

# Monitoring ozone-depleting substances and greenhouse gases



# Aiding atmospheric monitoring and research

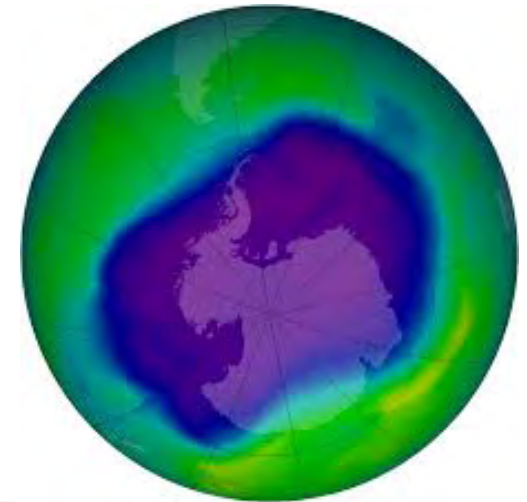
## Reliable direct monitoring of ultra-volatile ozone-depleting substances and halogenated greenhouse gases.

Ultra-volatile halogen-containing compounds have long been of concern to scientists because of their role as **ozone-depleting substances** (ODS) and, in many cases, because of their ability to act as potent **greenhouse gases** (GHGs). These compounds include:

- Chlorofluorocarbons (CFCs)
- Hydrofluorocarbons (HFCs)
- Alkyl halides, including tetrachloromethane ( $\text{CCl}_4$ )
- Nitrogen trifluoride ( $\text{NF}_3$ )
- Newly-developed 'replacement species', such as hydrofluoroolefins (HFOs).

To monitor compliance with regulations, assess the effectiveness of policies, and contribute to research and modelling efforts, reliable data is needed. This is best obtained by direct atmospheric monitoring, using either on-line systems or with canister/flask-based sampling followed by off-line analysis.

Markes International has over 25 years' experience of developing world-leading instrumentation for monitoring trace-level ultra-volatile, volatile and semi-volatile organic compounds in air and materials. We now present three cryogen-free preconcentration systems that couple with GC-MS instruments for the reliable monitoring of ultra-volatile ODS and GHGs.



**Direct air monitoring** is an essential tool for measuring atmospheric concentrations of ozone-depleting substances, aiding monitoring of compliance with the Montreal Protocol.



**Monitoring emissions** of halogenated greenhouse gases is necessary to understand their contribution to climate change.

# Markes' ODS and GHG monitoring portfolio

## Cryogen-free systems for on-line and canister/flask monitoring of ultra-volatiles

Monitoring ODS and halogenated GHGs is challenging due to their varying concentrations and ultra-volatility, complicated further by interference from water and CO<sub>2</sub>, and the need for both laboratory and field measurements.

As a result, there is no single instrument that is suitable for all monitoring situations. However, between them, Markes' portfolio of preconcentration systems for GC-MS covers every scenario.

Key features are:

- Cryogen-free on-line and canister/flask sampling offered on all systems
- All systems suitable for laboratory or field measurements
- Detection of all the important ODS and halogenated GHGs, including 'replacement species'
- Sampling of a range of atmospheres, with method detection limits from ppm (or above) down to sub-ppt.

With detection limits from ppm down to sub-ppt and with a range of compatible compounds, Markes' portfolio of systems for monitoring ODS and GHGs ensures that monitoring objectives can always be met.

### UNITY-CIA Advantage-xr



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### NuVo 200



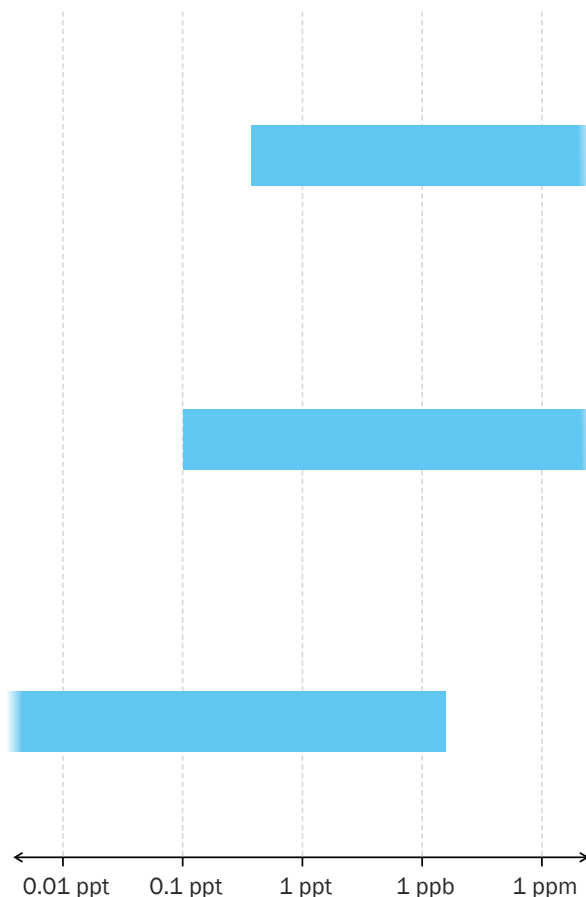
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### Medusa



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### Method detection limits



### Compatible species

Most ODS & halogenated GHGs  
NF<sub>3</sub> & CF<sub>4</sub>  
Replacement species

✓

✓

✓

✓

✓

✓

# UNITY-CIA *Advantage-xr*<sup>™</sup>

## Reliable, routine monitoring of industrial air

UNITY-CIA *Advantage-xr* systems are ideal for routine monitoring of industrial air for ODS and GHGs down to ppb levels or even below. Operating entirely without liquid cryogen and capable of performing on-line measurements or taking up to 27 canister samples, they can monitor all controlled ODS and halogenated GHGs (apart from CF<sub>4</sub> and NF<sub>3</sub>), including those as volatile as C<sub>2</sub>.

Samples from stack/fugitive sources and industrial fencelines can have very variable concentrations of analytes, which can significantly exceed the instrument's calibration range. With the UNITY-CIA *Advantage-xr*, samples can be screened via a gas sampling loop, removing this uncertainty. In addition, its inert, uniformly heated, low-volume flow path recovers rapidly from accidental overloading with high-concentration samples.

## Key advantages of UNITY-CIA *Advantage-xr*

### Maximum instrument uptime

- Highly efficient purging and flow path design eliminate carryover, meaning fewer blanks and higher uptime.
- Cryogen-free cooling and compatibility with hydrogen carrier gas provides continuous running with no downtime.

### Versatility

- Low-volume loop sampling accommodates high-concentration samples.
- Precisely-controlled MFC sampling of larger volumes allows trace-level detection.
- Compatible with pressurised and unpressurised samples.
- Compatible with all major GC-MS systems.

### Future-proof

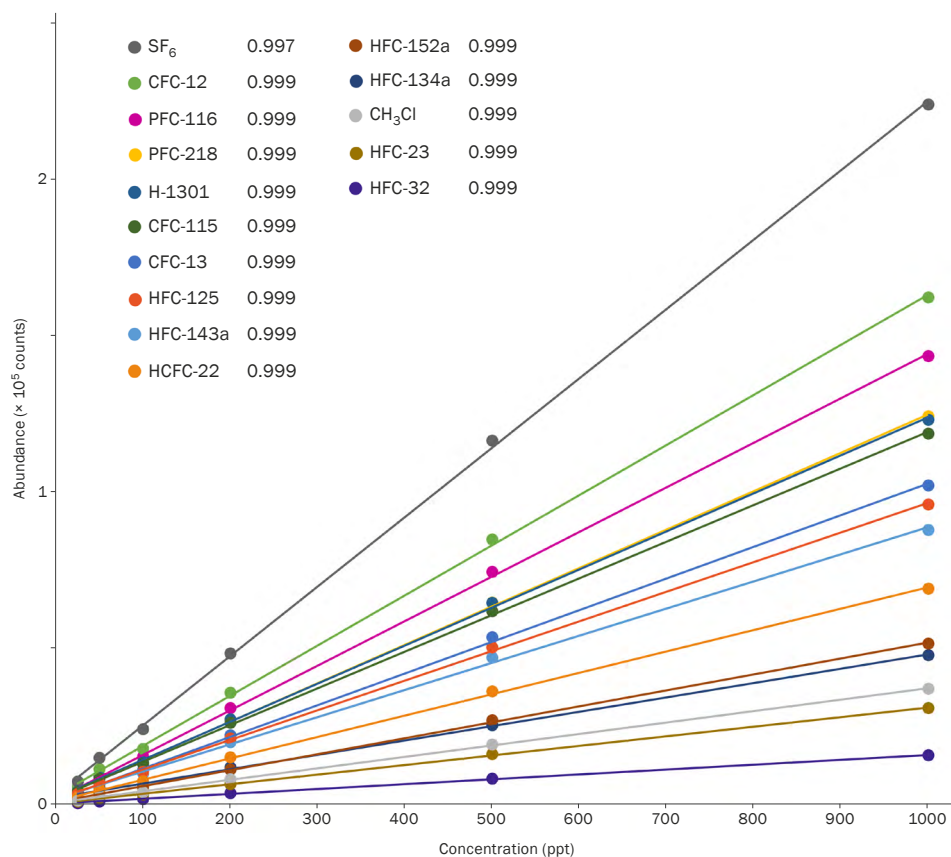
- Easy upgrading from the regular 14-canister capacity to 27 canisters for longer unattended sequences.



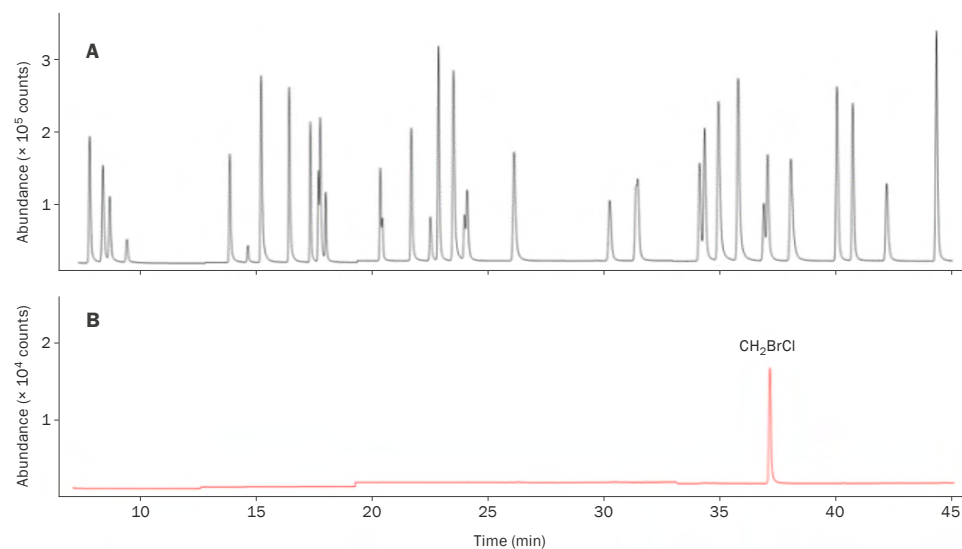


## UNITY-CIA Advantage-xr: High-throughput analysis from ppm to ppt

Using UNITY-CIA Advantage-xr, you can monitor from hexafluoroethane (PFC-116) to tribromomethane at concentration ranges from ppt up to ppm. At the same time, high throughput can be achieved due to the system's capability to use hydrogen carrier gas, and its ability to overlap sampling and analysis.



**Calibrations over three orders of magnitude** are possible with the UNITY-CIA Advantage-xr, thanks to its wide dynamic range and easy accommodation of the linear range of the GC detector. This calibration curve shows the highly linear results from 5 ppt to 1000 ppt for a range of species at 50% relative humidity.



**Excellent system recovery** is demonstrated by challenging the UNITY-CIA Advantage-xr with (A) a sample at double the concentration of the highest calibration point, followed by (B) a blank. Note the complete absence of carryover in the blank run, with the only peak being the internal standard.

# NuVo 200™

## Precise urban and industrial monitoring of all controlled species

NuVo 200 is an inert, 14-channel system for precise, automated monitoring in urban and industrial areas, which builds on the capabilities of the UNITY–CIA *Advantage*-xr by offering quantitative retention of all ODS and halogenated GHGs, including NF<sub>3</sub> and CF<sub>4</sub>, as well as management of interferents (H<sub>2</sub>O and CO<sub>2</sub>).

The ability of NuVo 200 to reach detection limits below the background level for most species, as well as analysing ppm levels, makes it perfectly suited for this type of monitoring. Small changes in concentration can be measured accurately, and it also offers fast recovery from high-concentration events.

## Key advantages of NuVo 200

### Maximum instrument uptime

- Confident reporting of concentrations for all controlled ODS and halogenated GHGs, with comparable results to Medusa systems.
- Water and CO<sub>2</sub> management enhance analytical repeatability, avoid analyte suppression, and increase instrument uptime.
- Cryogen-free cooling and ability to use hydrogen carrier gas provides continuous running with no downtime, for convenient operation in the field.

### Versatility

- Suitable for laboratory or field measurements.
- Compatible with all major GC–MS systems.

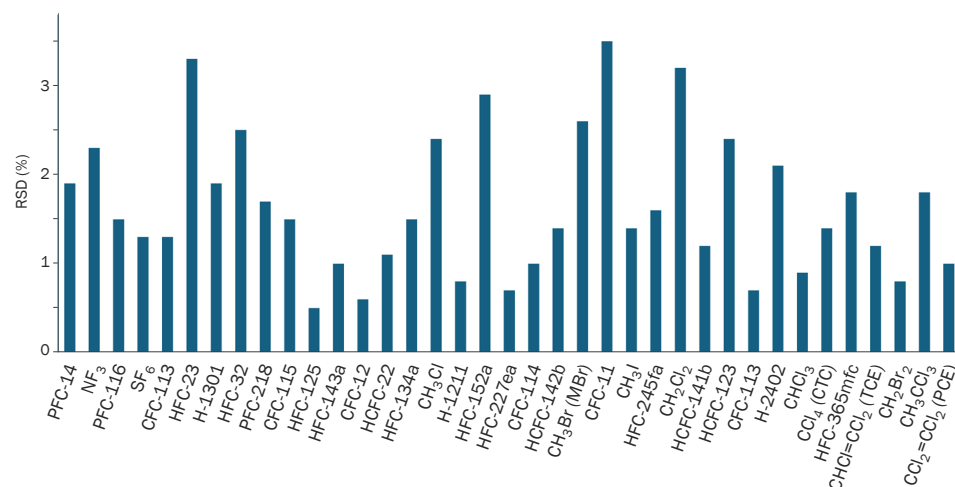
### Future-proof

- Compatible with samples or standard pressures from sub-ambient to 50 psig.
- Compatible with concentrations from sub-ppt to ppm level.

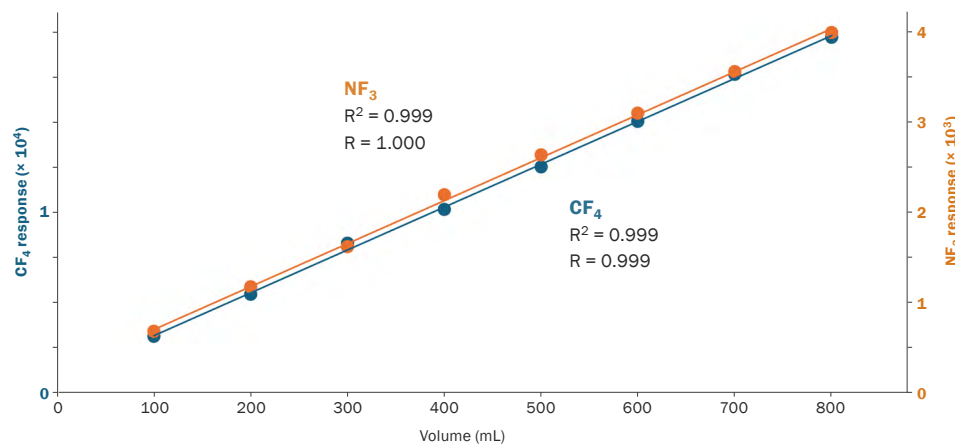


## NuVo 200: Comprehensive analyte coverage from ppm to sub-ppt

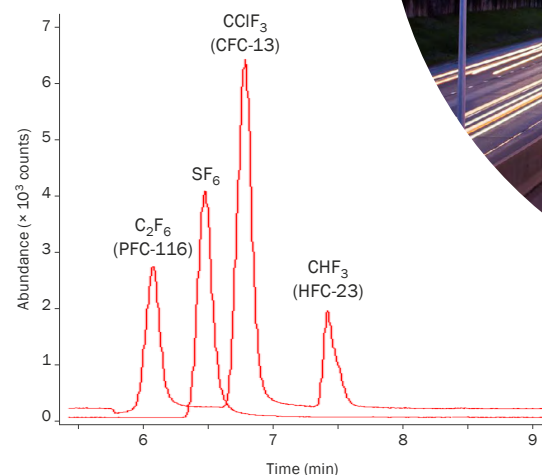
Capable of quantitatively analysing all species controlled under the Montreal protocol and its amendments, as well as some 'replacement' species, NuVo 200 is the ideal instrument for assessment of ODS and halogenated GHGs.



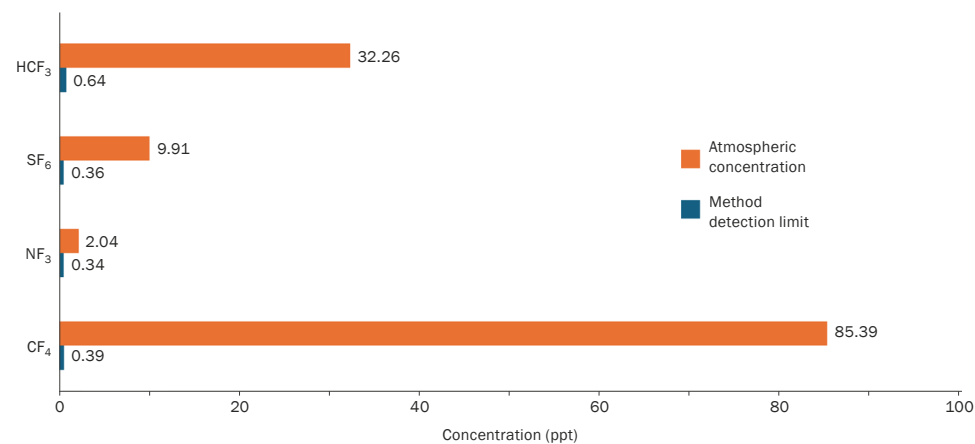
**Repeatable performance** at and below 10 ppt is achievable using NuVo 200, with relative standard deviations under 4%.



**Confident reporting of all species** can be achieved using NuVo 200, with sample volumes of up to 800 mL for the most volatile compounds of interest.



**Efficient management of interferences** on NuVo 200 is demonstrated here by the excellent peak shape (and no suppression) for four species that would normally co-elute with CO<sub>2</sub>.



**Monitoring changes in background concentration** for all species is possible on NuVo 200, thanks to the comprehensive reporting and ultra-low detection limits.



# Medusa™

## Maximum performance for monitoring atmospheric background

Medusa provides the ultimate in performance for the low-level monitoring of *all* ODS and halogenated GHGs, including  $\text{NF}_3$  and  $\text{CF}_4$ , and has been used globally by the AGAGE network for over 20 years to monitor all relevant species at background levels (<2 ppt).

Developed by researchers at the Scripps Institution of Oceanography<sup>1,2</sup> and built by Markes International, Medusa stands out from other air-monitoring instruments because of its ability to take 2 L air samples, allowing quantitation of certain species at levels as low as 0.01 ppt. This makes it well-suited to tracking background concentrations of controlled species, as well as their much lower-level replacements, such as hydrofluoroolefins (HFOs).

## Key advantages of Medusa

### Maximum instrument uptime

- Water and  $\text{CO}_2$  management enhance analytical repeatability, avoid analyte suppression, and increase instrument uptime.

### Versatility

- The only instrument with proven capability to measure  $\text{NF}_3$  in ambient air samples at background levels (2–4 ppt).
- Six channels, with canister and on-line capability.
- Suitable for laboratory or field measurements.
- Cryogen-free cooling provides continuous, economical running.

### Future-proof

- Reliably monitors over 50 ODS and halogenated GHGs.
- Low-level, non-targeted analysis enables addition of replacement species as needed.



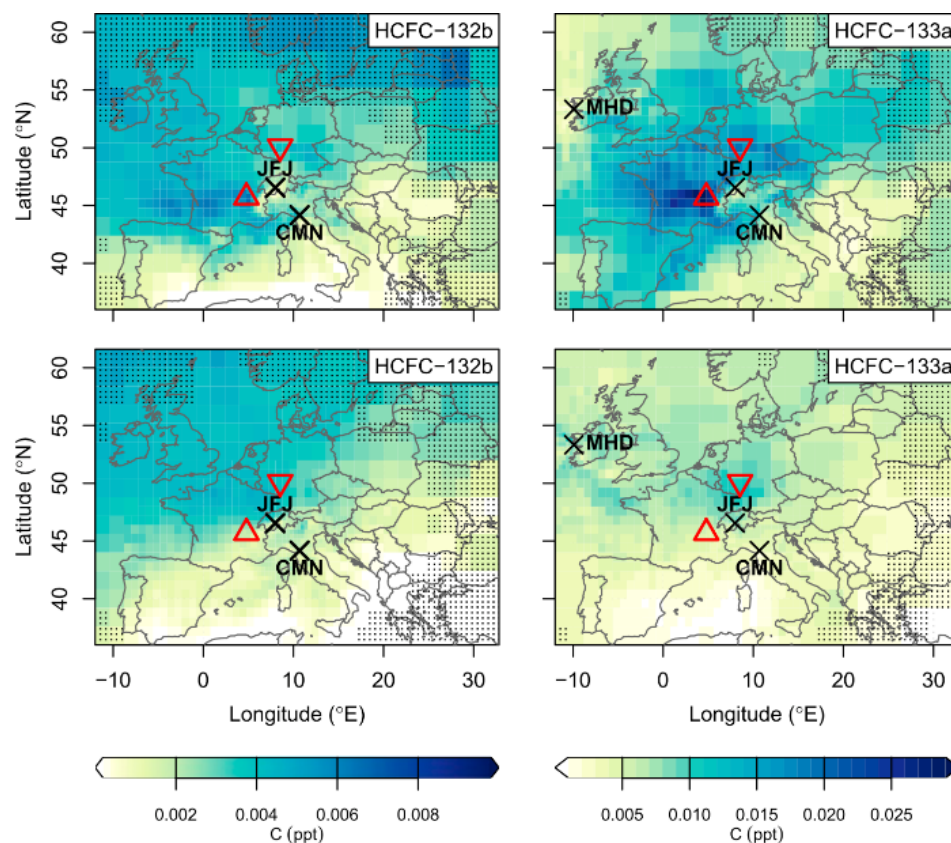
<sup>1</sup> B.R. Miller *et al.*, Medusa: A sample preconcentration and GC/MS detector system for *in situ* measurements of atmospheric trace halocarbons, hydrocarbons, and sulfur compounds, *Analytical Chemistry*, 2008, 80: 1536–1545, DOI: 10.1021/ac702084k.

<sup>2</sup> T. Arnold *et al.*, Automated measurement of nitrogen trifluoride in ambient air, *Analytical Chemistry*, 2012, 84: 4798–4804, DOI: 10.1021/ac300373e.

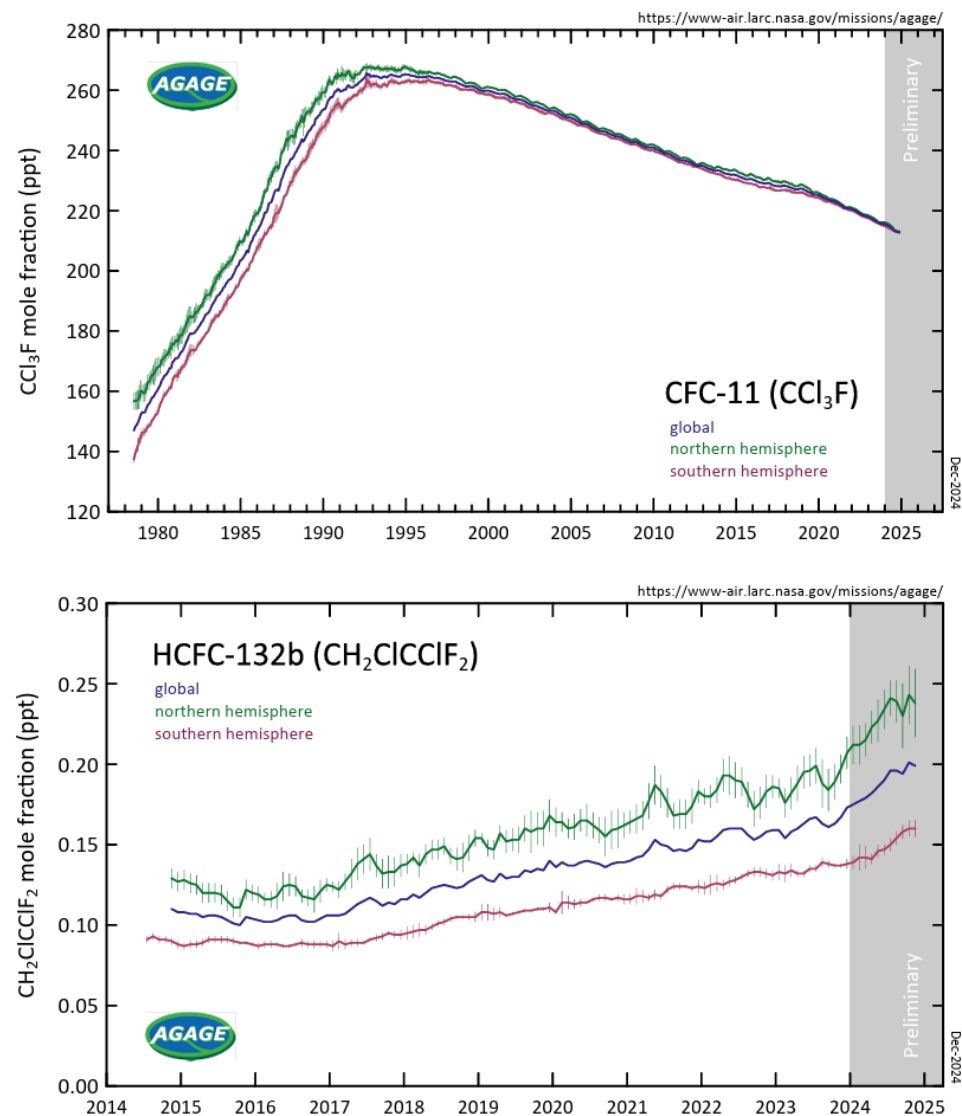


## Medusa: Complete analyte coverage down to 0.01 ppt

Because of its ability to trap up to 2 L of air, Medusa enables confident measurement of concentrations well below the ppt level. In addition, reliable data collection is assured thanks to its management of interferences, including removal of water, CO<sub>2</sub> and noble gases. With a linear response over a wide range of sample concentrations and the ability to alternate samples with a standard for ambient air samples, Medusa provides precise, consistent measurements critical for atmospheric research.



**Confident modelling of regional fluctuations** in pollutant levels is derived from Medusa data using online monitoring at background sites. Source: M.K. Vollmer *et al.*, Unexpected nascent atmospheric emissions of three ozone-depleting hydrochlorofluorocarbons, *Proceedings of the National Academy of Sciences, U.S.A.*, 2021, 118: DOI: 10.1073/pnas.2010914118.



**Defensible data** for controlled species and their replacements is routinely acquired using Medusa, as illustrated by this AGAGE data. Source: <https://www-air.larc.nasa.gov/missions/agage/data/>

# Markes International

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

For nearly 30 years, Markes International has been at the forefront of innovation for enhancing the measurement of trace-level VOCs and SVOCs by TD–GC. Our instruments – which include the flagship automated TD100-xr™ and Centri® platforms – are valued by customers around the world for their quality and reliability, enhanced further by our renowned expertise in applications ranging from air monitoring through to food analysis.

We're headquartered in Bridgend, UK, and support customers in over 60 countries through a network of offices and distribution partners.

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