Monitoring Produced Gases From PFAS Destruction Technologies Using OTM-50

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Monitoring volatile fluorinated compounds as markers for incomplete destruction of PFAS

Closing the fluorine mass balance

PFAS will ultimately need to be destroyed to be removed from the environment – this should be monitored.

TDGCMS provides a method for monitoring destruction efficiency.

Analytical systems must offer a robust and flexible solution to challenges posed by this task.

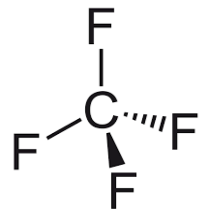
Products of incomplete destruction (PIDs)

Canister sampling at PFAS destruction facilities to monitor mineralization

- PFAS need to be removed from the environment, and disposed of responsibly when used in products
- If destruction is not complete volatile fluorinated species are formed.

- CF_4 is a key compound for monitoring destruction efficiency
- Incredibly difficult to breakdown
  - >1440 °C required to achieve 99.99% destruction

- US EPAs OTM-50 aims to monitor this process



Freon 14

Other Test Method 50

Sampling and Analysis of Volatile Fluorinated Compounds from Stationary Sources Using Passivated Stainless-Steel Canisters

Overview

Method – OTM-50

- Developed by the EPA to measure 30 target PFAS compounds and non-targets in air
- 30 targets are "volatile fluorinated compounds" (VFCs)

- Expected initial use will be monitoring source emissions linked to PFAS destruction.

- Second of four OTMs expected from the US EPA looking at PFAS emissions from sources.
  - OTM 45 was the first (HPLC method)
  - OTM 50 is a GCMS method

How can samples be taken?

Monitoring PFAS destruction efficiency

- Volatile fluorinated compounds related to incomplete destruction can be sampled into canisters
- Sample trains required remove:
  - Condensing water
  - Acid gases
- Once taken the sample poses challenges for analysts

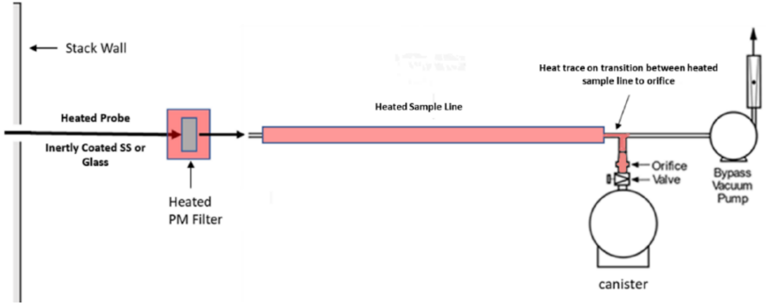


Figure OTM-50-1. Direct VFC Sampling System

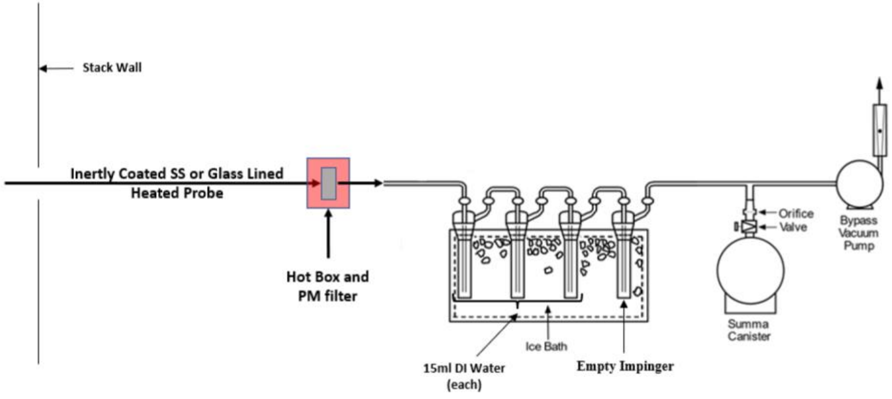


Figure OTM-50-2. VFC Canister Sampling System with Water/Acid Gas Management

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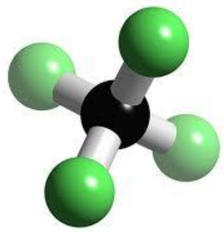
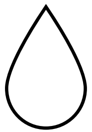
Challenges

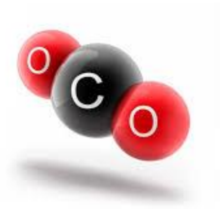
- **Incredibly volatile target compounds** which results in very specific analytical set-ups and low sample volumes for the most volatile species.



- **High humidity** which if not managed correctly will impact repeatability and long-term functioning of the analytical system. 100% relative humidity expected.



- **Varying CO_2 levels** which can be very high - up to 15% of the matrix has been reported.



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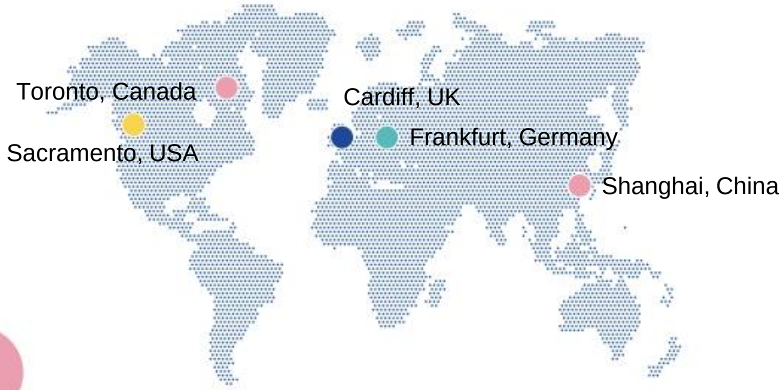
Over 25 years of Ambient Air monitoring expertise

- Wide range of products for sampling and analysis of trace volatile and semi-volatile organic compounds
- Expertise in VOCs and SVOCs analysis
- Future-proof instruments – hydrogen compatible
- Global presence and distribution network



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Compound List

Name	CAS	Name	CAS
Tetrafluoromethane	75-73-0	Tetradecafluorohexane	355-42-0
Hexafluoroethane	76-16-4	1H-Perfluoropentane	375-61-1
Chlorotrifluoromethane (CFC-13)	75-72-9	Hexadecafluoroheptane	335-57-9
Trifluoromethane	75-46-7	Heptafluoropropyl-1,2,2,2-tetrafluoroethyl ether	3330-15-2
Octafluoropropane	76-19-7	1H-Perfluorohexane	355-37-3
Difluoromethane	75-10-5	1H-Perfluoroheptane	375-83-7
1,1,1-Trifluoroethane (HCFC-143a)	420-46-2	2H-Perfluoro-5-methyl-3,6-dioxanonane (E2)	3330-14-1
Octafluorocyclobutane (FC-C318)	115-25-3	1H-Perfluorooctane	335-65-9
Perfluorobutane	355-25-9	Octadecafluorooctane	307-34-6
Dodecafluoropentane	678-26-2	1H-Nonafluorobutane	375-17-7
Tetrafluoroethyene	116-14-3	1H-Heptafluoropropane	2252-84-8
Fluoromethane	593-53-3	1,1,1,2-Tetrafluoroethane (HCFC-134a)	811-97-2
Pentafluoroethane	354-33-6	Chlorodifluoromethane (HCFC-22)	75-45-6
Hexafluoropropene	116-15-4	Octafluorocyclopentene (FC-C1418)	559-40-0
Hexafluoropropene oxide	428-59-1	Trichloromonofluoromethane (CFC-11)	75-69-4

At time of testing no commercially available standard. Compounds able to test in **bold**

Analysis QC requirements and performance

Requirement	Performance
MDL	0.03 – 0.011 ppbv
ICAL	Minimum 5 points. RRF ≤20% RSD.
Lab blank	Sample analytes <3 x MDL *or* <50% of project-required reporting limit
Precision	% RSD n = 7 less than 25%
Accuracy	% recovery n = 7 within +/- 30%
CO_2 bias check	**Target compounds with +/- 30% of standard value at known CO_2 concentration.**
MDL confirmation	Canister prepared at MDL, 3 times S/N

System Configuration

- Stainless steel passivated canister:
  - 6L
- UNITY-Kori-CIA *Advantage* HL-xr
  - Focusing trap designed for volatile fluorocarbons (U-T25ODS-2S)

- Column: Gas Pro
- Agilent 8890 GC
- Agilent 5977b MS

Restrictor Column	Analytical Column	Guard Column
5m x 180µm (160-2615-10) Agilent	60m x 320µm (113-4362) Agilent	2m x 320µm (60340) Alltech

Solving challenge 1 & 2

Incredibly volatile target compounds and high humidity

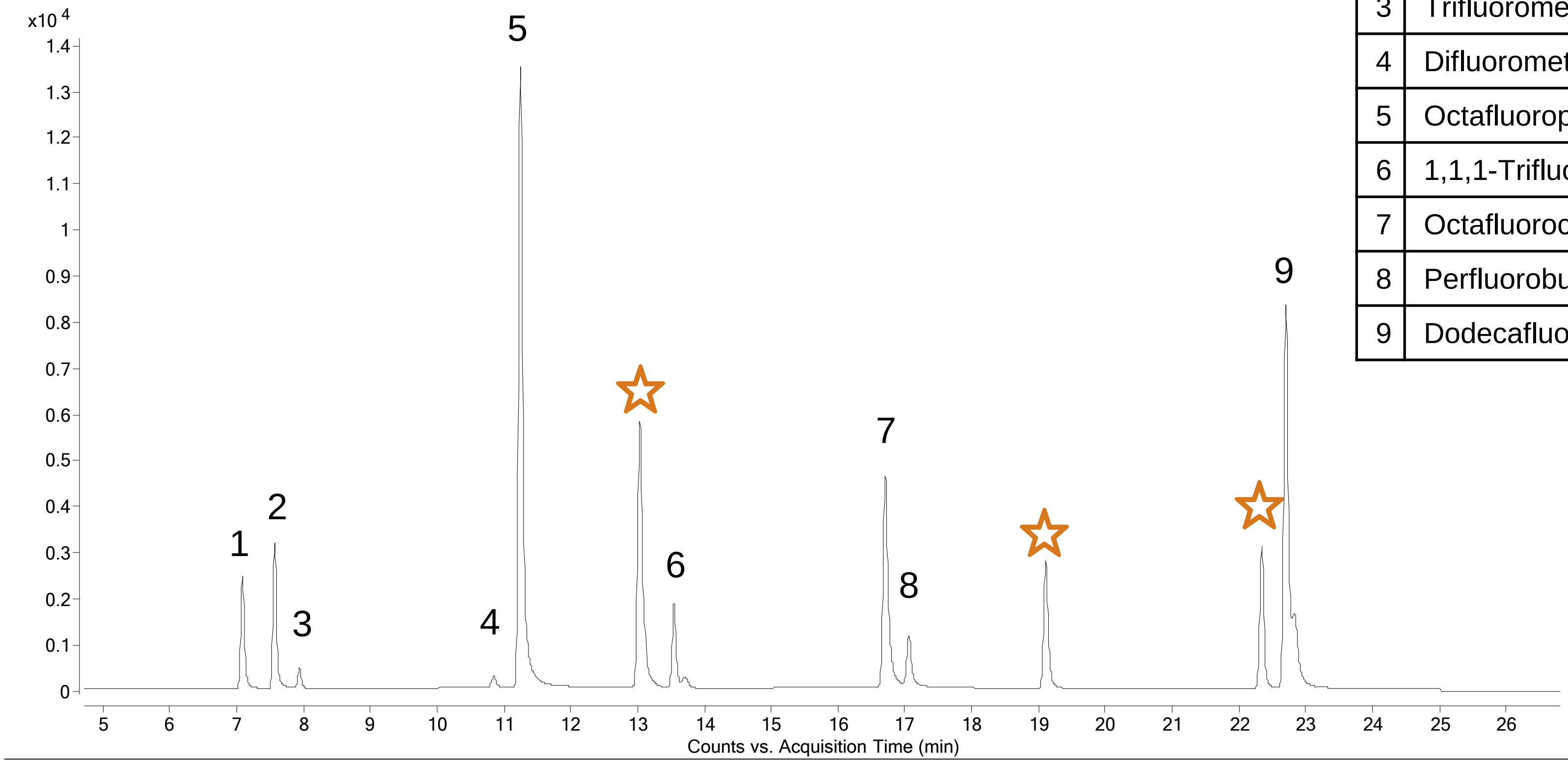
- Due to the volatility of CF_4 two methods have been developed:
  - **CF_4** only, sampled volume 20ml
  - Remaining 29 **OTM-50** compounds, sampled volume 200ml
  - *Methods referred to from here as CF_4 and OTM-50*

- OTM-50 outlines that this may be necessary.
  - Tested by the US EPA using these conditions on the UNITY-CIA *Advantage*-xr

- All testing carried out assuming a 3x dilution to manage CO_2
  - 33% RH (100% at source)
  - Max CO_2 level in canister tested 5% (15% at source)

Chromatography testing with non-targets

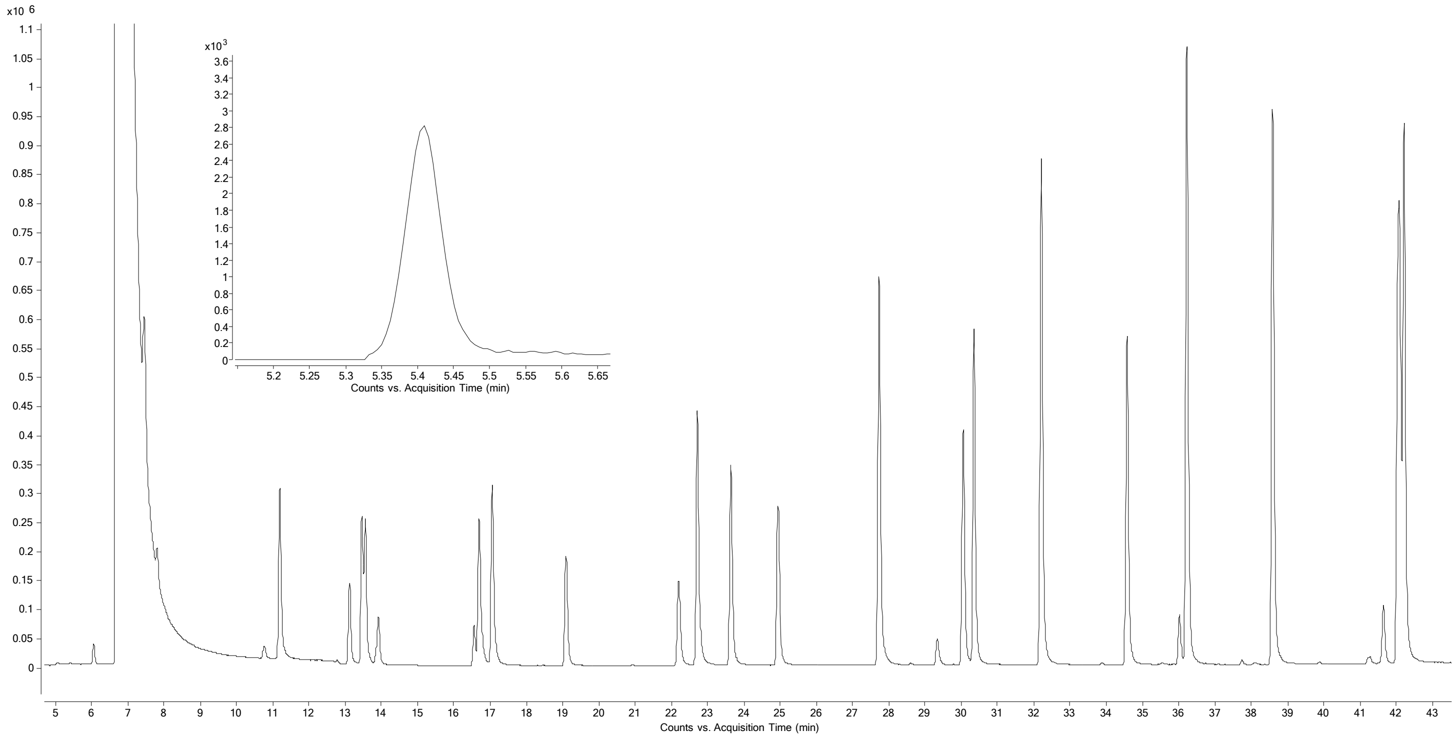
OTM-50 EIC, 10ppb standard



#	Compound
1	Hexafluoroethane
2	Chlorotrifluoromethane
3	Trifluoromethane
4	Difluoromethane
5	Octafluoropropane
6	1,1,1-Trifluoroethane
7	Octafluorocyclobutane
8	Perfluorobutane
9	Dodecafluoropentane

OTM-50 Standard

200ml – Inset 69 ion for CF_4

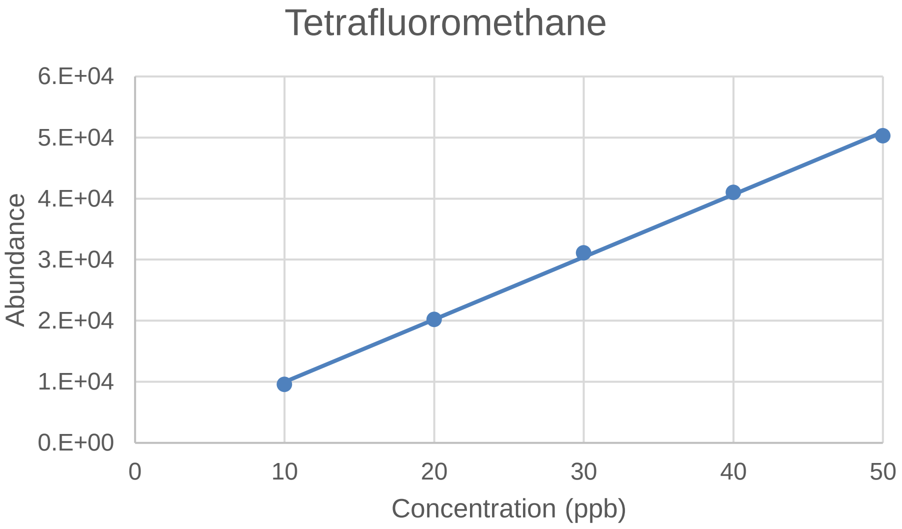


Proof of concept that it's possible to run the full OTM-50 standard with this method.

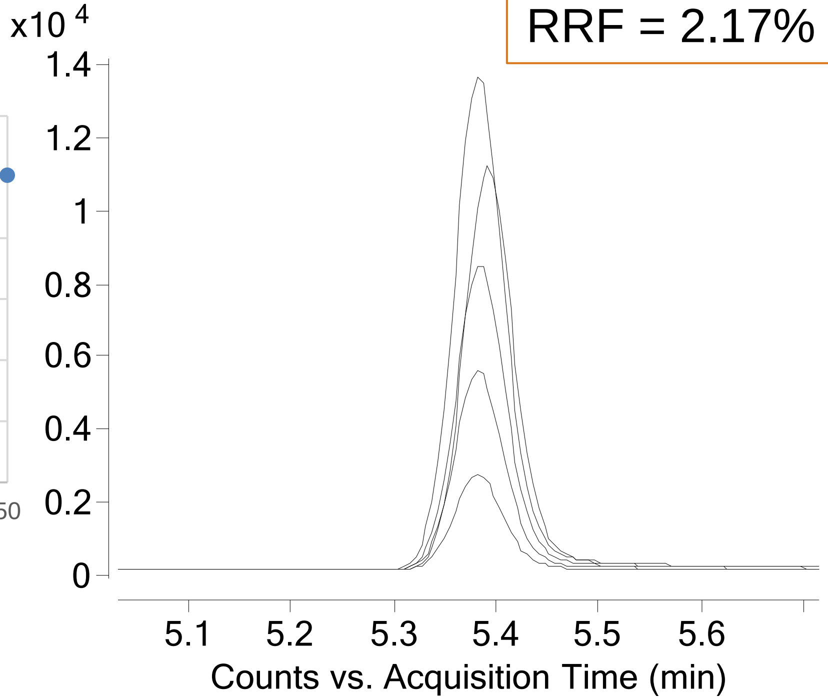
Full 30 compounds donated by US EPA.

ICAL: Minimum 5 points. RRF ≤20% RSD

CF_4, 20mL volume, 10 to 50ppb (33% RH)



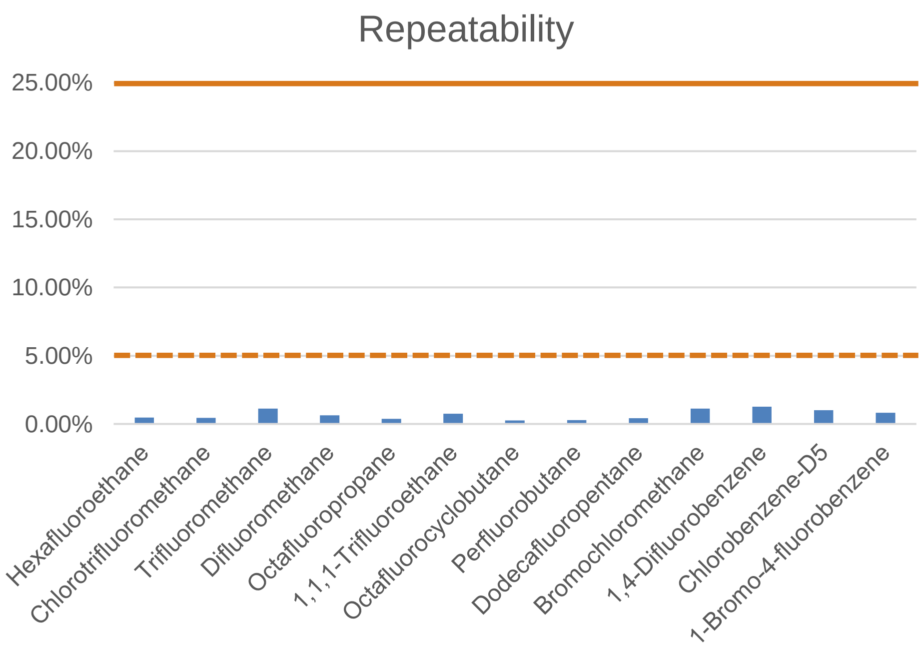
RRF = 2.17%



Calibration performed with **5 individual canisters** at 10, 20, 30, 40 and 50ppb. As recommended by OTM-50.

Precision: % RSD n = 7 less than 25%

OTM50 5ppb (33% RH) – n = 10



Compound	%RSD
Hexafluoroethane	0.48%
Chlorotrifluoromethane	0.44%
Trifluoromethane	1.13%
Difluoromethane	0.64%
Octafluoropropane	0.38%
1,1,1-Trifluoroethane	0.76%
Octafluorocyclobutane	0.26%
Perfluorobutane	0.29%
Dodecafluoropentane	0.43%
Bromochloromethane (INSTD)	1.14%
1,4-Difluorobenzene (INSTD)	1.28%
Chlorobenzene-D5 (INSTD)	1.02%
1-Bromo-4-fluorobenzene (INSTD)	0.83%
Average (All)	0.70%
Average (Targets)	**0.54%**

Summary Data

Compound	R2	Relative Response Factor (RRF)	Repeatability (5 ppb) n = 10	MDL (0.5 ppb)	Carryover (post 50 ppb)	Passes OTM 50 criteria
Tetrafluoromethane	0.9990	2.17%	2.03%	30ppt	ND	Yes
Compound	**R2**	**RRF**	**Repeatability (5 ppb) n = 10**	**MDL (0.25 ppb)**	**Carryover (post 25 ppb)**	**Passes OTM 50 criteria**
Hexafluoroethane	0.9999	1.86%	0.48%	6 ppt	25 ppt (0.03%)	Yes
Chlorotrifluoromethane	0.9977	2.52%	0.44%	8 ppt	38 ppt (0.10%)	Yes
Trifluoromethane	0.9977	5.12%	1.13%	10 ppt	13 ppt (0.15%)	Yes
Difluoromethane	0.9993	3.11%	0.64%	11 ppt	13 ppt (0.05%)	Yes
Octafluoropropane	0.9996	7.64%	0.38%	14 ppt	53 ppt (0.21%)	Yes
1,1,1-Trifluoroethane	0.9988	5.33%	0.76%	13 ppt	53 ppt (0.21%)	Yes
Octafluorocyclobutane	0.9998	7.14%	0.26%	11 ppt	35 ppt (0.14%)	Yes
Perfluorobutane	0.9995	4.00%	0.29%	9 ppt	18 ppt (0.07%)	Yes
Dodecafluoropentane	0.9989	7.65%	0.43%	9 ppt	5 ppt (0.02%)	Yes
Average	**0.9990**	**4.65%**	**0.60%**	**12 ppt**	**27 ppt (0.10%)**	**Yes**

CO_2 Bias Test

Challenge 3

CO_2 Bias Testing

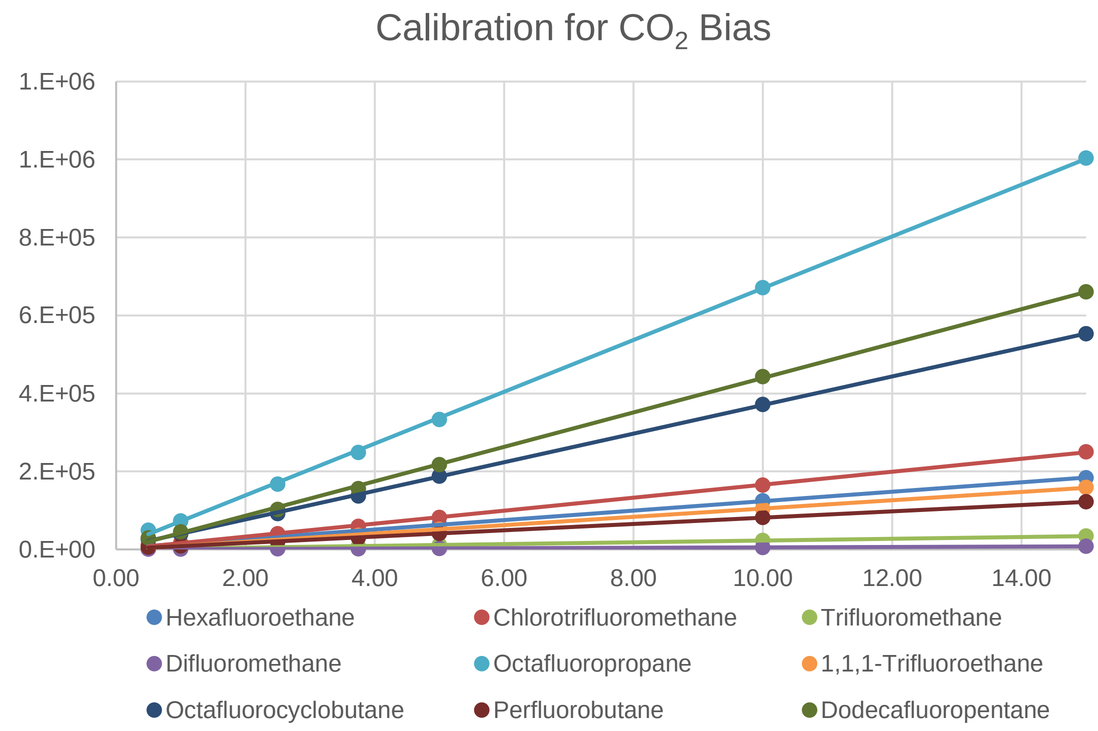
Unique design of Markes instruments makes CO2 management possible.

- CO_2 has a similar volatility to many of the compounds of interest.
  - If you are retaining your compounds, you will also retain CO_2!
- In the OTM-50 analysis it can be removed
  - However, if not managed correctly for the OTM-50 method this can lead to bias.
- In the CF_4 analysis due to the small retention volume CO_2 cannot be managed prior to injection.
  - This will likely lead to bias depending on the CO_2 concentration.
  - Bias is acceptable and is simply noted when reporting.

- The bias check is designed to quantify this.
- The acceptance criteria for this test is no deviation from the CO_2 standard above ±30% when compared with the non-CO_2 standard

CO_2 Bias – OTM-50

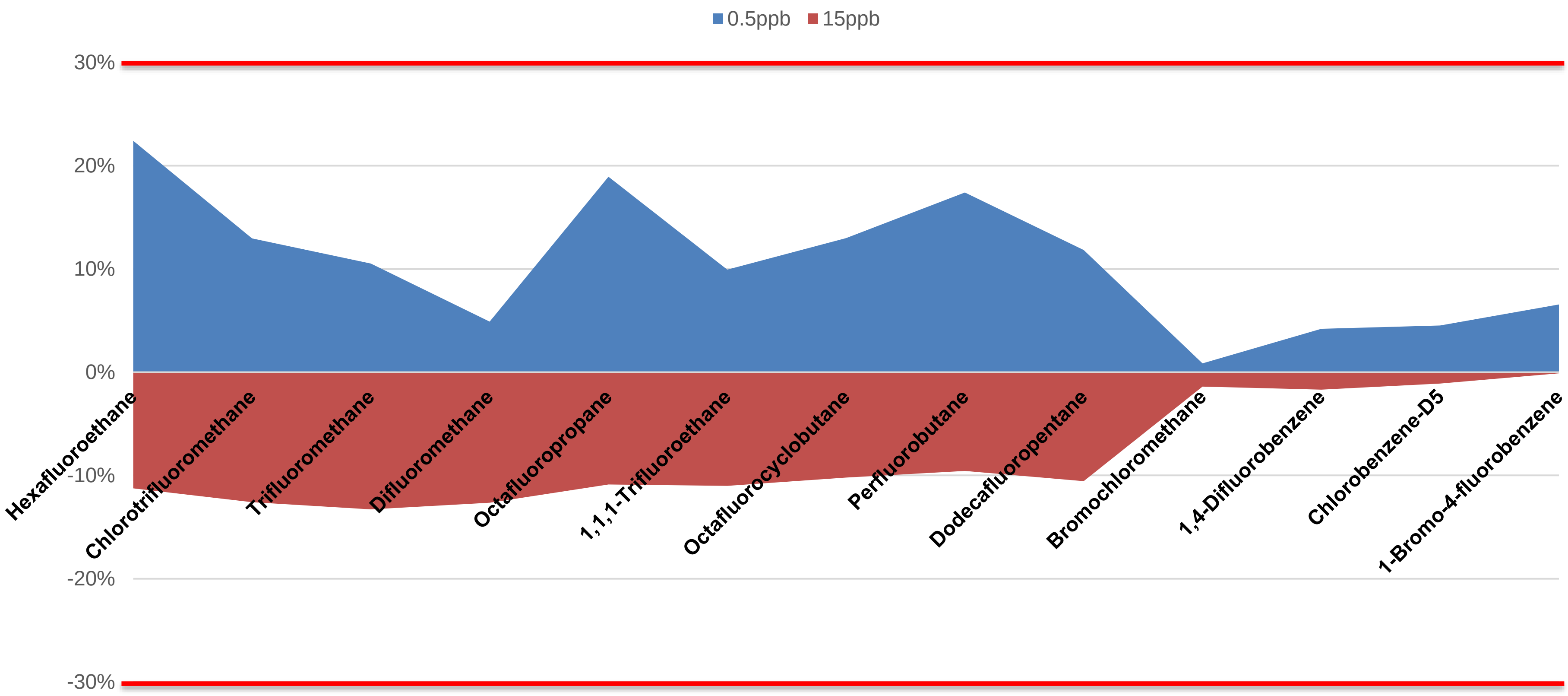
Bias Check at 5% CO_2



Compound	R2
Hexafluoroethane	0.9999
Chlorotrifluoromethane	0.9995
Trifluoromethane	0.9995
Difluoromethane	0.9994
Octafluoropropane	0.9998
1,1,1-Trifluoroethane	0.9990
Octafluorocyclobutane	0.9998
Perfluorobutane	0.9997
Dodecafluoropentane	0.9994

Calibration between 0.5 and 15ppb each from **individual canisters** sampled at 200ml.

CO_2 Bias OTM-50: 15% CO_2 diluted to 5%



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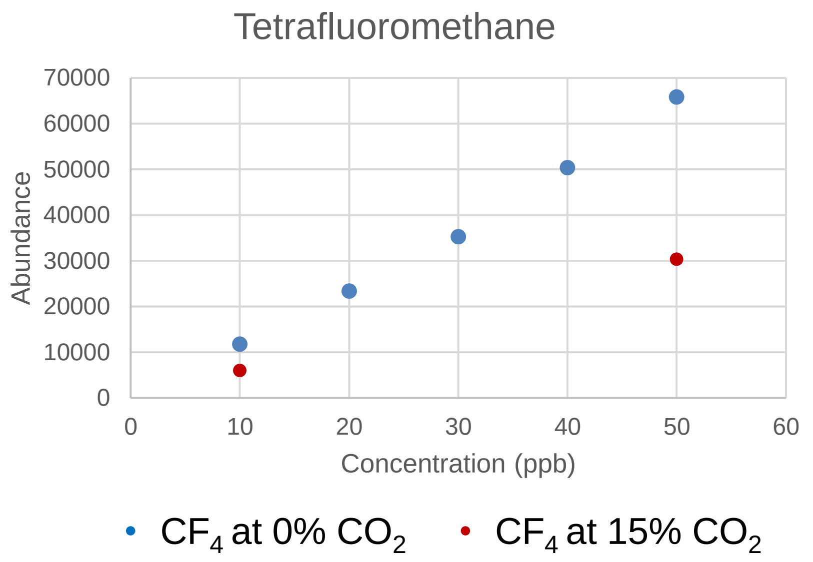
The Importance of Matrix Matching – CF_4

CO_2 Bias Check: 15% CO_2 diluted to 5%

	10ppb	50ppb
Tetrafluoromethane	**97%**	**117%**
Bromochloromethane (IS)	1%	5%
1,4-Difluorobenzene (IS)	2%	4%
Chlorobenzene-D5 (IS)	5%	7%
1-Bromo-4-fluorobenzene (IS)	13%	15%

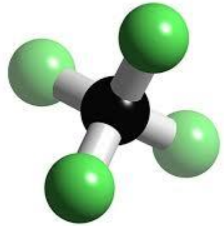


- Confident CF_4 quantitation is possible with a matrix matched calibration.
- Alternatively, CF_4 can be recorded as biased in reports.

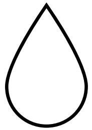
Can each challenge be addressed?

Summary

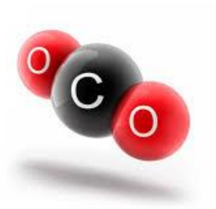
- **Incredibly volatile target compounds**
  - Two runs enabling ultra-volatile CF4 and the other OTM 50 compounds
  - No changes hardware or consumables needed.



- **High humidity**
  - Dilution likely to be part of the SOP due to CO_2
  - 33% RH proven for all compounds.
  - 100% RH proven in other studies



- **Varying CO_2 levels**
  - CO_2 bias check show that for 29/30 compounds there will be no bi
  - CF_4 likely to be biased at 15% CO_2 level but if desired a matrix matched calibration can be performed.



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