

Introduction

Ozone, or trioxigen, is a gas made up of three oxygen atoms (O₃). Naturally occurring in the stratosphere (upper atmosphere), ozone protects life on Earth from the Sun's ultraviolet (UV) radiation. However, the tropospheric ozone formation occurs when nitrogen oxides (NO_x), carbon monoxide (CO) and volatile organic compounds (VOCs) react in the atmosphere in the presence of sunlight, specifically the UV spectrum. NO_x, CO and VOCs are known as the ozone precursors. These ozone precursors cause a negative impact on plants and animals. Although VOCs are naturally emitted by biological organisms, NO_x and VOCs are emitted during combustion of farming equipment and burning of biological materials.

It is vital that the environment is not only protected from these ozone precursors but the level of ozone precursors are monitored. The United States Air Cleansing Act (1970) empowered the Environmental Protection Agency (EPA) to maintain air cleanliness and protect public health. EPA requires states in the US to identify problematic areas through comprehensive monitoring of NO_x, CO and VOCs (known as Photochemical Assessment Monitoring Stations; PAMS).

In the PAMS monitoring program, there are 57 specified target compounds, mainly non-methane hydrocarbons ranging from C₂ to C₁₂. This application note describes the process for monitoring these 57 ozone precursors in ambient air.

Experimental

A SCION 8500 GC, equipped with a split/splitless injector, deans switch, liquid nitrogen cooling column module and FID detector was coupled to the Scion mass spectrometer (MS). Additional instrumentation used throughout this application included an atmospheric preconcentrator, has dilution device, tank cleaning device, concentrator autosampler, stainless steel sampling tank (3.2L, 6L capacity) and a liquid nitrogen tank.

A PAMS ozone precursor gas (containing 57 target compounds) at 1µmol/mol was diluted using high purity nitrogen to 20nmol/mol. The internal standard calibration gas comprised of chloro-bromo-methane, 1,2-difluorophenyl, chlorobenzene-d₅ and 4-bromo-fluorobenzene at 1µmol/mol and was diluted to 100nmol/mol with pure nitrogen.

Ambient air samples were collected in the sample tank and pressurised to 101kPa with high purity nitrogen. 400mL of sample, with 50mL of internal standard was analyzed.

Calibration standards were prepared at 1.25, 2.5, 5, 10, 15 and 20nmol/mol with the addition of 12.5nmol/mol internal standard to each standard.

Table 1 details the instrument conditions for the analysis of ozone precursors.

Table 1. Analytical conditions of the GC-FID:MS

Conditions	
S/SL	200°C
Column 1	Scion Plot Q 30m x 0.32mm x 20µm
Column 2	Scion-1MS 60m x 0.25mm x 1µm
Oven Programme	5°C (6 min), 5°C/min to 170°C (5 min), 15°C/min to 190°C (10 min)
Carrier Gas	Helium 1mL/min constant
FID	250°C
MS	Full Scan 30amu to 300amu
Ion Source	250°C
Temperature Line	250°C

Results

Calibration curves were obtained for each target compound, with linear correlation coefficients all greater than 0.997 (majority of compounds had an R² of 0.999). Figures 1a-1f highlights the calibration curves of six target compounds.

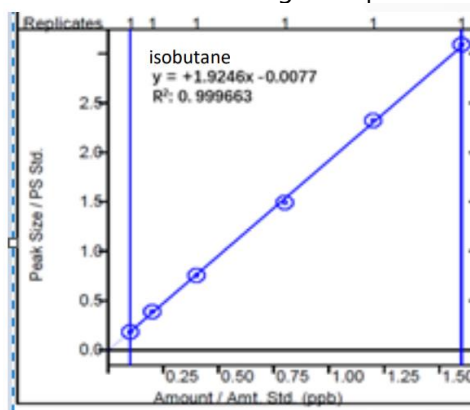


Figure 1a. Calibration curve of isobutane

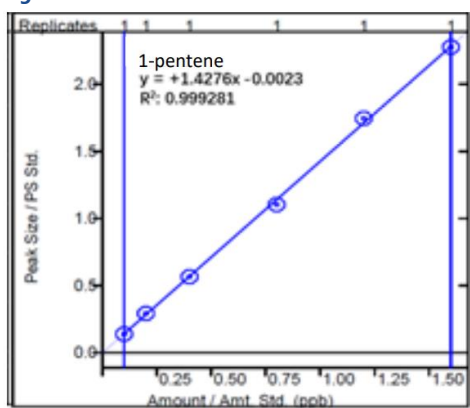


Figure 1b. Calibration curve of 1-pentene

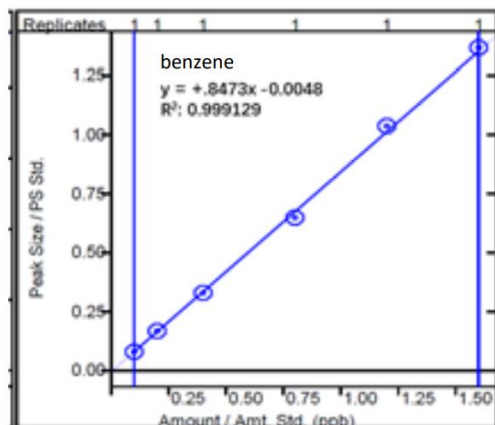


Figure 1c. Calibration curve of benzene

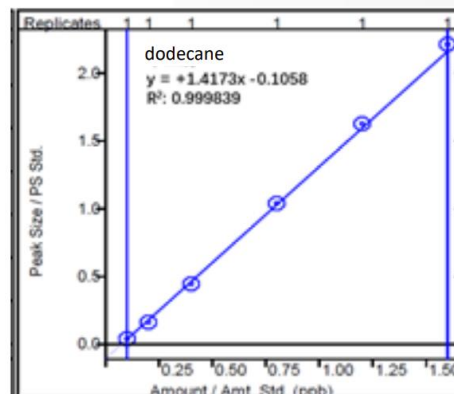


Figure 1f. Calibration curve of dodecane

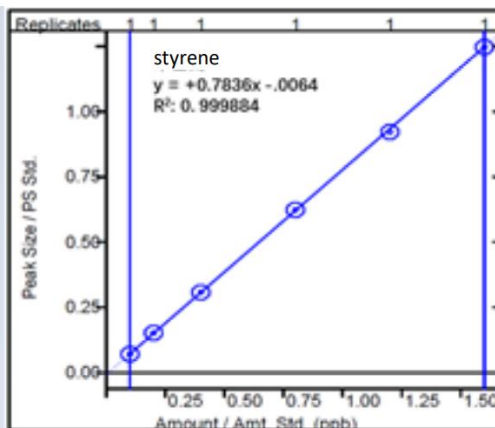


Figure 1d. Calibration curve of styrene

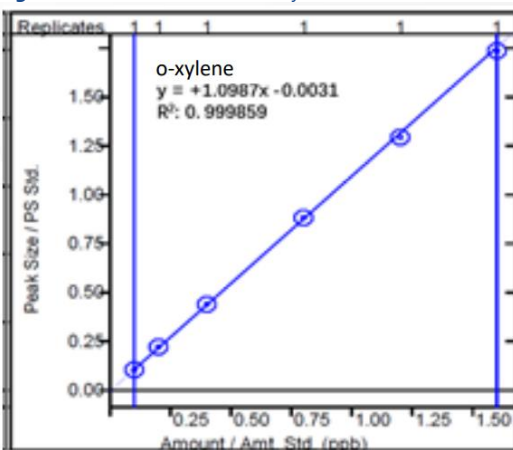


Figure 1e. Calibration curve of o-xylene

Table 2. Compound ID, retention times, corresponding internal standards and correlation coefficients for all 57 target compounds

Compound	Retention Time	Internal Standard	R ²
Isobutane	11.958	Chloro-bromo-methane	0.9997
1-butene	12.919	Chloro-bromo-methane	0.9994
Butane	13.297	Chloro-bromo-methane	0.9994
t-2-butene	13.741	Chloro-bromo-methane	0.9994
Ethylene	13.986	-	0.9995
c-2-butene	14.387	Chloro-bromo-methane	0.9994
Acetylene	14.649	-	0.9997
Ethane	15.125	-	0.9996
Isopentane	16.894	Chloro-bromo-methane	0.9990
1-pentene	17.667	Chloro-bromo-methane	0.9993
Pentane	18.280	Chloro-bromo-methane	0.9993
Isoprene	18.523	Chloro-bromo-methane	0.9989
t-2-pentene	18.686	Chloro-bromo-methane	0.9995
c-2-pentene	19.109	Chloro-bromo-methane	0.9992
2,2-dimethyl butane	20.235	Chloro-bromo-methane	0.9996
Cyclopentane	21.788	Chloro-bromo-methane	0.9981
2-methyl-pentane	22.059	Chloro-bromo-methane	0.9984
Propylene	22.085	-	0.9995
Propane	22.720	-	0.9991
3-methyl-pentane	22.829	Chloro-bromo-methane	0.9986
1-hexene	23.108	Chloro-bromo-methane	0.9990
Hexane	23.969	1,2-difluorophenyl	0.9985
Methylcyclopentane	25.198	1,2-difluorophenyl	0.9977
2,4-dimethylpentane	25.284	1,2-difluorophenyl	0.9986
Benzene	26.430	1,2-difluorophenyl	0.9991
Cyclohexane	26.940	1,2-difluorophenyl	0.9986
2-methylhexane	27.138	Chlorobenzene-d5	0.9994
2,3-dimethylpentane	27.307	Chlorobenzene-d5	0.9993
3-methylhexane	27.538	Chlorobenzene-d5	0.9996
2,2,4-trimethylpentane	28.302	Chlorobenzene-d5	0.9998
Heptane	28.682	Chlorobenzene-d5	0.9987
Methylcyclohexane	29.972	Chlorobenzene-d5	0.9991
2,3,4-trimethylpentane	31.201	Chlorobenzene-d5	0.9985
Toluene	31.472	Chlorobenzene-d5	0.9978
2-methylheptane	31.724	Chlorobenzene-d5	0.9992
3-methylpentane	32.087	Chlorobenzene-d5	0.9995
Octane	33.177	Chlorobenzene-d5	0.9997
Ethylbenzene	35.599	Chlorobenzene-d5	0.9998
p,m-xylene	35.968	Chlorobenzene-d5	0.9999
Styrene	36.680	Chlorobenzene-d5	0.9999
o-xylene	36.925	Chlorobenzene-d5	0.9999
Nonane	37.247	Chlorobenzene-d5	0.9994
Isopropylbenzene	38.161	4-bromofluorobenzene	0.9996
Propyl benzene	39.323	4-bromofluorobenzene	0.9998
1-ethyl-3-methylbenzene	39.557	4-bromofluorobenzene	0.9998

Table 2 details correlation coefficients for all target compounds along with compound identifiers, retention times and corresponding internal standards.

1-ethyl-4-methylbenzene	39.675	4-bromofluorobenzene	0.9998
1,3,5-trimethylbenzene	39.845	4-bromofluorobenzene	0.9998
1-ethyl-2-methylbenzene	40.363	4-bromofluorobenzene	0.9998
1,2,4-trimethylbenzene	40.941	4-bromofluorobenzene	0.9999
Decane	41.117	4-bromofluorobenzene	0.9997
1,2,3-trimethylbenzene	42.217	4-bromofluorobenzene	0.9998
1,3-diethylbenzene	43.159	4-bromofluorobenzene	0.9998
1,4-diethylbenzene	43.485	4-bromofluorobenzene	0.9998
Undecane	45.247	4-bromofluorobenzene	0.9994
Dodecane	49.389	4-bromofluorobenzene	0.9998

C₂ to C₃ (five compounds) are detected on the FID whilst C₄ to C₁₂ are detected using the MS. Utilising the Dean Switch allows the dual detector system from a single injection. Figure 2a details the chromatogram of the five compound FID chromatogram whereas Figure 2b details the 54 target compounds plus four internal standards (MS chromatogram).

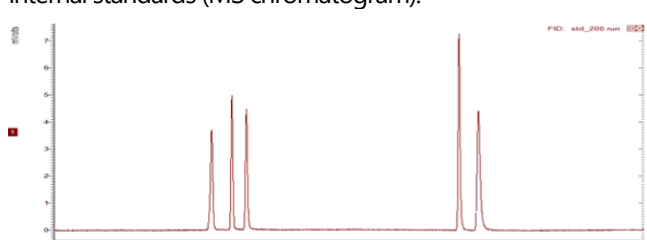


Figure 2a. C₂-C₃ target ozone precursors

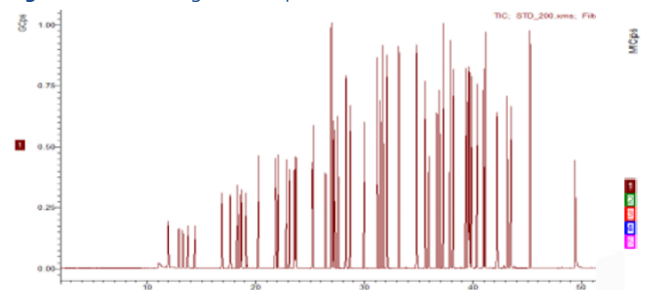


Figure 2b. C₄-C₁₂ target ozone precursors

Repeatability of the SCION analyzer was determined through five consecutive injections of 5nmol/mol gas standard, as shown in Figures 3 and 4.

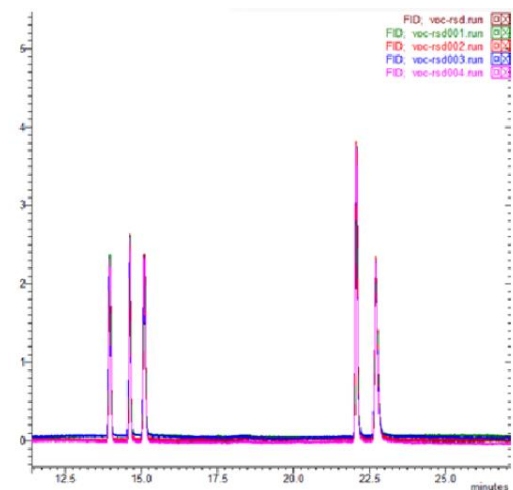


Figure 3. Chromatogram overlay of C₂-C₃ ozone precursors (n=5)

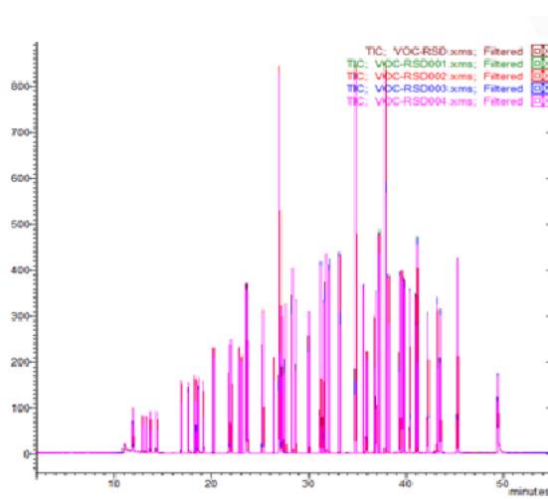


Figure 4. Chromatogram overlay of 52 ozone precursors (n=5)

Conclusion

The SCION 8500 equipped with a deans switch and FIDMS configuration offered excellent repeatability with exceptional linear range for the analysis of 57 ozone precursors in ambient air, in a single injection.

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