PRODUCT NOTE

GAS CHROMATOGRAPHY

On-line Ozone Precursor Analyzers

From the Leader in Thermal Desorption Technology

PerkinElmer On-line Ozone Precursor System, comprising of a Clarus Gas Chromatograph (left) and a TurboMatrix Thermal Desorber (right).

Global importance

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. The six parameters routinely measured in ambient air were expanded in 1990 to include volatile organic compounds (VOCs). Volatile organic compounds, carbonyl compounds and NOx are generally regarded as precursors to ground-level ozone formation in urban and industrial areas and may be present in the atmosphere at low part per billion (ppb) concentrations. These measurements are implemented through a program known as Photochemical Assessment Monitoring Stations (PAMS). Similar recommendations by other regulatory agencies have also been made around the globe.

For example, Europe follows the United Nations Economic Commission for Europe (UNECE) protocol on the control of emissions of VOCs. The target components for ozone precursor monitoring are listed in Table 1 (Page 2).

Proven monitoring now made easier with PPC

PerkinElmer, in conjunction with the U.S. EPA, originally developed an analyzer and methodology to collect and measure C_2-C_{12} hydrocarbons automatically, in the field, without the use of liquid cryogen. This established method, which has been successfully employed for many years with PerkinElmer® Ozone Precursor Analyzers, now includes fully integrated technologies incorporating PPC in both the Clarus® GC and TurboMatrix™ Thermal Desorber (TD) components of the system.

Key Benefits

- Complete, unattended operation
- Offsite system control and data access
- Data produced hourly for synchronous monitoring
- Programmable pneumatic control (PPC) allows easy setup and drift-free operation
- Cryogen-free for inexpensive and remote operation
- Unique “heartcut” device enables parallel chromatography for increased throughput and chromatographic resolution
- Trap impedance measurement ensures cold trap packing integrity
- Ozone precursor and air toxics analyses from the same TurboMatrix 650 ATD

PerkinElmer® precisely.

A choice of five new Ozone Precursor analyzers is now available with manual or fully integrated PPC configurations. Table 2 (Page 3) summarizes the features included in each of the TurboMatrix Thermal Desorber analyzer configurations. To complement the choice in pneumatic systems on the thermal desorbers, a similar choice is provided in the GC pneumatics as shown below.

A. Clarus 500 GC with
   - Dual FIDs with manual pneumatics
   - Heartcut device with manual pneumatics

B. Clarus 500 GC with
   - Dual FIDs with PPC
   - Heartcut device with PPC

Continuous, on-line monitoring

The requirements of on-line air monitoring systems include:

- Continuous unattended operation
- Sampling at regular intervals with minimal idle time (1 analysis/hr, 24 results/day)
- Ability to trap a wide volatility range of samples
- Operation without liquid cryogen
- Rapid transfer of analytes from the focusing device to the GC for high-resolution capillary chromatography
- Automatic calibration
- Sub-ppb detection limits using Flame Ionization Detector (FID)
- Stable retention times
- Precise and accurate quantitative performance

Table 1. Year 2000 Volatile Ozone-Precursor Target Compounds.

Compound	CAS Registry Number	Compound	CAS Registry Number
Ethane	43202	2,3-Dimethylpentane	43291
Ethylene	43203	3-Methylhexane	43249
Propane	43204	2,2,4-Trimethylpentane	43250
Propylene	43205	n-Heptane	43232
Isobutane	43214	Methylcyclohexane	43261
n-Butane	43212	2,3,4-Trimethylpentane	43252
Acetylene	43206	Toluene	45202
t-2-Butene	43216	2-Methylheptane	43960
1-Butene	43280	3-Methylheptane	43253
c-2-Butene	43217	n-Octane	43233
Cyclopentane	43242	Ethylbenzene	45203
Isopentane	43221	m&p-Xylenes	45109
n-Pentane	43220	Styrene	45220
t-2-Pentene	43226	o-Xylene	45204
1-Pentene	43224	n-Nonane	43235
c-2-Pentene	43227	Isopropylbenzene	45210
2,2-Dimethylbutane	43244	n-Propylbenzene	45209
2,3-Dimethylbutane	43284	m-Ethyltoluene	45212
2-Methylpentane	43285	p-Ethyltoluene	45213
3-Methylpentane	43230	1,3,5-Trimethylbenzene	45207
Isoprene	43243	o-Ethyltoluene	45211
2-Methyl-1-pentene	43246	1,2,4-Trimethylbenzene	45208
n-Hexane	43231	n-Decane	43238
Methylcyclopentane	43262	1,2,3-Trimethylbenzene	45225
2,4-Dimethylpentane	43247	m-Diethylbenzene	45218
Benzene	45201	p-Diethylbenzene	45219
Cyclohexane	43248	n-Undecane	43954
2-Methylhexane	43263		

The PerkinElmer Ozone Precursor Analyzers meet all of these requirements in robust and cost-effective packages.

PPC enhances ease-of-use and reliability

PPC allows easy setup of pressure and flow control automatically taking into account, through built-in firmware, pressure-drop relationships with trap impedance, different column and transfer-line dimensions, as well as temperature and carrier gas type.

Figure 1 (Page 3) shows the pneumatics screen, making it possible to perform a number of PPC system diagnostic checks such as the new column leak test feature.

PPC provides the following system benefits:

- Less susceptibility to drift, providing consistent performance

- Real-time monitoring and control of all flow rates
- The Log file lists all pneumatic deviations
- Better control at low outlet split ratios
- Less baseline artifacts because of direct control of pressure entering column
- All settings are in a single method for ease-of-setup
- In-sequence trap-clean and trap-test functions

New manifold design minimizes leaks and optimizes performance

All PerkinElmer Ozone Precursor Analyzers incorporate a manifold design which houses critical components, including mass flow controllers and solenoid valves. This manifold also reduces the number of fittings in the system and the potential for leaks and contamination, which is especially important for improved performance should the system also be used with GC/MS for air toxics analysis.

New drier accessory reduces dry air demand

The total demand for compressed air by the thermal-desorption system is about 2.5 L/min. Only 150 mL/min of this is used to purge the Peltier cooler for the cold trap to prevent the build-up of ice; the rest is used by the pneumatic actuators to drive the mechanics of the thermal desorber. The drying of the whole air intake in a field situation is often not convenient so a drier accessory (as shown in Figure 2, Page 4) is available to reduce the dew point of just the purge air to below the required dew point of -50 ˚C.

TotalChrom with Remote Control Software provides a single point of control

The TurboMatrix Remote Control Software (RCS) supports PPC and the other new features. The RCS is now accessible through TotalChrom® to provide integral control of the thermal desorber's methods and sequences. Access to the TurboMatrix TD and ATD settings is as shown in Figure 3 (Page 4). Configured this way, TotalChrom serves as a single point of control for the complete ozone precursor system, including the TurboMatrix TD, Clarus GC and data handling.

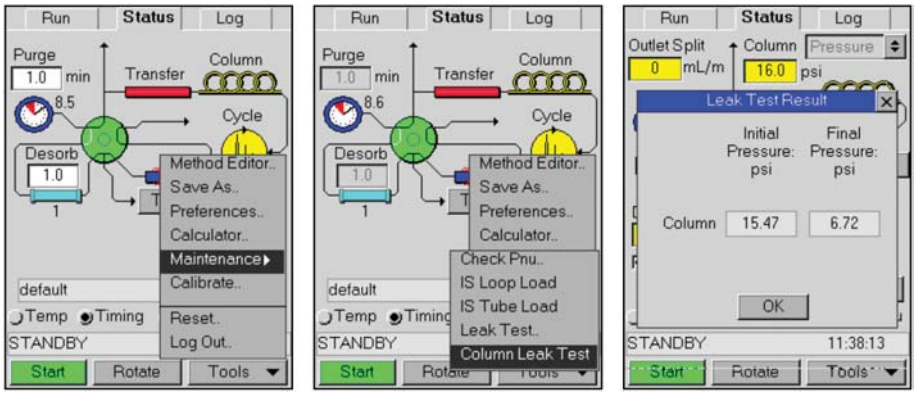

Figure 1. TurboMatrix Thermal Desorber pneumatics screens showing column leak test.

Table 2. Features of the Five New Thermal Desorbers.

Feature	TurboMatrix 100 TD	TurboMatrix 150 ATD	TurboMatrix 300 TD	TurboMatrix 350 ATD	TurboMatrix 650 ATD
Autosampler for tube analyses		●		●	●
PPC control of all flows and pressures			●	●	●
Sulfinert-coated metal transfer line	●	●	●	●	●
Air drier to prevent ice build-up on cold trap	○	○	○	○	○
Tube by-pass kit for robust long-term use	●	●	●	●	●
Trap-impedance monitoring					●
Air toxics analysis with tube dry purge					●
Remote control software for PC control	●	●	●	●	●
Fully integrated control from TotalChrom 6.3	○	○	○	○	○
Third-party software for control via telephone, internet, etc.	○	○	○	○	○

● = standard; ○ = optional

For users requiring offsite control and data access, the whole system may be accessed via the internet with external application software such as pcAnywhere™.

Automated trap impedance measurement monitors system integrity

For a thermal-desorption analysis to be successful, the adsorbent inside the secondary trap must be properly packed. Any voids in the packing may allow channeling of the gas flow during desorption, thus degrading the adsorption and desorption efficiencies. Furthermore, the adsorbent may be damaged during improper packing, rough handling or by thermal shock, giving rise to small fragments (fines) that fill the interstices between the packing particles and so serve to partially block the flow of gas during sampling and desorption.

Any degradation of the trap packing by the formation of channels or fines will alter the pneumatic impedance of the trap. Such degradation could be detected by monitoring the pressure drop across the trap while a known flow rate of carrier gas passes through it.

The TurboMatrix 650 ATD incorporates a fully automated procedure to measure variances in trap impedance, thereby ensuring an efficient and instant assessment of the condition of the trap. This provides additional confidence in the analytical data and allows instant identification of the need for remedial action, should it be required.

Operational overview

A schematic of the system for on-line mode operation is shown in Figure 5 (Page 5). The TurboMatrix Thermal Desorbers can sample air directly from the atmosphere being monitored or from a canister. Air is drawn through the PerkinElmer air-monitoring cold trap (Part Number M0413628) over a fixed time period (40 min), using a small vacuum pump. An electronic mass flow controller is set by the method and ensures that the volume sampled remains constant. A Nafion® drier is included in the sample flow-path and upstream of the trap to remove excessive quantities of water that would otherwise be collected from humid atmospheres. The external valve,

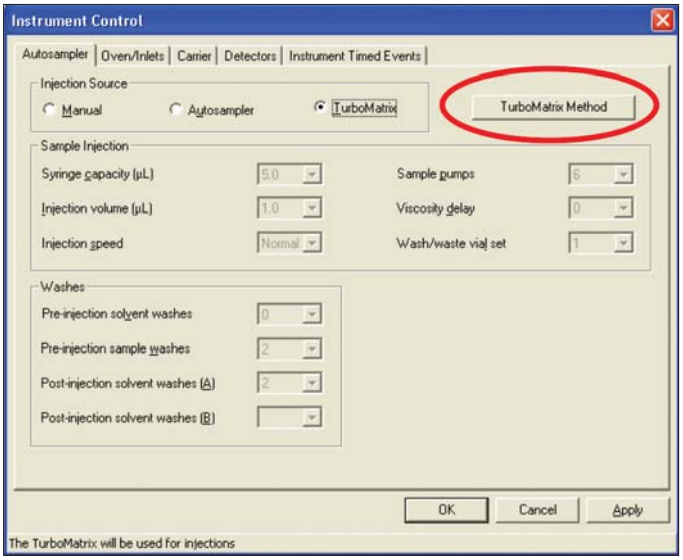

Figure 3. TotalChrom button now accesses TD and ATD settings.

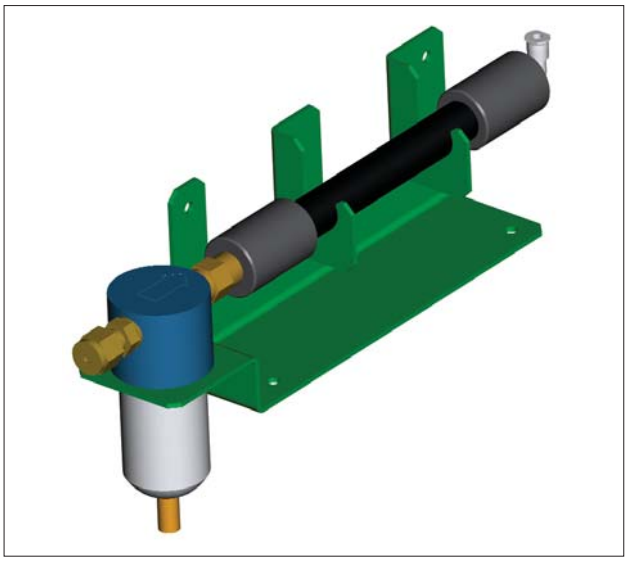

Figure 2. New drier accessory reduces dry air demand.

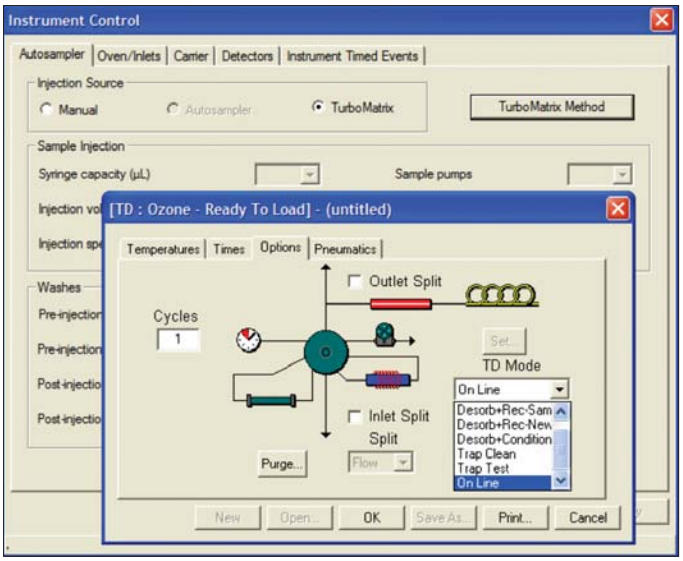

Figure 4. TotalChrom provides a gateway to the TD/ATD RCS.

marked "Valve 2" (Figure 5), is used to automatically switch between the sample air stream and a standard-calibration gas mixture at user-defined intervals for automatic system recalibration.

Cryogen-free operation

The TurboMatrix Thermal Desorbers incorporate Peltier cooling of the trap, which eliminates the need for liquid N_2. The Peltier-cooled trap can retain all the ozone precursor target analytes (C_2 to C_{12}) at -30 °C without liquid cryogen, using a combination of multi-bed adsorbents.

The rugged retention of C_2 components on this trap is shown in Figure 6. This demonstrates that acetylene is quantitatively retained from 600 mL of air. The retention volumes at -30 °C for other C_2 hydrocarbons exceed 1.2 L and for C_3 hydrocarbons exceed 4 L.

Chromatographic separation of ozone precursors

The chromatographic method was developed to achieve excellent resolution of the full suite of compounds in less than one hour. PerkinElmer achieves this goal by using a pressure-balanced switching technology based on the Deans' principle to distribute and separate the analytes between two columns.

Using this approach, components desorbed from the Peltier-cooled trap are transferred to the initial BP-1 capillary column. Early eluting peaks, which are poorly resolved on this column, are allowed to pass onto the Alumina PLOT column for more effective separation of the highly volatile components.

Later eluting peaks, which are effectively separated on the BP-1 column, are switched through uncoated, deactivated fused silica to a second FID, bypassing the PLOT column using a Dean's pressure switch. Carrier gas continues to pass through the Alumina PLOT column to the first FID after the switch.

This way, both chromatograms proceed in parallel without the need for liquid cryogen to cool either the trap or the GC column.

The excellent resolution obtained from such a system is shown in Figure 7. The resolution and shortened chromatography combine to yield near-continuous pollution-profiling information.

Table 3 (Page 6) shows the excellent quantitative and retention-time precision and the linearity possible from this system to give the highest confidence in the results generated.

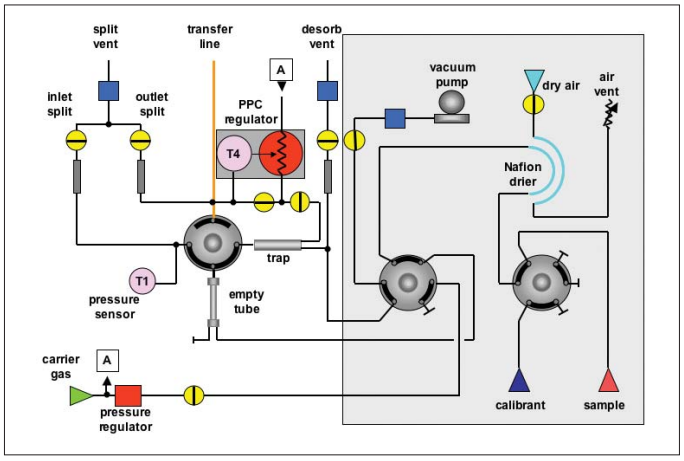

Figure 5. TurboMatrix 300 TD coupled with an on-line air sampling accessory.

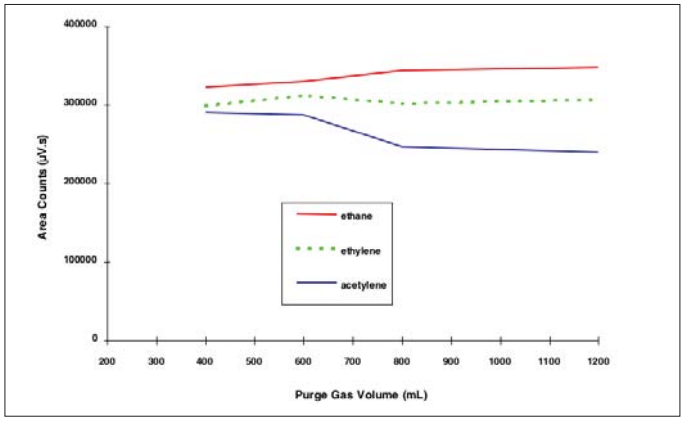

Figure 6. C_2 hydrocarbon recovery vs. sample gas volume (16-19 ng per component).

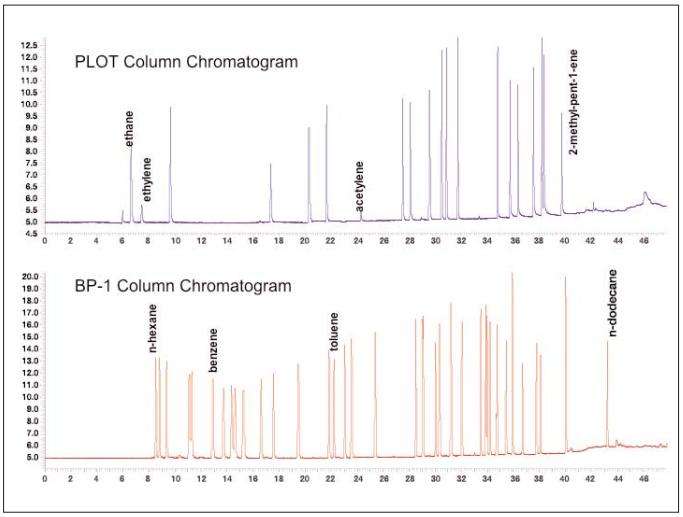

Figure 7. Dual-column separation of a 2-ppb standard of ozone-precursor target compounds.

Comprehensive service and support

With over 60 years of experience, and as a world leader in analytical instrumentation, PerkinElmer is the right partner for the environmental industry. In concert with global distribution of instruments, turnkey systems and consumables, we provide factory-trained global service and support.

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Table 3. System Performance Data from a TurboMatrix 300 TD.

Compound Name	Retention Time, RSD% (n=15)	50 ppb Peak Area RSD% (n=15)	1 to 50 ppb Linearity	Column
Ethane	0.042	2.33	0.9998	PLOT
Ethylene	0.125	3.53	0.9998	PLOT
n-Butane	0.155	2.70	1.0000	PLOT
Acetylene	0.263	3.09	0.9996	PLOT
Cyclopentane	0.094	2.79	1.0000	PLOT
Isoprene	0.113	3.69	0.9977	PLOT
n-Hexane	0.280	2.69	1.0000	BP-1
Benzene	0.308	2.75	0.9999	BP-1
Toluene	0.128	2.72	1.0000	BP-1
Styrene	0.044	2.73	1.0000	BP-1
1,2,3-Trimethylbenzene	0.015	2.86	0.9997	BP-1
n-Dodecane	0.009	2.65	0.9990	BP-1

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