

# Next-generation laboratory solutions for VOC air monitoring

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## Abstract

Air pollution remains a global concern, and there is increasing pressure on analytical laboratories to provide analyses at ever-lower detection limits without compromising overall analysis time. Hazardous air pollutants ranging in volatility from Freon to hexachlorobutadiene and ozone precursor hydrocarbons in the volatility range acetylene to trimethyl benzene have to be monitored at sub-ppb to low-ppb levels using on-line or canister systems. This work presents a powerful combination of sorbent capacity, cold trap dimensions and electrical cooling that allows quantitative retention of these compounds without the need for cryogen cooling, and simultaneous analysis of oxygenated and polar species.

## Introduction

Two sets of compounds are routinely monitored in ambient air using on-line or canister systems: the volatile organic compounds (VOCs) included in the US EPA Method TO-15<sup>1</sup> and ozone precursor compounds. TO-15 encompasses a wide range of polarity and volatility with compounds typically at sub-ppb to low-ppb concentration levels requiring hundreds of milliliters of sample and splitless analysis to ensure sufficient sensitivity by GC-MS. The O<sub>3</sub> precursor compounds are hydrocarbons in the volatility range of acetylene to trimethyl benzene. However, more demanding air monitoring applications are being established, and require not only high sensitivity for C<sub>2</sub> – C<sub>9</sub> ozone precursor hydrocarbons, but simultaneous analysis of polar species such as those found in EPA Method TO-15. Current techniques that incorporate the two lists of compounds require liquid cryogen, firstly to remove water from the sample and secondly to cool the GC oven. This can lead to lengthy analysis times. This presents a challenge: is it possible to quantitatively analyse C<sub>2</sub> hydrocarbons and polar species in a single analysis, without using liquid cryogen, while effectively managing the humidity that may be expected in ambient air? In this study, a cryogen free system that have been designed to allow canister samples with a wide range of analyte concentrations to be analyzed without the need for dilution is presented.

## Experimental

The thermal desorption system used is a Markes UNITY™ 2 – CIA Advantage-HL, an advanced system for automated analysis of VOCs in canister samples. The efficient design of the electrically-cooled cryogen-free UNITY 2 focusing trap, integrated into every CIA Advantage system, even allows quantitative retention of acetylene using sample volumes up to 1.5 L. Internal standard addition capability is included as standard for optimum reproducibility.



Figure 1: Markes' CIA Advantage system.

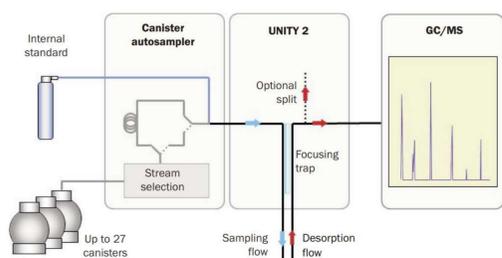


Figure 2: Schematic of CIA Advantage operation.

### Overview of operation

Metered by gas loop or mass flow controller, each air/gas sample is introduced directly into the electrically-cooled, sorbent-packed focusing trap. Sorbents and trapping temperatures are optimised for retention of organic components and simple/effective elimination of water and CO<sub>2</sub>.

The trap then heats rapidly in a reverse stream of carrier gas to transfer the retained compounds into the analytical system. This transfer can be performed splitless for maximum sensitivity. Flow path heating to 200 °C and uniquely effective line purging between samples eliminates carryover. This minimises the requirement for blanks and boosts productivity. The samples of ozone precursor gas standards and TO-15 gas standards were all run with the conditions described in Table 1.

Table 1. Thermal desorption and GC-MS systems conditions

Thermal desorption		GC-MS	
Sampling volume	Various at 20 mL/min	Oven	35 °C (6 min), 9 °C/min to 270 °C (8 min)
Cold trap	Universal trap (two-bed)	Column	Thermo Scientific TRACE TG Bond Q, 30 m x 0.32 mm x 10 µm with particle trap post-column
Cold trap	5 °C to 280 °C for 2 min	Column flow	2.5 mL/min constant-flow
Trap heating rate	40 °C/s	Data rate	4 Hz; m/z 24–300
Line purge	1 min at 50 L/min	Ion source	250 °C
Trap purge	Various at 20 mL/min	Transfer line	250 °C
Split ratio	2:1	Ionization voltage	70 eV
Flow path	120 °C		

## References

- Determination of Volatile Organic Compounds in Air Collected in Specially-Prepared Canisters and Analyzed by Gas Chromatography/Mass Spectrometry. METHOD TO-15 of the U.S. Environmental Protection Agency.
- New Jersey Department of Environmental Protection Site Remediation Program (NJDEP - SRP) Modified Low Level TO-15 Method, March 2007, March 2009 revision.

## Results

### Breakthrough tests

When designing a new method for monitoring the C<sub>2</sub> compounds ethane, ethylene and acetylene, one of the first tests that should be performed is determining the maximum sample volume (*i.e.* breakthrough volume). Breakthrough volumes for C<sub>2</sub> compounds when employing a Nafion dryer and a trap temperature of –30 °C are in the order of liters for the CIA Advantage system (Figure 3). However, the Nafion dryer removes some of the light polar compounds present in the TO-15 mix. In order to avoid collection of water on the trap, and without having to use cryogen to remove water, the best method is to employ a higher trap temperature.

Breakthrough tests were carried out using a focusing trap temperature of 5 °C and the specifically designed 'Universal' trap. A linear relationship was observed for the majority of compounds up to and above 100 mL, but ethane and ethylene breakthrough at this level with the cold trap at this comparatively high trapping temperature – see Figure 4. (Note when including purge volumes, the total volume through the trap was 130 mL).

For further tests, the sample volume was kept below 50 mL and the trap temperature at 5 °C, to ensure efficient trapping of the C<sub>2</sub> compounds whilst managing water.

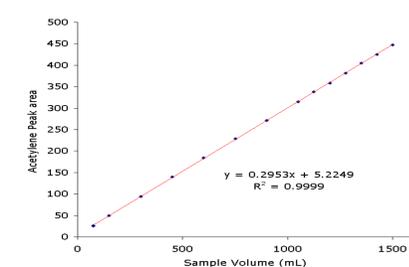


Figure 3: Peak area versus volume sampled for acetylene.

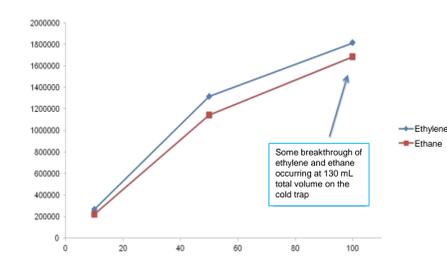


Figure 4: Peak area versus volume sampled for ethane and ethylene with the focussing trap at 5 °C.

### Instrument Detection Limits (IDLs)

Detection limits of 0.2 ppbV for the combined list of compounds had to be reached, and with the small volume sampled this meant that a very sensitive and selective detector had to be used.

IDLs (Table 2) exceeded the required detection limits (0.2 ppbV) for a 45 mL sample volume of a 75% RH standard. Canister cleanliness is an important factor in determining IDL levels, and in line with the requirement to reach lower levels (*e.g.* TO-15 Low Level NJ method<sup>2</sup>), changes to existing method require more stringent cleaning procedures and acceptance of cleanliness to be based on method performance.

Table 2: IDLs for a range of VOCs using a 45 mL sample

Ion	Name	IDL (ppbV)	Ion	Name	IDL (ppbV)	Ion	Name	IDL (ppbV)
26	Ethylene	0.083	41	Propene	0.049	56	Acrolein	0.071
26	Acetylene	0.040	43	Isobutane	0.026	45	IPA	0.017
30/27	Ethane	0.060	43	Butane	0.012	43	Pentane	0.009
50	Chloromethane	0.011	45	Ethanol	0.061	41	n-Hexane	0.010
29	Propane	0.088	43	Isopentane	0.020	43	Heptane	0.013

Figure 5 shows air toxics analyses carried out using the Markes' CIA Advantage system. Trap desorption efficiency is illustrated by the excellent peak shape of early eluting components, without the use of liquid cryogen, including polar species such as isopropanol (IPA). See also in close-up in Figures 6 and 7.

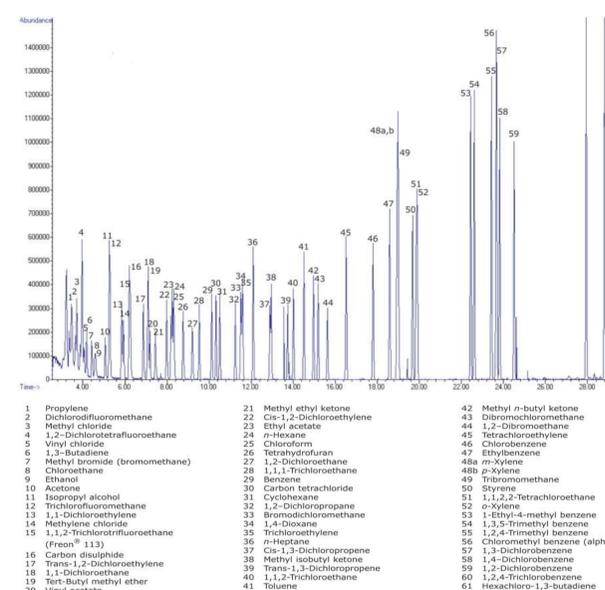


Figure 5: Chromatogram of 100 mL, 25 ppb TO-15 standard

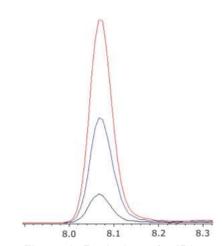


Figure 6: Peak shape for IPA at 0.6 ppb (red), 0.3 ppb (blue) and 0.1 ppb (black) analyzed splitless using extracted mass ion 45.

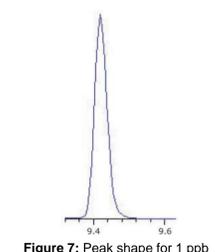


Figure 7: Peak shape for 1 ppb IPA analyzed splitless, using extracted mass ion 45.

## Conclusion

This work shows how with small sample volumes, water is managed effectively with a cryogen free thermal desorber. The negligible carryover means that canister analysis can be confidently undertaken on samples of unknown concentration, facilitating automation and therefore increasing productivity. The thermal desorber presented is adept at compounds as volatile as O<sub>3</sub> precursors without liquid cryogen coolant, due to the combination of trap dimensions, sorbent capacity and electrical cooling.