylene	Isoprene	Ethylbenzene
Propane	Trans-2-Pentene	m&p-Xylene
Isobutane	Cis-2-Pentene	o-Xylene
1-Butene	2-Methylpentane	1,3,5-Trimethylbenzene
n-Butane	n-Hexane	1,2,4-Trimethylbenzene
Trans-2-Butene	Benzene	1,2,3-Trimethylbenzene
Cis-2-Butene	2,2,4-Trimethylpentane	1,3-Butadiene

Table 3. 2017 Revised PAMS Target List.

Existing Priority Compounds	Optional Compounds
1,2,3-Trimethylbenzene	1,3-Butadiene
1,2,4-Trimethylbenzene	1,3,5-Trimethylbenzene
1-Butene	1-Pentene
2,2,4-Trimethylpentane	2,2-Dimethylbutane
Acetaldehyde	2,3,4-Trimethylpentane
Benzene	2,3-Dimethylbutane
Cis-2-Butene	2,3-Dimethylpentane
Ethane	2,4-Dimethylpentane
Ethylbenzene	2-Methylheptane
Ethylene	2-Methylhexane
Formaldehyde	2-Methylpentane
Isobutane	3-Methylheptane
Isopentane	3-Methylhexane
Isoprene	3-Methylpentane
M/P Xylene	Acetone
M-Ethyltoluene	Acetylene
N-Butane	Alpha Pinene
N-Hexane	Benzaldehyde
N-Pentane	Beta Pinene
O-Ethyltoluene	Cis-2-Pentene
O-Xylene	Carbon Tetrachloride
P-Ethyltoluene	Cyclohexane
Propane	Cyclopentane
Propylene	Ethanol
Styrene	Isopropylbenzene
Toluene	M-Diethylbenzene
Trans-2-Butene	Methylcyclohexane
	Methylcyclopentane
	N-Decane
	N-Heptane
	N-Nonane
	N-Octane
	N-Propylbenzene
	N-Undecane
	P-Diethylbenzene
	Tetrachloroethylene
	Trans-2-Pentene



Figure 3. Clarus GC Ozone Precursor System.

Key Features of System

- Fully complies with U.S. EPA "Technical Assistance Document for Sampling and Analysis of Ozone Precursors," EPA/600-R-98/161
- Unattended operation
- Simultaneous chromatography on two columns
- Unique heartcut device enables parallel chromatography for increased throughput and chromatographic resolution
- Hourly sampling
- Simultaneous sampling and chromatography
- Automatic system calibration
- Full data processing
- Optional total-system remote control of the thermal desorber, the gas chromatograph and the data processing via telephone, internet or local area network
- Cryogen-free operation
- Sample information inserted into result files
- Complete analytical package supplied and supported by a single vendor

Experimental

The full instrumental conditions for this analysis are given in Table 4.

Table 4. Instrument Conditions.

Chromatograph	Clarus 590/690 GC with Swafer heartcut device
Column Set	60M 0.25 mm Elite-624Sil MS (N9316581)
Oven Program	45 °C for 15 minutes, ramp at 5 °C/min to 170 °C then ramp at 15 °C/min to 200 °C and hold for 6 minutes
Detector	Dual Wide Range Flame Ionization Detectors at 250 °C, 0.011" Jets, 300 mL/min Air, 30 mL/min H ₂
Carrier Gas	38.7 psig helium at pre-column inlet
Thermal Desorber	TurboMatrix™ TD with online sampling accessory
Trap	Air Monitoring and Investigative Enhanced Air Monitoring trap
Trap Low	-30 °C
Trap High	325 °C
Transfer Line	150 °C
Operating Mode	On Line
Inlet Split	Off
Outlet Split	3 mL/min (~1:2 split ratio)
Data Handling System	TotalChrom®
Air Sampling	15 mL/min for 40 min (600 mL total)
Heartcut Time	13 minutes

The Clarus 590/690 also incorporates a new wide range flame ionization detector (WR-FID) that is able to run a sample of greatly varying concentration without the need to change ranges or attenuations.

New Trap Design

Modern adsorbents, when used in combination, are effective in retaining all the target analytes at the TurboMatrix Thermal Desorber (TD) Peltier-cooled trap temperature of -30 °C. This totally eliminates the need for liquid cryogen. Figure 4 shows the classic PerkinElmer Air Monitoring Trap used on this system to collect the air sample. This same trap is also used in the PerkinElmer Air Toxics System for analyses of toxic volatile organic compounds in ambient air, according to U.S. EPA Methods TO-14, TO-15 and TO-17.

The new trap design incorporates a small guard zone as the leftmost of the three sorbent bed as shown in Figure 5. This zone will trap and release a number of our targets of interest but more importantly it will also release higher molecular weight non-targeted compounds that otherwise would remain on the old style trap thus gradually causing contamination. The center zone is also improved in its ability to capture lower molecular weight targets; this will leave the strongest bed on the right to capture only the most volatile analytes.

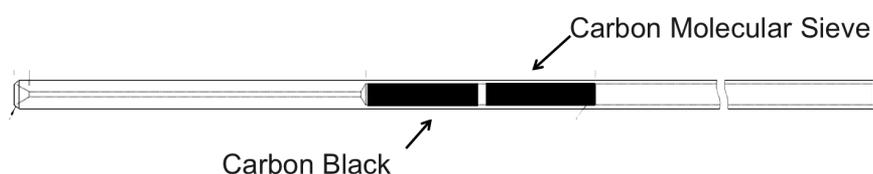


Figure 4. Classic Air Monitoring Trap.

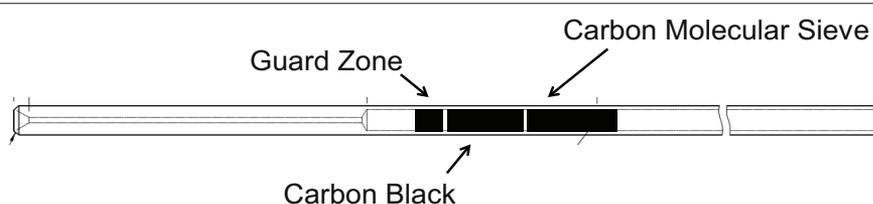


Figure 5. Investigative Enhanced Air Monitoring Trap.

Good peak shapes are produced from this trap during thermal desorption at carrier-gas flow rates within the range of 3 to 5 mL/min. These low flow rates mean that split ratios may be kept to a minimum as the vapors are transferred to the GC column.

The enhanced trap uses three adsorbents; the guard zone, the weaker (carbon black) adsorbent is towards the sample inlet/outlet and will retain the less volatile targets from the sample. The guard zone provides multiple functions such the ability to desorb high molecular weight non-targeted compounds that ultimately cause the trap to become contaminated. The middle zone is also composed of a carbon black adsorbent but a bit stronger than the guard zone so that it can trap the mid-range analytes. The strongest (carbon molecular sieve) adsorbent is positioned behind the two weaker adsorbents to catch the most volatile analytes (C2 to C4).

Gas Standards

Gaseous standards (PAMS and TCEQ) were purchased from Linde Gas and delivered to an in house built custom dynamic dilution system. This dynamic blending system also included the

ability to add and measure percent Relative Humidity (%RH), as described in Reference 5. Individual standards to verify Retention Times (RT) were purchased from MilliporeSigma® and either spiked into a 1L Tedlar bag or 0.05uL of the target was directly spiked onto a PKI SVI tube.

The values reported here are in the units of PPBC which can be converted to the more familiar PPBV by dividing the ppbc by the number of carbons in the target analyte. For example, Pentane at 20 ppbc would be $20 \text{ ppbc} / 5 = 4 \text{ ppbv}$.

Performance

The 624 separation is shown in Figure 6 and compares favorably with the BP-1 separation shown in Figure 7. The obtained peak shape and separation enables accurate quantification of the analytes of interest using the 624 column.

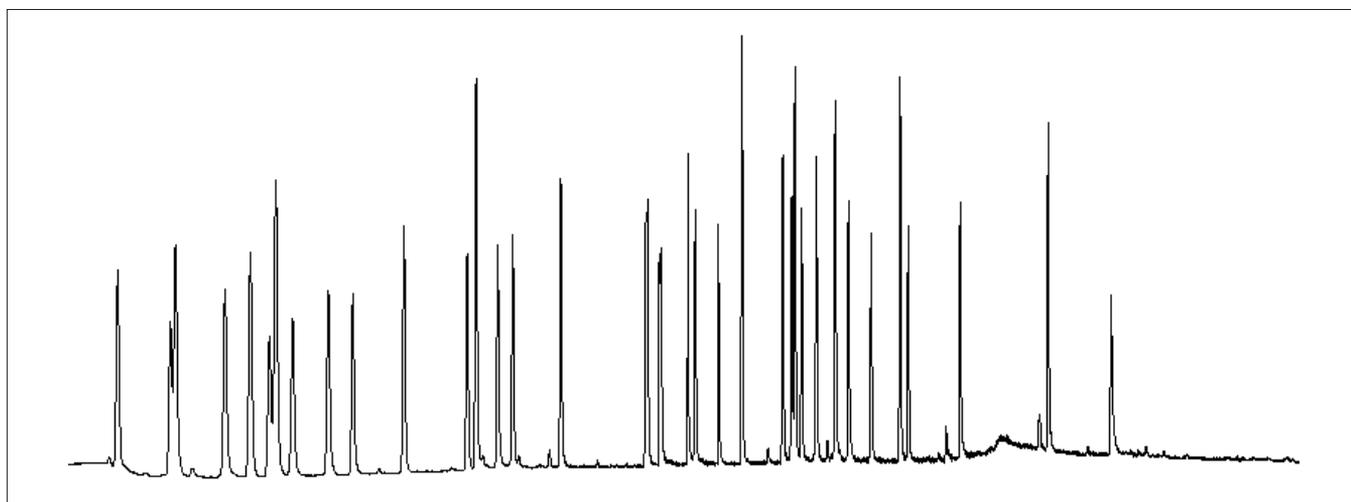


Figure 6. Classic BP-1 chromatogram at 12 ppb benzene.

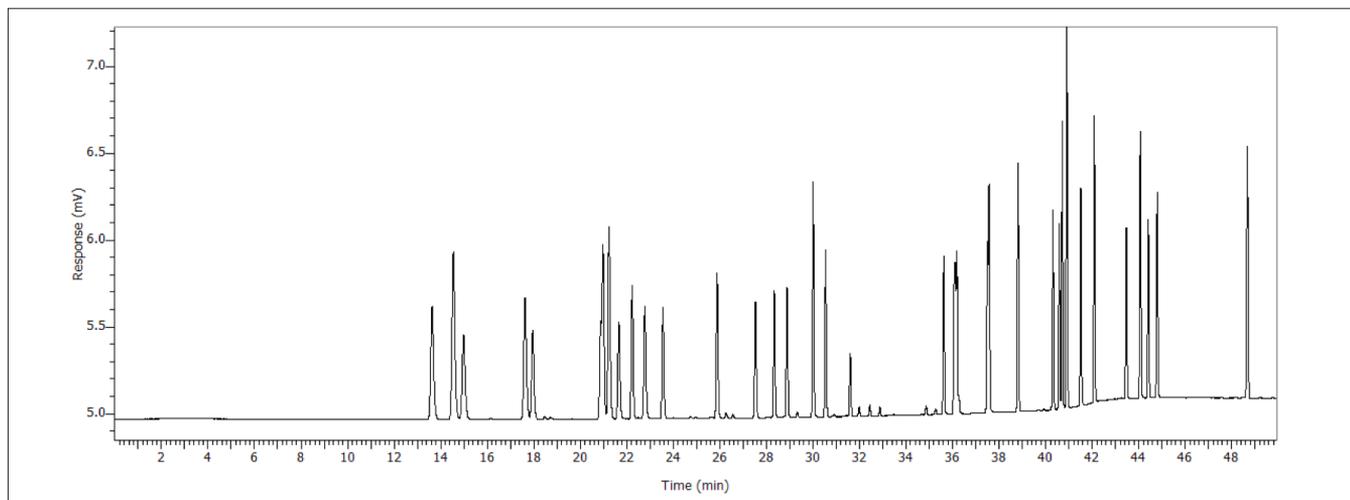


Figure 7. New 624Sil MS column using new wide range FID on Clarus 690 GC with stock EPA PAMS mix at 19-60 ppbc (3-10 ppbv).

Results

Linear Retention Index (LRI)

LRI is a logical extension of Retention (or Kovats) Index applied to a linear temperature programmed chromatography vs the classic isothermal Kovats Index. The LRI is fairly simple to calculate, the n-alkanes are defined as the number of carbons in the molecule multiplied by 100. Therefore hexane is C6 and its LRI is by definition 600, heptane is 700, octane is 800 and so on. An example: we have an unknown peak that elutes 85% of the way between C6 and C7 so its LRI would be $600 + 85\%(100)$ or simply $600 + 85 = 685$. If you look up 685 in the LRI column in Table 6 you will see it lines up

very nicely with benzene. LRI are very useful for comparing analytes on similar phases when column conditions differ. We used LRI as an orthogonal technique to verify component identification from literature that only contained retention time data. This retention time data was easily converted to LRI using Microsoft® Excel. Actual pure individual chemical standards were also run to confirm retention times in the most of cases, in addition, to mass spectral data, using a PerkinElmer Clarus SQ 8 GC/MS system.

The LRI agreement between literature and data reported here was excellent.

Data

Table 6. Shows the precision obtained from 30 samples of a 19-60-ppbc (3-10ppbv) calibration gas.

Component	Actual RT of Pams Std 0%RH	LRI Calculated	PAMS stock ppbc	75%RH 6.1:1 dilution %RSD Area (n=30)	75%RH 6.1:1 dilution %RSD Height (n=30)	MDL 75% humidity ppbc Area	MDL 75% humidity ppbc Height	MDL 0%RH 29:1 dilution ppbc Area	MDL 0%RH 29:1 dilution ppbc Height
3-Methylpentane	13.47		42	1.30	0.84	0.21	0.13	0.29	0.13
1-Hexene	14.39		60	1.70	1.07	0.42	0.26	0.19	0.10
n-Hexane	14.88	600	31	2.00	1.56	0.25	0.20	0.16	0.08
2,4-Dimethylpentane	17.56	631	42	1.30	1.39	0.22	0.24	0.10	0.06
Methylcyclopentane	17.89	635	26	1.90	1.02	0.20	0.11	0.09	0.05
2-Methylhexane	20.92	670	27	7.90	0.79	0.16	0.08	0.31	0.05
2,3-Dimethylpentane	21.19	673	53	1.20	1.14	0.19	0.19	0.37	0.10
3-Methylhexane	21.61	678	26	1.00	1.11	0.08	0.09	0.15	0.05
Benzene	22.18	685	31	1.70	0.83	0.21	0.10	0.18	0.06
2,2,4-Trimethylpentane	22.73	691	31	1.70	1.44	0.17	0.13	0.32	0.11
n-Heptane	23.51	700	26	4.60	3.75	0.40	0.31	0.13	0.12
Methylcyclohexane	25.84	733	32	1.30	1.48	0.17	0.18	0.06	0.04
2,3,4-Trimethylpentane	27.49	757	26	1.10	1.19	0.08	0.09	0.08	0.04
2-Methylheptane	28.30	768	26	1.30	1.52	0.08	0.09	0.06	0.04
3-Methylheptane	28.85	776	26	2.40	1.42	0.23	0.10	0.16	0.04
Toluene	29.98	792	42	1.10	0.94	0.17	0.16	0.11	0.11
n-Octane	30.51	800	31	0.02	1.2	0.09	0.10	0.08	0.03
Ethylbenzene	35.59	890	26	1.10	1.3	0.12	0.13	0.10	0.03
p-Xylene	36.07	899	42	1.60	1.08	0.26	0.16	0.55	0.08
m-Xylene	36.07	899	42	1.60	1.08	0.26	0.16	0.55	0.08
Nonane	36.15	900	41	1.90	1.27	0.18	0.11	0.10	0.04
o-Xylene	37.46	928	26	1.20	0.99	0.17	0.15	0.09	0.08
Styrene	37.53	929	41	1.00	1.05	0.10	0.10	0.08	0.05
Isopropylbenzene	38.78	956	40	0.90	0.97	0.12	0.15	0.07	0.06
n-Propylbenzene	40.27	987	30	1.10	1.03	0.13	0.12	0.09	0.04
m-Ethyltoluene	40.54	993	26	1.10	0.97	0.12	0.10	0.08	0.04
p-Ethyltoluene	40.68	996	43	1.10	1.11	0.19	0.19	0.08	0.07
1,3,5-Trimethylbenzene	40.87	1000	27	0.80	0.79	0.17	0.14	0.10	0.08
n-Decane	40.87	1000	32	0.80	0.79	0.17	0.14	0.10	0.08
o-Ethyltoluene	41.47	1015	43	1.00	1.07	0.11	0.13	0.18	0.05
1,2,4-Trimethylbenzene	42.05	1030	41	0.70	1.12	0.10	0.19	0.30	0.11
1,2,3-Trimethylbenzene	44.02	1081	27	3.50	1.98	0.51	0.30	0.34	0.14
m-Diethylbenzene	43.42	1066	41	0.70	0.89	0.08	0.09	0.08	0.05
p-Diethylbenzene	44.36	1090	26	0.70	0.92	0.09	0.10	0.18	0.06
n-Undecane	44.75	1100	33	0.80	0.92	0.08	0.11	0.13	0.06
n-Dodecane	48.60	1200	44	1.30	1.13	0.20	0.20	0.28	0.09

Conclusion

Air pollution is a global concern. Ground-level ozone has become an increasingly important issue in developed nations, as the health effects of smog are more clearly understood. The monitoring of VOC ozone precursor compounds will continue to play a role in defining and reducing air pollution in developed and developing nations in the next decade. The PerkinElmer On-line Ozone Precursor Analyzer has a proven record of several hundred thousand hours of reliable field operation. With quantitation limits below 0.1 ppb (FID) and the capability of sampling for 40 minutes of every hour, the system meets the requirements of this exacting method. Sophisticated network communications ensure that the Online Ozone Precursor Analyzer provides a robust, 24-hour monitoring solution, ideal for field operation.

The data presented here shows the excellent results of improved separation via Elite-624Sil MS column with real world samples, simplified column connections to the Dean Switching device and trap with modernized triple bed trap with guard zone technologies.

The TurboMatrix TD system has been shown to perform U.S. EPA ozone precursor analysis within the specifications required by the method.

References

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