The Determination of Vehicle Emissions in Exhaust Gases and Ozone Precursors in Ambient Air with a Built-in Preconcentrator/GC System

Application Note

INTRODUCTION

Internal combustion engine emissions are comprised of a long list of organic compounds from C2 to C12 hydrocarbons. Major sources of these are automobiles and trucks with lesser sources including industrial emissions and home powered tools such as lawnmowers and leaf blowers. These emissions are considered as ozone precursors in the ambient air since under atmospheric conditions in the summer months, they can interact with nitrogen oxides in the presence of sunlight to produce ozone, a criteria air pollutant under the United States Clean Air Act (1970).

The amount and identity of the saturated and unsaturated organics that make up the ozone precursors has a major impact on the amount of ozone produced since each precursor has a certain ozone formation potential. Concentration at the tailpipe of an automobile are much greater than those found in the ambient air, so any analytical system must be capable of analysing a wide range of concentrations. A custom SCION GC system combining a special preconcentrator and dual FID was used to evaluate a standard gas mixture which contained target precursors from C2 to C13 hydrocarbons.

EXPERIMENTAL

A 456 GC was fitted with a sample preconcentration trap (SPT), a nafion gas sample dryer, a three Valco valve system with dual flame ionisation detectors (FID's). Figure 1 shows the configuration of the gas analyser. Analytical parameters used throughout this application can be found in Table 1.

Approximately 100mL of sample is drawn through the dryer and then through the SPT multi-absorbent trap. The residual air is then flushed from the trap for one minute. The trap is then backflushed and desorbed at 220˚C. The trap contents are split to two 0.32mm i.d capillary columns. Column 1, a PLOT Al2O3/KCl column separated C_2 to C_6 whereas a SCION-1 column separated C_6 to C_{13}. During the chromatography, the external dryer is backflushed with any trace of the sample being flushed out of the system.

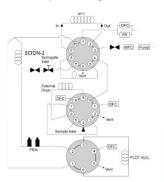**Table 1.** Analytical parameters

Sample	100mL, 100ppbc
SPT	Tenax/Carbotrap/Carbosieve
Trap	0˚C, desorb 220˚C
Column 1	PLOT Al2O3 50m x 0.32mm x 5.0µm; 2.5mL/min
Column 2	SCION-1 60m x 0.32mm x 1.0µm; 3.2mL/min
Oven	0˚C (hold 10 min), 10˚C/min to 200˚C (hold)

RESULTS

A chromatogram is produced from each of the detectors; one for hydrocarbons C2 to C6 (Figure 2) and a second for hydrocarbons C6 to C13 (Figure 3).
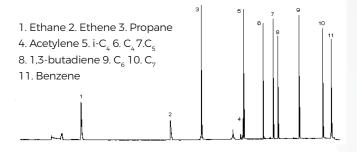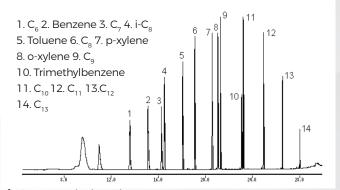

1. Ethane 2. Ethene 3. Propane
4. Acetylene 5. i-C_4 6. C_4 7.C_5
8. 1,3-butadiene 9. C_6 10. C_7
11. Benzene

Fig 2. C_2 to C_6 hydrocarbons

1. C_6 2. Benzene 3. C_7 4. i-C_8
5. Toluene 6. C_8 7. p-xylene
8. o-xylene 9. C_9
10. Trimethylbenzene
11. C_{10} 12. C_{11} 13.C_{12}
14. C_{13}

Fig 2. C_6 to C_{13} hydrocarbons

Fig 1. Schematic diagram for vehicle emissions/ ozone precursor

A series of nine replicates of a C6 to C12 standard were run and the retention time and area count precisions determined. The statistical data for the precision testing can be found in Table 2.

DISCUSSION

Gas exhaust components or ozone precursors are targeted by EPA for quantitative analysis due to their ozone formation potential. However, there are a number of unidentified components that may be present in a sample. In order to correctly identify compounds, mass spectrometry may be used. Retention time, peak area t precision and the recovery of analytes is also important for the accurate quantification of the components of interest. Obtaining high recoveries of target compounds in air is more difficult as boiling point increases. Excellent recoveries are obtained through C_{11} (C_6-C_9 100%, C_{10} 97%, C_{11} 86%) with recovery dropping to 50% for C_{12}.

CONCLUSION

The SCION custom analyser with built in preconcentrator, dual columns and dual FID's are capable of quantitatively analysing a wide range of hydrocarbon compounds found in vehicle emissions and ambient air. The high recovery and excellent precision ensure that targeted compounds are confidently identified and quantified.

Table 2. Retention time and Peak Area

Compound	% Standard Deviation of the nine injections	
	Retention Time (RSD%)	Peak Area (RSD%)
C_6	0.070	0.32
Benzene	0.051	0.37
C_7	0.041	0.30
i-C_8	0.040	0.29
Toluene	0.033	0.43
C_8	0.031	0.32
p-xylene	0.029	0.42
o-xylene	0.030	1.07
C_9	0.030	0.42
Trimethylbenzene	0.029	0.82
C_{10}	0.030	0.54
C_{11}	0.028	0.82
C_{12}	0.026	1.36