

Next-generation laboratory solutions for VOC air monitoring

Nicola Watson, David Wevill and Peter Grosshans
Markes International, Inc., 11126-D Kenwood Road, Cincinnati, Ohio 45242, USA.

Introduction

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. Two sets of compounds are routinely monitored in ambient air using on-line or canister systems: US EPA Method TO-15 and ozone precursor compounds. However, more demanding air monitoring applications are being established, and require not only high sensitivity for C₂ – C₆ ozone precursor hydrocarbons, but simultaneous analysis of polar species such as those found in US 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 high overhead costs and lengthy analysis times, both of which give the laboratory a disadvantage in the competitive market for air analysis.

This presents a challenge: is it possible to quantitatively analyse C₂ hydrocarbons and polar species in a single analysis, without using liquid cryogen, while effectively managing the humidity that may be expected in ambient air?

Experimental

Markes' CIA Advantage™ systems have been designed to allow canister samples with a wide range of analyte concentrations to be analyzed without the need for dilution. The addition of the BenchTOF-Select™ time-of-flight mass spectrometer (Markes International), with its speed, and sensitivity, results in a very productive and flexible tool for air monitoring of VOCs and SVOCs.

The samples of ozone precursor gas standards and TO-15 gas standards were all run with the conditions described below.

Thermal desorption system:
Markes UNITY™ 2 – CIA Advantage-HL

GC-MS system:
Agilent 7890A GC – Markes BenchTOF-Select™

Sampling volume: Various at 20 mL/min
Cold trap: Universal trap (two-bed)
Cold trap: 5°C to 280°C for 2 min
Trap heating rate: 40°C/s
Line purge: 1 min at 50 mL/min
Trap purge: Various at 20 mL/min
Split ratio: 2:1
Flow path: 120°C

Oven: 35°C (6 min), 9°C/min to 270°C (8 min),
Column: Thermo Trace TG Bond Q, 30 m x 0.32 mm
x 10 µm with particle trap post-column
Column flow: 2.5 mL/min constant-flow
Data rate: 4 Hz; mass range: m/z 24–300
Ion source: 250°C
Transfer line: 250°C
Ionization voltage: Various



Figure 1: CIA Advantage (left) and GC-BenchTOF-Select system (right) used in this study.

Method design

Breakthrough tests

When designing a new method for monitoring the C₂ compounds ethane, ethylene and acetylene, one of the first tests that should be performed is determining the maximum sample volume (i.e. breakthrough volume).

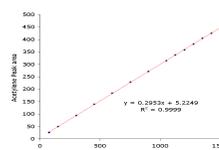


Figure 2: Peak area versus volume sampled for acetylene.

Breakthrough volumes for C₂ 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 2).

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 3. (Note when including purge volumes, the total volume through the trap was 130 mL).

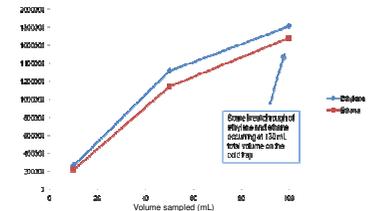


Figure 3: Peak area versus volume sampled for ethane and ethylene with the focusing trap at 5°C, showing the predicted breakthrough at a total volume of 130 mL (sample volume 100 mL).

For further tests, the sample volume was kept below 50 mL and the trap temperature at 5°C, to ensure efficient trapping of the C₂ compounds whilst managing water.

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.

Results

Instrument Detection Limits (IDLs) at 70 eV

IDLs (Table 1) 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), changes to existing method require more stringent cleaning procedures and acceptance of cleanliness to be based on method performance.

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

Table 1: IDLs for a range of VOCs using a 45 mL sample at 70 eV.

Variable-energy electron ionization

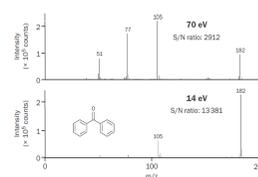


Figure 4: Benzophenone (MW 182) at 70 eV and 14 eV. Note the enhancement of sensitivity at the lower ionization energy.

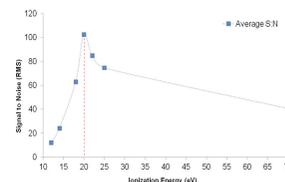


Figure 5: Ionization energy versus average signal-to-noise.

IDLs can be lowered even further for a number of compounds by employing Markes' variable-energy ion-source technology, Select-eV™. Select-eV enables signal intensity to be focused into fewer ions, often including the molecular ion, while enhancing signal-to-noise (S/N) at these m/z values. This is especially true when using an ionization energy of 14 eV (Figure 4).

For some of the lighter VOCs, 14 eV does not lead to an increase in sensitivity, or a large enhancement in the molecular ion signal.

To determine if Select-eV can increase sensitivity for VOCs from C₂ to C₁₀, S/N measurements were taken at 70, 25, 22, 20, 18, 14 and 12 eV. Figure 5 shows that the maximum S/N is at 20 eV, which is below the ionization potential of the carrier gas helium (24.58 eV).

Comparison of spectra at a range of ionization energies

Using Select-eV at a value of 20 eV gave an increase in S/N, by lowering the background and by increasing the overall intensity of the ions in the spectra. Figure 6 shows an example of heptane at 70 eV, 20 eV and 14 eV.

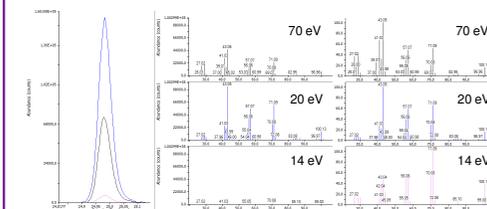


Figure 6: Comparison of chromatograms and mass spectra obtained at 70 eV (black), 20 eV (blue) and 14 eV (pink) for heptane. The mass spectra on the left show absolute intensity, and relative intensity on the right.

Instrument Detection Limits at 20 eV

Instrument IDLs are reported for 70 eV in Table 1 and exceeded the required detection limits for a 45 mL sample volume. Table 2 shows IDLs for compounds using a 45 mL sample of the same standard, but at 20 eV.

Ion	Name	IDL (ppbV)	Ion	Name	IDL (ppbV)	Ion	Name	IDL (ppbV)
26	Ethylene	0.035	41	Propene	0.019	56	Acrolein	0.025
26	Acetylene	0.030	43	Isobutane	0.018	45	IPA	0.006
30/27	Ethane	0.039	43	Butane	0.007	43	Pentane	0.003
50	Chloromethane	0.004	45	Ethanol	0.038	41	n-Hexane	0.006
29	Propane	0.049	43	Isopentane	0.013	43	Heptane	0.006

Table 2: IDLs for a range of VOCs using a 45 mL sample at 20 eV.

Conclusions

This poster has shown how the combination of thermal desorption and the BenchTOF time-of-flight mass spectrometer can produce a powerful air monitoring tool for combining the most challenging of air sampling applications. With small sample volumes, water is managed effectively, and with the sensitivity of the BenchTOF low IDLs are achieved. As IDLs become lower, canister cleanliness will also play a factor, with existing methods being changed to make the certification of cleanliness more stringent and to base acceptance on method performance (e.g. MDLs).

Select-eV also adds another aspect by lowering the IDLs even further (by a factor of 1.5 to 3 times) for the same sample volume or by maintaining the same IDLs (at 70 eV) but using smaller sample sizes, leading to a cleaner system and less downtime.