

Thermal Desorption Technical Support

Note 87: A cryogen-free method for monitoring trace greenhouse gases in air

Key Words:

Trace greenhouse gases, Kyoto Protocol, CFCs, HCFCs, UNITY 2, CIA 8, air toxics, GHG

Introduction

In response to the Kyoto Protocol, 'Clean Development Mechanism' (CDM) regulations are being enacted in a number of countries to facilitate and control greenhouse gas (GHG) emission trading. Many of the new regulations require the monitoring of bulk greenhouse gases such as carbon dioxide and methane and some require additional consideration of other lower level and more analytically challenging compounds. Examples of this include proposed amendments to the European Emission Trading Scheme Directive 2003/87/EC¹ and Australia's recent government white paper on a low pollution future².

Trace-level greenhouse gases of interest include chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). Improved methods for monitoring many such compounds in air have recently been reported using sorbent tube or canister-based air sampling methods together with thermal desorption (TD) - GC/MS analysis per US EPA 'air toxics' Methods TO-17 and TO-15 respectively (see Markes TDTS Notes 81 and 86). This work demonstrates detection limits below 100 ppt for all CFCs and HCFCs on the 'air toxic' list using a Markes electrically-cooled TD platform with GC/MS running in full scan mode.

However, not all trace level greenhouse gases are included on the standard US EPA list of target 'air toxics'. Perfluorocarbons for example, are a class of long lived greenhouse gases, the most volatile of which, carbon tetrafluoride (CF₄), has a boiling point of -128°C. CF₄ is present in the atmosphere at very low

concentrations, but has more than 5,000 times the 'global warming potential' (GWP) of CO₂ and a half life in the atmosphere of many thousands of years. The extreme volatility of CF₄ makes it very difficult to trap/concentrate and measure at low levels. Similarly, hexafluoroethane (C₂F₆), has a boiling point of -78°C and over 10,000 times the GWP of CO₂. Other analytically-challenging greenhouse gases, which don't appear on the air toxics list include CF₃Cl, nitrous oxide (N₂O) and sulphur hexafluoride (SF₆) - see table 1.

Compound	Boiling point (°C)	GWP (100 year) 2001 IPCC	Estimated atmospheric lifetime (years)
CF ₄	-128	5700	50000
C ₂ F ₆	-78	11900	50000
N ₂ O	-88	296	114
CF ₃ Cl	-81	14000	Info. not available
SF ₆	-64	23900	3200

Table 1: Greenhouse gases with high GWP, not found in the regular list of US EPA 'air toxics'

Not all of these ultra-volatile GHGs are readily available. CF₃Cl, for example, is banned in many countries and cannot be obtained as a standard. It was therefore decided to evaluate the applicability of the same cryogen-free TD-GC/MS technology used for air toxics monitoring (TDTS 81 and 86) for the most challenging ultra-volatile GHG species (CF₄, C₂F₆, SF₆ and N₂O). If successful, this would demonstrate that such a monitoring system could be used for both ultra-volatile GHGs plus higher boiling CFC & HCFC air toxics and, by extrapolation, any compound in between.

Description of the TD-GC/MS analytical system

The analytical system used for this study comprised a Markes International UNITY 2™ thermal desorber (TD) and Canister Interface Accessory (CIA 8) (with optional nafion dryer), coupled to a GC/MS. Using this TD system, controlled volumes of air/gas were transferred to an electrically-cooled, sorbent-packed focusing trap inside UNITY 2. A combination of Carbograph 1TD™ and Carboxen™ 1003 sorbents held at a trapping temperature of -30°C was found to work best, offering quantitative recovery and efficient release of target compounds. This trap is also compatible with analysis of conventional air toxics (US EPA Methods TO-15 or TO-17) – see below.

Once the process of transferring vapours to the focusing trap was completed, the flow of carrier gas was reversed and the trap heated rapidly (up to ~100°C/sec). Retained compounds were desorbed into the carrier gas stream and transferred/injected into the GC analytical column. Desorption of a UNITY 2 focusing trap is so efficient that splitless analysis is possible without significant peak broadening *i.e.* all of the retained compounds may be transferred to the analytical column in a narrow band of vapour, ensuring optimum sensitivity.

Analytical conditions

A custom gas standard containing CF₄, C₂F₆, N₂O and SF₆ at 1 ppm (balance nitrogen) was used for the experiments.

TD

Instrument configuration:
UNITY 2 + CIA 8 and nafion dryer accessory

Cold trap:
Greenhouse gas trap (part no U-T16GHG-2S)

Sampling time (flow rate):
Between 2.5 min (10 ml/min) and 20 min (50 ml/min)

Post sampling line purge (flow rate):
1 min (20 ml/min)

Pre-trap fire purge (flow rate):
1 min (20 ml/min)

Trap low: -30°C

Trap heating rate: 40°C/s

Trap high: 300°C
Trap high time: 3 min
Split: Splitless
Flow path: 120°C

GC

Column:
J & W GS-AL/KCl 50 m x 0.53 mm with 5 m 0.18 mm fused silica on MS end acting as a restrictor

Pressure: 18 psi

Mode: Constant pressure

Oven program:
60°C (4 min) then 8°C/min to 150°C (0 min)

Total run time: 15.25 min

MS

Quad temperature: 150°C

Source temperature: 230°C

Full scan range: 10 – 300 amu

SIM ions (dwell time):
30 (100), 69 (100), 119 (20), 127 (100)

Sample preparation

A 4 component 1 ppm custom gas standard in nitrogen was used to fill a 10 L Tedlar® bag. Successive dilutions of the bag contents with nitrogen were used to reach lower concentrations.

Results

The excellent peak shape of a 25 ml 100 ppb standard sample can be seen in figure 1 (overleaf).

Linearity/breakthrough

Figure 2 illustrates system linearity for increasing volumes of 15 ppb level gas standards, with R² values of 0.99 for C₂F₆ and SF₆. CF₄ and N₂O also had R² values of 0.99 up to their respective breakthrough volumes *i.e.* up to 25 ml and 150 ml respectively for CF₄ and N₂O.

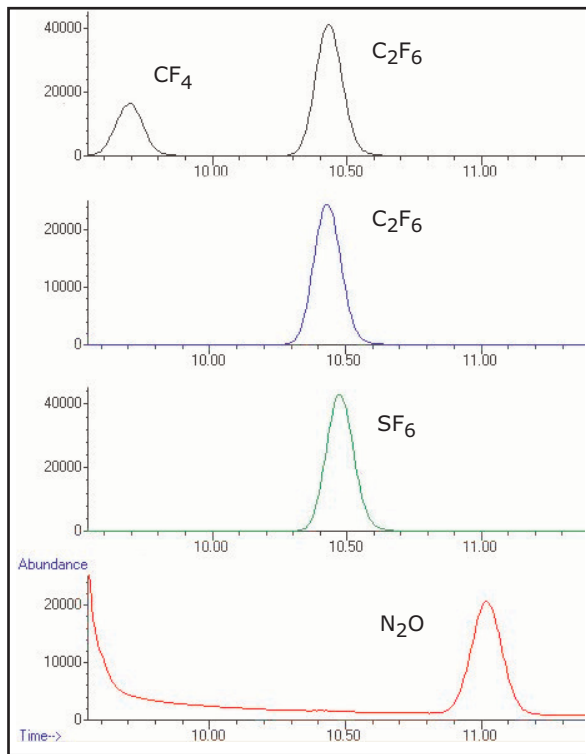


Figure 1: Extracted ions 69 (black), 119 (blue), 172 (green) and 30 (red) from a full scan analysis of 25 ml of a 100 ppb gas standard

Minimum detection limits

The minimum detection limits were determined with a 25 ml sample volume for CF_4 and 1 L for C_2F_6 and SF_6 . Due to problems with absorption and carryover of N_2O in the Tedlar bag, no reliable data could be obtained at low concentrations for this compound. Detection limits for N_2O were therefore determined by extrapolating S:N data at higher concentrations. The MS was run in selected ion monitoring (SIM) mode to give the greatest sensitivity. Figure 3 shows example data at low levels in real air.

Table 2 gives the sample volume, sampling flow, lowest measured detection limits, root mean square (RMS) signal:noise (S:N) and estimated minimum detection limit (with S:N > 3:1) for standards in nitrogen (Std) and real air samples (Air).

The high S:N values even at low concentrations are due to the very low noise levels of the SIM ions, the exception is N_2O where the 30 ion background is high in real air samples and impacts the estimated minimum detection limit.

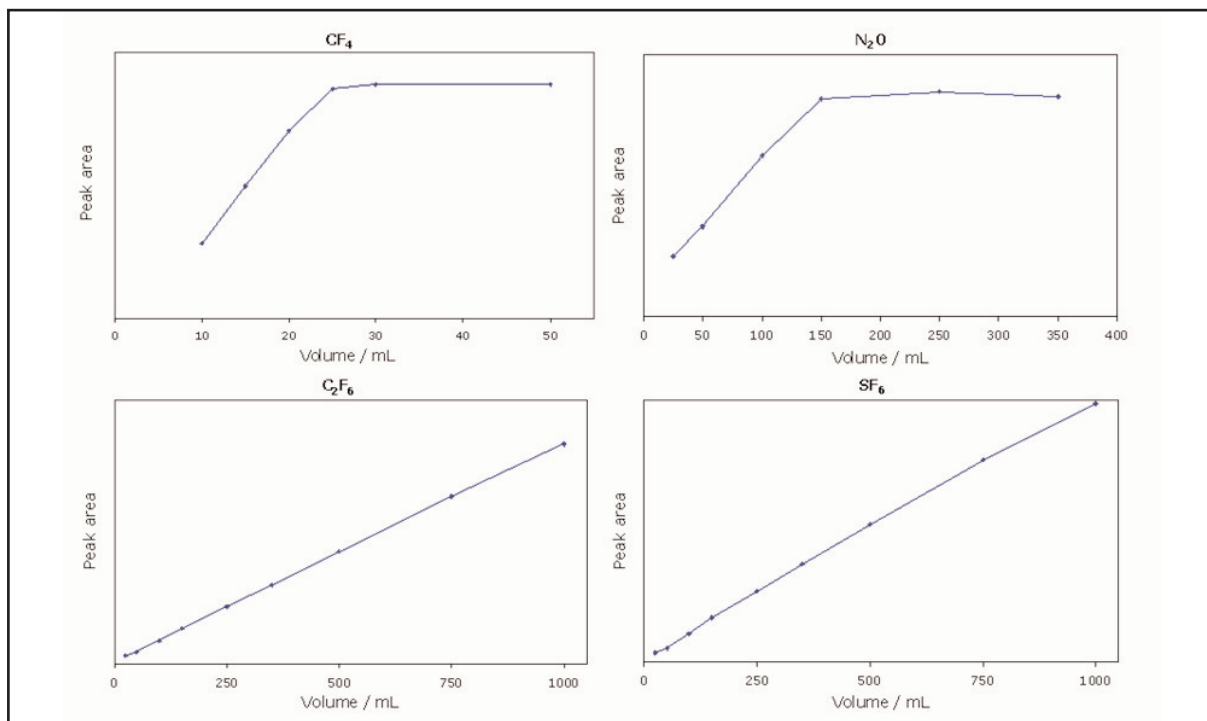


Figure 2: Linearity plots for CF_4 , C_2F_6 , N_2O and SF_6 using a 15 ppb standard concentration, full scan extracted ion

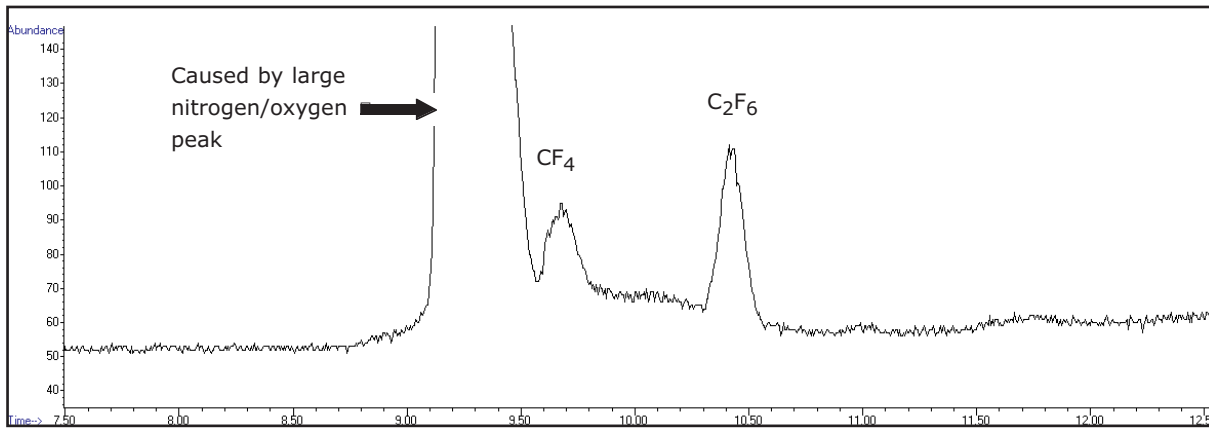


Figure 3a: Chromatogram showing extracted SIM ion 69 for 0.3 ppb CF_4 and 0.1 ppb C_2F_6 in real air. Sample volume was 25 ml; 1 L sample used for C_2F_6 detection limit data

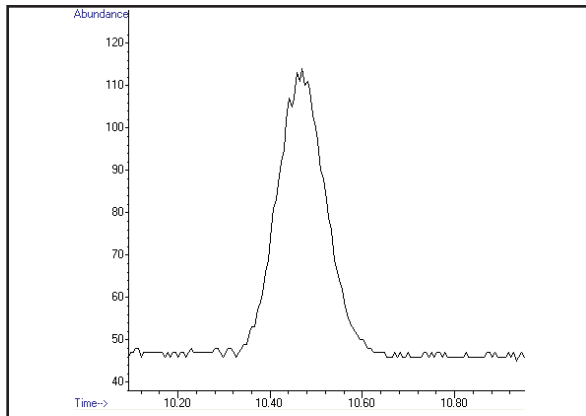


Figure 3b: Chromatogram showing extracted SIM ion 127 for 0.1 ppb SF_6 in real air. Sample volume was 25 ml; 1 L sample used for detection limit data

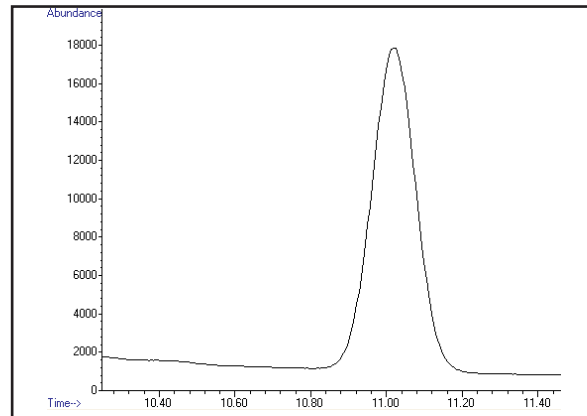


Figure 3c: Chromatogram showing extracted SIM ion 30 for 400 ppb N_2O in real air. Sample volume was 25 ml; 150 mL sample used for detection limit data

Compound	Sample volume (ml)	Sampling flow (ml/min)	Lowest measured concentration (std) (ppt)	RMS S:N (std)	Estimated minimum detection limit (std) (ppt)	Lowest measured concentration (air) (ppt)	RMS S:N (air)	Estimated minimum detection limit (air) (ppt)
CF_4	25	10	70	40:1	<10	300	20:1	50
N_2O	150	30	N/A	N/A	<5*	400	5400:1	200*
C_2F_6	1000	50	6	80:1	0.2	100	2000:1	0.2
SF_6	1000	50	1.5	80:1	0.05	100	5500:1	0.05

Table 2: Sampling and detection limit data, determined in SIM mode for standards in nitrogen (std) and real air samples (air).

**Detection limit extrapolated from higher concentration data*

System reproducibility

System reproducibility was determined at three different sample volumes: 25, 150 and 1000 ml. Six samples of a 70 ppt standard dilution were taken at each volume. N₂O % RSD values were obtained from 150 ml of a higher concentration standard because of the sorption and carryover effects observed with lower level standards using Tedlar bags.

Table 3 shows the % RSD (n=6) for the different volumes. Values are not reported for CF₄ at 150 and 1000 ml as these volumes are above its breakthrough volume.

Compound/ volume	25 ml	150 ml	1000 ml
CF ₄	4.1%		
N ₂ O		5.1%*	
C ₂ F ₆	3.7%	1.8%	2.4%
SF ₆	1.1%	0.8%	1.5%

Table 3: Compound % RSD values at 3 different volumes; SIM mode; 70 ppt diluted standard. *determined at 15 ppb

Analysis of TO-15/17 'Air Toxics' using a UNITY 2-CIA 8 system configured for monitoring ultra-volatile GHG compounds

TD

Instrument configuration:
UNITY 2 + CIA 8

Cold trap:
Greenhouse gas trap (part no U-T16GHG-2S)

Pre-trap fire purge (flow rate):
2 min (20 ml/min)

Trap low: +25°C

Trap heating rate: Maximum

Trap high: 320°C

Trap high time: 3 min

Split: Splitless

Flow path: 140°C

GC

Column:
J & W DB-624 60 m x 0.32 mm x 1.80 µm

Pressure: 10 psi

Mode: Constant pressure

Oven program:
35°C (5 min) then 5°C/min to 230°C (0 min)

MS

Quad temperature: 150°C

Source temperature: 230°C

Full scan range: 33 – 300 amu

Sample preparation

A 62 component 1 ppm mixed air toxics gas standard was used for the experiments.

Results

The excellent peak shape of a 10 ml sample of the 1 ppm, equivalent to 1 L at 10 ppb, standard can be seen in figure 4 (overleaf).

Further information on the excellent performance of Markes cryogen-free TD technology for analysis of 'Air Toxics' in canisters, as per US EPA Method TO-15, can be found in TDTS 81.

Conclusion

Markes series 2 UNITY-CIA 8 thermal desorption system combined with conventional GC/MS, as used for the analysis of CFC and HCFC air toxics in canisters (TDTS 81), offers on- or off-line cryogen-free analysis of ultra-volatile greenhouse gases such as CF₄ (bp: -128°C), at levels below 50 ppt in air. The higher breakthrough volumes of other ultra-volatile compounds tested (C₂F₆ and SF₆) facilitate even lower detection limits in these cases – namely <<1 ppt for SF₆ and C₂F₆.

The estimated lower detection limit for N₂O is 200 ppt. This is due to high background levels of the selected ion in real air samples.

Though unavailable as a standard, the reduced volatility of CF₃Cl relative to CF₄ would enable limits of detection significantly below 5 ppt for this compound, using the analytical system and conditions described.

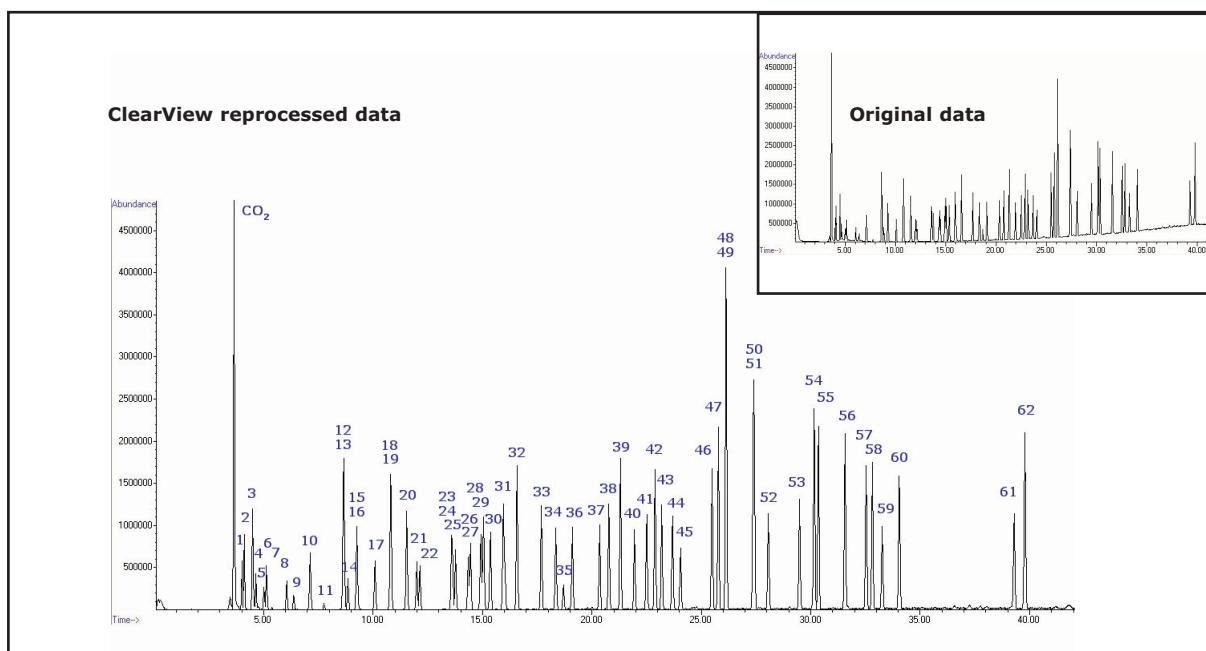


Figure 4: Chromatogram of a 10 ml sample of a 1 ppm standard run splitless and in full scan mode, ClearView reprocessed. Inset shows original (un-reprocessed) data

1 Propylene	22 Vinyl acetate	43 Methyl n-butyl ketone
2 Dichlorodifluoromethane	23 Trans-1,2-dichloroethylene	44 Dibromochloromethane
3 1,2-Dichlorotetrafluoroethane	24 Methyl ethyl ketone	45 1,2-Dibromoethane
4 Methyl chloride	25 Ethyl acetate	46 Chlorobenzene
5 Chloroethane	26 Tetrahydrofuran	47)
6 1,3-Butadiene	27 Chloroform	48) <i>o</i> -, <i>m</i> -, <i>p</i> -Xylene
7 Vinyl chloride	28 1,1,1-Trichloroethane	49) + ethylbenzene
8 Methyl bromide (bromomethane)	29 Cyclohexane	50)
9 1,2-Dichloroethane	30 Carbon tetrachloride	51 Styrene
10 Trichlorotrifluoroethane (Freon® 113)	31 Benzene	52 Tribromomethane
11 Ethanol	32 n-Heptane	53 1,1,2,2-Tetrachloroethane
12 1,1-Dichloroethylene	33 Trichloroethylene	54 Trimethylbenzene
13 1,1,2-Trichlorotrifluoroethane	34 1,2-Dichloropropane	55 Trimethylbenzene
14 Acetone	35 1,4-Dioxane	56 1-Ethyl-4-methyl benzene
15 Carbon disulfide	36 Bromodichloromethane	57 Dichlorobenzene
16 Isopropyl alcohol	37 Cis-1,3-dichloropropene	58 Dichlorobenzene
17 Methylene chloride	38 Methyl isobutyl ketone	59 Chloromethylbenzene (alpha)
18 Tert-butyl methyl ether	39 Toluene	60 Dichlorobenzene
19 Cis-1,2-dichloroethylene	40 Trans-1,3-dichloropropene	61 1,2,4-Trichlorobenzene
20 n-Hexane	41 1,1,2-Trichloroethane	62 Hexachloro-1,3-butadiene
21 1,1-Dichloroethane	42 Tetrachloroethylene	

Table 4: Elution order for the chromatogram shown in figure 4

The excellent detection limits and method performance data shown here demonstrate that cryogen-free on- and off-line monitoring of ultra-volatile greenhouse gases in air can be achieved at the lowest concentrations of interest.

References and associated explanatory notes

1. Directive 2003/87/EC: EU Directive establishing European Union Emission Trading System (EU ETS). This is the largest multi-national, emissions trading scheme in the world

covering CO₂ and methane. As of January 2008, the European Commission proposed a number of changes to the scheme, including the inclusion of other specified greenhouse gases, such as nitrous oxide and perfluorocarbons. These changes are likely to come into effect from January 2013 onwards.

2. CARBON POLLUTION REDUCTION SCHEME: 'Australia's low pollution future' White Paper, 15 December 2008.

Applications were performed using the stated analytical conditions. Operation under different conditions, or with incompatible sample matrices, may impact the performance shown.