GAS

CHROMATOGRAPHY

Ozone Precursor Analysis Using the TurboMatrix Thermal Desorption GC System



Figure 1. Areas not reaching ozone attainment goals (www.epa.gov).

Introduction

In the United States, the Clean Air Act of 1970 gave the 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 , PM_{10} (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,

as shown in Figure 1. These measurements are implemented through a program known as Photochemical Assessment Monitoring Stations (PAMS). Similar recommendations have also been made in Europe following the 1992 Ozone Directive and United Nations Economic Commission for European protocol on controlling VOC emissions. Although this program has been in place in the U.S. for a number of years, a recent EPA press release indicates that ozone concentration was reduced only 4% over the last ten years and remains a major health concern.¹

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The analysis of C₂ to C₁₂ volatile organic ozone-precursor compounds can present a serious technical challenge to the analytical chemist. Low concentrations in the atmosphere coupled with the need to monitor frequently to assess diurnal variations means that a preconcentration step on the sample before analysis by gas chromatography (GC) is required. 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 C_2 VOCs can be trapped on solid sorbents if those sorbents are cryogenically cooled. However, this presents a serious cryogen-use problem. It is difficult to get liquid nitrogen routinely delivered to remote locations and its use can make these analyses costly and dangerous.

This application note describes a method developed by PerkinElmer in conjunction with the U.S. EPA to collect and measure C_2 to C_{12} automatically, in the field, without the use of liquid cryogen.² This system has been updated to support the use of a new Thermal Desorption (TD) system, the TurboMatrixTM TD.

System requirements

Table 1 lists the 54 (meta and para xylenes are counted as one compound) 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. This document is available from the U.S. EPA web site at: http://www. epa.gov/ttn/amtic/files/ambient/ pams/newtad.pdf These target compounds vary tremendously in their volatilities and therefore place special 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.

Table 1. Ozone Precursor Target Analytes.						
Ethylene	2,3-Dimethylbutane	n-Octane				
Acetylene	2-Methylpentane	Ethylbenzene				
Ethane	3-Methylpentane	m and p-Xylene				
Propylene	n-Hexane	Styrene				
Propane	Methylcyclopentane	o-Xylene				
Isobutane	2,4-Dimethylpentane	n-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				

System overview

Figure 2 gives a schematic diagram of the key components that comprise the PerkinElmer® On-line Ozone Precursor Monitoring System. A TurboMatrix TD with installed On-line Sampling Accessory is responsible for collecting the sample – either directly from ambient air or from a sample previously stored in a passivated canister. The TD extracts the analytes from the sample onto a cooled adsorbent trap. The trapped analytes are thermally desorbed and carried through a heated transfer line by carrier gas into the Clarus® 500 Gas Chromatograph. The GC contains two columns and a heartcut device to separate, by volatility, the analytes into two fractions. The more volatile fraction is separated on a PLOT (Porous Layer Open Tubular) column whereas the less volatile fraction is separated on a methyl silicone column. A flame ionization detector monitors the chromatography on each column. The PC runs the TotalChrom[®] data-handling system and the TurboMatrix Remote Control software to provide the automated control and review of the settings and conditions that control the GC, the TD and the data processing. As an option, thirdparty remote control software may be used to provide access to the PC and the applications running on it from a remote location.



Figure 2. Key components of the PerkinElmer On-line Ozone Precursor Monitoring 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
- · Allows 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 desorption system, 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 which is supplied and supported from a single vendor

Sample collection

Modern adsorbents, when used in combination, are effective in retaining all the target analytes at the minimum TurboMatrix TD Peltier-cooled trap temperature of -30 °C. This totally eliminates the need for liquid cryogen. Figure 3 shows a photograph of the PerkinElmer 'Air Toxics 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.

Figure 4 shows a diagram of the trap's internal geometry. The sample is drawn into the cooled trap from the left-hand side in the drawing. When the trap is heated, the desorbed vapors exit again from the left-hand side. This section of the trap is reduced in diameter (0.7 mm) to minimize vapor dilution, which would result in chromatographic



Figure 3. Photograph of the PerkinElmer Air Toxics Trap.



Figure 4. Internal geometry of the PerkinElmer TurboMatrix TD trap.



Figure 5. C₂ hydrocarbons recovery vs. sample gas volume (16 to 19 ng per component).

peak-shape broadening and degradation in detection limits. The fast trap heat-up rate (2400 °C/min) also serves to minimize peak broadening. Good peak shapes are produced from this trap during thermal desorption at carrier gas flow rates within the range 3 to 5 mL/min. These low flow rates mean that split ratios may be kept to a minimum (1:1 is typical) as the vapors are transferred to the gas chromatographic column.

This trap uses two adsorbents, the weaker (carbon black) adsorbent is towards the sample inlet/outlet and will retain the less volatile analytes from the sample. The stronger (carbon molecular sieve) adsorbent is positioned behind the weaker adsorbent to catch the most volatile analytes $(C_2 \text{ to } C_4)$. When the trap is heated, the desorbed analytes are backflushed from the trap - this ensures that the less volatile components never make contact with the stronger adsorbent. Using just a single adsorbent would require that the trap is operated over a much greater temperature range and thus this dualadsorbent arrangement facilitates the retention and desorption of all the ozone precursor target analytes, without recourse to liquid cryogen. The retention of C_2 components on this trap is shown in Figure 5. This demonstrates that acetylene is quantitatively retained from 600 mL of air. The retention volumes for other C₂ hydrocarbons exceed 1.2 L at -30 °C and over 4 L for C₃ hydrocarbons.

The use of glass-fiber filter disks keeps the packing beds apart without introducing dead volumes into the flow path. The adsorbent is retained by the reduced-trap inner walls at one end and by a spring at the other end, so the adsorbents are kept in their optimum position during operation.

The thermal desorption system

Figures 6 to 9 show schematic diagrams of the thermal desorption system used for this application. These figures represent only a few of the stages necessary to perform this analysis, but they should illustrate how the system collects and desorbs the sample analytes in the gas chromatograph. The core TD technology is to the left and the On-line Sampling Accessory is to the right of the dotted line in Figures 6 to 9.

A rotary valve (*RVC*) selects whether a sample or a calibration standard mixture is to be run. The position of this valve is controlled from the TotalChrom data-handling sequence so that scheduled automatic recalibration of the system is possible.



Figure 6. The PerkinElmer TurboMatrix TD thermal desorption system with fitted On-line Sampling Accessory – idle position.



Figure 7. The PerkinElmer TurboMatrix TD thermal desorption system with fitted On-line Sampling Accessory – sampling position.

Once the sample (or standard) passes through RVC, it is fed through a Nafion[™] membrane drier to remove moisture. Nafion is a perfluorosulfonic acid polymer that is permeable to water molecules and is very effective in this application. The membrane will also remove many polar compounds, particularly aliphatic alcohols, ketones, ethers and esters. However, as none of these are on the target list of analytes, this is a direct benefit to this application, since possible interferents will be removed from the sample. A flow of dry air is supplied via an electrical solenoid valve (ISV2) to remove the extracted water and to keep the membrane operating under optimum conditions.

When the system is idle, the sample stream is directed through another rotary valve (*RVB*) to an electronic flow controller and a vacuum pump. This arrangement allows the system to sample air at ambient pressures or even (in the case of canister samples) at pressures below ambient at a user-settable sampling rate. An electrical solenoid valve (*ISV1*) will close in the event of a power interruption so that the loss of an expensive standard gas mixture does not occur under these circumstances.

To take a sample, *RVB* is rotated as shown in Figure 7. This directs the sample stream through an empty tube (used just as a conduit), through *RVA* and into the cooled trap where the analytes are retained. The outlet of the trap is taken back through *RVB* and out to the electronic flow controller and vacuum pump. The sample will be collected at the set flow rate for a set period of time – both are settable by the user. Note that while sample is being collected, carrier gas continues to flow to the GC column so chromatography of the current sample may occur simultaneously with the collection of the next sample. This approach to overlapping the chromatography with sample collection enables the system to meet one of the primary requirements of the method – to collect sample over a period of at least 40 minutes, yet deliver a result each hour. The overlapped timing is shown in Figure 8.

Once the sample has been collected onto the trap, RVB returns to its previous position and RVA rotates and SV2 switches to direct carrier gas through the trap and into the GC column (Figure 9). The trap is heated at this point and desorbed analytes are backflushed into the GC column and chromatography of the analytes is initiated. A small split is applied at the trap outlet by opening SV4 – this sharpens the early-eluting peaks.

The system will now chromatograph the current sample and initiate the collection of the next sample early in the run.

Figure 10 shows a photograph of the thermal desorption instrument with fitted On-line Sampling Accessory. Figure 11 shows the same system from the rear with the covers removed to display the key components of the sampling system.

RVB

filter

ISV1

electronic flow controller



Figure 8. Overlapped functions allow sample collection, chromatography and data collection to occur within each hour.



drier por

Figure 11. Cover removed from On-line Sampling Accessory showing key components.



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Gas chromatography

Once the desorbed sample vapor is delivered to the gas chromatograph, the 55 target components given in Table 1 must be separated, identified and quantified within about 50 minutes in order for the GC to be cooled and ready to start the next analysis an hour later. It would be very difficult to achieve a satisfactory separation of all 55 compounds on a single GC column without recourse to subambient oven temperatures. This would clearly defeat the benefit of eliminating the liquid cryogen from the thermal desorption system.

To separate the very volatile compounds (such as ethane, ethylene and acetylene), a very retentive column such as an alumina PLOT would be required. Although this type of column is ideal for the separation of the light compounds, it has a temperature limit of about 200 °C and would be unable to elute compounds much heavier than hexane.

This limitation is overcome by the addition of a methyl silicone column which is coupled to the PLOT column with a heartcut switch as shown in Figure 12.

The heartcut technology used here is based on the Deans principle of pressure-balanced switching and has the advantages of being simple, highly inert, low thermal mass and low internal dead-volume.

There are two pressure regulators employed. The first (P1) is on the TD and controls the pressure at the inlet of the methyl silicone column. The second regulator (P2) is attached to the heartcut device in-between the two columns. For correct operation, P1 > P2 > ambient pressure. The difference in pressures between P1 and P2 represents the pressure drop across the methyl silicone column and will control the flow rate of carrier gas through it. The pressure P2 represents the pressure across the PLOT column and hence the flow rate of carrier gas through that column. This arrangement allows simultaneous chromatography in both columns.

The heartcut device is used to separate the analytes into two fractions – the more volatile fraction elutes from the methyl silicone column and is directed into the PLOT column for further chromatography and detection on FID2. The heartcut device is now switched to its other position and the effluent from the methyl silicone column is directed to FID1.



Figure 12. Schematic diagram of gas chromatographic system showing dual columns configured with a heartcut device.

Figures 13 and 14 illustrate how this heartcut device works. By the simple switching of a solenoid valve mounted outside the GC oven, the effluent from the column is switched between the two outlets, D and E. The other port continues to be fed with pure carrier gas. In order for this to work, the pressure at point D must be very close to the pressure at point E. This is achieved by making the pneumatic impedance of the fused silica restrictor tubing in Figure 10 close to that of the PLOT column - hence the term "pressure balanced switching".

A needle valve is connected across the switching ports on the heartcut device. This maintains a trickle flow of carrier gas through the otherwise unswept plumbing lines to ensure that no sample material is lost or is reinjected as the analysis proceeds.

Figure 15 shows a chromatogram of a 10-ppb standard mixture with the effluent from the methyl silicone column directed to FID1 throughout the run (i.e., no heartcut).

As can be seen from Figure 15, separation of the compounds up to n-hexane is not very good but is acceptable for later-eluting compounds. The heartcut device is used, therefore, to direct those components eluting before n-hexane on to the PLOT column. Chromatography of both of the more volatile and less volatile fractions will proceed in parallel as shown in Figure 16. This approach eliminates the need for subambient chromatography and will produce 'double the chromatography' during the run.

Experimental

The full instrumental conditions for this analysis are given in Table 2.



Figure 13. Heartcut device, switching column effluent from point A to PLOT column at point E.



Figure 14. Heartcut device, switching column effluent from point A to FID1 at point D.



Figure 15. 10-ppb standard mixture chromatographed with effluent from methyl silicone column directed to FID1.



Figure 16. Parallel chromatography of the two sample fractions on the methyl silicone and PLOT columns.

Table 2. System Conditions for Ozone Precursor Analysis.				
Chromatograph	Clarus 500/AutoSystem XL with Heartcut Device and Integral LINK			
Column	Ozone Precursor Column Set: • 50 m x 0.22 mm x 1 µm methyl silicone column and • 50 m x 0.32 mm alumina/KC1 PLOT column			
Oven	45 °C for 15 minutes, then 5 °C/minute to 170 °C, then 15 °C/minute to 200 °C and hold for 6 minutes (48-minute chromatogram)			
Detector	Dual Flame Ionization Detectors at 250 °C			
Carrier Gas	48 psig (approx.) helium at the pre-column inlet 17 psig (approx.) helium at the heartcut device			
Thermal Desorber	TurboMatrix TD with On-line Sampling Accessory			
Тгар	Air-monitoring trap packed with carbonaceous sorbents			
Trap Low	-30 °C			
Trap High	400 °C			
Transfer Line	200 °C			
Operating Mode	On Line			
Inlet Split	Off			
Outlet Split	2 mL/min (~1:1 split ratio)			
Data Handling System	TotalChrom and TurboMatrix Remote Control software			
Air Sampling	15 mL/min for 40 min (600 mL total)			

Performance

The success of this analysis depends to a large extent on whether a few critical chromatographic separations are achieved.

Figures 17 and 18 give an overview of the critical separations.

Figure 19 shows critical separation 'A', a low concentration of isobutylene near several peaks often observed at higher concentration. This compound is thought to be produced as an artifact in the Nafion drier and therefore good detection at a low level is required.

Figure 20 shows critical separation 'B' between isopentane and cyclopentane. A good separation is seen between these two very similar compounds.

Figure 21 shows critical separation 'C' between the three compounds typically referred to as the *"Three Amigos"*. In ambient air, the 2methylpentane peak is usually the strongest, while the 2,3-dimethylbutane peak is the strongest in this standard.

Figure 22 shows critical separation 'D'. N-hexane is the first peak to elute from the methyl silicone column into FID1 after the heartcut has switched. A minimal baseline disturbance, like the one shown here, is sought.

Figure 23 shows critical separation 'E' highlighting the separation of toluene. Toluene is an important reference peak for this analysis and therefore needs to be well resolved.



Figure 17. Critical separations on the alumina PLOT column.



Figure 18. Critical separations on the methyl silicone column.



Figure 19. Critical separation 'A' – showing a low concentration of isobutylene.





Figure 20. Critical separation 'B' – a good separation between these two components is critical.

Figure 21. Critical separation 'C' – a good separation between the "Three Amigos" is desirable.



Figure 22. Critical separation 'D' – minimal baseline disturbance.



 $Figure\ 23.$ Critical separation 'E' – toluene reference peak well resolved.



Figure 24. Alumina PLOT column chromatogram with all the components identified.



Figure 25. Methyl silicone column chromatogram with all the components identified.

Table 3. Repeatability of the Peak Area and Retention Time for Fourteen Runs on the Alumina PLOT Column.

Compound	Area Average (Counts)	Area (%RSD)	Time (%RSD)		
ethane (ETHAN)	214638	1.5	0.06		
ethylene (ETHYL)	124128	1.5	0.18		
propane (PROPA)	312707	1.0	0.26		
propylene (PRPYL)	174052	1.0	0.46		
iso-butane (ISBTA)	195506	1.6	0.29		
n-butane (NBUTA)	312147	1.4	0.26		
acetylene (ACETY)	66870	2.2	0.32		
trans-2-butene (T2BTE)	203689	1.4	0.20		
1-butene (1BUTE)	231206	1.5	0.20		
cis-2-butene (C2BTE)	275002	1.3	0.18		
cyclopentane (CYPNA	A) 146311	1.5	0.15		
isopentane (ISPNA)	306789	1.2	0.16		
n-pentane (NPNTA)	195473	1.3	0.15		
trans-2-pentene (T2PNE)	194509	1.3	0.14		
1-pentene (1PNTE)	189573	1.5	0.15		
cis-2-pentene (C2PNE)	260427	1.3	0.14		
2,2-dimethylbutane (22DMB)	315273	1.3	0.14		
2,3-dimethylbutane (23DMB)	385742	1.4	0.13		
2-methylpentane (2MPNA)	156987	1.5	0.13		
3-methylpentane (3MPNA)	312026	1.4	0.13		
isoprene (ISPRE)	273503	1.4	0.14		
2-methyl-1pentene (2M1PE)*	60621	1.5	0.10		
* Compound not on target list.					

Figures 24 and 25 show the chromatography on the alumina PLOT and methyl silicone columns respectively, with all the components identified.

In addition to accurate quantification, the method must be precise and stable for reliable operation in remote areas. Table 3 shows the percent relative standard deviation (% RSD) for both area counts and retention time for 14 runs of the standard mixture for the alumina PLOT column. The same information for the methyl silicone column is shown in Table 4. The concentration ranged from 20-50 ppb in the sample, depending on the compound. *Table 4.* Repeatability of the Peak Area and Retention Time for Fourteen Runs on the Methyl Silicone Column.

Compound	Area Average (Counts)	Area (%RSD)	Time (%RSD)
n-hexane (nHEXA)	230493	1.3	0.19
2-methyl-2-pentene (2M2PEN)*	273184	2.0	0.18
methylcyclopentane (MCPNA)	144872	0.9	0.14
2,4-dimethylpentane (24DMP)	452231	1.6	0.14
benzene (BENZ)	233810	1.7	0.09
cyclohexane (CYHXA)	314890	1.6	0.08
2-methylhexane (2MHXA)	181874	1.4	0.07
2,3-dimethylpentane (23DMP)	416641	1.7	0.07
3-methylhexane (3MHEX)	208749	2.6	0.07
2,2,4-trimethylpentane (224TMP)	241903	1.9	0.05
n-heptane (nHEPT)	190584	1.4	0.05
methylcyclohexane (MCYHX)	225975	1.3	0.04
2,3,4-trimethylpentane (234TMP)	187354	1.4	0.03
toluene (TOLU)	287696	2.6	0.03
2-methylheptane (2MHEP)	192927	2.3	0.03
3-methylheptane (3MHEP)	193685	1.5	0.03
n-octane (nOCT)	223686	1.4	0.03
ethylbenzene (EBENZ)	182455	1.2	0.03
m,p-xylene (M/PXY)	276820	1.3	0.02
styrene (STYR)	207815	0.7	0.03
o-xylene (oXYL)	179952	1.4	0.03
n-nonane (NNON)	179411	1.5	0.03
iso-propylbenzene (ISPBZ)	259197	1.3	0.03
n-propylbenzene (nPBZ)	203292	1.5	0.03
m-ethyltoluene (mETOL)	234665	2.1	0.03
p-ethyltoluene (pETOL)	201955	2.8	0.03
1,3,5-trimethylbenzene (135TMB)	174842	1.5	0.03
o-ethyltoluene (oETOL)	209463	1.8	0.03
1,2,4-trimethylbenzene (124TMB)	263891	1.4	0.03
n-decane (NDEC)	204677	1.8	0.03
1,2,3-trimethylbenzene (123TMB)	162110	1.9	0.03
m-diethylbenzene (mDEBE	N) 258986	1.9	0.04
p-diethylbenzene (pDEBEN) 155525	2.3	0.04
n-undecane (nUNDC)	185384	1.4	0.03
* Compound not on target list			

Any new system that purports to perform this analysis should have its performance compared against that of existing systems. Figures 26 and 27 show how the recoveries on this new system match up against well validated and established systems that are run routinely.

The 'EPA' data was produced on the original standard mixture used for the other studies and was generated on a system using a single column (with subambient cooling). On this system, the 2-methyl-1-pentene and 2-methyl-2-pentene were not fully separated, which explains why these results for this particular system differed from all the others. The other systems are based on the PerkinElmer ATD-400 – the thermal desorption system that preceded the TurboMatrix range of products.

Excellent correlation between the new system and the reference systems is apparent.

Software control

The data processing and the gas chromatographic conditions are fully controlled by the PerkinElmer TotalChrom data-handling system. The TurboMatrix TD is controlled from the same PC using the TurboMatrix Remote Control software. Between these two software applications, the instrumentation is able to be fully automated for the unsupervised analysis of ozone-precursor target compounds each and every hour. The system is able to automatically run standard mixtures to recalibrate the system according to a predefined sequence. The sample collection and analysis times are logged.

Although this is not part of the standard product, third party software applications such as the Symantec pcAnywhere[™] may be used to remotely access the system via a telephone line, internet or local area network to check on system status, transfer data, adjust conditions, etc.

Conclusions

Air pollution is a global issue. 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 modem communications ensure that the On-line Ozone Precursor Analyzer provides a robust, 24-hour monitoring solution, ideal for field operation.

The new TurboMatrix TD system has been shown to perform U.S. EPA ozone precursor analysis within the specifications required by the method. In addition, the new PerkinElmer On-line Ozone Precursor system is smaller, easier to set up and allows total remote control of the system.



Figure 26. Comparison of TurboMatrix data and existing operating systems for alumina PLOT column data.



Figure 27. Comparison of TurboMatrix data and existing operating systems for methyl silicone column data.

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