Released: April 2024

THE QUEEN'S AWARDS FOR ENTERPRISE: INNOVATION 2019

Application Note 175

Detection of ozone-depleting substances and halogenated GHGs in industrial zones with a cryogen-free preconcentration–GC–MS system

Summary

This application note describes a cryogen-free method to collect and analyse ozone-depleting substances (ODS) and halogenated greenhouse gases (GHGs) in 100% humidity ambient air, which meets recent requirements for industrial monitoring in China. In this approach, automated canister sampling and preconcentration employs Markes' UNITY–CIA *Advantage*-xr equipment, and is used in conjunction with a Nafion dryer for management of water vapour, and a GC–MS using selected ion monitoring (SIM).

Introduction

To comply with the Montreal Protocol[1] and recent Five-Year Plans in China,[2,3] it has been decided to carry out pilot-scale monitoring of ozone-depleting substances (ODS) and greenhouse gases (GHGs) in factories or industrial parks that produce or use large quantities of these chemicals.

The chemicals of concern include chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), and other haloalkanes including chloromethane, bromomethane, bromochloromethane, 1,1,1-trichloroethane and carbon tetrachloride.

China has already phased out CFCs, and is gradually stepping-up the phase-out of HCFCs. HFCs, although they do not harm the ozone layer, have a very strong greenhouse effect, and were added to the Montreal Protocol in 2016 under the Kigali Amendment.

This application note demonstrates the quantitative analysis of ODS and halogenated GHGs without use of cryogen, in accordance with the requirements for detection limits and data quality stipulated in a document released by the China National Environmental Monitoring Centre.[4] The analysis system includes a canister autosampler, a device for water vapour removal, a thermal desorption instrument, and a GC–MS analyser used in SIM mode. The system is capable of monitoring samples with 100% relative humidity (RH) and achieving qualitative and quantitative analysis of 34 ODS and halogenated GHGs.

Analytical system

The analytical system used in this study includes a CIA *Advantage*-xr canister autosampler, a UNITY-xr thermal desorption (preconcentration) unit and a Nafion dryer, connected to a GC–MS system (Figure 1 and Figure 2).

The CIA *Advantage*-xr™ is an autosampler for analysing volatile organic compounds in sampling canisters (or bags), which can inject samples either with a 0.5 mL sample loop or a mass flow controller (MFC). The autosampler allows analysis of high- and low-concentration samples in a single sequence, avoiding reliance on diluting high-concentration samples, and the associated risk of quantitative error and introduction of contaminants. It also overcomes the limitations of traditional cryogen-based cooling techniques in analysing canister air, such as high cost and the risk of ice build-up. Moreover, with the CIA *Advantage*-xr it is possible to add an internal standard through a 1 mL sample loop, thus reducing the need for dilution and expensive standard gases by using a small amount of highly concentrated internal standard gas.

Figure 1: UNITY–CIA *Advantage*-xr.

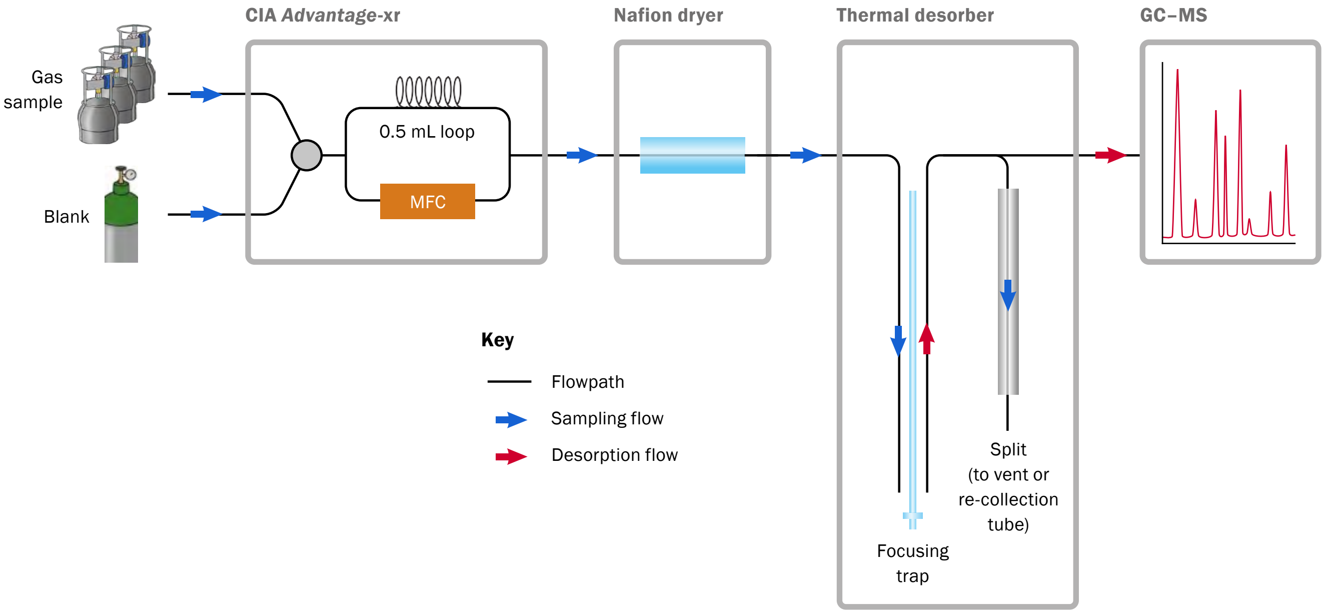

Figure 2: Instrument configuration.

Because ODS and other halogenated GHGs are present at extremely low levels in ambient air, a sample volume of at least 800 mL is required to ensure sufficient sensitivity. However, levels of water in the GC–MS system must also be maintained at very low levels.[5] To achieve this, in this study a Nafion dryer is used to remove water vapour, and the analytical settings have been optimised to enable analysis of trace or ultra-trace ODS and GHGs in 100% RH ambient air (see Figure 2).

The operation of the system is as follows: following sampling using the CIA *Advantage*-xr, the Nafion dryer is used to remove most of the water vapour from the sample. The sample then enters the electrically-cooled cold trap of the UNITY-xr™ thermal desorber, which is maintained at –30°C to achieve quantitative capture of the analytes. The carrier gas then purges the cold trap in the direction of sampling, eliminating oxygen and further reducing water vapour levels without causing loss or breakthrough of the components to be measured. Finally, the flow of carrier gas is reversed, and the cold trap is heated rapidly (up to 100°C/s) to inject the components onto the GC column.

Experimental

Standard gas:
A mixture of 1 µmol/mol ODS (Linde SPECTRA Environmental Gases, Inc.) and 1 µmol/mol HFCs (Air Liquide S.A.) was diluted with nitrogen to achieve two standard gas concentrations, 1 ppb and 100 ppt. The mixtures were stored in canisters and a humidity of 50% RH was achieved by injecting 182 µL pure water into the canister at ambient laboratory temperature (21°C). Components are listed in Table A1 (see Appendix).

Canister sampling:

Instrument:	CIA *Advantage*-xr™ (Markes International)
Pre-sampling purge:	4 min at 50 mL/min
Sampling rate:	80 mL/min
Sample volume:	80–800 mL
Post-sampling purge:	5 min at 50 mL/min
Water removal:	
Instrument:	Nafion dryer
Dryer setting:	20 psig, 240 mL/min

TD:

Instrument:	UNITY-xr™ (Markes International)
Cold trap:	'Ozone precursor/Freons' (U-T5O3F-2S)
Flow path:	120°C
Cold-trap purge:	2 min at 50 mL/min
Cold trap low:	–30°C
Cold trap high:	350°C, 5 min
Split vent:	3 mL/min

GC:

Carrier gas:	Helium, constant flow
Column flow:	1.5 mL/min
Temperature ramp:	35°C (10 min), then 10°C/min to 120°C (10 min), then 5°C/min to 230°C (2 min)
Run time:	52.5 min

Quadrupole MS:

Ion source:	230°C
Transmission line:	250°C
Quadrupole:	150°C
SIM settings:	See Table A1 (see Appendix)

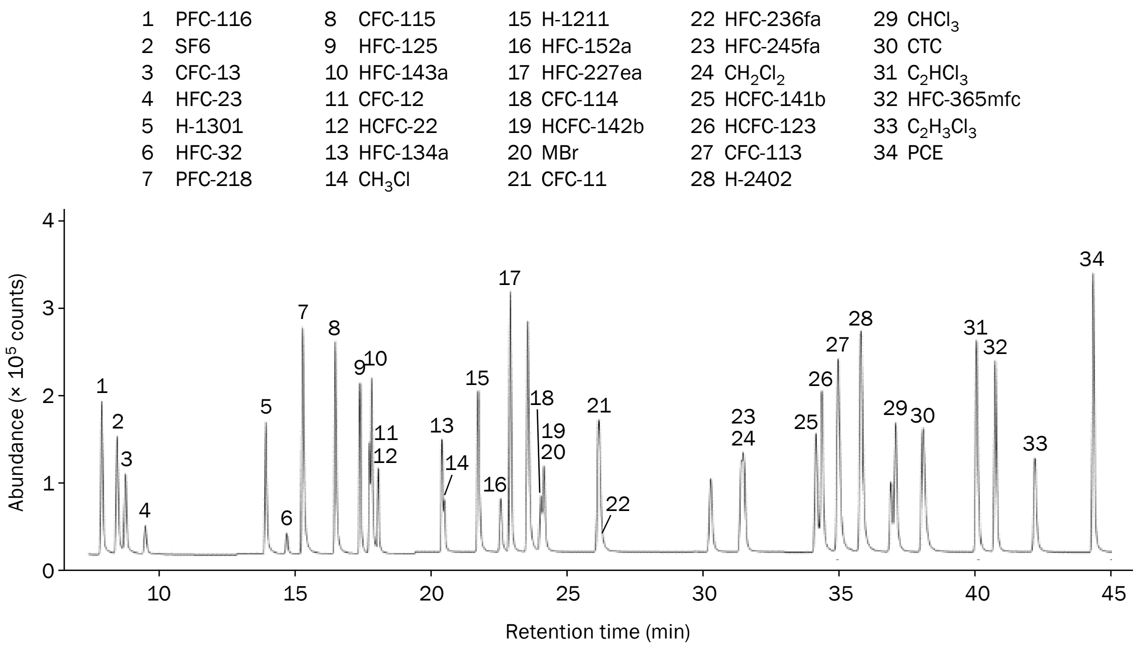

Figure 3: Total ion chromatogram showing separation of ODS and HFCs.

Results

1. Chromatography

The chromatographic columns typically used for ODS analysis are GS-GASPRO and PoraBOND Q, and in this case, the GS-GASPRO (60 m × 320 µm, Agilent Technologies) was chosen. A typical chromatogram is shown in Figure 3.

2. Linearity

Calibration with the 1 ppb standard used sample volumes of 800, 400, 160 and 80 mL; calibration with the 0.1 ppb standard used sample volumes of 400, 200, 80 and 40 mL. The relative response factors (RSDs) for all compounds were less than 30%, and the correlation coefficients for all compounds were ≥0.992. Full results are listed in Table A1 (see Appendix). Figure 4 shows the linearities of selected target compounds at 50% RH.

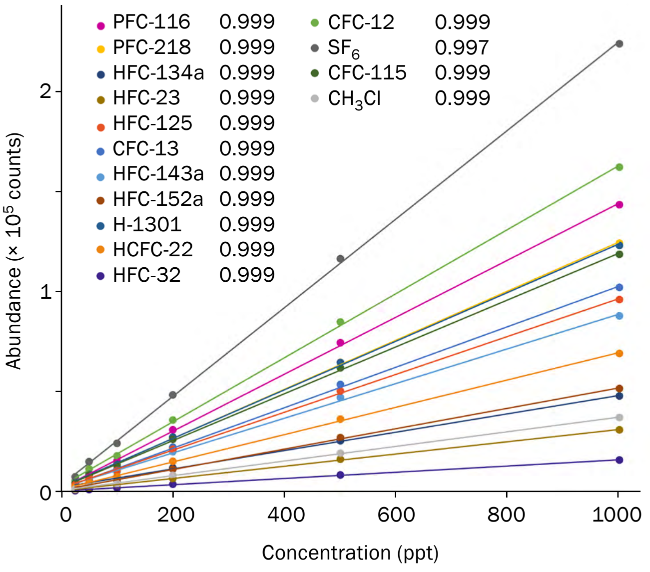

Figure 4: Linearity plots for selected compounds at 50% RH.

3. Limits of detection

According to HJ 168-2020,[6] the standard deviation of the method detection limit (MDL) is calculated by repeating the analysis of low-concentration blank spiked samples near the limit of detection (LOD) seven times according to the steps in the sample analysis. In this study, the calculated LOD ranges from 0.08 to 0.30 ppt, while the limit of quantitation (LOQ) ranges from 0.32 to 1.20 ppt, as shown in Table A1 (see Appendix). These values are therefore acceptable for monitoring fluctuations in the very small amounts of these compounds present in ambient air.

4. Precision and accuracy

To assess the precision of the measurements, standard gases with a concentration of 0.5 ppb and 50% RH were prepared using nitrogen as the matrix gas, and these standards were sampled continuously six times. Good precision was achieved, with value for individual compounds varying from 0.8% to 7.7%. Full results are given in Table A1 (see Appendix).

To assess the accuracy of the measurements, a blank nitrogen sample spiked with 500 ppt of the analytes was analysed. Recoveries were found to be in the range 93.5–101.5% indicating a robust method. Full results are given in Table A1 (see Appendix).

5. Cross-contamination and blanks

The concentrations of ODS and halogenated GHGs in ambient air are generally low, but due to the use of ODS in certain industries, concentrations can be higher in particular locations.

The 'HL' model of the CIA *Advantage*-xr is well-suited for analysing trace samples while also accommodating high-concentration samples from industrial areas. This model contains two sampling channels: high-concentration samples can be injected through the sample loop, while trace-level samples can be injected in larger volumes through the mass flow controller (MFC). By using these different sampling methods, cross-contamination between high- and low-concentration samples can be prevented.

This technology is also useful when analysing samples of unknown origin, where it is necessary to minimise cross-contamination between samples (for example, a sample with a concentration higher than that typically analysed may cause cross-contamination of a subsequent background air sample with trace-level VOCs, leading to errors in quantitation). In order to assess residual effects, 800 mL of a 2 ppb, 90% RH standard was analysed, followed immediately by 800 mL of pure helium, with 10 mL of 40 ppb bromochloromethane added as an internal standard.

The sample concentration in this case is twice the maximum calibration concentration standard. The results show that none of the target compounds were detected, except for the added internal standard. Figure 5 shows the TIC for the 2 ppb specimen, alongside the subsequent cross-contamination test.

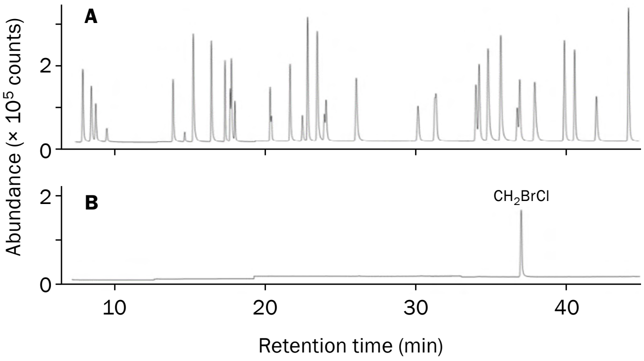

Figure 5: (**A**) TIC of a 2 ppb sample, and (**B**) a subsequent gas blank containing the internal standard bromochloromethane.

Conclusion

In summary, this application note has shown that the CIA *Advantage*–UNITY-xr system with Nafion dryer, using a cold trap dedicated to ODS analysis, is suitable for detecting ODS and halogenated GHGs in up to 800 mL of humidified industrial air.

The method detection limits found for the ODS and GHG targets are in the range 0.08–0.30 ppt, which is lower than the reference range of the global background concentration, enabling the tiny fluctuations of concentration in ambient air to be monitored. Alongside the use of GC–MS detection in SIM mode, this means that the system meets the technical requirements of the 'TRAIL' document[4] from China National Environmental Monitoring Centre.

A further advantage of the system is that it does not require cryogen, because the cold trap is electrically-cooled, and because of the use of an initial GC column temperature of 35°C. The use of a Nafion dryer further enables compatibility with humid air, so ensuring system stability, retention time stability, reproducibility of response values and method linearity.

When this optimised chromatographic method is used in conjunction with 'overlap' mode (adding the next sample into the cold trap while the current GC analysis is still running), laboratory efficiency is further increased.

In addition to providing full automation of sampling from up to 27 canisters, the CIA *Advantage*-xr is also suitable for gas bag sampling and unattended on-line monitoring in the field, without any modification. Two additional features of all Markes' TD systems, including the CIA *Advantage*–UNITY-xr system described here, are the ability to:

- Perform thermal desorption analyses of adsorbent tubes in accordance either with US EPA Method TO-17 or with China Method HJ 644.
- Re-collect samples for storage or repeat analysis. This involves the collection of split samples into clean sorbent tubes, allowing cleaning and sampling of the canister. In addition, programs for analysis of sorbent tubes or canisters can be pre-programmed and set to run sequentially, without user intervention.

References

1. The Montreal Protocol on Substances that Deplete the Ozone Layer (and the Kigali Amendment), UN Environment Program, https://ozone.unep.org/treaties/montreal-protocol#nolink.
2. 14th Five-Year Plan on Ecological Environment Monitoring (CNEMC), 2021, No. 117.
3. 14th Five-Year Plan on Coordinated Control and Monitoring Capacity Building Program of Fine Particulate Matter and Ozone (Requirement in CNEMC letter), 2021, No. 218.
4. Technical Requirements on Monitoring Ozone-Depleting Substances and Hydrofluorocarbons in Industrial Parks (TRAIL), China National Environmental Monitoring Centre, 2023.
5. M. Li *et al.*, Determination of ODS and other controlled halogenated hydrocarbons in ambient air by electronic refrigeration preconcentration-GC/MS, *Environmental Chemistry (China)*, 2022, 41: 2788–2792, http://hjhx.rcees.ac.cn/en/article/id/62da15dac59bc37b30739b95.
6. Technical Guidelines on Formulation of Standards for Environmental Monitoring and Analysis Methods (HJ 168-2020).

Trademarks

Air Server-xr™, CIA *Advantage*-xr™ and UNITY-xr™ are trademarks of Markes International.

Appendix

No.	Code	Compound name	CAS No.	RT (min)	Quant ion	Qual ion(s)	Linearity (R^2)	MDL (ppt)	500 ppt Precision (%)	500 ppt Recovery (%)
1	PFC-116	Hexafluoroethane	76-16-4	7.928	69	50,119	0.999	0.18	3.31	98.1
2	SF_6	Sulfur hexafluoride	2551-62-4	8.501	127	89	0.997	0.20	3.98	96.6
3	CFC-13	Chlorotrifluoromethane	75-72-9	8.795	69	85,50	0.999	0.15	2.38	98.6
4	HFC-23	Fluoroform	75-46-7	9.427	69	51	0.999	0.27	2.80	99.9
5	H-1301	Bromotrifluoromethane	75-63-8	14.172	69	129	0.999	0.24	2.49	99.4
6	HFC-32	Difluoromethane	27672	14.615	51	33	0.999	0.24	2.41	100.0
7	PFC-218	Perfluoropropane	76-19-7	15.602	69	169,113	0.999	0.17	2.12	99.7
8	CFC-115	Pentafluoroethyl chloride	76-15-3	16.839	85	119,135	0.999	0.21	2.27	97.7
9	HFC-125	Pentafluoroethane	354-33-6	17.593	101	51,69	0.999	0.24	2.79	98.7
10	HFC-143a	1,1,1-Trifluoroethane	420-46-2	17.903	65	69	0.999	0.21	3.73	98.7
11	CFC-12	Dichlorodifluoromethane	75-71-8	18.203	85	87	0.999	0.16	1.17	98.4
12	HCFC-22	Difluorochloromethane	75-45-6	18.252	51	67	0.999	0.20	1.82	98.2
13	HFC-134a	Norflurane	811-97-2	20.546	83	69	0.999	0.30	2.10	101.1
14	CH_3Cl	Chloromethane	74-87-3	20.631	50	52	0.999	0.19	1.79	98.9
15	H-1211	Bromochlorodifluoromethane	353-59-3	22.169	85	87,129	0.999	0.15	1.46	99.3
16	HFC-152a	1,1-Difluoroethane	75-37-6	22.591	65	51	0.999	0.17	2.31	99.6
17	HFC-227ea	1,1,1,2,3,3,3-Heptafluoropropane	431-89-0	23.183	69	82,151	0.999	0.15	1.86	98.9
18	CFC-114	1,2-Dichlorotetrafluoroethane	76-14-2	24.012	85	135,87	0.999	0.20	1.49	99.4
19	HCFC-142b	1-Chloro-1,1-difluoroethane	75-68-3	24.244	65	45,85	0.999	0.16	1.96	98.6
20	MBr	Bromomethane	74-83-9	24.444	94	96	0.995	0.18	4.70	101.5
21	CFC-11	Trichlorofluoromethane	75-69-4	26.650	101	103	0.999	0.14	3.87	95.0
22	HFC-236fa	1,1,1,3,3,3-Hexafluoropropane	690-39-1	26.941	69	133	0.999	0.17	0.80	99.5
23	HFC-245fa	1,1,1,3,3-Pentafluoropropane	460-73-1	31.659	49	84,86	0.999	0.16	4.20	98.2
24	CH_2Cl_2	Dichloromethane	75-09-2	31.679	64	115	0.999	0.20	2.67	98.5
25	HCFC-141b	1,1-Dichloro-1-fluoroethane	1717-00-6	34.518	81	83	0.999	0.25	2.24	94.0
26	HCFC-123	Dichloro(trifluoromethyl)methane	306-83-2	34.737	83	85,69	0.999	0.13	2.14	95.8
27	CFC-113	1,2,2-Trichlorotrifluoroethane	76-13-1	35.475	101	103,151	0.999	0.08	2.75	95.4
28	H-2402	1,2-Dibromotetrafluoroethane	124-73-2	36.325	179	181,129	0.999	0.15	4.20	96.9
29	$CHCl_3$	Trichloromethane	67-66-3	37.571	83	85	0.999	0.10	4.22	99.3
30	CTC	Tetrachloromethane	56-23-5	38.697	117	119,121	0.999	0.23	4.47	93.5
31	C_2HCl_3	Trichloroethylene	79-01-6	40.564	95	130,132	0.999	0.10	2.09	97.8
32	HFC-365mfc	1,1,1,3,3-Pentafluorobutane	406-58-6	40.994	133	69	0.999	0.24	3.81	96.5
33	$C_2H_3Cl_3$	1,1,1-Trichloroethane	71-55-6	42.665	97	99	0.999	0.17	1.74	95.1
34	PCE	Tetrachloroethylene	127-18-4	44.878	166	164,129	0.999	0.17	1.06	96.9

Table A1: Performance data for ODS and halogenated greenhouse gases.