

# 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 C<sub>2</sub> to C<sub>12</sub> 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 C<sub>2</sub> to C<sub>13</sub> hydrocarbons.

### EXPERIMENTAL

A 456 GC was fitted with a sample pre-concentration 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 Al<sub>2</sub>O<sub>3</sub>/KCl column separated C<sub>2</sub> to C<sub>6</sub> whereas a SCION-1 column separated C<sub>6</sub> to C<sub>13</sub>. During the chromatography, the external dryer is backflushed with any trace of the sample being flushed out of the system.

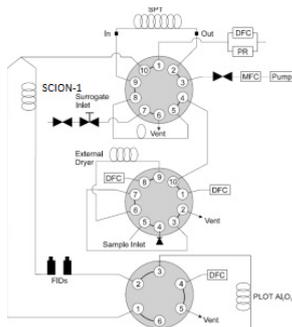


Fig 1. Schematic diagram for vehicle emissions/ ozone precursor

Table 1. Analytical parameters

<b>Sample</b>	100mL, 100ppbc
<b>SPT</b>	Tenax/Carbotrap/Carbosieve
<b>Trap</b>	0°C, desorb 220°C
<b>Column 1</b>	PLOT Al <sub>2</sub> O <sub>3</sub> 50m x 0.32mm x 5.0µm; 2.5mL/min
<b>Column 2</b>	SCION-1 60m x 0.32mm x 1.0µm; 3.2mL/min
<b>Oven</b>	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 C<sub>2</sub> to C<sub>6</sub> (Figure 2) and a second for hydrocarbons C<sub>6</sub> to C<sub>13</sub> (Figure 3).

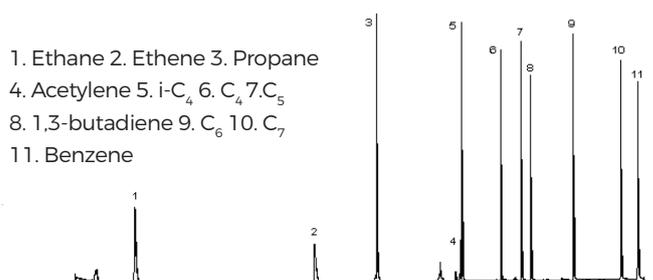


Fig 2. C<sub>2</sub> to C<sub>6</sub> hydrocarbons

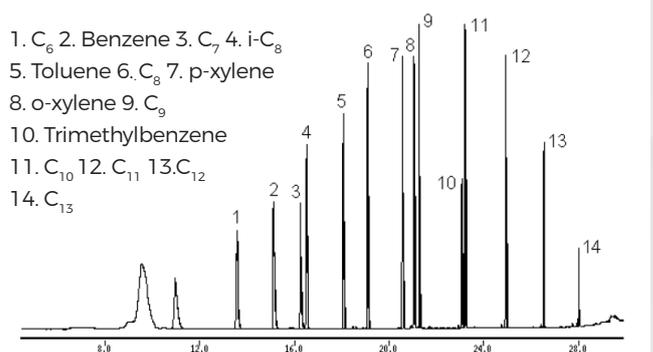


Fig 2. C<sub>6</sub> to C<sub>13</sub> hydrocarbons

A series of nine replicates of a C<sub>6</sub> to C<sub>12</sub> 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 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<sub>11</sub> (C<sub>6</sub>-C<sub>9</sub> 100%, C<sub>10</sub> 97%, C<sub>11</sub> 86%) with recovery dropping to 50% for C<sub>12</sub>.

## 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 <sub>6</sub>	0.070	0.32
Benzene	0.051	0.37
C <sub>7</sub>	0.041	0.30
i-C <sub>8</sub>	0.040	0.29
Toluene	0.033	0.43
C <sub>8</sub>	0.031	0.32
p-xylene	0.029	0.42
o-xylene	0.030	1.07
C <sub>9</sub>	0.030	0.42
Trimethylbenzene	0.029	0.82
C <sub>10</sub>	0.030	0.54
C <sub>11</sub>	0.028	0.82
C <sub>12</sub>	0.026	1.36