

Ozone Precursor System

Key Features:

- Most reliable analysis of ozone precursors
- Fully U.S. EPA compliant
- Total end-to-end solution from sampling to reporting

The EPA Gold Standard for Over 24 Years

Introduction

In the United States, the Clean Air Act of 1970 gave the U.S. Environmental Protection Agency

(EPA) responsibility for ensuring clean air by monitoring six analytes routinely in ambient air, including SOx, NOx, PM10 (particulates $<10~\mu$), Pb, CO and ozone. In 1990, amendments to the Clean Air Act, expanded the measurements to include fifty four (54) volatile organic compounds (VOCs) that are precursors to the formation of ground-level ozone, implemented through a program known as Photochemical Assessment Monitoring Stations (PAMS). In 2008 the National Ambient Air Quality Standards (NAAQS) for ground-level ozone was reduced to 0.075 ppm for an 8-hour period. An ozone precursor list was also established in Europe, following the 1992 Ozone Directive and United Nations Economic Commission for Europe's protocol on controlling VOC emissions.

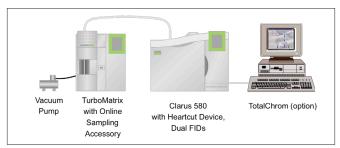
The analysis of C_2 to C_{12} volatile organic ozone-precursor compounds can present a serious technical challenge to the analytical chemist. Low concentrations in the atmosphere coupled with the need to monitor frequently to assess diurnal variations means that a preconcentration step of the sample before analysis by thermal desorption is required. While the samples can be collected in the field and returned to the laboratory, remote, field-based analysis is desired which 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 adsorbents if those adsorbents are cryogenically cooled.



It is difficult to get liquid nitrogen routinely delivered to remote locations and its use can make these analyses costly and dangerous. PerkinElmer resolves this by using an electronic Peltier device enabling cooling to -30°C, there is no need for liquid cryogen. In 1992, PerkinElmer developed a system 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, utilizing the PerkinElmer On-Line Thermal Desorber (ATD) coupled with the PerkinElmer Gas Chromatograph. As a result, this system has become the gold standard for carrying out the measurement of ozone precursors using the PAMS method.

Single-source for a Complete Solution

The key components of the PerkinElmer Online Ozone Precursor Analyzer are shown in Figure 1.



 $\label{thm:components} Figure~1.~Key components~of~the~PerkinElmer~Online,~Field-Based~Ozone~Precursor~Analyzer.$

A TurboMatrix TD with installed online sampling accessory is responsible for collecting the sample, either directly from ambient air or from a sample previously stored in a passivated canister. The sample enters the cooled adsorbent trap at a known flow rate and time so the volume of sample is known. After sampling onto the focusing trap, the sample is thermally desorbed removing the target analytes from the trap into a heated transfer line by carrier gas into the Clarus® Gas Chromatograph. The Clarus GC contains two columns and a heartcut device to separate the analytes. The more-volatile fraction is separated on a PLOT (Porous Layer Open Tubular) column whereas the less-volatile fraction is separated on a dimethyl siloxane column. A flame ionization detector (FID) monitors the chromatography on each column. The PC runs the 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. Since the systems are typically placed in field-based locations, remote control software is used to monitor the system; change parameters if needed; run a blank and/or standard instead of a sample and review data all from an off-site location.

Sample Collection Requirements

Modern adsorbents, when used in combination with the On-Line TurboMatrix TD Peltier-cooled trap, are effective in retaining all the target analytes. This totally eliminates the need for liquid cryogen. Figure 2 shows a diagram of the trap's internal components used to collect the air sample.

Why PerkinElmer?

- Fully complies with U.S. EPA "Technical Assistance Document for Sampling and Analysis of Ozone Precursors" (EPA/600-R-98/161)
- Unattended field operation for more than 24 years
- Unique heart-cutting device enables parallel separation for increased throughput and chromatography resolution
- Hourly sampling
- Automatic system calibration
- Full data processing
- Complete turnkey solution supplied and supported by a single vendor

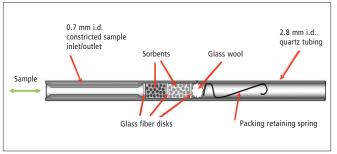


Figure 2. Internal components of the Peltier-cooled trap

The sample is drawn into the cooled trap from the left-hand side in the schematic. 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 volume, which would result in chromatographic peak broadening and degradation in detection limits. The fast trap heat-up rate (99°C/sec) 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 of 3 to 5 mL/min. This design enables the use of very low split ratios (1:1 is typical) enhances minimum detection limits. This trap uses two adsorbents; the weaker adsorbent is situated towards the sample inlet/outlet and will retain the less volatile analytes from the sample. The stronger adsorbent is positioned behind the weaker adsorbent to catch the most volatile analytes (C2 to C3). When the trap is heated, the desorbed analytes are back-flushed from the trap – this ensures that the less volatile compounds never make contact with the stronger adsorbent. The dual adsorbent arrangement facilitates the retention and desorption of all the ozone precursor target analytes, without the need for liquid cryogen.

While a sample is being collected, carrier gas continues to flow to the GC column from the carrier-gas source, so chromatography of the current sample may occur simultaneously with the collection of the next sample, ensuring optimized throughput and the required sampling every hour. Using this sampling approach, < 0.1 ppb detections limit is achievable by sampling 600 mL of air.

Parallel Chromatography

Using this dual sampling approach, chromatography of both of the more-volatile and less volatile fractions will proceed in parallel, which eliminates the need for sub-ambient chromatography as shown in Figure 3.

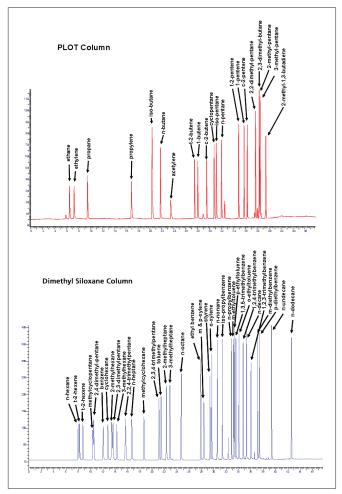


Figure 3. Parallel chromatography of two sample fractions on the PLOT and dimethylsiloxane columns.

A Proven Track Record

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 over the next decade. The PerkinElmer On-line Ozone Precursor Solution 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, such as the Photochemical Assessment Monitoring Stations (PAMS).

Over the last 24 years, there is no question that our Clarus 580 GC and Online TurboMatrix TD system is the gold standard in performing U.S. EPA ozone precursor analysis. We do it more accurately and reliably than anyone in the industry – helping to protect the health and safety of our environment.

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