APPLICATION NOTE

US EPA Method TO-15 Volatile Organic Compounds in Ambient Air

AN023v1; SCION Instruments

Introduction

Many volatile organic compounds (VOCs) that occur in ambient air are the result of emissions from mobile, industrial sources, landfills and hazardous waste sites. The levels of these compounds in air frequently regulated by national or local government agencies. Additionally, it is vital to monitor the VOCs to determine the effect they have on human health, the environment and the global climate.

Detection of toxic organic compounds in ambient air is undoubtedly one of the most difficult analyses in gas chromatography, due to the trace levels needed to be quantified and due to the large number of target compounds. Samples must be concentrated into a small volume in order to enhance detection limits.

The United States Environmental Protection Agency (US EPA) developed a harmonised test method (TO- 15) for the measurement of VOCs in ambient air when analysed by gas chromatography with mass spectrometry (GC-MS). US EPA TO-15 specifies that air must be collected in specially prepared canisters. TO-15 measures toxic organics at a target linear range of 0.5nmol/mon (ppbv) to 30nmol/mon (ppbv), with expected detection limits less than 0.2nmon/mol, for a dynamic concentration range of 100.

This application note details the analysis of ambient air using the SCION 8500 GC together with SCION 8700 MS(SQ) tailored for the test method TO-15.

Figure 1. SCION Instruments 8500 GC coupled with the 8700 MS(SQ).

Experimental

The SCION TO-15 analyser consists of a SCION 456 GC, with built in sample preconcentration trap (SPT) and single quad MS specifically designed for the analysis of ambient air in accordance to US EPA TO-15 specifications. With its patented Extended Dynamic Range Detector (EDR), the TO-15 analyser is capable of accurately measuring a wide concentration range of VOCs in air.

Multi-point calibration levels were prepared and analysed. One 1µmol/mol (ppmV) standard was serially diluted into working standards from 0.01nmol/mol to 100nmol/mol with a Lotus Consulting Pressure Station (model PS-1)1. Bromochloromethane, chlorobenzene-d5 and 1,4- difluorobenzene were used as internal standards and automatically added to the adsorbent trap.

Water was added to all evacuated canisters to deactivate polar surfaces inside the canisters for analyte preservation.

A mass flow controller (MFC) was used for sample loading. By varying the loading times to the trap, multiple calibration levels were generated. The sample is directed onto a hydrophobic mixed-bed adsorbent trap, with water, methane and carbon dioxide passed to vent, before the sample is passed onto the SPT, where the VOCs are isolated, and sample components reduced to a smaller volume, ready for the injection into the analytical system. Samples are loaded through a 16 position automated sampler. Analytical parameters for the SCION TO-15 analyser can be found in Table 1.

Table 1. Instrumentation operating conditions.

Part	Settings
Adsorbent Trap	55˚C (9.1 min), 200˚C/min to 202˚C (51.3 min)
MFC	50 mL/min
Column	SCION-1MS 30m x 0.32mm x 1.0µm
Oven Program	50 ˚C, -100˚C/min to 0 ˚C (11.10 min), 5˚C/min to 50˚C, 8˚C/min to 150˚C, 25˚C/min to 220˚C (0.10 min)
Carrier Gas	2 mL/min, constant
Source	200˚C
Transfer Line	170˚C
Mode	Selected Ion Monitoring
EDR	Activated
Software	MSWS

Results

Figure 2 shows the chromatogram from a 100ppb V/V calibration mixed standard. However, due to the vast number of analytes analysed, Toluene will be discussed as a representative analyte. Toluene is typical of all analytes analysed and detected as it is the most prevalent hydrocarbon in the troposphere, with it is dispersion dependent upon atmospheric reactivity.

As Toluene is very pervasive in the atmosphere, special efforts must be taken to minimise interferences within the analytical system. This allows a very wide dynamic concentration range, including low concentrations in ambient air samples to be analysed. Due to the extensive concentration range, of over 100,000, calibration curves were generated using a display of log[area] verses log[concentration]. Figure 3 details the calibration curve for Toluene, which is representative of the calibration curves obtained for each compound in the calibration standard.

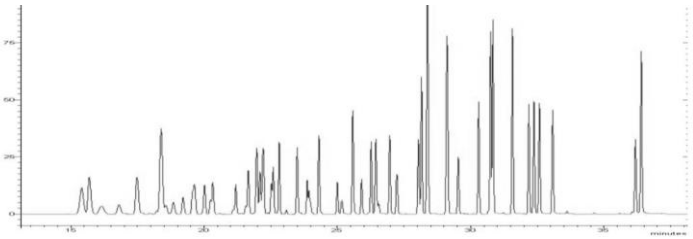

Figure 2. Chromatogram of 100ppb (v/v) calibration standard.

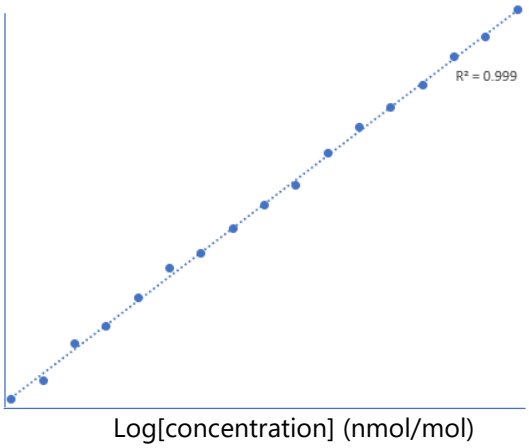

Figure 3. Linear calibration of toluene over a very wide concentration range (1-10000 nmol/mol).

The linearity of the Toluene over a wide concentration range was 0.999; this was reflected throughout the analysis of the other VOCs. Consistent linearity is demonstrated by constant response factors over the concentration range.

Figure 4 displays a plot of relative response factors (RRF) versus log[concentration] for toluene covering a range from 0.33pmol/mol to 100nmol/mol, for a dynamic range in of excess of 300,000. This excellent linearity was obtained due to the extended dynamic range of the SCION MS.

The EPA method TO-15 specifies that an acceptable range must possess relative standard deviation for response factors over the proposed concentration range of less than 30% for each analyte. However, two RRFs may deviate but they must still be less than 40%.

Figure 4 shows that the response factors of Toluene are consistent, passing the strict criteria of the method, thus highlighting the capability of the MS.

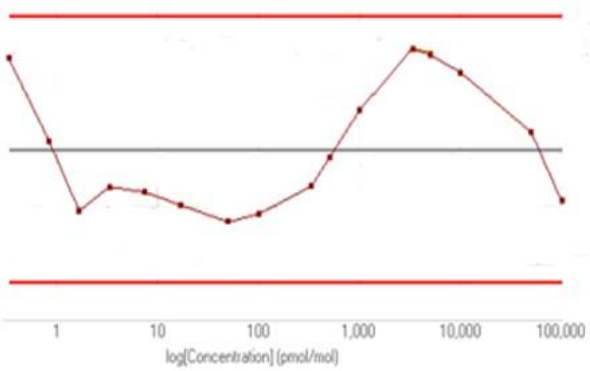

Figure 4. RRF plot of toluene over a wide concentration range.

Figures 5 and 6 detail the extracted chromatogram of ion 91, which is the quantifier ion of Toluene, at both 333 fmol/mol and 100 nmol/mol.

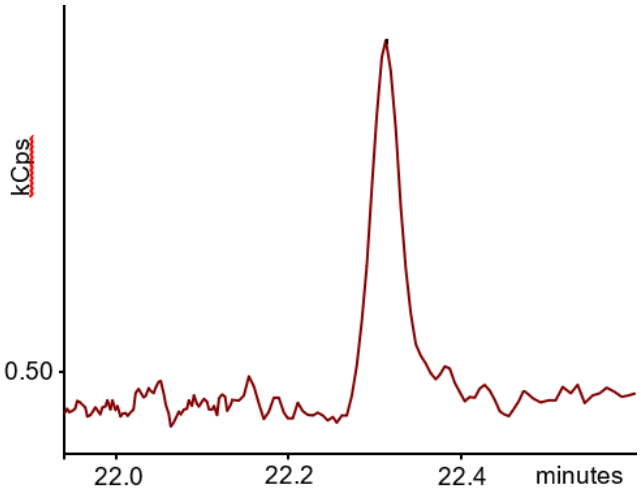

Figure 5. Extracted 91 ion of Toluene at 333 fmol/mol.

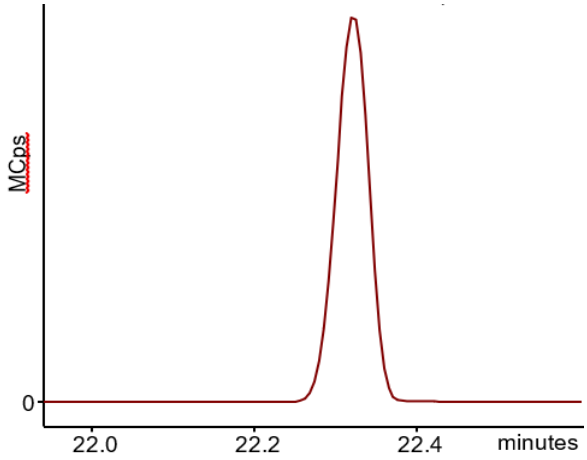

Figure 6. Extracted 91 ion of Toluene at 100 nmol/mol.

Both figures show the excellent capability of the SCION MS to accurately measure a very wide dynamic range from fmol/mol to nmol/mol without altering operating conditions; this is due to the EDR.

Table 2 details the detection limits for selected compounds analysed under TO-15 specifications. The quantifier ion and standard concentration analysed are also detailed. The sample volume was 300mL to the adsorbent trap.

Effective trapping and remarkable performance of the SCION MS enables low fmol/mol detection limits when only 300mL of sample is loaded onto the SPT.

Table 2. Detection limits, SIM ions and standard concentration of selected compounds.

Compound	Ion	Detection Limit (µmol/mol)	Standard concentration (µmol/mol)
CCl3F	85	0.008	0.028
diCl diF Methane	62	0.012	0.030
Cl Ethene	101	0.008	0.030
13Butadiene	54	0.006	0.024
Bromomethane	94	0.006	0.031
diCl Methane	49	0.008	0.064
12 diCl Ethane	62	0.007	0.024
Chloroform	83	0.006	0.025
111triClEthane	97	0.006	0.024
Benzene	78	0.006	0.026
12DiCl Propane	76	0.004	0.014
C13diCl Propene	75	0.009	0.028
Toluene	91	0.006	0.032
T13diCl Propene	75	0.004	0.030
TetraCl Ethene	166	0.005	0.031
Cl Benzene	112	0.010	0.031
Eth Benzene	106	0.009	0.035
m/p xylene	106	0.013	0.069
Styrene	104	0.008	0.022
o-xylene	106	0.008	0.040
13diCl Benzene	146	0.006	0.029
14diCl Benzene	146	0.007	0.031
12diCl Benzene	146	0.007	0.031
Hexachlorobutadiene	225	0.009	0.041

Conclusions

The SCION 8500 GC coupled with the SCION 8700 SQ (MS) is specifically designed for the analysis of ambient air for the presence of VOCs. With the extended dynamic range of the MS and the built in sample preconcentration trap, it is possible to accurately analyse a very wide concentration range of VOCs, including trace levels. The capability of the system to analyse such a wide concentration range eliminates the necessity for sample re-runs and also without the need for modification of the analytical setup to keep analyte levels within the systems operating range. The SCION instrument eliminates the difficult and time consuming restraints of alternative gas chromatography analysers.

SCION AIR Analyser Key Features

- Built in sample preconcentration trap.

Order Information

Ordering Information for the 8300 GC	
Part	**Part Number**
SCION 8500 GC + SCION 8700 SQ PREMIUM EI ONLY (120V)	SCIONSQ85PRE531
SCION 8500 GC + SCION 8700 SQ PREMIUM EI ONLY (230V)	SCIONSQ85PRE532
SCION 8500 GC + SCION 8700 SQ PREMIUM EI+CI (120V)	SCIONSQ85PRC531
SCION 8500 GC + SCION 8700 SQ PREMIUM EI+CI (230V)	SCIONSQ85PRC531

Suggested Consumables	
Part	**Part number**
15% Graphite/85% Vespel Ferrule 1/16" with 0.4 mm hole pk/10	41312148
BTO Septa 9 mm, pk/50	CR298713
SCION-1MS 30m x 0.32mm x 1.0µm	SC32135

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