Advances in comprehensive ambient air monitoring

Hannah Calder[1], Nicola Watson[2], Tarun Anumol[3] and Jan Peter Mayser[1]

[1]Markes International, Gwaun Elai Medi-Science Campus, Llantrisant, RCT, UK. [2]Markes International, Inc., 2355 Gold Meadow Way, Gold River, Sacramento, CA 95670, USA. [3]Agilent Technologies Inc, 2850 Centerville Road, Wilmington, DE, 19808, USA.

Introduction

With the Chinese Environmental Air Volatile Organic Compound Monitoring Program, there is a plan to combine the sampling and analysis of TO-15 air toxics, PAMS ozone precursors and OVOCs into one run (Figure 1). Research is being carried out to find a way to detect all 117 compounds of interest from high humidity samples in one run, without the use of a cryogen.

This poster describes the successful application of Markes' innovative on- and offline method coupled with Agilent's powerful GC–MSD, which combines sampling and analysis in a single run with a cycle time under one hour, ensuring consistent hourly monitoring of all compounds, even remotely.

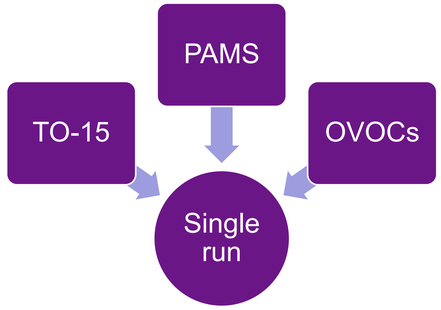

Figure 1: The sampling and analysis of TO-15 compounds, PAMS and OVOCs can be combined into one run.

Compounds of interest:

- **Ozone precursors (PAMS)** are listed under the US EPA Photochemical Assessment Monitoring Scheme (PAMS) and are monitored using on-line techniques (for continuous monitoring) or remote canister sampling. Both techniques require water removal and preconcentration of the sample before injection into a GC, usually in a dual column/Deans switch configuration with dual flame ionisation detection (FID).
- **Air toxics (TO-15)** comprise polar and non-polar VOCs, as well as a number of halogenated compounds. Methodology and performance criteria are detailed in US EPA Method TO-15 and the Chinese EPA Method equivalent, HJ 759. Samples are collected in canisters, with water removal and sample preconcentration taking place prior to injection into a single-column GC–MSD system.
- **Oxygenated volatile organic compounds (OVOCs)** are a more recent addition to target lists for air monitoring, and include a range of aldehydes and ketones. They are typically monitored using derivatisation and high-performance liquid chromatography, as specified in Chinese EPA Method HJ 683 and US EPA Method TO-11A. However, these protocols require manual preparation, the use of solvents and two analytical platforms, which add significant time and cost to the analysis as a whole.

Experimental

The analytical system (Figure 2) comprises a canister autosampler (**CIA *Advantage*-xr™**), water removal device (**Kori-xr™**), thermal desorber (**UNITY-xr™**) and dual-column GC–MSD/FID (**Agilent 7890-5977**). The system enables the unattended, continuous monitoring of samples at up to 100% relative humidity (RH), offering optimum responses for the three C_2 and two C_3 hydrocarbons monitored using FID, as well as confident compound identification and high sensitivity quantitation for the remaining compounds monitored using MS.

Figure 2: Markes and Agilent TD–GC–MS equipment configuration.

Dry-Focus3

The highly efficient removal of water from air achieved with Markes' **cryogen-free Dry-Focus3™** (Figure 3) combined with a cryogen-free GC oven program enables the oven to start at the relatively high temperature of 35°C. This allows more efficient operation without compromising analyte peak shape, and reducing the cost per sample.

(1) Air sampling and water removal
Canister or whole-air samples pass through the drying trap (where vapour-phase water is selectively deposited as ice), so that VOCs are concentrated on the focusing trap.

(2) Purging of residual water
Optional temperature-programmed dry-purging of the focusing trap with carrier gas (between -30°C and 50°C) selectively eliminates any residual water while retaining 100% of target analytes.

(3) Trap desorption
The focusing trap is rapidly heated in a reverse flow of carrier gas to transfer analytes to the GC. Simultaneously, the drying trap is heated in a flow of gas to expel the trapped ice and regenerate it, ready for the next sample.

Figure 3: Operation of Dry-Focus3.

Results and discussion

Chromatography and peak shape

Good peak shape is obtained across the analyte range, including the least volatile compounds in the list (Figure 4). In addition, the expansion of the 30.5–31.2-minute range demonstrates identification of seven closely-eluting compounds using their extracted ions. It is important to note that the sampling and analysis are achieved within a sample-to-sample cycle time of <60 minutes without the use of liquid cryogen in the thermal desorber or the GC oven. This run time results from the GC oven's relatively high starting temperature (35°C) and the thermal desorber's overlap mode, in which the next sample is loaded into the focusing trap while the current GC analysis is still running, maximising sample throughput.

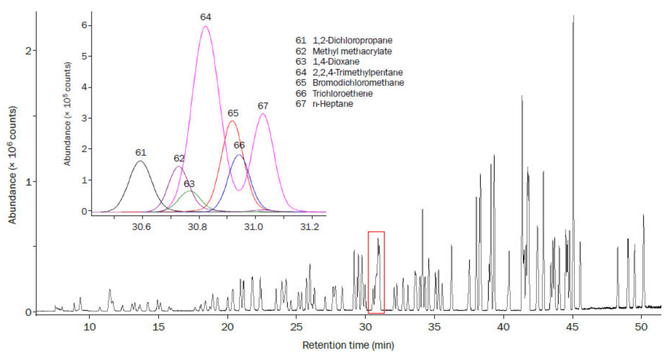

Figure 4: Total ion chromatogram of 400 mL of the 10 ppb 100% RH standard containing the 117 target compounds. The inset shows overlaid EIC responses from seven closely-eluting analytes.

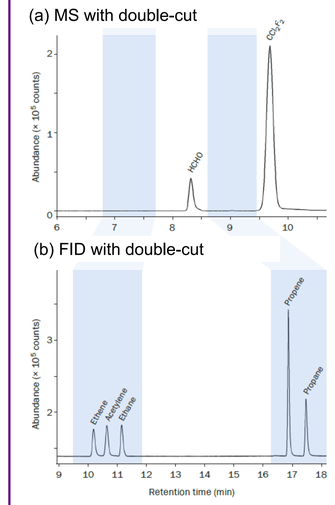

Figure 5: Analysis of 400 mL of the 10 ppb 100% RH standard containing the 117 target compounds analysed using: (a) Composite MS (primary column) with double-cut and (b) FID (secondary column) with double-cut.

Deans switch method optimisation: Using a double-cut Deans switch method, optimum sensitivity, together with excellent peak shape, retention time stability and reproducibility were obtained for this complex target list in a 52-minute chromatographic run. The C_2 hydrocarbons ethene, acetylene and ethane respond best to FID detectors, whereas formaldehyde responds best to MS detection. It is therefore important to achieve sufficient separation between the C_2 hydrocarbons and formaldehyde to allow the first cut of this method. The columns used to achieve this separation were a GS-CARBONPLOT (secondary) and a CP-Volamine (primary). The excellent peak shape and resolution of the C_2 and C_3 hydrocarbons resulting from this method are shown in Figure 5(b), with formaldehyde and dichlorodifluoro-methane shown on the MS trace in Figure 5(a).

Relative response factors and linearities
System linearity was assessed by sampling 50, 100, 200, 300, 400 and 600 mL of the 10 ppb 100% RH mixed standard (Figure 6). This represents the equivalent mass of each compound that would be sampled from 400 mL of samples with concentrations of 1.25, 2.5, 5, 7.5, 10 and 15 ppb, respectively. Relative response factors (RRFs) and their relative standard deviations (RSDs) were calculated from the results in accordance with HJ 759 and EA-VOC-MP. The mean RRF RSD over the six-point calibration was 5% with a maximum of 12%, therefore well within the 30% limit specified in the methods.

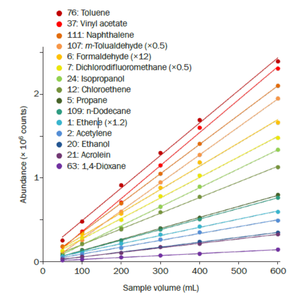

Figure 6: Linearity plots for selected compounds from the 10 ppb 100% RH standard, over the range 50–600 mL.

Method detection limits
MDLs are reported with 99% confidence that the measured concentration is distinguishable from method blank results. MDLs are calculated based on data from seven replicate samples with a concentration at or near the detection limit. In this study, MDLs were determined using a 0.5 ppb standard, with the resulting concentrations for each measurement being multiplied by 3.14 (the Student's t-value for 99% confidence for seven values) to determine MDL values in ppb. Data for the 13 duplicate compounds was generated using a single PAMS standard. The average MDL was 0.052 ppb.

Conclusions

Successful PAMS, TO-15 and OVOC analysis requires:

- Quantitative retention of very volatile to volatile organic compounds in a single analysis.
- Sampling at any humidity level (up to 100% RH).
- Automated internal standard addition.
- Ability to sample from pressurised or unpressurised sources.
- Automated unattended analysis with ability to sequence between different techniques.
- Trapping and separation of 117 compounds with <60-minute cycle times without liquid nitrogen.

The **UNITY–CIA *Advantage*-xr** preconcentration system with **Dry-Focus3** technology allows simultaneous, cryogen-free analysis of **PAMS** ozone precursors, **TO-15** air toxics and **OVOCs** listed in the EA-VOC-MP. The implementation of **Agilent dual-column/Deans switch 7890-5977/FID** provides confident identification and quantitation, with maximum sensitivity achieved in this challenging application.

MARKES international

T: +44 (0)1443 230935 **E:** enquiries@markes.com **W:** www.markes.com
@MarkesInt www.linkedin.com/company/markes-international

Agilent