Ozone Precursor Measurements in Ambient Air with the Saturn GC/MS

GC/MS

Varian Application Note
Number 20

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Key Words: *Air, VOCs, Hydrocarbons, Cryotrapping, Full Scan Spectra*

Ozone is the most commonly measured contaminant to characterize air quality. It is formed through photochemical reactions of volatile organic compounds (VOCs) and nitrogen oxides and is always found in urban smog. In the USA the National Ambient Air Quality Standard (NAAQS) for ozone is 120 ppb volume/volume* and in some European countries is set at 60 ppb (120μg/m^3). Daily one hour average ozone concentrations which have been found to range between 50-300 ppb can have adverse health effects [1,2]. While these data refer to the USA, similar conditions have been observed in other countries.

In order to reduce ozone concentration, the reduction of ozone precursor VOCs is necessary. Title I of the US Clean Air Act Amendments of 1990 requires that the air districts which do not meet the NAAQS take action to monitor and reduce these precursor levels.

The measurement of toxic air contaminant VOCs is usually done by EPA method TO-14.[3] This method is specific to air toxics, but by using appropriate trapping conditions the ozone precursors may be measured the same way. Table 1 lists the ozone precursors specified by EPA for monitoring. These precursors have been studied using the Saturn Air System described in GC/MS Application Note #18 [4].

Instrumentation and Conditions

Cryogenic concentrator:

- Variable Temperature Adsorption Trap (VTAT), 5 cm of 60/80 mesh silanized glass beads
- Two automated valves capable of sample and internal standard (I.S.) introduction
- Electronic mass flow controller with readout box
- Vacuum pump (metal diaphragm)

Pneumatics:

Air sample flow: 20 mL/min
Column flow: 1 mL/min
Auxiliary flow: 20 mL/min

Temperatures:

VTAT: -180°C for 4 min, 180°C/min to 120°C, hold
Valves: 160°C
Column: -60°C for 6 min, 8°C/min to 160°C, hold

Column:

DB-1, 60m x 0.32 mm ID, 1 μm film

MS:

Scan range: 35-260u
Scan rate: 0.8 sec/scan (3 μ scan/analytical scan)
RF storage level: 125 DAC steps
Background mass: 33u
Segment Breaks: 70/78/150
Tune factors: 120/70/100/70
AGC Target: 12000
Emission Current 20 μA **
Manifold temperature: 100°C

*ppb volume/volume is defined as 1 nL analyte in 1L sample; the weight/volume concentration can be calculated considering the analyte molecular weight.

**Optimized parameters might vary instrument to instrument.

Table 1. List of Ozone Precursors

**Ethylene	t-2-Pentene	Methylcyclopentane	3-Methylheptane
*Ethane	c-2-Pentene	2,4-Dimethylpentane	n-Octane
*Acetylene	2-Methyl-2-Butene	1,1,1-Trichloroethane	Perchloroethylene
Propylene	2,2-Dimethylbutane	Benzene	Ethylbenzene
Propane	Cyclopentene	Cylohexane	m-Xylene
Isobutane	4-Methyl-1-Pentene	2-Methylhexane	p-Xylene
1-Butene	Cyclopentane	2,3-Dimethylpentane	Styrene
n-Butane	2,3-Dimethylbutane	3-Methylhexane	o-Xylene
t-2-Butene	2-Methylpentane	Trichloroethylene	n-Nonane
c-2-Butene	3-Methylpentane	2,2,4-Trimethylpentane	Isopropylbenzene
3-Methyl-1-Butene	2-Methyl-1-Pentene	n-Heptane	alpha-Pinene
Isopentane	n-Hexane	Methylcyclohexane	n-Propylbenzene
1-Pentene	Chloroform	2,3,4-Trimethylpentane	1,3,5-Trimethylbenzene
n-Pentane	t-2-Hexene	Toluene	beta-Pinene
Isoprene	c-2-Hexene	2-Methylheptane	1,2,4-Trimethylbenzene

*These compounds are detected by FID

To successfully measure the ozone precursors in the 0.1-15 ppb concentration range, an air sample must be concentrated. The precursors are trapped on glass beads at -180°C in a built-in automated concentrator. The duration of this trapping process is user defined, so different sample volumes can be concentrated. In this study 60-100 mL sample volumes were analyzed. The resulting chromatogram of a standard for 57 components with concentrations between 4-10 ppb is shown in Figure 1. The combination of the efficient concentrator and the Saturn system's superb sensitivity allows the qualitative and quantitative determination of ozone precursors at and below the required concentration (1 ppb) using only 60 mL sample volumes instead of the commonly used 400-500 mL.

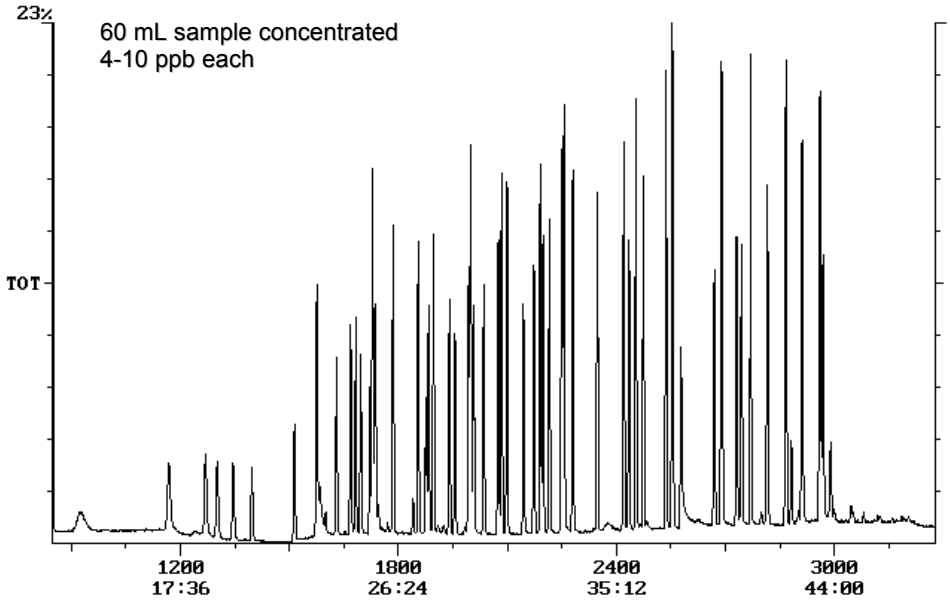

Figure 1. 57 Component Hydrocarbon Mixture

The system's sensitivity is demonstrated in Figure 2, where a chromatogram of a 0.1 ppb hexane standard is shown. The signal to noise (S/N) ratio is 84 when 90 mL of the standard was concentrated, and the NIST library reverse fit was 902 of 1000. Similar library search data was observed for the light (propene), medium (pentane) and heavy (nonane) precursors as shown in Figure 3.

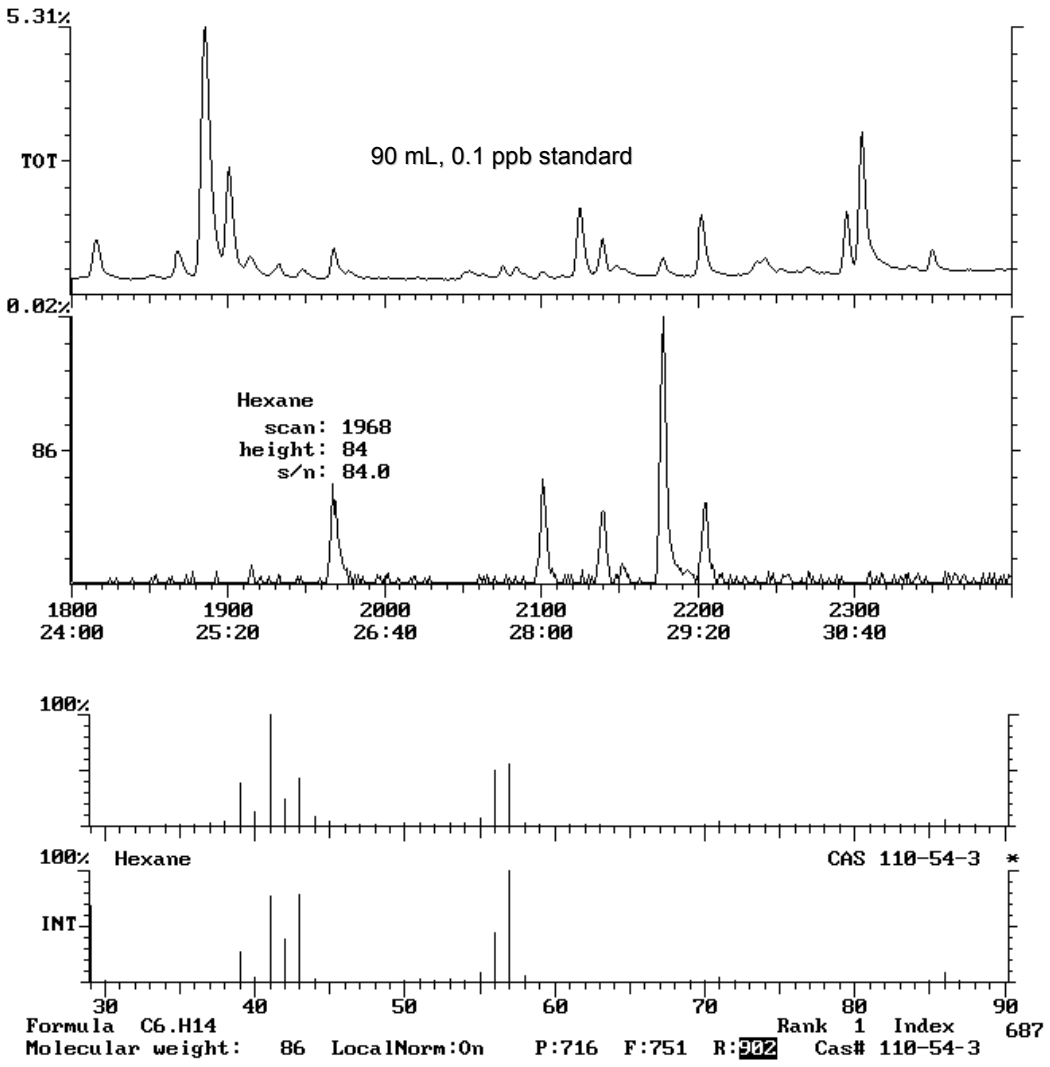

Figure 2. Sensitivity and Library Search for Hexane

The Saturn Air System's hardware is capable of the measurement of both ozone precursors and air toxics by modifying some of the method parameters. The need for a sample dryer is eliminated because small sample volumes are concentrated. The analysis time and LN_2 consumption are reduced since the concentration takes place in 3-5 minutes instead of the commonly used 20-30 minutes. The system footprint is small, the concentrator is integrated into the GC and all components (concentrator, GC, MS detector) are controlled from one PC.

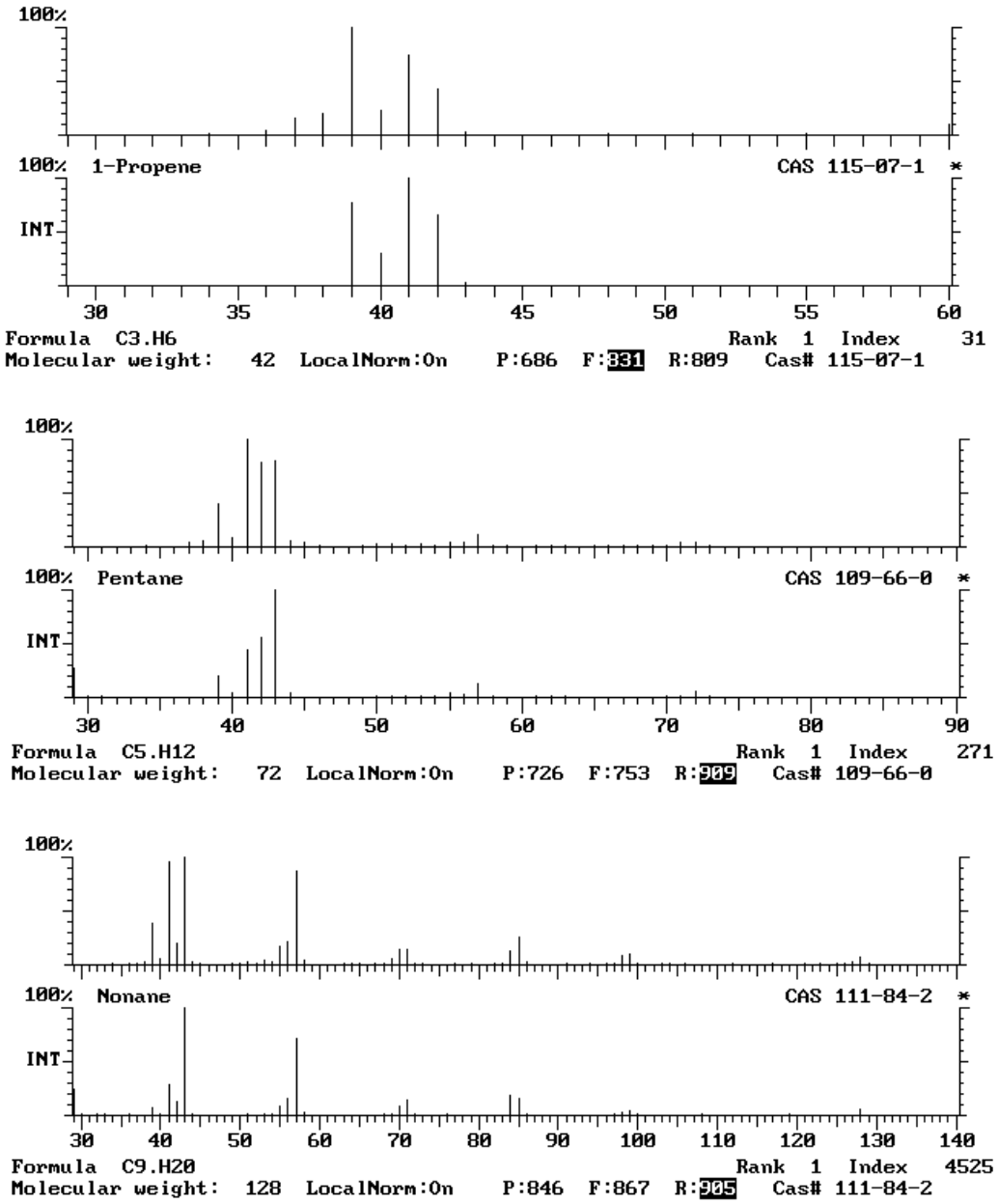

Figure 3. NIST Library Search of 1-Propene, Pentane and Nonane

References

1. Lippmann, M., "Health Effects of Ozone: A Critical Review", Journal of Air and Waste Management Association, 39, 672-694, 1989.

2. L. Stockburger, K. Knapp, T. Ellestad, "Overview and Analysis of Hydrocarbon Samples During the Summer Southern California Air Quality Study" 82nd Annual AWMA meeting, paper 89-139.1.

3. Compendium Method TO-14, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711, 1988.

4. E. Almasi, N. Kirshen; The Determination of Volatile Organic Compounds (VOCs) in Air by the TO-14 Method Using the Saturn II GC/MS, Varian GC/MS Application Note#18.

These data represent typical results.
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