



MARKES
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 **Metrohm**

Determination of Non-targeted Fluorine in Air Using Combustion Ion Chromatography

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Today, I will discuss....

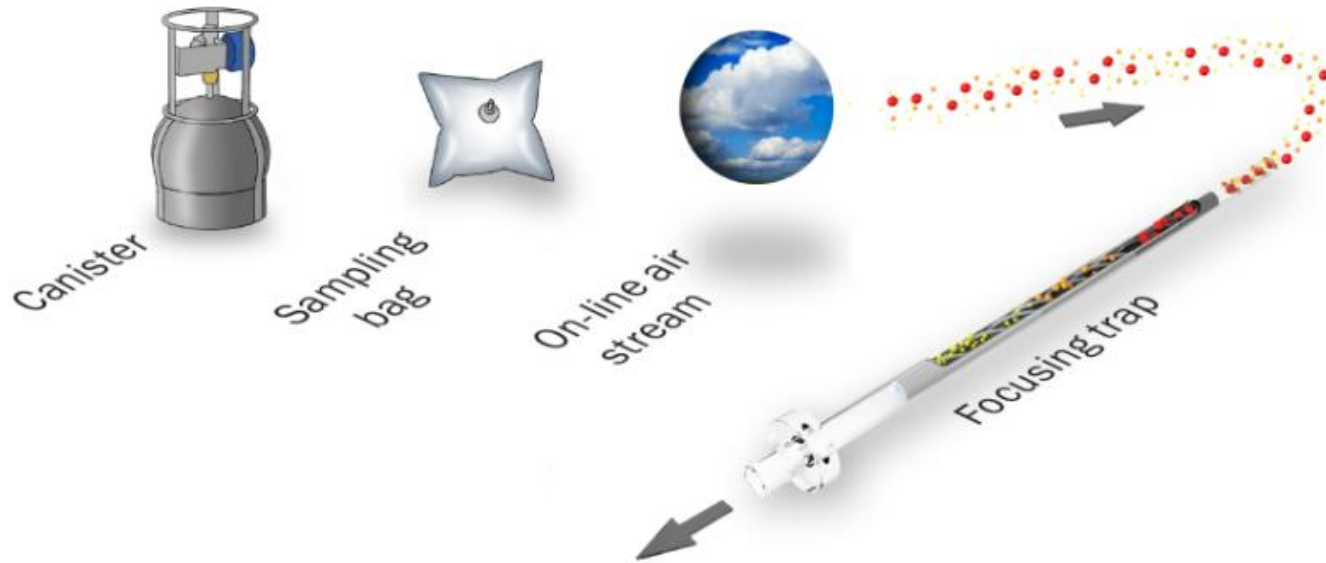
- **Approaches to measuring non-targeted PFAS in Air**
- **ASTM Method –**
 - D8591 – TD/GCMSMS
 - D8560 – Guide for PFAS in indoor air
- **Instrumentation**
 - **Markes International (Sample prep Unit)**
 - **Metrohm Combustion IC**
- **Instrument Integration and Data**
- **Q&A**



Monitor/measure Volatile PFAS?

- ✓ In recent years, there is major PUSH towards reduction of PFAS use
- ✓ At the same time, assessment of PFAS and destruction of PFAS compounds in environment
- ✓ Global movement to BAN and REPLACE AFFF types of PFAS – Fire fighting foams
- ✓ There are several innovative PFAS remediation technologies developed
 - ✓ Multiple effective technologies involve some kind of high temperature degradation to completely “mineralized” PFAS into inorganic salts of Fluoride
- ✓ What are the products of incomplete degradation? VOLATILE PFAS compounds

The analytical thermal desorption process



Stage 1: On-line/canister/bag sampling

Whole air/gas samples, from canisters, bags or manifolds, are introduced directly to the focusing trap at controlled flows and/or for precise time intervals

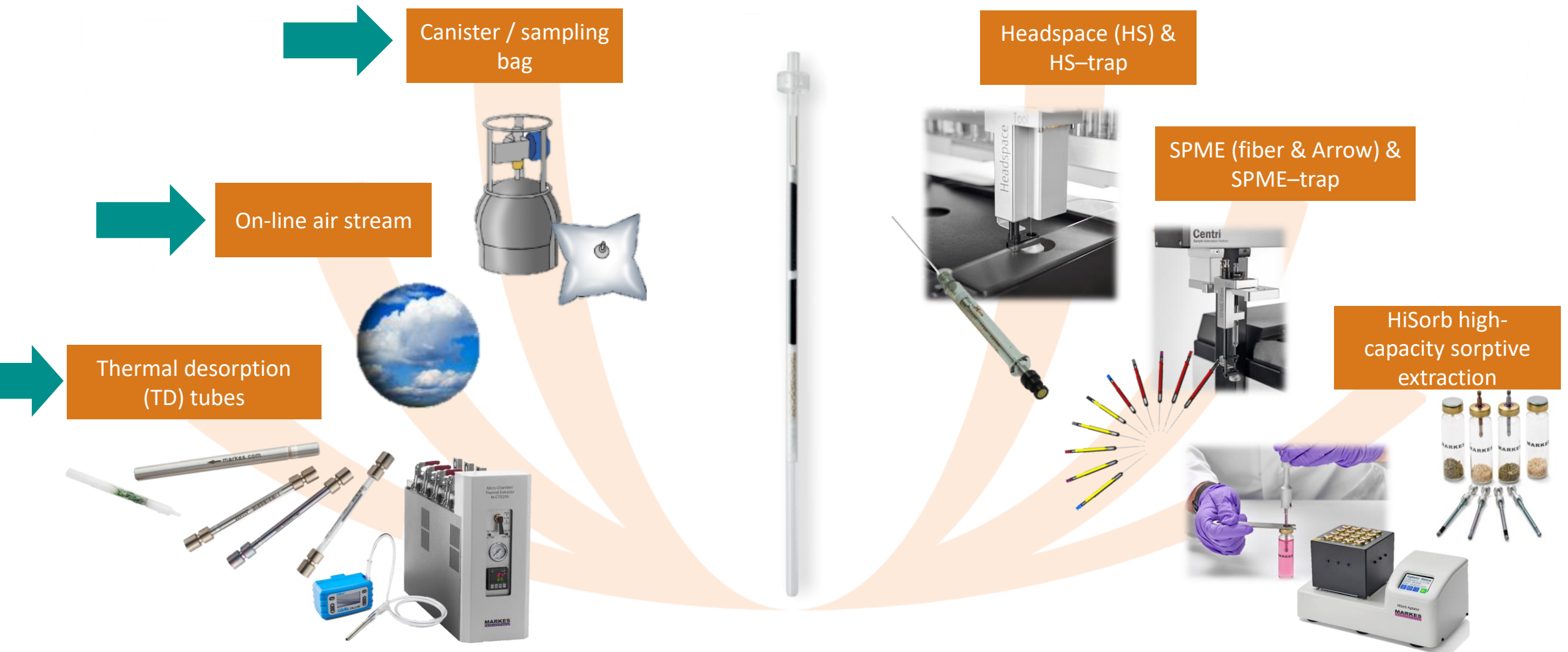
Stage 2: Trap desorption

- Focused sample is rapidly heated, at rates up to $100\text{ }^{\circ}\text{C s}^{-1}$, in a reverse flow of carrier gas to release retained compounds



...but how do you get your sample onto the trap?

Volatile organics: Accessories & consumables for sample collection & introduction



Innovation at the heart of every instrument...

Cryogen-free, backflush focusing trap and inert, low-volume valve

This powerful combination allows:

Analyte preconcentration and enrichment to **increase analytical sensitivity** for **Total Fluorine** analysis.

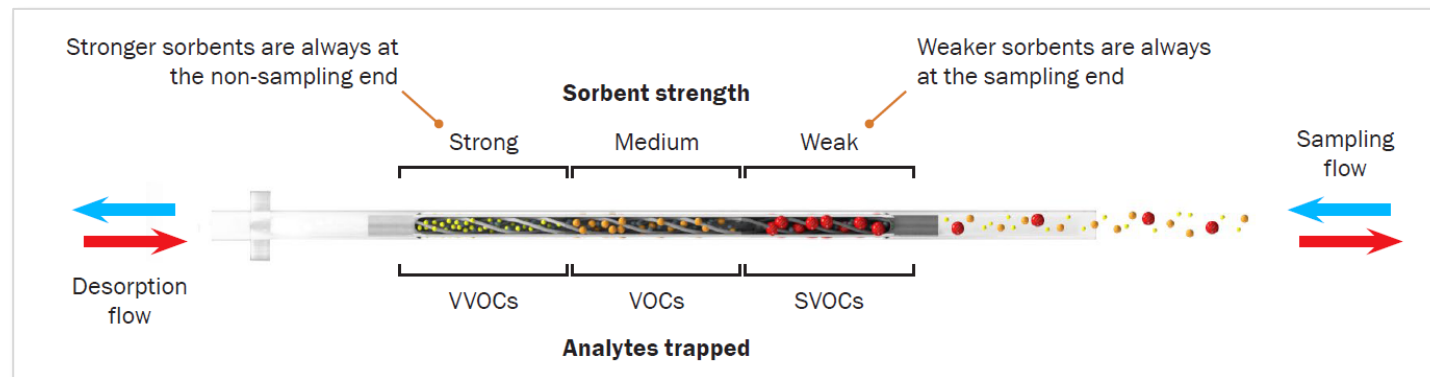
Backflush operation, for compatibility with multi-bed sorbents, thus **analysis of a wide compound range** in a single run.

Analysis of challenging VVOCs, by combining multi-sorbents with electrical cooling down to -30°C .



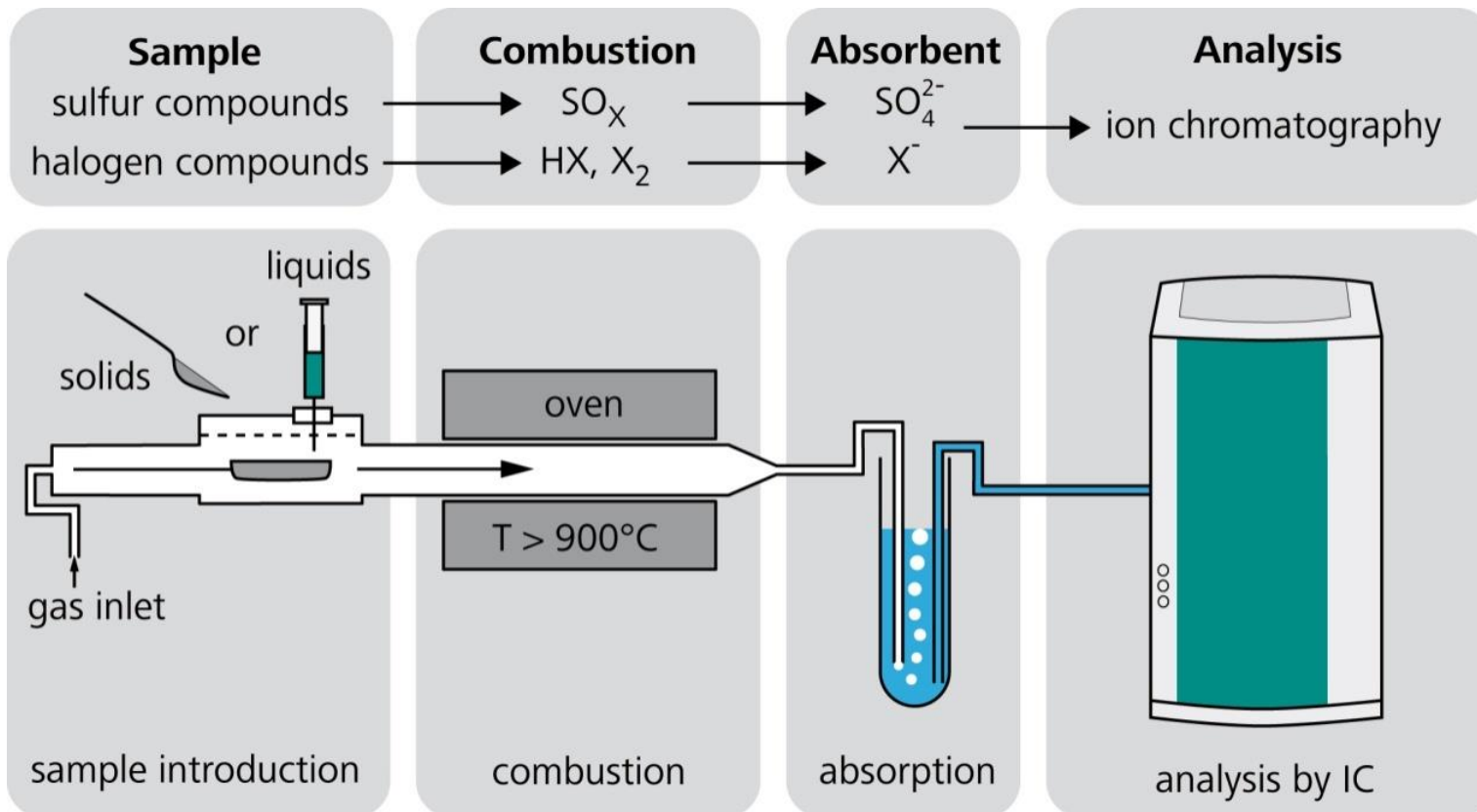
Patented TD valve

Low volume, inert, uniformly-heated. Enables split re-collection, backflush & unique application range.



Basic Principle of C-IC instrument

- A sample undergoes Heat + Oxygen - Breaks covalent bonds to remove halogens from organic molecules
- SO_x, H_x, X₂ are absorbed (H₂O₂) and injected into IC (16 min run)



	1	2	13	14	15	16	17	18
	la							VIIla
1 (K)	H							He
2 (L)	Li	Be	B	C	N	O	F	Ne
3 (M)	Na	Mg	Al	Si	P	S	Cl	Ar
4 (N)	K	Ca	Ga	Ge	As	Se	Br	Kr
5 (O)	Rb	Sr	In	Sn	Sb	Te	I	Xe
6 (P)	Cs	Ba	Tl	Pb	Bi	Po	At	Rn
7 (Q)	Fr	Ra	Uut	Uuq	Uup	Uuh	Uus	Uuo

Metrohm CIC



Ion Chromatography

Liquid Handling

Combustion Oven and ABD

Sample Preparation Device from Markes International

Unity xr – Heated X-fer Line
to CIC

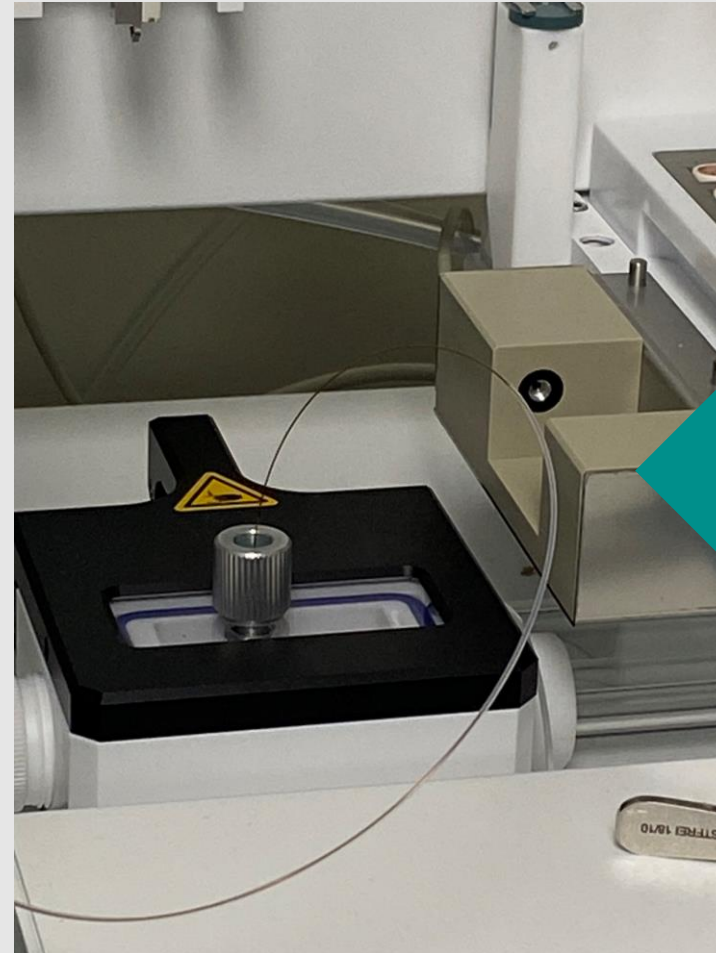
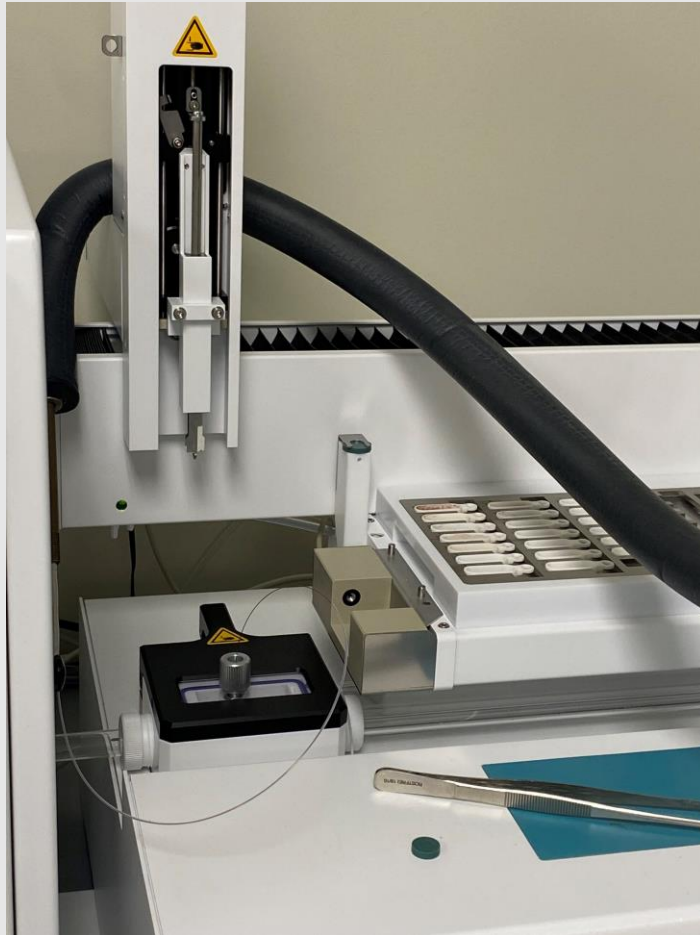
CIA Advantage – Canister
Autosampler (14 Canisters)

Unity xr – Focusing trap for
VOA compounds

Canisters for Air Sampling (pressurized
with N₂ gas for CIC)



Sample Preparation Device from Markes International interfaced with Metrohm C-IC



0.25mm ID Fused silica x-fer line
inserted into sample port of CIC

Sample – MagIC Net

Time program				
Main program	sample	dose absorber solution	prepare absorber solution	rinsing
Time	Device	Module	Command	Parameter
			Sequence	Prep
			Wait	Continue after 5 s.
			Wait	Continue after 5 s.
0.0	Remote Box		Set lines	*****g**
	Remote Box		Scan lines	*****1**, Timeout 10 min
			Wait	Continue after 5 s.
			Sequence	Combustion
0.0	Remote Box		Set lines	*****1**
			Wait	Continue after 5 s.
0.0	920 Absorber Module 1	10-port valve	Change port	Port 8, automatic
	UPW (5 mL)		Aspirate	Port 3, Volume 0.5 mL, Rate 2 mL/min
0.0	920 Absorber Module 1	10-port valve	Change port	Port 10, automatic
	UPW (5 mL)		Dosing	Port 3, Volume 0.5 mL, Dosing rate 5 mL/min, Filling rate 1.0 mL/min
0.0	920 Absorber Module 1	10-port valve	Change port	Port 9, automatic
	UPW (5 mL)		Wait	Continue after 1 s.
			Aspirate	Port 3, Volume 0.1 mL, Rate 5 mL/min
			Wait	Continue after 2 s.
0.0	920 Absorber Module 1	10-port valve	Change port	Port 8, automatic
	UPW (5 mL)		Aspirate	Port 3, Volume 3 mL, Rate 2 mL/min
			Wait	Continue after 5 s.
0.0	920 Absorber Module 1	10-port valve	Change port	Port 1, automatic
	UPW (5 mL)		Dosing	Port 3, Volume 0.5 mL, Dosing rate 5 mL/min, Filling rate 1.0 mL/min

Time program				
Main program	sample	dose absorber solution	prepare absorber solution	rinsing
Time	Device	Module	Command	Parameter
			Sequence	Prep
			Wait	Continue after 5 s.
			Set lines	*****g**
0.0	Remote Box		Scan lines	*****1**, Timeout 10 min
			Wait	Continue after 5 s.
			Sequence	Combustion
0.0	Remote Box		Set lines	*****1**
			Wait	Continue after 5 s.
0.0	920 Absorber Module 1	10-port valve	Change port	Port 8, automatic
	UPW (5 mL)		Aspirate	Port 3, Volume 0.5 mL, Rate 2 mL/min
0.0	920 Absorber Module 1	10-port valve	Change port	Port 10, automatic
	UPW (5 mL)		Dosing	Port 3, Volume 0.5 mL, Dosing rate 5 mL/min, Filling rate 1.0 mL/min
0.0	920 Absorber Module 1	10-port valve	Change port	Port 9, automatic
	UPW (5 mL)		Wait	Continue after 1 s.
			Aspirate	Port 3, Volume 0.1 mL, Rate 5 mL/min
			Wait	Continue after 2 s.
0.0	920 Absorber Module 1	10-port valve	Change port	Port 8, automatic
	UPW (5 mL)		Aspirate	Port 3, Volume 3 mL, Rate 2 mL/min
			Wait	Continue after 5 s.
0.0	920 Absorber Module 1	10-port valve	Change port	Port 1, automatic
	UPW (5 mL)		Dosing	Port 3, Volume 0.5 mL, Dosing rate 5 mL/min, Filling rate 1.0 mL/min

Status	Sample Type	Comment	Method	CIA Advantage Deviation	Trap Fire Time	UNI
1 Complete	Sample		Trap Blank Metrohm (1)		2025/06/24 09:37:45	
2 Complete	Sample		Trap Blank Metrohm (1)		2025/06/24 10:00:49	
3 Complete	Sample		Trap Blank Metrohm (1)		2025/06/24 10:22:24	
4 Active	Sample		Trap Blank Metrohm (1)			
5	Sample		Trap Blank Metrohm (1)			
6	Sample		Trap Blank Metrohm (1)			
7	Sample		Trap Blank Metrohm (1)			
8	Sample		Trap Blank Metrohm (1)			
9	Sample		Trap Blank Metrohm (1)			
10	Sample		Trap Blank Metrohm (1)			

Temperatures (°C)	Actual	Set
UNITY cold trap	24.9	25
UNITY interface	119.9	120
UNITY heated valve	119.9	120
UNITY transfer line	120.2	120
CIAIS oven	45.4	45
CIA valve oven	120.4	120
CIA canister lines	120	120
CIA interconnector	120	120
Pressures (psi)		
Purge gas	On	---
UNITY split gauge	34.4	---
CIA vent gauge	-0.1	---
CIA canister gauge	-0.3	---
MFC flows (mL/min)		
UNITY split	19.7	20
UNITY trap	50	50

Input 1 on 2 will allow switch to Combustion when Markes device – Trap heating

Combustion – MagIC Net

Time program						
Main program	sample	dose absorber solution	prepare absorber solution	rinsing	water inlet	prepare water inlet
Time	Device	Module	Command	Parameter	Comment	No.
0.0	Remote Box		Parallel	dose absorber solution		105
0.0	Remote Box		Parallel	water inlet		110
			Wait	Continue after 480 s.		111
			Sequence	post rinse		112
0.0	Remote Box		Set lines	*****1**		101
0.0	Remote Box		Wait	Continue after 5 s.		98
0.0	920 Absorber Module 1	10-port valve	Change port	Port 8, automatic	port 8: absorber vessel	8

Status	Sample Type	Comment	Method	CIA Advantage Deviation	Trap Fire Time	UNI
1	Complete	Sample	Trap Blank Metrohm (1)		2025/06/24 09:37:45	
2	Complete	Sample	Trap Blank Metrohm (1)		2025/06/24 10:00:49	
3	Complete	Sample	Trap Blank Metrohm (1)		2025/06/24 10:22:24	
4	Active	Sample	Trap Blank Metrohm (1)		2025/06/24 10:44:11	
5		Sample	Trap Blank Metrohm (1)			
6		Sample	Trap Blank Metrohm (1)			
7		Sample	Trap Blank Metrohm (1)			
8		Sample	Trap Blank Metrohm (1)			
9		Sample	Trap Blank Metrohm (1)			
10		Sample	Trap Blank Metrohm (1)			

Instruments

Trap Desorb Elapsed: 2.8 min
GC Ready?

	Actual	Set
Temperatures (°C)		
UNITY cold trap	349.8	350
UNITY interface	120	120
UNITY heated valve	120	120
UNITY transfer line	120.3	120
CIAIS oven	44.8	45
CIA valve oven	120.3	120
CIA canister lines	119.9	120
CIA interconnector	119.9	120
Pressures (psi)		
Purge gas	On	---
UNITY split gauge	34.2	---
CIA vent gauge	-0.1	---
CIA canister gauge	-0.3	---
MFC flows (mL/min)		
UNITY split	0	0
UNITY trap	0	0

Time program						
Main program	sample	dose absorber solution	prepare absorber solution	rinsing	water inlet	prepare water inlet
Time	Device	Module	Command	Parameter	Comment	No.
0.0			Parallel	dose absorber solution		105
0.0			Parallel	water inlet		110
			Wait	Continue after 480 s.		111
			Sequence	post rinse		112
*						

			Wait	Continue after 5 s.		95
			Sequence	Combustion		7
0.0	Remote Box		Set lines	*****1**		101
			Wait	Continue after 5 s.		98
0.0	920 Absorber Module 1	10-port valve	Change port	Port 8, automatic	port 8: absorber vessel	8

After combustion- GC switched to inactive

Sample Nesting – MagIC Net

Time program											
Main program	sample	dose absorber solution	prepare absorber solution	rinsing	water inlet	prepare water inlet	sample nested	fill loop sample	post rinse	Prep	Combustion
Time	Device	Module	Command	Parameter		Comment		No.			
			Sequence	Prep				104			
			Wait	Continue after 5 s.				107			
0.0	Remote Box		Set lines	*****g**				113			
	Remote Box		Scan lines	*****!**, Timeout 10 min				114			
			Wait	Continue after 5 s.				115			
			Sequence	Combustion				116			
0.0	Remote Box		Set lines	*****! **				117			
			Wait	Continue after 5 s.				99			
0.0	920 Absorber Module 1	10-port valve	Change port	Port 8, automatic		port 8: absorber vessel		54			
	UPW (5 mL)		Aspirate	Port 3, Volume 0.5 mL, Rate 2 mL/min		precondition absorber vess...		55			
0.0	920 Absorber Module 1	10-port valve	Change port	Port 10, automatic		port 10: waste		56			
	UPW (5 mL)		Dosing	Port 3, Volume 0.5 mL, Dosing rate 5 mL/min, Filling rate 1.0 mL/min		empty buffer tube		57			
0.0	920 Absorber Module 1	10-port valve	Change port	Port 9, automatic		port 9: air		58			
			Wait	Continue after 1 s.				59			
	UPW (5 mL)		Aspirate	Port 3, Volume 0.1 mL, Rate 5 mL/min		air gap		60			
			Wait	Continue after 2 s.				61			
0.0	920 Absorber Module 1	10-port valve	Change port	Port 8, automatic		port 8: absorber vessel		62			
	UPW (5 mL)		Aspirate	Port 3, Volume 3 mL, Rate 2 mL/min		aspirate sample into buffer ...		63			
			Wait	Continue after 5 s.				64			
0.0	920 Absorber Module 1	10-port valve	Change port	Port 1, automatic		port 1: 6-port valve		65			
	UPW (5 mL)		Dosing	Port 3, Volume 0.5 mL, Dosing rate 5 mL/min, Filling rate 1.0 mL/min		pre-condition dead volume ...		66			
*											

Markes device waiting to switch to active after prep steps

Instruments

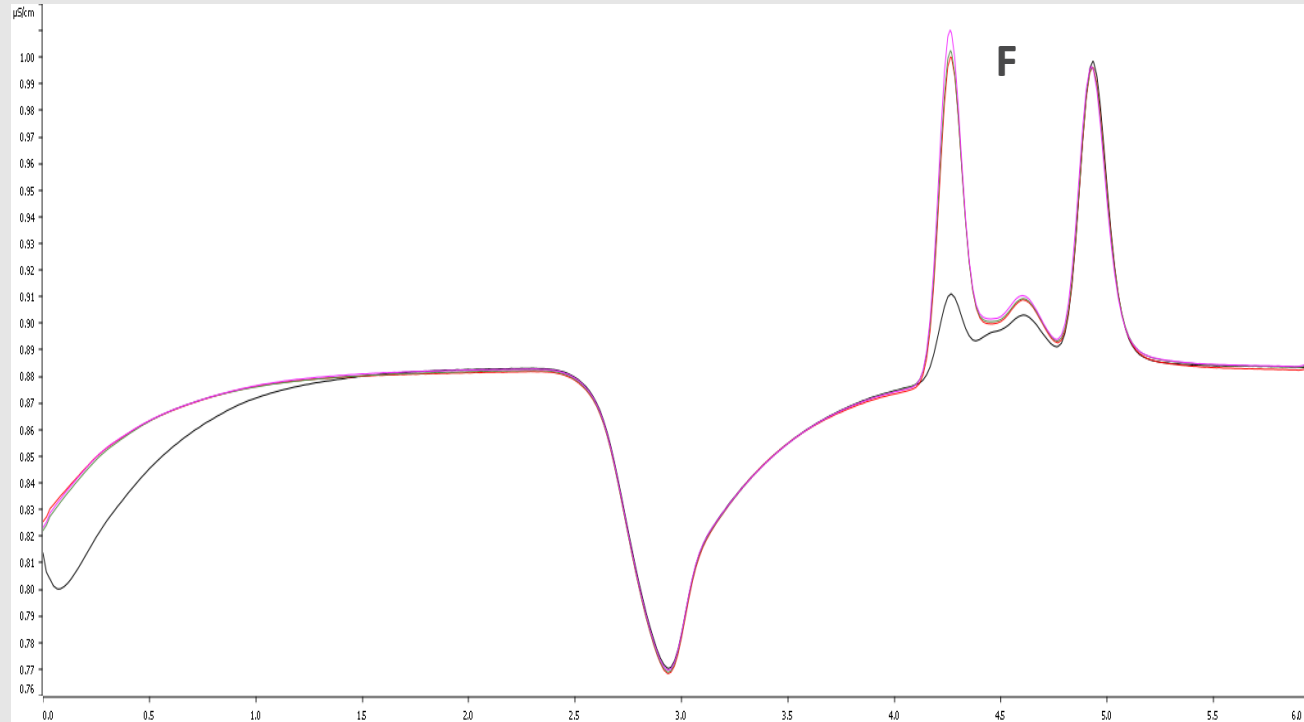
Waiting for GC Ready 2 Active

Elapsed: 0.2 min

GC Ready? X

	Actual	Set
Temperatures (°C)		
UNITY cold trap	25.2	25
UNITY interface	119.7	120
UNITY heated valve	119.7	120
UNITY transfer line	119.9	120
CIAIS oven	44.8	45
CIA valve oven	120.8	120
CIA canister lines	119.9	120
CIA interconnector	120.4	120
Pressures (psi)		
Purge gas	On	---
UNITY split gauge	35.1	---
CIA vent gauge	-0.1	---
CIA canister gauge	-0.3	---
MFC flows (mL/min)		
UNITY split	9.3	10
UNITY trap	0	0

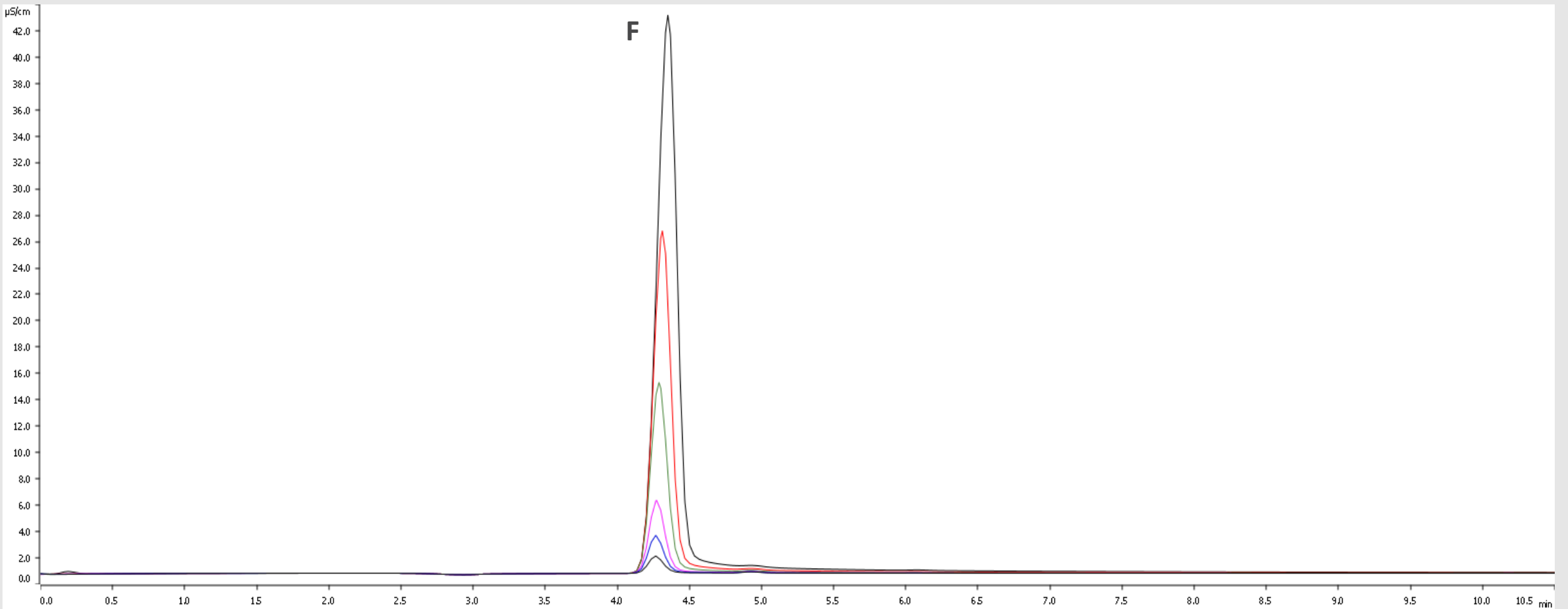
Blank Analysis before analyzing any samples



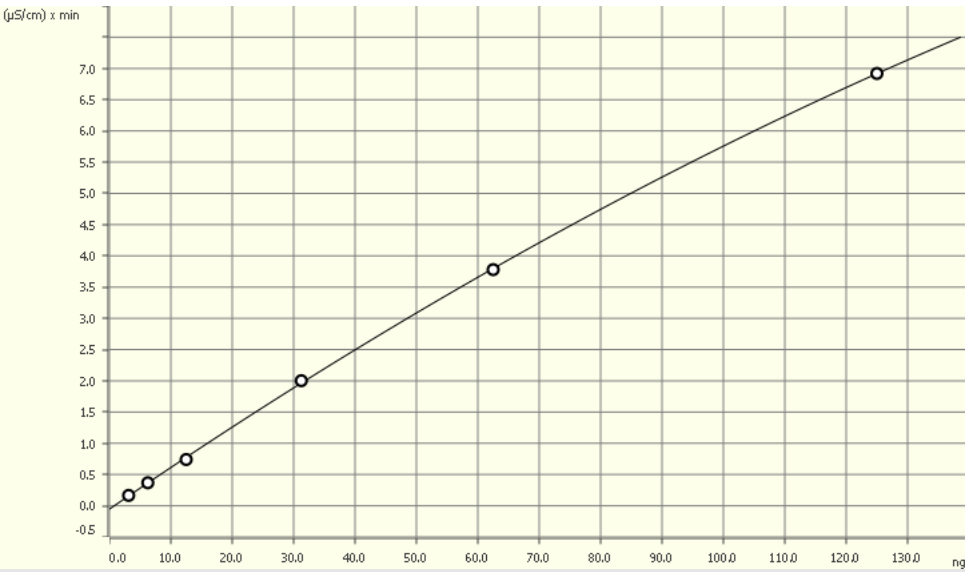
- Black Trace – CIC system Blank
- Red Trace – X-fer line Blank
- Green Trace – Focusing Trap Blank

	Date ▲	Number	Ident	Sample type	Volume	Dilution	Sample amount	Method	Analysis	Leg...	Display
1	2024-08-27 12:55:40 UTC-5	1	CIC System Blank	Sample	200.0	1.0	1.0	CIC_Gases_Simplified 082024_Variable Volume IC inj	Anions	—	<input checked="" type="checkbox"/>
2	2024-08-27 15:23:19 UTC-5	2	TD_CIC X-ferline Blank	Sample	200.0	1.0	1.0	CIC_Gases_Simplified 082024_Variable Volume IC inj	Anions	—	<input checked="" type="checkbox"/>
3	2024-08-27 16:53:04 UTC-5	3	TD_CIC Focusing Trap Blank	Sample	200.0	1.0	1.0	CIC_Gases_Simplified 082024_Variable Volume IC inj	Anions	—	<input checked="" type="checkbox"/>
▶ 4	2024-08-28 10:34:02 UTC-5	4	TD_CIC Focusing Trap Blank	Sample	200.0	1.0	1.0	CIC_Gases_Simplified 082024_Variable Volume IC inj	Anions	—	<input checked="" type="checkbox"/>

Calibration Overlay (3ng – 125ng F)



Calibration Curve

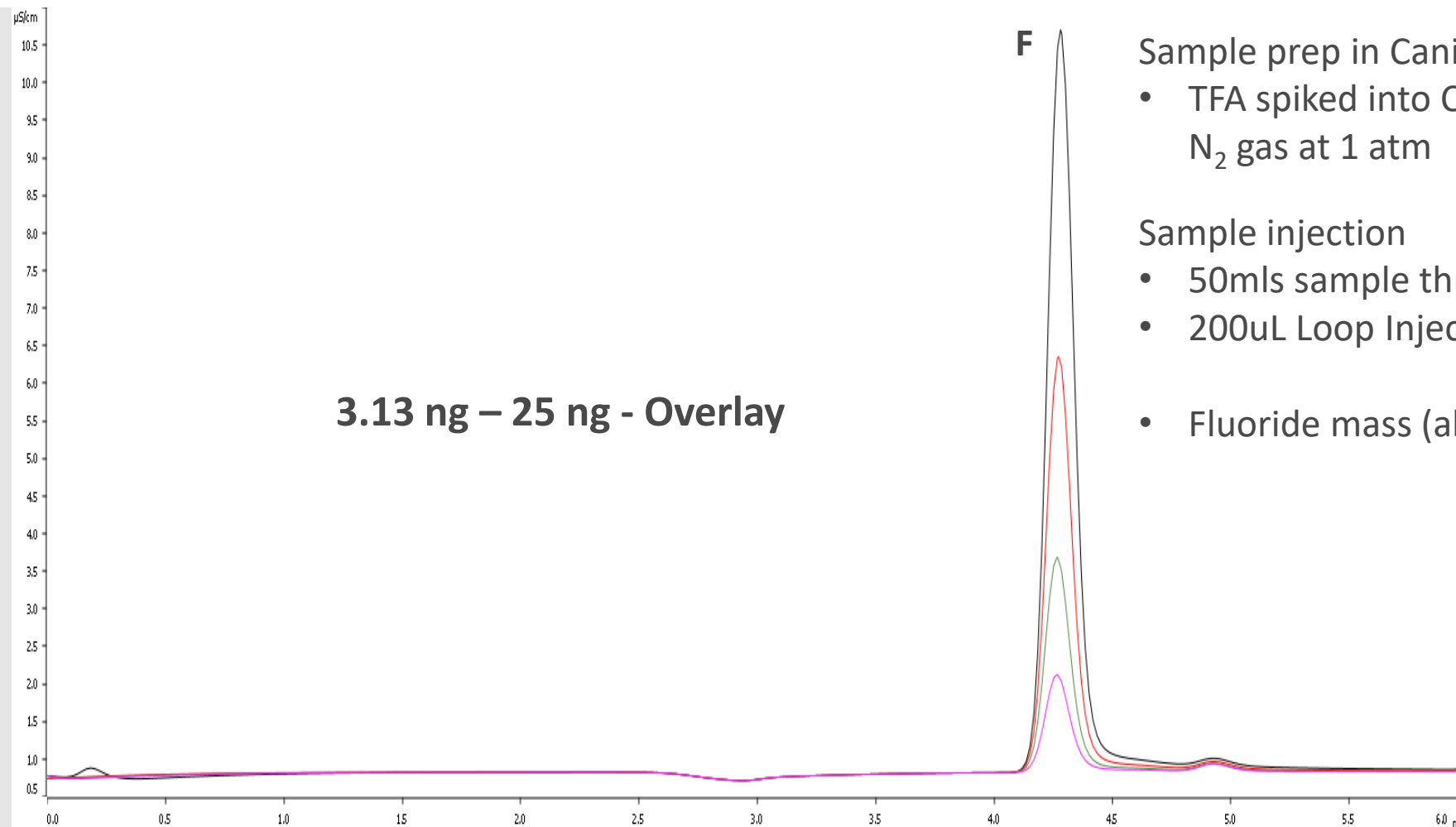


Function: $A = -0.0534810 + 3.37314E-4 \times Q - 2.33921E-9 \times Q^2$

Relative standard deviation	1.391%
Correlation coefficient	0.999954
Curve type	Quadratic
Weighting	1

	Sample type	Index	Conc.	Volume	Dilution	Sample amount	Area	Ident	Date ▲	Used	Conc.(calc.)	Conc.(dev., %)
▶ 1	Standard 6	1	125.000	200.0	1.0	1.0	6.91972	TD_CIC 50mls of TFA sample for CIC	2024-08-28 13:41:55 UTC-5	☑	125.054	0.04
2	Standard 5	1	62.500	200.0	1.0	1.0	3.77968	TD_CIC 50mls of TFA sample for CIC	2024-08-28 14:24:19 UTC-5	☑	62.182	-0.51
3	Standard 4	1	31.250	200.0	1.0	1.0	2.00201	TD_CIC 50mls of TFA sample for CIC	2024-08-28 14:47:22 UTC-5	☑	31.878	2.01
4	Standard 3	1	12.500	200.0	1.0	1.0	0.73990	TD_CIC Canister#2 50mls TFA sample for desorption	2024-08-29 13:21:10 UTC-5	☑	11.959	-4.33
5	Standard 2	1	6.250	200.0	1.0	1.0	0.36772	TD_CIC Canister#2 50mls TFA sample for desorption	2024-08-29 13:48:54 UTC-5	☑	6.298	0.78
6	Standard 1	1	3.130	200.0	1.0	1.0	0.16557	TD_CIC Canister#2 50mls TFA sample for desorption	2024-08-29 14:10:46 UTC-5	☑	3.262	4.21

Canister # 2



Sample prep in Canister #2

- TFA spiked into Canister and pressurized with N_2 gas at 1 atm

Sample injection

- 50mls sample through CIA and Unity focusing trap
- 200uL Loop Injection (MiPT used for Calib Curve)
- Fluoride mass (absolute) 0.025 ug \rightarrow 25ng

Canister # 2 – lowest concentration replicates

IC Detail overview - Results



Result Concentration

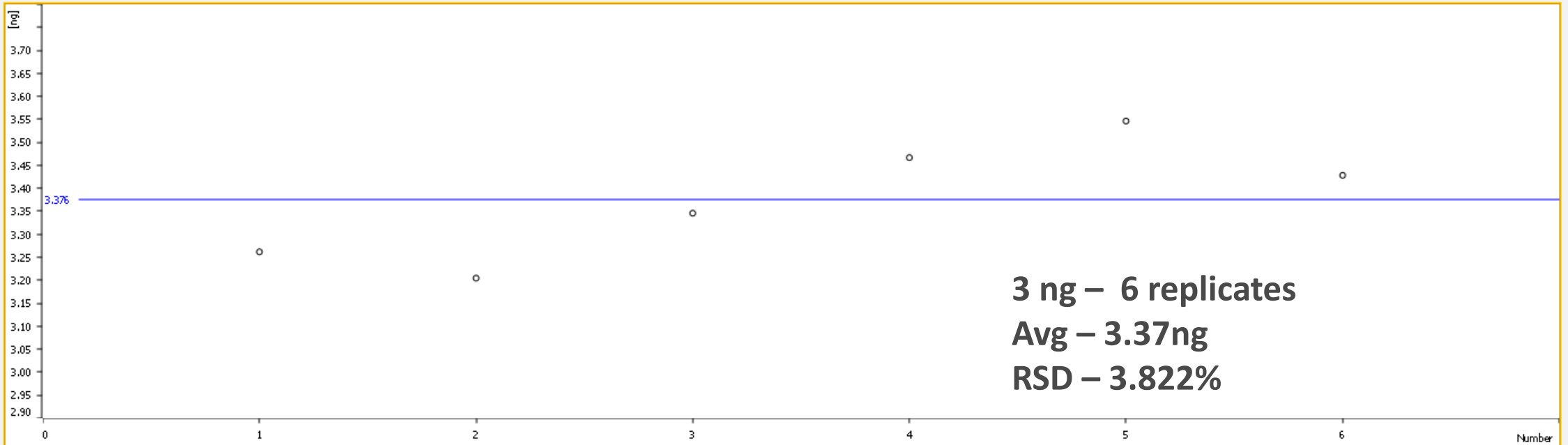


Results

Fluoride



Control chart



3 ng – 6 replicates
Avg – 3.37ng
RSD – 3.822%

Statistics Mean value:	3.376 ng	Absolute standard deviation:	0.129 ng
Minimum:	3.205 ng	Relative standard deviation:	3.822 %
Maximum:	3.546 ng	Number of determinations:	6

Houston Lab Air sampling and analysis

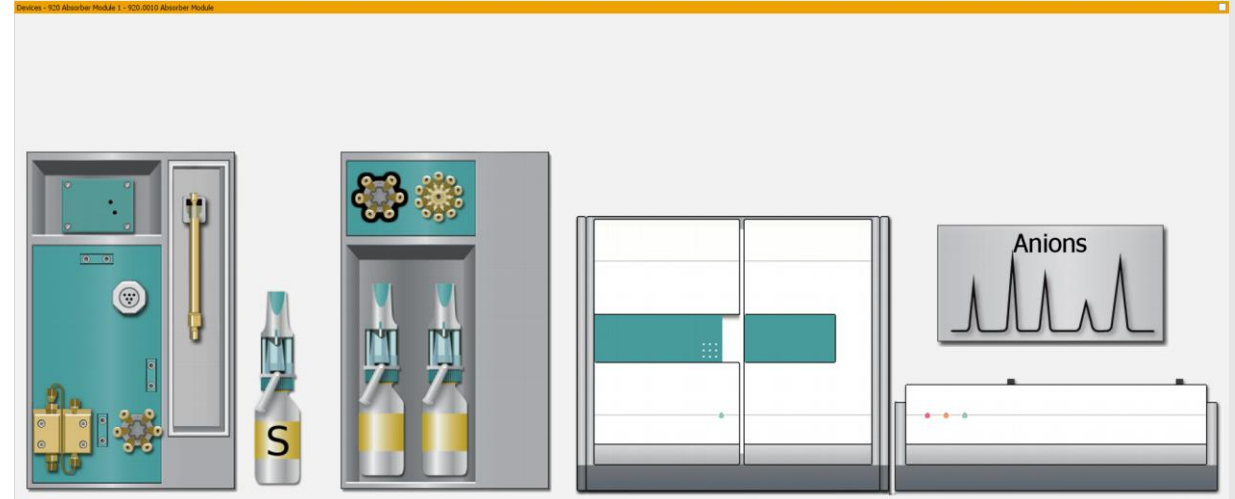


- 500mls of House air sampled (10 minutes)
- Desorbed into CIC

- Total Fluorine in MUSA Pasadena Lab Air = 522 picogram (only 2 data points)

Conclusions

- **Metrohm USA** and **Markes International** created an innovative technique to compliment OTM-50 method (targeted compounds) for monitoring **Total Fluoride in Air**
- This technique is canister-based technique which is very common in Air Monitoring methods like TO-14 and TO-15
- Limit of quantitation (LOQ) can be extremely low depending on the volume of sample trapped and injected on the IC



Metrohm CIC Advantages



1

Expertise in CIC Analysis

2

Innovative technology for
Inorganic Fluoride removal

3

Flexible Calibration and Sample
Handling Options

4

Streamlined Software Integration

5

Single Vendor Support for
Entire System

Thank You



Questions? Please contact us at communications@metrohmusa.com