

Round-the-Clock, Online and Cryogen-Free Monitoring of Hydrocarbons in Ambient Air Using Thermal Desorption-Gas Chromatography

An application of the UNITY[™]-Air Server thermal desorber system

Technical Overview

Background

The presence of volatile hydrocarbons in urban atmospheres is believed to contribute to the formation of ground level ozone, one of the main constituents of urban smog. The compounds of interest range in volatility from ethyne (acetylene) to trimethylbenzene and are generally referred to as 'ozone precursors'.

Vehicle emissions are thought to be the main source of these compounds. Recent European and US regulations^{1, 2} require round-the-clock monitoring of target species in all major urban centers to establish and monitor the link between periods of high traffic density and high pollution levels. Key compounds include: benzene, toluene, xylene, and 1,3-butadiene. Continuous real-time monitoring provides an insight into emission episodes from local industry and can be used to monitor the effect of weather conditions such as wind direction, precipitation, and temperature inversion.

Introduction

The UNITY[™]-Air Server is a new, cost-effective thermal desorber for round-the-clock speciated measurement of multiple trace-level volatile organic compounds (VOCs) in air or pure gases. It combines automated, controlled-flow sampling with cryogen-free concentration technology. The

²1990 US Clean Air Act Amendment

system can be coupled to an Agilent gas chromatograph (GC) or a gas chromatograph/mass spectrometer (GC/MS), and is designed for unattended operation in remote field locations.

In summary, sample air is pulled through an optionally incorporated permeable membrane dryer directly onto an electrically-cooled, sorbentpacked focusing trap at a controlled flow rate. No liquid cryogen is required. The membrane dryer selectively eliminates water and other low molecular weight polar components, reducing the risk of interference from unknown species. It facilitates the use of flame ionization detection (FID) rather than MS detection.

To avoid contamination, sampling flows are controlled by an electronic mass flow controller and pump located downstream of the focusing trap. All sampling parameters are selected by the user and monitored by UNITY-Air Server software as an integral part of the analytical method. After sample collection, the flow path is purged with carrier gas to prevent carryover and to eliminate oxygen from the focusing trap. The trap then heats rapidly, at rates approaching 100 °C/s, to inject retained analytes into the capillary column as a highly concentrated band of vapor. This transfer may be performed splitless for maximum sensitivity. Once the trap has desorbed, it recools, re-equilibrates to the trapping temperature, and begins collection of the next sample while analysis of the previous sample is ongoing.





¹Council Directive 96/62/EC: On ambient air quality assessment and management, and its "daughter" directive - 2000/69/EC relating to limit values for benzene and carbon monoxide in ambient air.

The UNITY-Air Server also offers automatic interchange between three sample channels (typically sample, reference, and blank) for remote system calibration/validation as per user requirements. Six or eight channel options are also available.

This application note describes validation of the system for online monitoring of the 27 ozone precursors specified by European regulators, plus 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, and isoprene. Table 1 in the Appendix shows the full list of 30 compounds.

Operation of the system for compliance with the 56-component US EPA ozone precursor list is also demonstrated. Table 2 in the Appendix shows the list of 56 compounds. Key factors taken into account when developing this method included the need for a system that could operate round-the-clock unattended, hence the requirement for cryogen-free operation. The system should allow hourly sample collection with as much of the hour as possible dedicated to sampling. Finally, detection limits should be below 0.5 ppb - ideally 0.1 ppb.

Defining the Ideal Cold Trap

Initial tests were carried out using the 30-component ppb-level certified gas standard described above

(National Physical Laboratory, Teddington, UK). Individual concentrations are listed in Table 1 in the Appendix. Two types of ozone precursor focusing traps were tested:

Trap 1 - Three-bed trap: porous polymer sorbent (5 mm), graphitized carbon black (8 mm), and carbon molecular sieve (~45 mm).

Trap 2 - Four-bed trap: porous polymer sorbent (5 mm), graphitized carbon black (8 mm), carbon molecular sieve 1 (15 mm), and carbon molecular sieve 2 (30 mm).

Trap 1 is the stronger of the two, retaining the highly volatile compounds to a greater extent than trap 2. However, the strength of the sorbents in trap 1 caused slight broadening of early eluting peaks under the splitless conditions used for optimum sensitivity (sub ppb). Figure 1 shows a chromatogram of a splitless injection using the four-bed trap specifically designed for this application.

Breakthrough Tests

All the C2 hydrocarbons are highly volatile species. Ethyne (acetylene) has a boiling point of -89 °C and is the most difficult to trap. To retain it quantitatively without liquid cryogen requires careful selection of the cold trap sorbent(s) and focusing temperature.



Figure 1. Chromatogram showing a splitless injection of 150 mL of calibration standard.

Breakthrough volume experiments were performed on the selected cold trap using the ppb-level certified gas standard generated by the National Physical Laboratory, Teddington, UK. Steadily increasing volumes of the gas standard were introduced and a graph of detector response versus sampled volume traced. Breakthrough occurs when the data deviates from a linear relationship, that is, when the species of interest are no longer quantitatively retained. Data from the low volumes of standard introduced were also used to estimate detection limits.

Analytical conditions used for determining the breakthrough volumes:

Column:	J&W GasPro, $30 \text{ m} \times 0.32 \text{ mm}$
GC Program:	40 °C (hold 5 min)
	Ramp 1: 5 °C/min to 90 °C
	Ramp 2: 20 °C/min to 260 °C
	Hold (10 min)
Prepurge time:	2 min
Sampling rate:	10 mL/min
Sampling time:	Various
Purge time:	1 min
Cold trap:	Ozone precursor trap
Cold trap low:	−15 °C
Cold trap high:	300 °C
Cold trap hold:	5 min
Transfer line:	100 °C

Figure 2 shows peak area versus sampled volume

of calibration gas for acetylene and propane. Propane is a less volatile component that has a breakthrough volume of many liters on the cold trap used in these experiments.

Figure 2 shows that there is good reproducibility and negligible breakthrough for acetylene, even up at 600 mL of sampled gas. Field sampling volumes of 450 mL (45 min sampling at 10 mL/min) may therefore be used.

Detection/Quantitation Limits

Signal-to-noise ratios for the 150 mL volume of standard using the GC-FID are in the order of 300:1 for the light hydrocarbons at ~6 ppb. For compounds from n-butane upwards, which are at ~2 ppb concentration level, signal-to-noise ratio is 150:1. Assuming a minimum detection signal-tonoise ratio of 3:1 and a minimum quantifiable signal of double that, approximate detection/quantitation limits for 450 mL air samples were

calculated as follows:

HydrocarbonsDetection ppbQuantificationC2 to C30.050.1C4+0.030.06



Figure 2. Peak area vs. volume sampled for acetylene and propane.

Reproducibility of Peak Area and Retention Time

Figure 3 shows four repeat analyses of the ozone precursor calibration standard on a J&W $30 \text{ m} \times 0.32 \text{ mm}$ GasPro column. Although some coelution of C5 hydrocarbons was observed, excellent retention time (<1% RSD) and peak area (<2% RSD) precision were found across the analyte range for sequence of 12 analyses.



Figure 3. Repeat analyses of 200 mL gas standard run before 5-day field monitoring study.

Suburban Air Monitoring

Analyzer performance for an unattended field operation was evaluated during a 5-day trial at one of Europe's leading centers for standardization in environmental monitoring. Figure 4 shows a sequence of ambient air profiles running from before dawn through the height of the rush hour in a suburban environment. These data were collected at the end of the trial and show that good analytical performance was maintained. No user intervention was required during the 5-day trial. Detection limits in this relatively clean environment were also satisfactory.

Figure 5 describes a two-column configuration suitable for GC-FID detection and quantitation of low molecular weight hydrocarbons.



Figure 4. A series of suburban air profiles from 06:30 to 10:30 on 24th January 2000.



Figure 5. Schematic representation of the two-column ozone precursor analytical system.

Figures 6 and 7 show chromatograms obtained using the 30- and 56-component calibration gas standards respectively, using the described two-column GC system. Peak identifications are given in Tables 1 and 2 in the Appendix. This configuration makes it possible to separate all of the components in these two standard mixtures.



Figure 6. Thirty-component calibration gas injection on two-column analytical system.



Figure 7. Fifty six-component calibration gas injection on two-column analytical system.

Figures 8 and 9 show linearity plots for five selected compounds.



Figure 8. Detector response vs. sampled volume for ethene, propane, and 1,3-butadiene.



Figure 9. Detector response vs. sampled volume for heptane and toluene.

Appendix

Compound Ethane (1)	Concentration (mole fraction by ppb) 5.94	Uncertainty (mole fraction by ppb) ±0.15
Ethene (2)	9.31	±0.20
Ethyne (7)	7.75	±0.20
Propane (3)	2.25	±0.05
Propene (4)	5.86	±0.15
Propyne (15)	2.53	±0.05
n-Butane (6)	2.27	±0.05
<i>iso</i> -Butane (5)	2.63	±0.05
<i>iso</i> -Butene (10)	2.49	±0.05
1-Butene (9)	2.91	±0.05
trans-2-Butene (8)	1.94	±0.05
cis-2-butene (11)	2.08	±0.05
1,3-Butadiene (14)	4.66	±0.10
n-Pentane (13)	2.32	±0.05
i-Pentane (12)	1.04	±0.02
trans-2-Pentene (16)	3.54	±0.10
cis-2-Pentene (17)	1.35	±0.03
lsoprene (20)	1.61	±0.04
2-Methylpentane (18)	2.78	±0.05
3-Methylpentane (19)	3.18	±0.05
Cyclohexane (23)	2.92	±0.05
n-hexane (21)	1.55	±0.04
Benzene (22)	3.00	±0.05
n-Heptane (24)	2.43	±0.05
Toluene (25)	2.82	±0.05
Ethylbenzene (26)	1.55	±0.04
o-Xylene (28)	0.88	±0.02
m-Xylene (27)	1.23	±0.03
1,2,4-Trimethylbenzene (30)	0.99	±0.02
1,3,5-Trimethylbenzene (29)	0.81	±0.02

Table 2. Details of ppb-Level 56-Component Gas Standard

Peak number	Compound
1	Ethane
2	Ethylene
3	Propane
4	Propylene
5	iso-Butane
6	n-Butane
7	Acetylene
8	trans-2-Butene
9	1-Butene
10	<i>cis</i> -2-Butene
11	Cyclopentane
12	Isopentane
13	n-Pentane
14	trans-2-Pentene
15	1-Pentene
16	<i>cis</i> -2-pentene
17	2,2-Dimethylbutane
18	2,3-Dimethylbutane
19	2-Methylpentane
20	3-Methylpentane
21	Isoprene
22	2-Methyl-1-Pentene
23	Hexane
24	Methylcyclopentane
25	2,4-Dimethylpentane
26	Benzene
27	Cyclohexane
28	2-Methylhexane
29	2,3-Dimethylpentane
30	3-Methylhexane
31	2,2,4-Trimethylpentane
32	n-Heptane
33	Methylcyclohexane
34	2,3,4-Trimethylpentane
35	Toluene
36	2-Methylheptane
37	3-Methylheptane
38	n-Octane
39	Ethylbenzene
40	m/p-Xylene
41	Styrene
42	o-Xylene
43	n-Nonane
44	Isopropylbenzene
45	n-Propylbenzene
46	m-Ethyltoluene
4/	p-Ethyltoluene
4ð	1,3,5-Irimetnyibenzene
49 50	0-EUIYITOIUENE
50 E1	
บ 1 52	1.2.2 Trimothylbonzonc
52 52	
55 E4	
54 55	p-Dietriyiberizerie
55	n-ondecane
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