MARKES international

Monitoring trace VOCs in humid air

Novel water management solutions for thermal desorption

THE QUEEN'S AWARDS FOR ENTERPRISE: INNOVATION 2019

Unparalleled expertise in air monitoring

Global regulations with expanding target lists are driving a need for more versatile air monitoring tools – a need that is met by thermal desorption (TD) with GC–MS.

Air streams monitored using tubes, canisters or by on-line methods frequently contain high levels of water vapour. However, moisture can lower sensitivity, cause poor chromatography (peak shape and repeatability), and reduce column and detector lifetime.

Removing water without using liquid cryogen is essential to achieve good results and minimise the running and maintenance costs of the entire analytical system.

With 20 years at the forefront of TD innovation and applications development, Markes International can recommend the three best solutions for water management:

- Kori-xr water condenser for canister and on-line monitoring.
- Nafion dryer for routine on-line air monitoring with conventional GC detectors.
- Dry-purging of sorbent tubes and traps (standard in every TD system).

Markes ‘xr’ series of thermal desorbers offers outstanding versatility for the monitoring of volatile and semi-volatile organic compounds (VOCs and SVOCs) in air streams:

- E**x**tended analytical **r**ange – from C_2 to C_{44}, including reactive and thermally labile species.
- E**x**tended **r**e-collection capability, available for tubes, canisters and on-line.
- E**x**tended **r**eliability.

Water management options

Selecting the best approach for your application

The three complementary water management solutions offered by Markes enable users to optimise their TD system for each application challenge. Whatever the target compounds, analyte level or sampling method, one or more of these options will guarantee best possible performance across a wide range of sample humidities.

Description	Key features	C_2	Non-polar C_3	Polar VOCs	Mono-terpenes	Typical applications
Kori-xr	▪ Cryogen-free trap placed before sorbent trap enables water to be removed from the sample. ▪ **No** loss of polar and non-polar compounds. ▪ Ideal for GC–MS analysis of complex air samples.	✓	✓	✓	✓	**Canister** or **on-line** monitoring of: ▪ VOCs and VVOCs (US EPA Method TO-15, PAMS Method or Chinese EPA Method HJ 759). ▪ Oxygenates (OVOCs).
Nafion dryer	▪ Hydrophilic co-polymer widely used for the analysis of C_2–C_{10} ozone precursors. ▪ Polar VOCs and monoterpenes are purged along with the water. ▪ Ideal for GC–FID analysis of VOCs.	✓	✓	✗	✗	**Canister** or **on-line** monitoring of: ▪ Ozone precursors (PAMS Method). ▪ VOCs and VVOCs (Chinese EPA Method HJ 759). ▪ Hazardous air pollutants.
Dry-purging	▪ Selection of appropriate sorbent materials and trap temperature eliminates most of the water. ▪ Very volatile species cannot be trapped under these conditions. ▪ No additional hardware needed.	✗	✓	✓	✓	**Tube**, **canister** or **on-line** monitoring of: ▪ VOCs and SVOCs (US EPA Methods TO-15 and TO-17). ▪ Fenceline emissions (US EPA Method 325). ▪ Stack emissions (CEN/TS 13649 or Chinese EPA Method HJ 734).

Kori-xr™

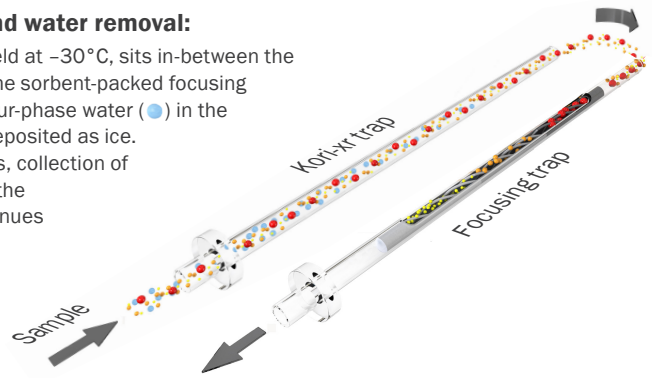
High-performance water removal

Markes' new water management device, Kori-xr, delivers outstanding results for on-line and canister analysis of humid air by TD–GC–MS without any need for liquid cryogen. The efficient removal of water by Kori-xr permits lower temperatures to be used in the focusing trap without risk of ice formation, allowing quantitative retention of VOCs, VVOCs, oxygenates and monoterpenes on the UNITY-xr™ thermal desorber.

How Kori-xr works

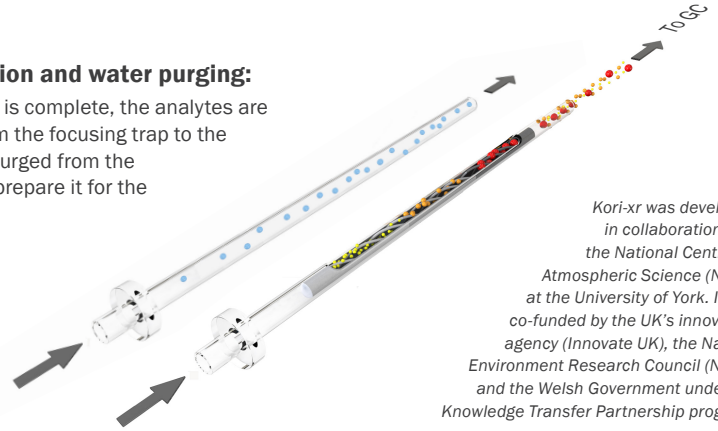
1 **Air sampling and water removal:**

The Kori-xr trap, held at –30°C, sits in-between the sample inlet and the sorbent-packed focusing trap, causing vapour-phase water ( ) in the air sample to be deposited as ice. During this process, collection of VOCs ( ) on the focusing trap continues unaffected.



2 **Trap desorption and water purging:**

When sampling is complete, the analytes are transferred from the focusing trap to the GC, and ice is purged from the Kori-xr trap, to prepare it for the next sample.

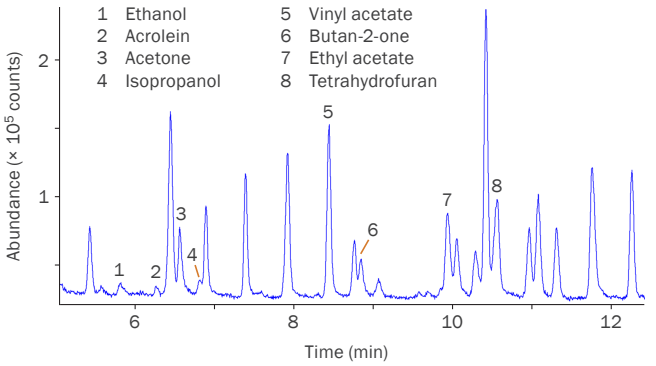


Kori-xr was developed in collaboration with the National Centre for Atmospheric Science (NCAS) at the University of York. It was co-funded by the UK's innovation agency (Innovate UK), the Natural Environment Research Council (NERC) and the Welsh Government under the Knowledge Transfer Partnership program.

When should I choose Kori-xr?

- When you need to analyse polar and non-polar VOCs and VVOCs by GC–MS.
- When your sample has high relative humidity.
- When you need to reliably quantify compounds from C_2 to C_{12}.
- When you need to reach very low MDLs.
- When you need to fully characterise unknown atmospheres.

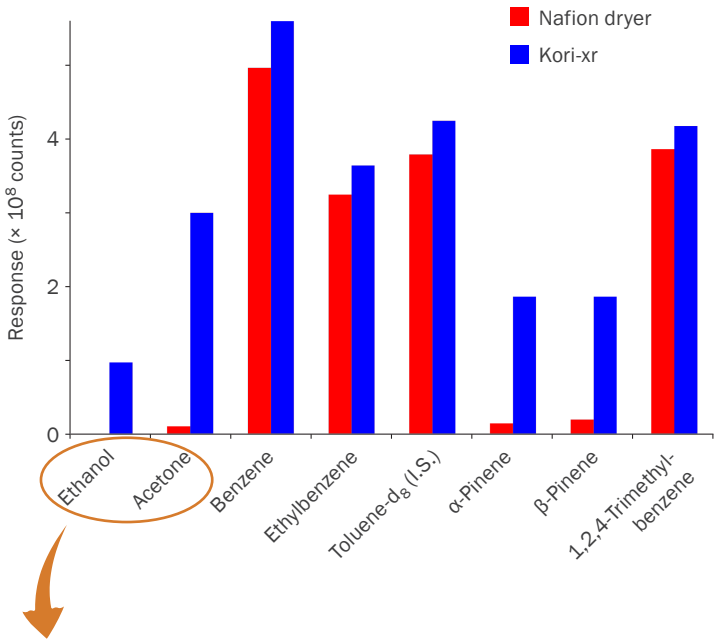
Monitoring TO-15 compounds in humid air



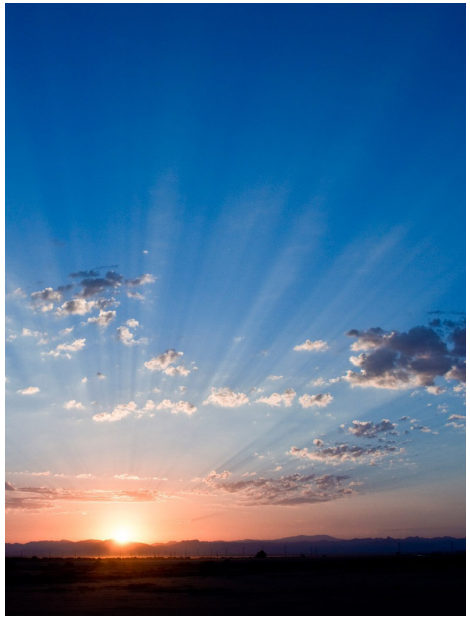
Using Kori-xr and Markes' UNITY–CIA *Advantage*-xr™ system to analyse humid air allows interference-free monitoring of polar and non-polar compounds cited in US EPA Method TO-15 for canister sampling and analysis.

Improved retention of ultra-volatile and polar species

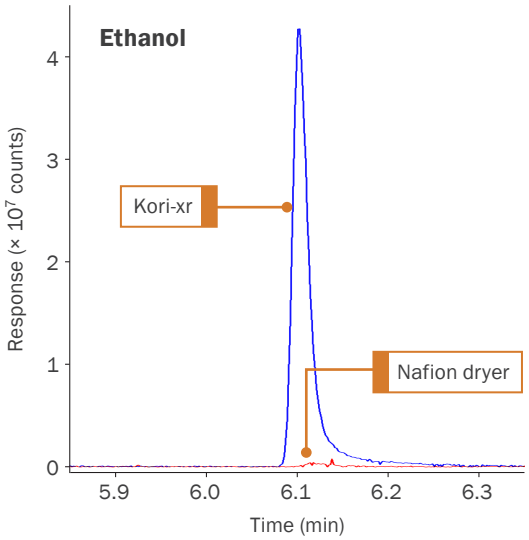
Compound	Detected using Nafion dryer?	Detected using Kori-xr?	Response linearity (R^2) using Kori-xr
Ethanol	✗	✓	0.973
Acetone	✓	✓	0.993
Toluene-d_8 (I.S.)	✓	✓	1.000
Ethylbenzene	✓	✓	0.999
α-Pinene	✗	✓	0.999
β-Pinene	✗	✓	0.997
1,2,4-Trimethylbenzene	✓	✓	0.999

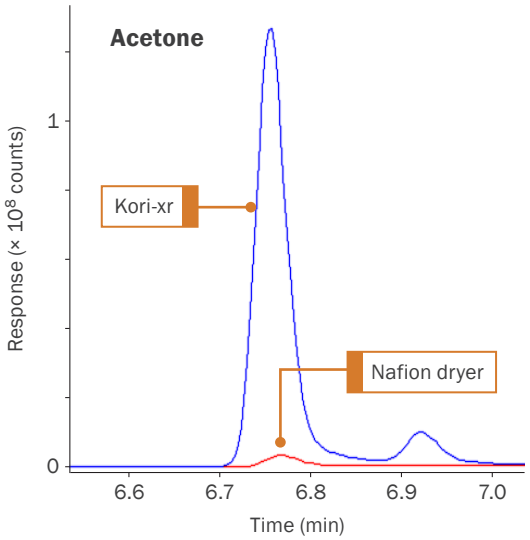


Kori-xr shows enhanced recovery of low-boiling and polar VOCs from an air stream with 80% RH, compared to use of a Nafion dryer.



Strong responses from highly polar compounds





Ethanol and acetone are scarcely visible in this 80% RH air stream when it is monitored using a Nafion dryer. In contrast, Kori-xr allows quantitative analysis of these important polar compounds.

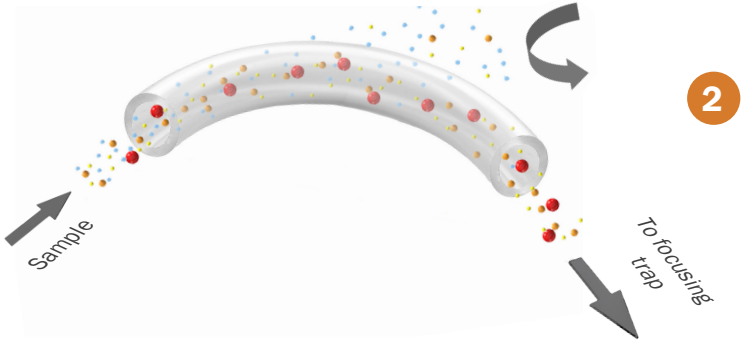
Nafion™ dryer

Efficient membrane-based water removal

Membranes constructed of hydrophilic co-polymers such as Nafion are widely used to remove water from humid air streams, especially for the analysis of C_2–C_{10} hydrocarbons, known as 'ozone precursors'. However, many polar VOCs (such as alcohols, aldehydes, ketones, esters and glycol ethers) plus key monoterpenes (such as α- and β-pinene) also migrate through the membrane. This can be a major advantage for routine air monitoring applications carried out using Markes' UNITY–Air Server-xr™ with conventional GC detection – enabling confident analysis of target compounds with minimal interference from unknowns.

How Nafion dryers work

1 **Air sampling:**
The air sample containing water ( ) and VOCs ( ) passes through a Nafion polymer tube before reaching the sorbent-packed focusing trap.

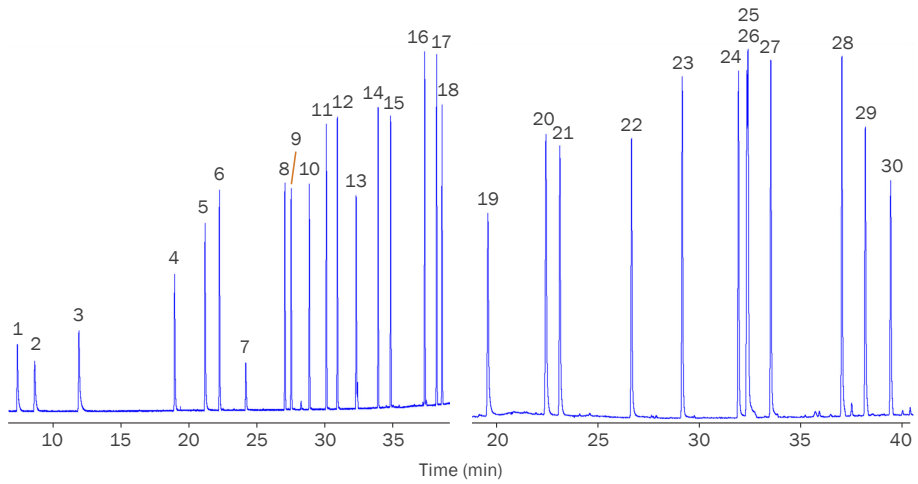


2 **Water removal:**
Water in the air stream is adsorbed onto the polymer surface and, driven by the humidity gradient, passes through to be removed by a stream of purge gas. However, the presence of strongly acidic groups on the polymer surface means that some polar compounds also migrate through.

When should I choose Nafion dryers?

- When you are not interested in analysis of polar compounds.
- When you run VOC analysis by GC–FID.
- When you need an affordable and reliable solution for sulfur compounds.

Reliable analysis of ozone precursors



1	Ethane	16	2-Methylpentane
2	Ethene	17	Isoprene
3	Propane	18	n-Hexane
4	Propene	19	Benzene
5	2-Methylpropane	20	2,2,4-Trimethylpentane
6	n-Butane	21	n-Heptane
7	Acetylene	22	Toluene
8	*trans*-But-2-ene	23	n-Octane
9	But-1-ene	24	Ethylbenzene
10	*cis*-But-2-ene	25, 26	*m-/p*-Xylene
11	2-Methylbutane	27	*o*-Xylene
12	n-Pentane	28	1,3,5-Trimethylbenzene
13	Butadiene	29	1,2,4-Trimethylbenzene
14	*trans*-Pent-2-ene	30	1,2,3-Trimethylbenzene
15	Pent-1-ene		

Using a Nafion dryer allows interference-free analysis of ozone precursors using a dual-column setup and GC–FID, at levels well below the 0.5 ppb required for the PAMS Method.

Dry-purging

The built-in option for water removal

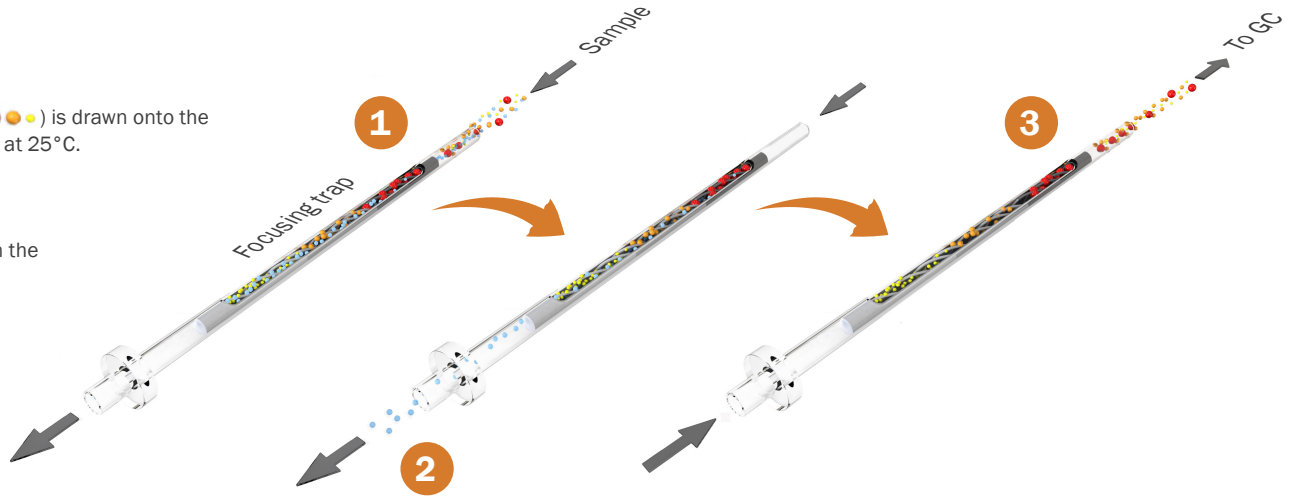
Dry-purging is a powerful and versatile tool for selectively eliminating water and other unwanted interferences prior to air analysis. It harnesses the sorbent selection expertise and precise temperature control available with Markes' instruments, and can be applied to all air sampling methods – sorbent tubes, canisters, bags and on-line air monitoring. However, a drawback of this approach is that C_2 hydrocarbons are not quantitatively retained by the focusing trap, and therefore cannot be reliably reported.

How trap dry-purging works

1 Sample trapping:
The air sample containing water ( ) and VOCs ( ) is drawn onto the sorbent-packed focusing trap, which is usually held at 25°C.

2 Water removal:
Water is purged from the trap with dry carrier gas in the sampling direction.

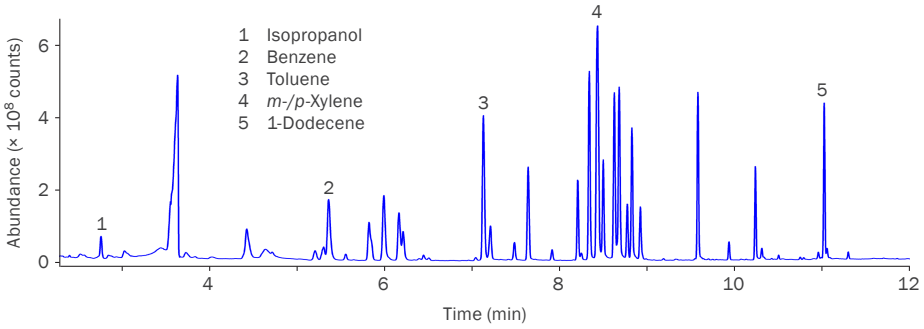
3 Trap desorption:
The flow of carrier gas is then reversed and the trap heated rapidly in the usual way, to desorb the analytes.



When should I choose dry-purging?

- When your analyte range is C_3–C_{44}.
- When you need compatibility with tube (passive and pumped), on-line and canister analysis.
- When you would prefer not to use additional hardware.

Analysis of humid stack emissions



Use of tube and trap dry-purging gives excellent results for tubes containing the CEN/TS 13649 standard at 100 ng per analyte.

Markes International – The TD experts

World-leading instruments and unmatched expertise in VOC and SVOC monitoring

Markes International has for 20 years been at the forefront of innovation for enhancing the measurement of trace-level VOCs and SVOCs by thermal desorption–gas chromatography. Our suite of instruments for thermal desorption sets the benchmark for quality and reliability:

TD100-xr™
High-throughput 100-tube automated thermal desorber.

UNITY-xr™
Single-tube thermal desorber featuring sample re-collection of all split flows.

UNITY–Air Server-xr™
Versatile on-line VOC monitoring system.

ULTRA-xr™
High-throughput 100-tube autosampler for UNITY-xr.

CIA *Advantage*-xr™
Cryogen-free automated canister autosampler and pre-concentrator.

TT24-7™
Twin-trap instrument for near-real-time on-line monitoring.

L0075 (110321-7)

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