



Series 2  
**Air Server**  
Thermal Desorption  
Options

**Automated canister and on-line air/gas analysis**



## Series 2 Air Server

A range of accessories for series 2 UNITY thermal desorbers offering automated canister analysis and on-line air/gas monitoring

### Thermal desorption technology

Thermal desorption (TD) is a highly versatile, sensitive and labour-saving sample preparation technique for the measurement of volatile and semi-volatile organic compounds (VOC and SVOC) in air and materials. It is applicable to GC-compatible organics ranging in volatility from acetylene to n-C<sub>40</sub> and a few inorganic gases; including nitrous oxide, SF<sub>6</sub>, CS<sub>2</sub> and H<sub>2</sub>S. Key applications include:

- Environmental and workplace air monitoring
- Civil defence and forensic analysis
- Materials and materials emissions testing
- Food, flavour and fragrance profiling

Many material samples such as drugs, foods, textiles, polymers, paints *etc.* can be directly thermally desorbed by weighing them into empty TD sample tubes.

Alternatively, vapours in gas or air can be concentrated on- or off-line onto sorbent traps/tubes before TD-GC(MS) analysis.

### Innovation and excellence in thermal desorption

Since 1997, Markes International has re-engineered analytical thermal desorption for the 21st century. Harnessing unparalleled technical expertise, the company has developed a suite of "universal" TD systems and unique sampling accessories incorporating key proprietary innovations such as:

- SecureTD-Q™ and automated sample re-collection using a single TD autosampler<sup>1</sup>
- RFID tube tagging (TubeTAG™)<sup>2</sup>
- Diffusion-locking for effective tube sealing and robust automation<sup>3</sup>
- Innovative low volume valving specifically designed for TD<sup>4</sup>

Many of these innovations now set the standard for TD instrumentation worldwide.

1. Patent# GB 2395785 (Automated re-collection using a single TD autosampler), 2. Patent# US 6,446,515 B2, 3. Patent# GB 2337513 US 6,564656 B1  
4. Patent# GB 2336649

## Air Server 2 Main Features

- Adds **automated canister and on-line air/gas stream** analytical capability to any series 2 (ULTRA-)UNITY thermal desorption (TD) system.
- **Cryogen-free** operation and low consumption of gas supplies for lower running costs and higher uptime.
- Minimum 3 channels for sequencing between sample, zero and standard air/gas streams during **unattended on-line monitoring**.
- **Up to 8 channel** operation available for high throughput analysis of whole-air/gas samples – canisters, bags, etc.
- **Quantitative retention of ultra-volatiles** such as acetylene from increased sample volumes (up to 1.5 L) combined with peerless high-resolution capillary chromatographic performance (even under splitless conditions) ensure optimum sensitivity. Parts per trillion (ppt) levels are readily detected.
- Method compliant **tube desorption capability** included with every system. Can be automated.
- **Thermostatted flow path and internal standard addition** options for compliance with standard canister methods.
- **Negligible sample carryover** plus versatile sampling flows & flexible splitting options allow analysis of both high and low concentration samples.
- Small footprint: Especially useful for installation in mobile labs.
- Versatile **water management** options for analysis of both dry and humid air/gas samples.
- Connects to any commercial GC/GCMS and offers enhanced selective purging for compatibility with real-time detectors such as process MS and sensor-arrays.

## Introducing the series 2 Air Server range

Series 2 Air Server modules add to any series 2 (ULTRA-)UNITY system to allow a controlled flow of whole-air or gas to be introduced directly into the electrically-cooled focusing trap of the desorber. The combined systems operate **cryogen-free** (to minimise running costs/maintenance) and offer optimum analytical performance/sensitivity.

With 3- and 8-channel options available, method-compliant series 2 (ULTRA-)UNITY-Air Server systems are suitable for both automated analysis of canister/bag samples and round-the-clock unattended monitoring of on-line air/gas streams.

Key applications include:

- Continuous monitoring of **ozone precursors** ( $C_2$  to  $C_{10}$  hydrocarbons) in ambient air and/or vehicle emissions
- On- or off-line **odour monitoring** e.g. measuring reduced sulphur species such as  $H_2S$ , mercaptans and sulphides in canisters, bags or on-line air streams at sub- to low-ppb levels

- **"Air Toxics"** in ambient air e.g. US EPA Method TO-(14)15
- **Industrial process control** of gas purity and odour
- **Atmospheric research** e.g. global background pollution levels, pollution transport and kinetic studies, such as monitoring diurnal changes in urban air pollution or biogenic emission profiles

Series 2 (ULTRA-)UNITY-Air Server systems connect to standard GC/GCMS technology and/or real-time process detectors.



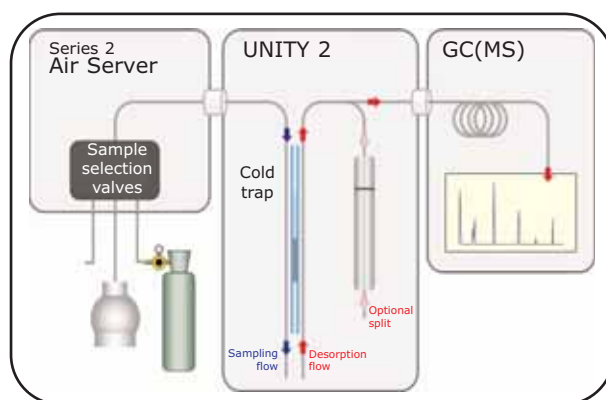


## Overview of Air Server operation

Series 2 Air Servers connect to any series 2 UNITY or ULTRA-UNITY TD system. They contain 3- or 8- inert sample/stream selection valves uniquely configured to eliminate dead volumes and prevent carryover. Each whole air/gas sample (pressurised or at (sub-)atmospheric pressure) is introduced directly into the electrically-cooled, sorbent-packed, focusing trap of the UNITY 2 thermal desorber for a user-specified sampling time. Conventional sorbent sampling tubes are not used in this process.

The sampling flow is regulated by an electronic mass flow controller (MFC) and optional pump located downstream of the trap to eliminate risk of contamination. Focusing trap sorbent and trapping temperatures are selected for quantitative retention of the compounds of interest and for selective purging of potential interferences such as CO<sub>2</sub> and water. No liquid cryogen is required and only inert, non-emitting components come into contact with the sample. All sampling parameters are monitored by system software as an integral part of the analytical method.

At the end of sample introduction, the flow path is purged with carrier gas to prevent carryover and eliminate oxygen from the focusing trap. The trap then heats rapidly in a reverse stream of carrier gas to inject/transfer retained compounds into the measurement system and trigger the analysis. This transfer/injection may be performed splitless for **maximum sensitivity**. (See UNITY 2 brochure for more details.)



Schematic of Air Server 3 operation

Once the focusing trap has desorbed, it cools and re-equilibrates at the trapping temperature. Focusing of the next air/gas sample in the sequence may begin while analysis of the previous sample is ongoing to optimise throughput.

## Series 2 Air Server range

The series 2 Air Server range includes products for 3- and 8-channel sequencing. The table below highlights the differences between the products:

**Note:** Air Server 3 and 8 modules are integrated with UNITY 2 prior to shipment or during field installation to minimize bench space in confined locations such as mobile labs or remote monitoring stations. The CIA 8 is a separate module.

	Air Server 3	Air Server 8	Canister Interface Accessory (CIA 8)
Number of channels	3	8	8
Thermostatted flow path	✗	✗	✓
Internal standard addition	✗	✗	✓

# Up to 8-channels for optimum throughput

## Intuitive user interface

Series 2 (ULTRA-)UNITY-Air Server control is intuitive and integrated with the UNITY 2 TD software to provide one comprehensive and easy to understand user interface (UI).

The UI offers a specific mode for on-line/canister operation (see figure opposite) and, once selected, users are prompted to enter the relevant sampling parameters such as sampling time, flow rate and purge times.

## Sequence building

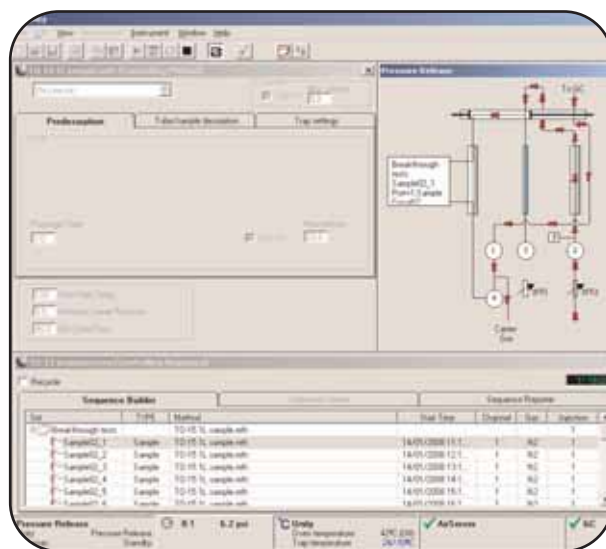
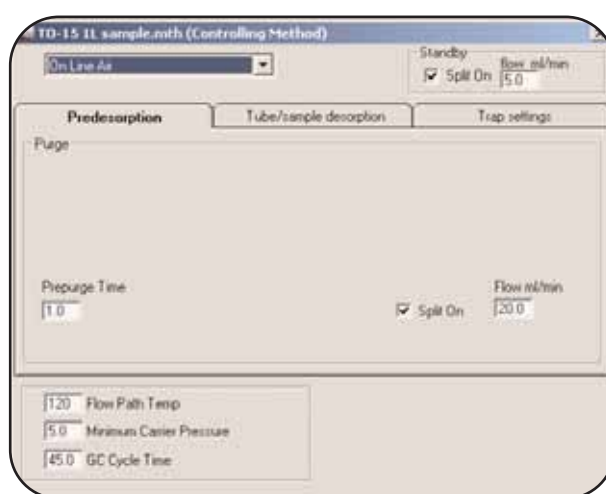
Automated sequences for on-line monitoring and/or automated canister/bag analysis are easily constructed *via* the sequence builder. Samples may be assigned individual desorption methods. Each sample is classified as sample, calibrant or blank and all sequences may be stored and recalled for future reference or repeat use.

## Graphical sequence viewer

The sequence viewer presents a clear graphical display of current sequence status.

## Sequence reporting

Information associated with each analysis, such as the time, date and any deviations, are all recorded in the sequence reporter. Any sample sequence failure triggers the GC(MS) system to start a blank run to keep the analyser in step with the autosampler.



Control method screen (top) of user interface.  
Complete user interface screen (bottom)



# Round-the-clock, cryogen-free monitoring

## On-line operation

On-line monitoring systems typically comprise a series 2 UNITY with integrated **3- or 8-channel Air Server module**. The combined system is programmed to repeatedly introduce air/gas from the sample stream(s) and to automatically sequence **calibration gas and zero air/gas** at user-defined frequencies, typically once every 24 hours. Sequences may be recycled indefinitely to minimise system programming.

**Continuous monitoring of ozone precursors** ( $C_2 - C_{10}$  hydrocarbons) in urban air, as required by both European and US regulations<sup>1,2</sup>, is a key application for series 2 UNITY-Air Server 3 (or 8) systems.

1. Council Directive 96/62/EC: On ambient air quality assessment and management, and the daughter directive - 2002/3/EC relating to ozone in ambient air

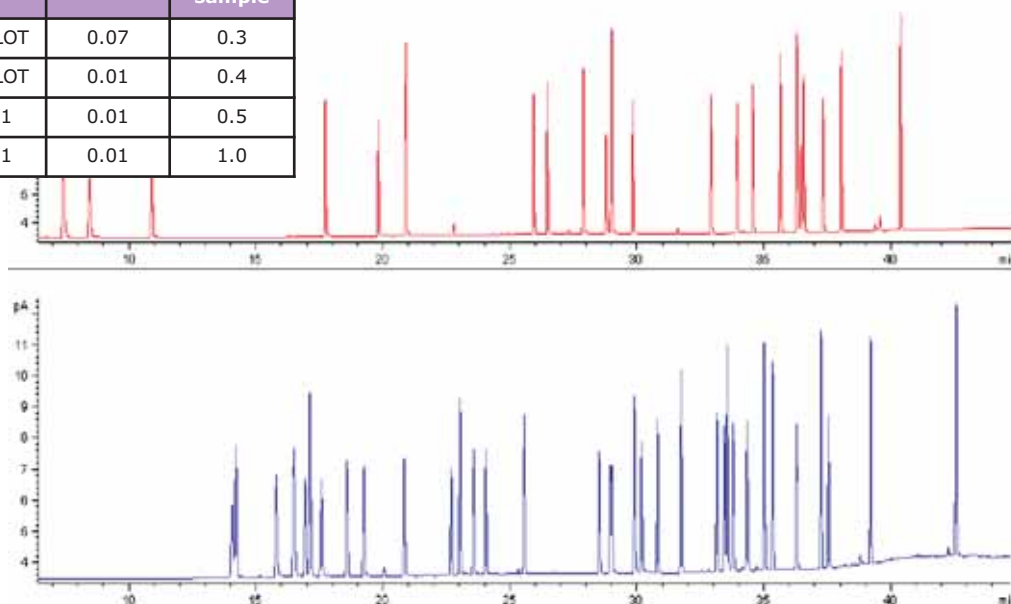
2. 1990 US Clean Air Act Amendment

Key advantages of Markes series 2 UNITY-Air Server systems for ozone precursor monitoring include:

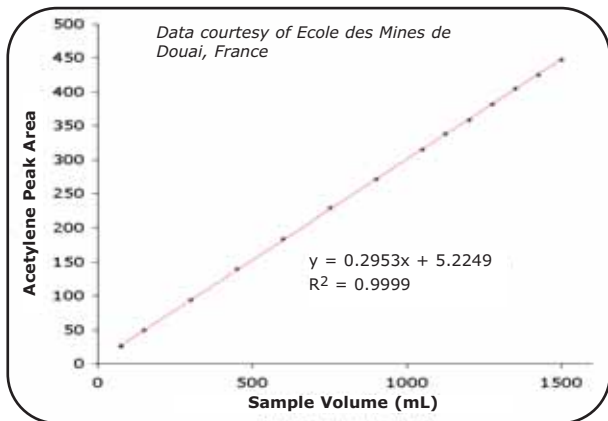
- Unattended operation for extended periods:** Cryogen-free operation and low consumption of gases simplify installation in mobile labs and offers extended periods of unattended operation in remote field monitoring stations. Markes' cryogen-free series 2 UNITY-Air Server systems consume only 40 ml/min dry gas/air when configured without a Nafion dryer and less than 200 ml/min when a dryer is configured. This is between 3 and 10 times less than other cryogen-free ozone precursor monitoring systems and allows extended operation without cylinder replacement
- Sensitivity:** Quantitative retention of ultra-volatiles such as acetylene from up to 1.5 L air sample volumes combined with efficient splitless desorption at low (<2 ml/min) flows ensures best possible detection limits (typically 1-50 ppt levels)

Compound	Det limti (ppb) 450 ml sample	Column	%RSD (n=12) $R_t$ 450 ml sample	% RSD (n=12) peak area 450 ml sample
Ethane	0.026	AI PLOT	0.07	0.3
Butane	0.010	AI PLOT	0.01	0.4
Hexane	0.019	DB1	0.01	0.5
Octane	0.017	DB1	0.01	1.0

Data courtesy of Ecole des Mines de Douai, France



**Splitless desorption of 56-compound US EPA mix of ozone precursors using series 2 UNITY-Air Server 3 with dual column/dual FID GC with Dean's switch**



**Cryogen-free trapping of ultra-volatile compounds including acetylene (ethyne) from up to 1.5 L of air**

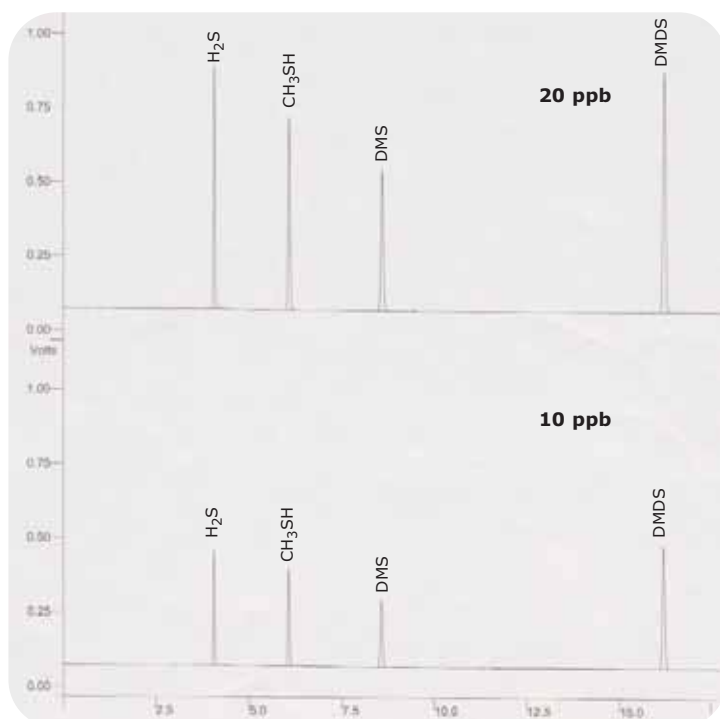
- **Reliably excellent chromatographic performance:** Great resolution, stable retention times and repeatable concentration data minimise measurement uncertainty and simplify data interpretation/validation
- **Small footprint:** The Series 2 UNITY with integrated 3- or 8-channel Air Server is only 22 cm (9-inches) wide

## Timed start

Series 2 UNITY-Air Server systems allow the start of a monitoring sequence to be programmed for a specific date and time (e.g. noon on Monday May 1st) and for the period between each sampling cycle to be fixed. The sampling cycle used for ozone precursor monitoring for example, is typically 1 hour. In this case air is usually sampled into the UNITY 2 focusing trap for 40 minutes of every hour starting on the hour.



## On-line odour monitoring - Another key application for series 2 UNITY with integrated Air Server 3 option



Compound	Minimum Detection Limit (ppb)	%RSD (n=10, 20ppb)
Hydrogen sulphide (H <sub>2</sub> S)	0.15	4.1
Methyl mercaptan (CH <sub>3</sub> SH)	0.15	1.8
Dimethyl sulphide (C <sub>2</sub> H <sub>6</sub> S)	0.15	0.8
Dimethyl disulphide (C <sub>2</sub> H <sub>6</sub> S <sub>2</sub> )	0.10	0.8

Data courtesy of ITC, South Korea



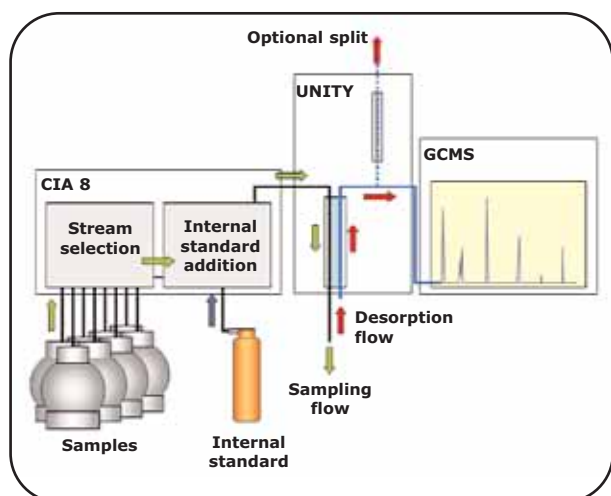
**Field-proven, robust on-line monitoring of H<sub>2</sub>S and other reduced sulphur compounds down to sub-ppb levels in ambient air**



## Automated off-line analysis of canister/bag samples

Key issues associated with automated canister analysis include throughput, running costs, sensitivity, water management and method compliance. A typical Markes Air Server system configuration in this case would be the series 2 (ULTRA)-UNITY with an 8-channel **Canister Interface Accessory (CIA 8)**.

This system features a **thermostatted sample flow path and internal standard (IS) addition** to the focusing trap. It is **fully compliant with relevant standard methods** such as US EPA Method TO-15.



**Schematic of series 2 UNITY - CIA 8 operation**  
**Versatile sample splitting options offer compatibility with vapour concentrations ranging from ppt to ppm**

## Air toxics analyzers

Key advantages of Markes series 2 (ULTRA)-UNITY-Air Server technology for air toxics monitoring and for canister air analysis generally include:

- **Productivity:** Markes systems offer 8-channels for automated operation over an extended period. Confirmatory repeat analysis of each canister may be included in the automation sequence
- **Cost reduction. Cryogen-free operation** minimises:
  - Capital costs (no liquid nitrogen dewar required)
  - Running costs (cryo-cooled systems require fresh supplies of liquid coolant as often as every 2 or 3 days)
  - Manpower (changing/refilling of liquid coolant dewars takes time and effort)
  - Downtime (replenishing liquid cryogen often interrupts an automated sequence)
- **Analytical excellence:** Super-efficient trap desorption and reliably excellent chromatographic performance, even under splitless conditions and without on-column focusing (see Series 2 UNITY brochure), optimise sensitivity and simplify identification of target air toxic analytes even in complex backgrounds.
- **Versatile water management:** Markes systems offer selective purging of water, sophisticated sample splitting and the option of in-line dryers for effective water management under any air monitoring conditions.

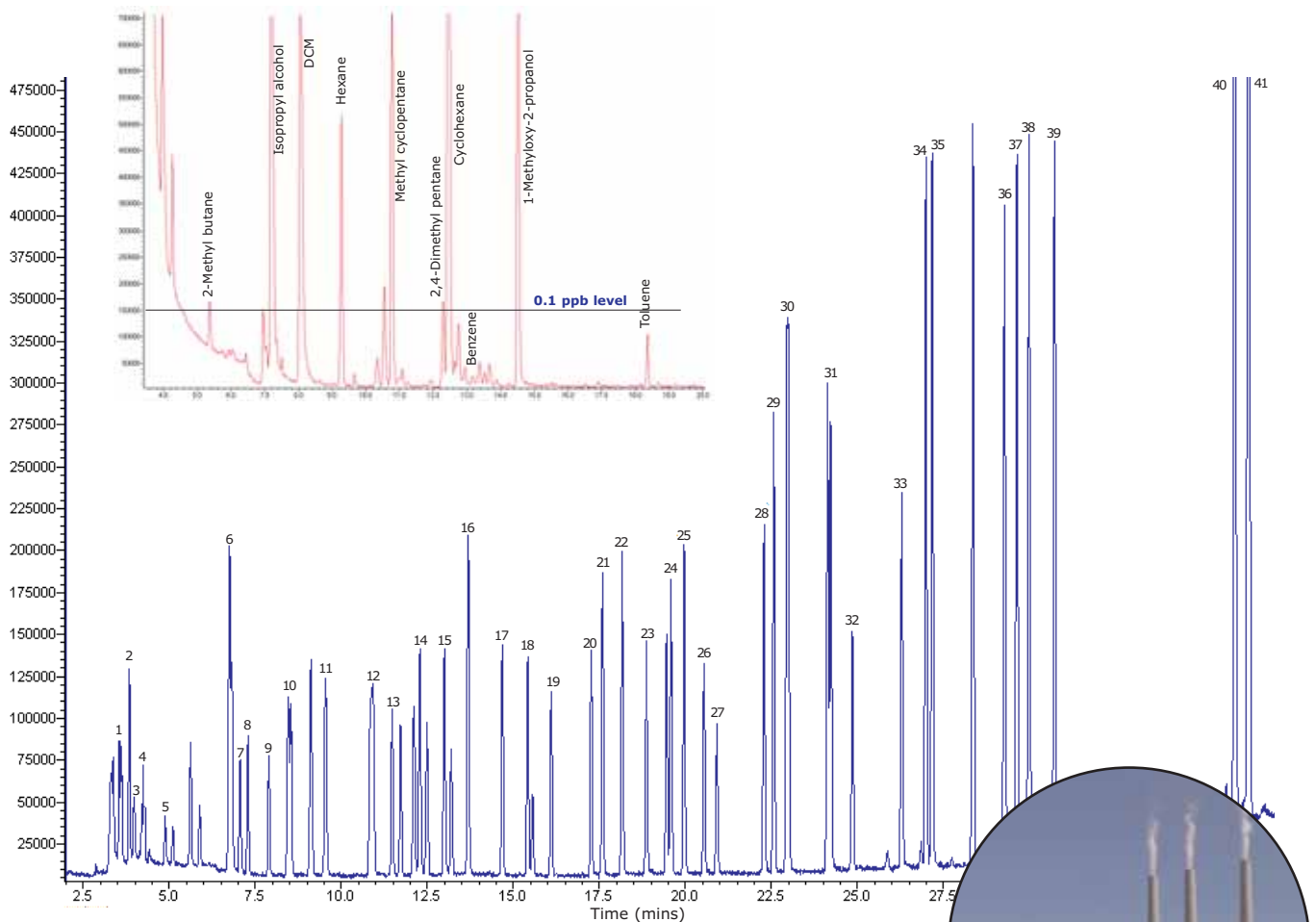
**Cryogen-free operation saves thousands of dollars a month...**



# Canisters, bags and sorbent tubes

TO-15 standard chromatogram (1 ppb in 1 L) (main) and real air sample (insert)

- |  |                              |                                |
|--|------------------------------|--------------------------------|
| 1 Dichlorodifluoromethane              | 15 Benzene                   | 29 Ethylbenzene                |
| 2 1,2-Dichlorotetrafluoroethane        | 16 n-Heptane                 | 30 Xylene                      |
| 3 Methyl chloride                      | 17 Trichloroethylene         | 31 Styrene                     |
| 4 1,3-Butadiene                        | 18 1,2-Dichloropropane       | 32 Tribromomethane             |
| 5 Methyl bromide                       | 19 Bromodichloromethane      | 33 1,1,2,2-Tetrachloroethane   |
| 6 Trichlorotrifluoroethane (Freon 113) | 20 Trans-1,3-dichloropropene | 34 1,2,4-Trimethylbenzene      |
| 7 Isopropyl alcohol                    | 21 Methyl isobutyl ketone    | 35 1,3,5-Trimethylbenzene      |
| 8 Carbon disulfide                     | 22 Toluene                   | 36 1,2-Dichlorobenzene         |
| 9 Methylene chloride                   | 23 Cis-1,3-Dichloropropene   | 37 1,3-Dichlorobenzene         |
| 10 Tert-butyl methyl ether             | 24 Tetrachloroethylene       | 38 Chloromethylbenzene (alpha) |
| 11 1,1-Dichloroethane                  | 25 Methyl n-butyl ketone     | 39 1,4-Dichlorobenzene         |
| 12 Ethyl acetate, methyl ethyl ketone  | 26 Dibromochloromethane      | 40 1,2,4-Trichlorobenzene      |
| 13 Tetrahydrofuran                     | 27 1,2-Dibromoethane         | 41 Hexachloro-1,3-butadiene    |
| 14 Cyclohexane                         | 28 Chlorobenzene             |                                |





ppm...ppb...ppt

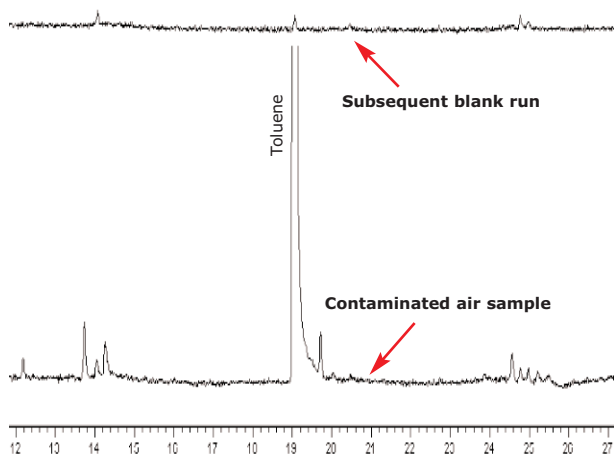
## Versatility

### The application range of series 2 Air Server technology

Series 2 (ULTRA-)UNITY-Air Server systems offer quantitative and cryogen-free retention, even of ultra-volatile species such as freons and C<sub>2</sub> hydrocarbons, together with complete recovery across the air toxics boiling range. Labile, odorous analytes, such as H<sub>2</sub>S and mercaptans may also be measured at sub-ppb concentrations. Markes systems are compatible with the highest boiling compounds that can be recovered from canisters or ambient temperature air/gas streams.

New improved stream selection valves and an inert flow path **eliminate sample carryover** even when monitoring over a wide concentration range (ppt to ppm). This allows ambient air samples to be calibrated with small volumes of relatively concentrated standard gas. It also allows automated sequencing of samples varying widely in concentration without fear of contamination.

Compatibility with samples over a wide concentration range is further enhanced by sophisticated, electronically-controlled sample splitting during trap desorption (and during tube desorption, if applicable).



Negligible carryover with series 2 UNITY-Air Server

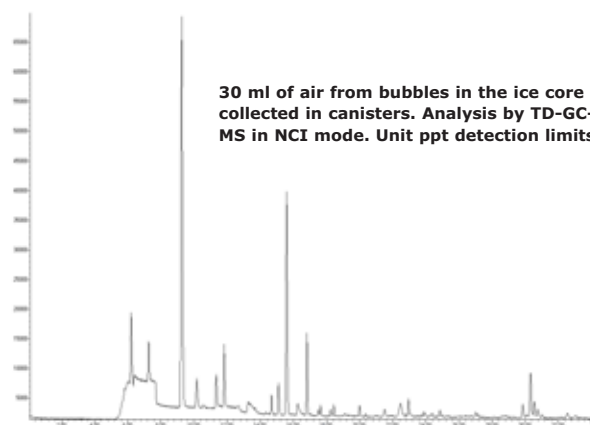
### On-line monitoring, canisters/bags and tube desorption

Whether they are used for on-line monitoring or off-line canister/bag analysis, all systems incorporating series 2 Air Server technology, offer complementary tube desorption.

Every series 2 Air Server is connected to a Markes (ULTRA-)UNITY 2 system. The UNITY 2 TD platform offers method-compliant desorption of single tubes and the addition of a series 2 ULTRA allows automatic analysis of up to 100 sorbent tubes. Series 2 (ULTRA-)UNITY systems are described in detail in the associated brochures and their performance is not compromised in any way by the addition of an Air Server module.

In summary, key advantages of series 2 (ULTRA-)UNITY systems for tube desorption include:

- **Application versatility.** Series 2 (ULTRA-)UNITY systems are compatible with every TD application on one analytical platform; ultra-volatiles (e.g. C<sub>2</sub> hydrocarbons), semi-volatiles (up to n-C<sub>40</sub>) and reactive compounds. Samples for tube desorption either comprise sorbent tubes used to collect organic vapours or material samples (solid or liquid) weighed directly into empty TD sample tubes for direct desorption. Splitless, single or double split options allow analysis of samples ranging in concentration from ppt to percent without overloading the analytical system



Detection of trace level analytes aids atmospheric research

# Real time monitoring - real time detection

- **Method compliance.** Markes tube desorption technology complies with all key standard methods; US EPA Method TO-17 (ambient and indoor air), EN ISO 16017 (workplace, ambient and indoor air), ISO 16000 (materials emission testing), NIOSH 2549 (workplace indoor air), *etc.* Important features for method compliance include effective tube sealing during automation, stringent (ambient-temperature/no-flow) leak testing, cryogen-free cooling and the option of IS addition
- **Repeat analysis.** Markes proprietary SecureTD-Q facility is supplied as standard with every series 2 (ULTRA-)UNITY system. It offers quantitative re-collection of any split flow (during tube or trap desorption) facilitating repeat analysis and simplifying method/data validation. ***SecureTD-Q overcomes the one-shot limitation of other thermal desorbers***
- **High throughput.** 100-tube capacity and overlap mode (the ability to begin desorption of a subsequent sample while analysis of a previous sample is ongoing) optimise productivity/revenue generation
- **Compatibility with RFID tagged tubes (TubeTAG)** for enhanced tube/sample traceability

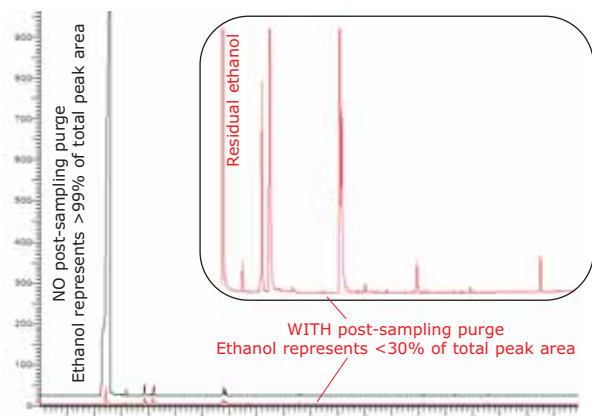
## Measurement system

The majority of TD systems incorporating Markes series 2 Air Server technology are connected to standard or portable GC(MS) systems. However, it is also possible to configure the TD system with real-time detector technology, either in parallel with the GC(MS) or as an alternative to GC(MS).

Most environmental monitoring applications require the resolution of capillary GC(MS) because of the diversity and variability of organic vapour profiles which can occur in most atmospheres. However, for some industrial process applications or for monitoring well characterized atmospheres (where the various failure modes are known) it can be advantageous to combine the on-line TD system with simpler real-time detection technologies; process MS, sensor arrays, infra-red, *etc.*

## Trademarks

SecureTD-Q™ and TubeTAG™ are trademarks of Markes International Ltd.



**Aroma profiling of whisky vapours with e-nose showing differentiation of whiskey types**

**Purging of water and ethanol from whisky headspace vapours allows selective concentration of olfactory compounds. Analysis with GCMS & e-nose**

**Markes International Ltd.**

Gwaun Elai Medi Science Campus  
Llantrisant  
RCT  
CF72 8XL  
United Kingdom

**T:** +44 (0)1443 230935 **F:** +44 (0)1443 231531  
**E:** [enquiries@markes.com](mailto:enquiries@markes.com) **W:** [www.markes.com](http://www.markes.com)