On-line, monitoring of trace-level ultra-volatile fluorinated compounds with high GWPs

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Overview

- Regulations
- Measuring Air Toxic compounds
- Description of the analytical system
- Results for 'TO15' analysis
- Analytical challenges of Freon compounds including results of analyses
- Re-evaluation of system for Air Toxic compounds

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Regulations

- Kyoto Protocol 'Clean Development Mechanism' (CDM)
- New regulations require the monitoring of bulk greenhouse gases e.g. CO_2, CH_4 plus lower level analytically challenging compounds
- New regulations include proposed amendments to the European Emission Trading Scheme Directive 2003/87/EC1 and Australia's recent government white paper on a low pollution future

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Measuring Air Toxics

TO15 TO17

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Description of the TD-GC/MS analytical system

CIA 8-TD parameters
Cold Trap: Markes Air Toxics Analyser/Soil Gas trap
Cold trap low temp.: 25°C
Cold trap high temp: 320°C for 3 min
Split ratio: splitless
Trap heating rate: 40°C/s
TD flow path: 140°C

GC parameters
60 m x 0.32 mm x 1.80 µm column for purgeable volatiles
Pressure: 10 psi (Constant pressure)
Oven Program: 40°C (5 min), 5°C/min to 230°C (0 min)

MS conditions
MS source temperature: 230°C
MS quadrupole temperature: 150°C
MSD transfer line temperature: 200°C
Full scan 35 - 300 amu

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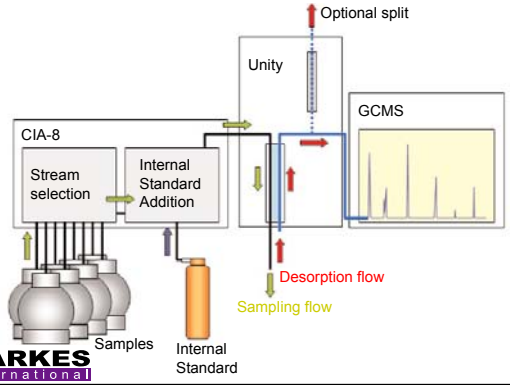
Analytical System Overview



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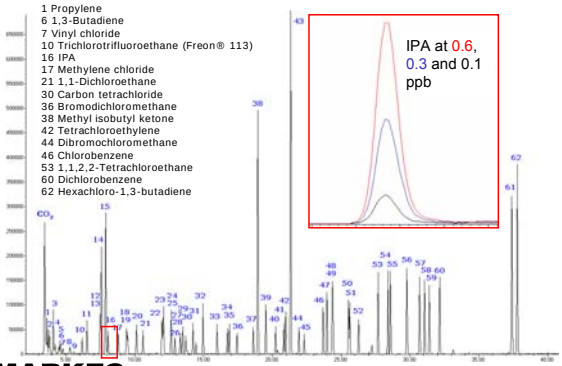
Analytical system – TO15 results

1 Propylene
6 1,3-Butadiene
7 Vinyl chloride
10 Trichlorotrifluoroethane (Freon® 113)
16 IPA
17 Methylene chloride
21 1,1-Dichloroethane
30 Carbon tetrachloride
36 Bromodichloromethane
38 Methyl isobutyl ketone
42 Tetrachloroethylene
44 Dibromochloromethane
46 Chlorobenzene
53 1,1,2,2-Tetrachloroethane
60 Dichlorobenzene
62 Hexachloro-1,3-butadiene



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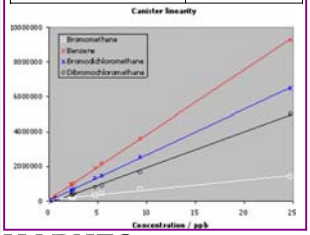
Linearity / Limit of detection

Analyte	R^2
Benzene	0.99
Bromodichloromethane	0.99
Dibromochloromethane	0.99
Bromomethane	0.98



Analyte	Mean Peak Area (n=4)	% RSD
Benzene	13,967	0.85
Toluene	18,715	0.81
Xylene	22,507	0.77

Compound	% RSD
Dichlorodifluoromethane	2.8
IPA	4.0
Carbon Disulphide	2.8
Dichloroethylene	3.3
THF	2.2
Benzene	1.9
Vinyl chloride	4.0
1,2,4-trichlorobenzene	4.5

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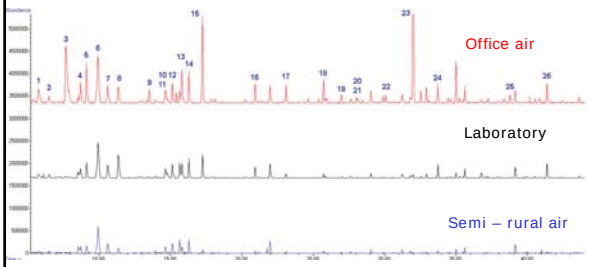
Real air samples

1 Methanol	8 Hexane	15 1-Methyl-2-propanol	22 Alpha-myrcene
2 2-Methyl butane	9 Ethyl acetate	16 Toluene	23 D-limonene
3 Ethanol	10 2-Methyl hexane	17 Hexanal	24 Phenol
4 Acetone	11 Cyclohexane	18 Xylene	25 Menthol
5 Isopropyl alcohol	12 3-Methyl hexane	19 Xylene	26 2-Phenoxy ethanol
6 2-Methyl pentane	13 Heptane	20 Alpha-pinene	
7 3-Methyl pentane	14 Acetic acid	21 Cyclohexanone	



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Global Warming Potentials

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

Compound	Boiling Point (°C)	CWP (100 year) 2001 IPCC	Estimated atmospheric lifetime (years)
CF_4	-128	5,700	50,000
C_2F_6	-78	11,900	50,000
N_2O	-88	296	114
CF_3Cl	-81	14,000	Information not available
SF_6	-64	23,900	3,200

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Description of the TD-GC/MS analytical system

TD Conditions
Cold trap: Greenhouse gas trap
Sampling time (flow rate): Between 2.5 min (10 ml/min) and 20 min (50 ml/min)
Trap low: -30°C
Trap heating rate: 40°C/s
Trap high: 300°C (3 min)
Split: Splitless
Flow path: 120°C

GC
Column: GS-Al/KCl 50 m x 0.53 mm with 5 m x 0.18 mm fused silica on MS end acting as a restrictor
Pressure: 18 psi (Constant pressure)
Oven program: 60°C (4 min) then 8°C/min to 150°C (0 min)
Total run time: 15.25 min

MS
Full scan range: 10 – 300 amu
SIM ions (dwell time): 30 (100), 69 (100), 119 (20), 127 (100)

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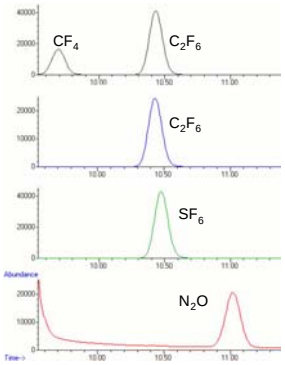
Results – Peak Shape



Extracted ion 69

Extracted ion 119

Extracted ion 127

Extracted ion 30

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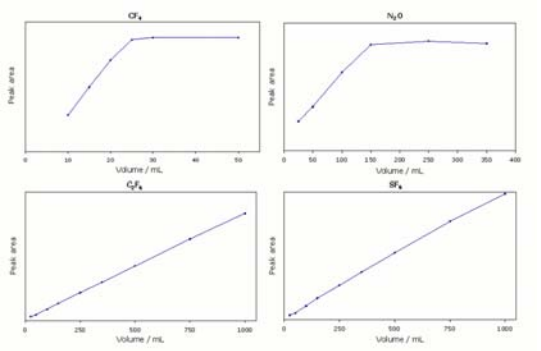
Results Linearity



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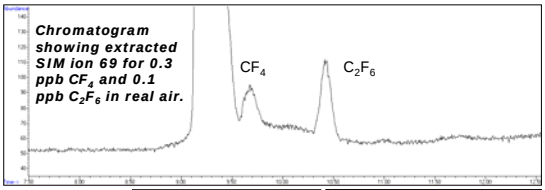
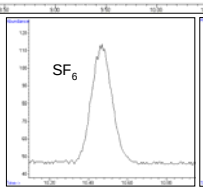
Results – detection limits

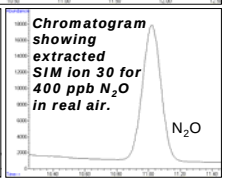


Chromatogram showing extracted SIM ion 69 for 0.3 ppb CF_4 and 0.1 ppb C_2F_6 in real air.

Chromatogram showing extracted SIM ion 127 for 0.1 ppb SF_6 in real air.



Chromatogram showing extracted SIM ion 30 for 400 ppb N_2O in real air.



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Results – detection limits

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)	MS 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	5,400:1	200*
C_2F_6	1,000	50	6	80:1	0.2	100	2,000:1	0.2
SF_6	1,000	50	1.5	80:1	0.05	100	5,500:1	0.05

Detection limit extrapolated from higher concentration data

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

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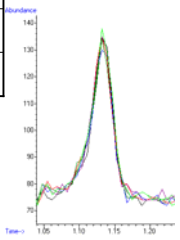
Results reproducibility

Compound \ Volume	25 ml	150 ml	1000 ml
CF_4	4.1%		
N_2O		5.1%*	
C_2F_6	3.7%	1.8%	2.4%
SF_6	1.1%	0.8%	1.5%

***determined at 15 ppb**

Compound % RSD values at 3 different volumes; SIM mode; 70 ppt diluted standard.

CF_4 precision



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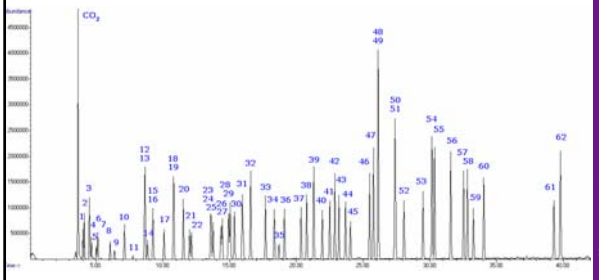
Re-evaluation of instrumentation for TO15/TO17



Chromatogram of a 10 ml sample of a 1 ppm standard run splitless and in full scan mode

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Compound list

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

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Conclusions

- Analytical system combined with conventional GC/MS, used for
  - the analysis of CFC and HCFC air toxics in canisters (TDTS 81), and
  - on- or off-line cryogen-free analysis of ultra-volatile greenhouse gases such as CF4 (bp: - 128°C),
- Excellent detection limits at levels **below 50 ppt** in air (**<<1 ppt for SF_6 and C_2F_6**)
- Method performance data show that cryogen-free on- and off-line monitoring of ultra-volatile greenhouse gases in air can be achieved at the lowest concentrations of interest.
- Acknowledgements
  - Dr. David Wevill

Thank you

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