

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



Application Note

AN0021

INTRODUCTION

Many volatile organic compounds (VOCs) that occur in ambient air are the result of emissions from mobile, industrial, landfills and hazardous waste sites. The levels of these compounds in the air are 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 needing to be quantified. 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 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 0.2nmol/mol, for a dynamic concentration range of 100.

This application note details the analysis of ambient air using the SCION TO-15 analyser.

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. 1 μ mol/mol (ppmV) standards were 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. 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 of low level analytes. The sample is directed onto a hydrophobic mixed-bed adsorbent trap, with water, methane, carbon dioxide and carbon monoxide passed to vent, before the sample is passed onto a cryofocus trap 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 four automated valves on a 16 position automated sampler.

Analytical parameters for the SCION TO-15 analyser can be found in Table 1.

Table 1. Analytical conditions of the SCION Analyser

Conditions	
Adsorbent Trap	55°C (9.1mins), 200°C/min to 202°C (51.3 mins)
Cryofocus Trap	79°C (2.6mins), -200°C to -146°C (8.10mins), 200°C/min to 202°C (48.4mins)
MFC	50mL/min
Column	SCION-1MS 30m x 0.32mm x 1.0 μ m
Oven Programme	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 (0.10mins)
Carrier Gas	2mL/min, constant
Source	200°C
Transfer Line	170°C
Mode	Selected Ion Monitoring
EDR	Activated

RESULTS

Figure 1 shows the chromatogram from a 100ppb V/V calibration mixed standard. However, due to the vast number of analytes analysed, Toluene will be discussed throughout this application note. Toluene is representative of all analytes analysed and detected as it is the most prevalent hydrocarbon in the troposphere, with its dispersion dependant 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, calibration curves were generated using a display of log[area] verses log[concentration]. Figure 2 details the calibration curve for Toluene, which is representative of the calibration curves obtained for each compound in the calibration standard.

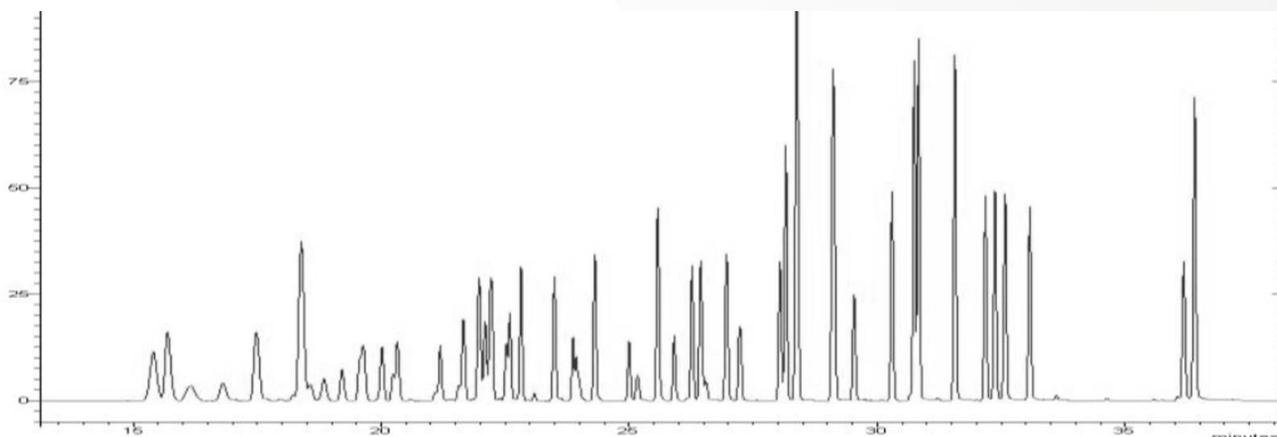


Fig 1. Chromatogram of 100ppb (v/v) calibration standard

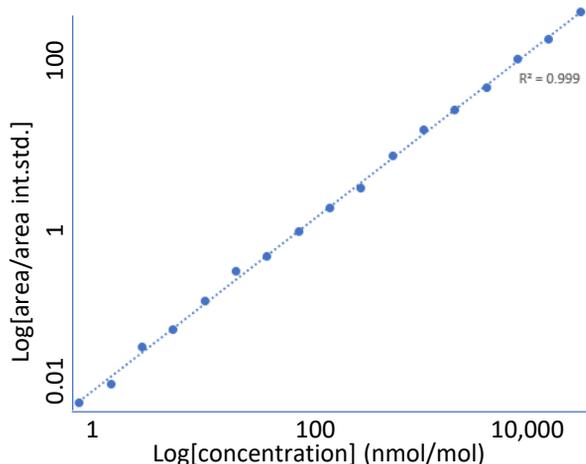


Fig 2. Linear calibration of toluene over a very wide concentration range.

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 3 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 333,333. 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 3 shows that the response factors of Toluene are consistent, passing the strict criteria of the method, thus highlighting the capability of the MS.

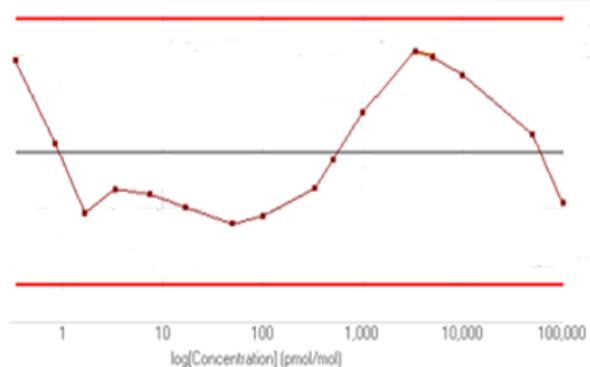


Fig 3. RRF plot of toluene over a very wide concentration range

Figures 4 and 5 detail the extracted chromatogram of ion 91, which is the quantifier ion of Toluene, at both 333 fmol/mol and 100 nmol/mol.

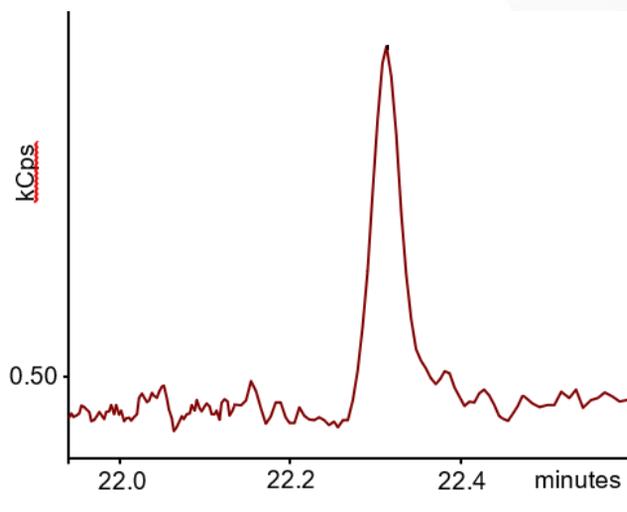


Fig 4. Extracted 91 ion of Toluene at 333 fmol/mol .

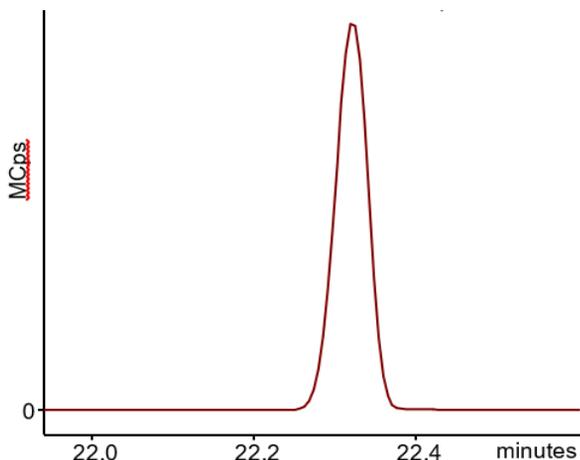


Fig 5. Extracted 91 ion of Toluene at 100 nmol/mol.

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 with an injection volume of 5 μ L.

Effective trapping and remarkable performance of the SCION MS enables low ppb V/V 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 (ppb V/V)	Standard Conc. (ppb V/V)
diCl diF Methane	85	0.008	0.028
Cl Ethene	62	0.012	0.030
CCl ₃ F	101	0.008	0.030
1,3-Butadiene	54	0.006	0.024
Bromomethane	94	0.006	0.031
diCl Methane	49	0.008	0.064
1,2-diCl Ethane	62	0.007	0.024
Chloroform	83	0.006	0.025
1,1,1-triCl Ethane	97	0.006	0.024
Benzene	78	0.006	0.026
1,2-DiCl Propane	76	0.004	0.014
c ¹³ diCl Propene	75	0.009	0.028
Toluene	91	0.006	0.032
t ¹³ diCl 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
1,3-diCl Benzene	146	0.006	0.029
1,4-diCl Benzene	146	0.007	0.031
1,2-diCl Benzene	146	0.007	0.031
Hexachlorobutadiene	225	0.09	0.041

CONCLUSION

The SCION TO-15 analyser 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. The SCION TO-15 analyser eliminates the difficult and time consuming restraints of alternative gas chromatography analysers.

Acknowledgements

Lotus Consulting, Long Beach, CA.

References

- [1] Bramston-Cook, R. (2018). *Air Scion Brochure*. 1st ed. [pdf] CA: Lotus Consulting, pp.1-8. Available at: <http://lotusinstruments.com/wp/wp-content/uploads/Air-Scion-456-Brochure.pdf> [Accessed 22 Feb. 2019].