

When low levels are no longer good enough

Moving toward trustable quantification of trace levels



Introduction

Why trace-level quantification is becoming critical

Acceptable limits are continuously decreasing, reaching **sub-ppm and ppb levels**.

While analyzers can now detect extremely low concentrations, **reliable calibration and measurement confidence have become the real challenges**.

Examples across key industries:

- ✓ **Hydrogen purity (ISO 14687)**
Sub-ppm / ppb limits for CO, NH₃, H₂S and formic acid to prevent fuel cell catalyst poisoning.
- ✓ **Environmental monitoring**
Ambient air limits often below 50 ppb for NO₂ and SO₂, requiring calibration gases at even lower levels.
- ✓ **Semiconductor manufacturing**
HF, NH₃ and siloxanes below 10 ppb to avoid wafer damage and yield loss.

➔ **As acceptable limits go lower**, reliable and traceable quantification becomes essential

The Calibration Challenge

- Trace calibration gases are often unavailable commercially
- And when they are, the lower the concentration :
 - The higher the cost
 - The higher the uncertainty
 - The shorter the lifetime
 - The longer the delivery lead time

\$



RSD



Lifetime



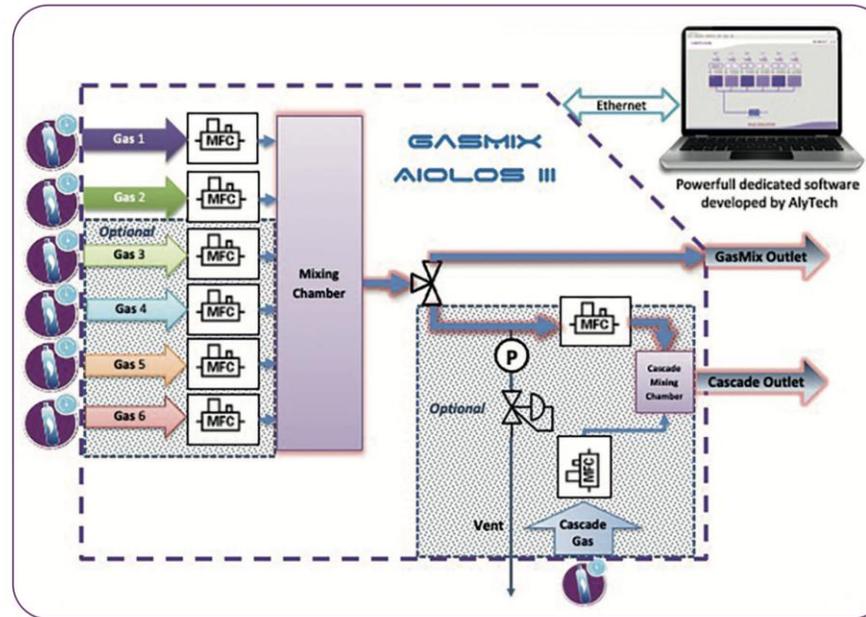
A solution – Dynamic gas mixture

- 1 way to tackle this challenges is through dynamic gas generation :
 - ✓ On-site generation of trace calibration gases
 - ✓ Flexible and immediately available
 - ✓ Full traceability
 - ✓ Following an international standard
- Generate dynamic gas mixture - **ISO 6145 methods**



Dynamic Dilution via ISO 6145-7

- High-accuracy mass flow controllers -> combined uncertainty below +/-1% of the set flow
- Can dilute to 10^8 with a 2nd stage dilution (ie from 100% to approx. 10ppb)
- Automated system for dynamic gas generation
- Compliant with aggressive gases & trace analysis: SS316 tubing with inert coating, zero dead volume



Trace Analysis

- At trace level, adsorption or memory effect is no longer negligible
- The system between the gas cylinder and the analyzer shall be designed for trace analysis
- Special care is to be taken for all parts in contact with the gas (diluter and pipings) -> Inert coating

Example: Ammonia NH₃, a very sticky gas

Metal / coating	Adsorption* (10 ¹² molecules/cm ²)	St. deviation (10 ¹² molecules/cm ²)
SilcoNert 2000	5.7	0.6
SilcoNert 1000	14.6	0.9
EP SS316L	72	11
Dursan	101	5
SS316L	138	21

*Average of 3 measurements

NH₃ conc = 420 ppb, p (tube) = 176 mbar

Traceability and Metrology

- Mass flow controllers calibration are NIST traceable (volumetric flowmeters used for the calibration certified by an accredited ISO 17025 lab)
- Complete audit trail and mixture generation certificates with generated concentrations and associated uncertainties

Uncertainties calculations

- For a final concentration, the main uncertainty contributions are:
 - ✓ Initial gas standard uncertainty
 - ✓ MFC calibration flow meter uncertainty
 - ✓ MFC uncertainty

👉 Each contribution is expressed as a **standard uncertainty** u_i

- Combination (GUM)
 u_c = **combined standard uncertainty**

$$u_c = \sqrt{u_1^2 + u_2^2 + \dots}$$



Uncertainties calculations

- Expanded uncertainty

$$U = k \times u_c$$

Where:

- u_c is the combined standard uncertainty (GUM)
- k is the coverage factor

For routine industrial measurements:

- $k = 2$
- Confidence level $\approx 95\%$

	Case 1	Case 2	Case 3	Case 4
u1 = Initial gas standard uncertainty	0,0%	0,5%	1,0%	2,0%
u2 = MFC calibration flow meter uncertainty	0,6%	0,6%	0,6%	0,6%
u3 = Repeatability or standard deviation	0,5%	0,5%	0,5%	0,5%
uc = Combined standard uncertainty	0,8%	0,9%	1,3%	2,1%
U = Expanded uncertainty	1,5%	1,8%	2,5%	4,3%

Application 1: Hydrogen Purity (ISO 14687)

Maximum concentrations of individual compounds are listed in the ISO 14687 method :

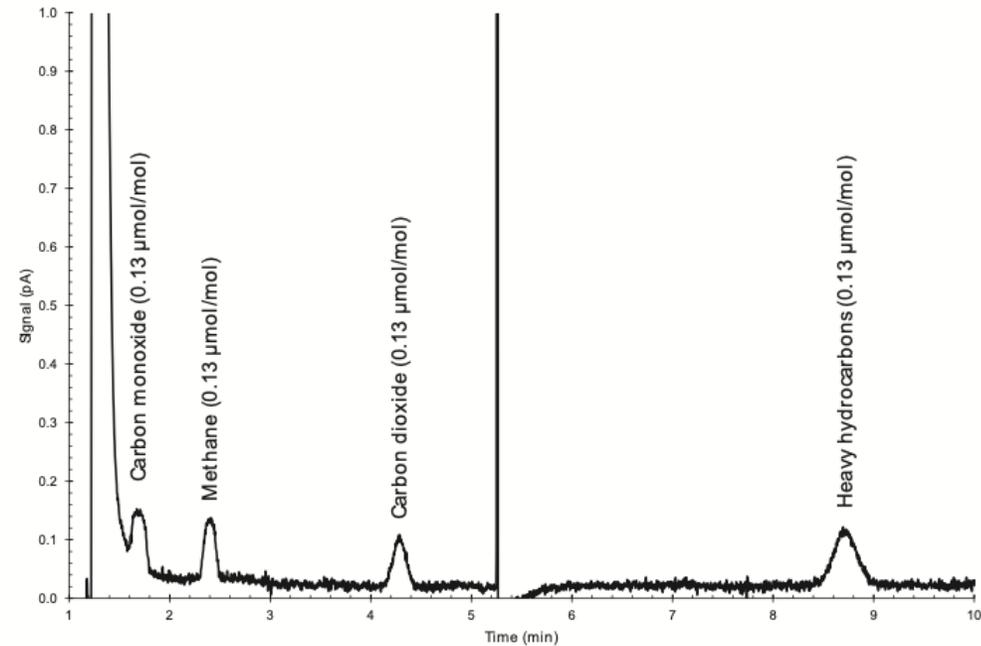
Characteristics (assay)	Grade D Specification
	umol/mol
Water (H ₂ O)	5
Total hydrocarbons except methane (C1 basis)	2
Methane (CH ₄)	100
Oxygen (O ₂)	5
Helium (He)	300
Nitrogen (N ₂)	300
Argon (Ar)	300
Carbon dioxide (CO ₂)	2
Carbon monoxide (CO)	0.2
Total sulphur compounds (H ₂ S basis)	0.004
Formaldehyde (HCHO)	0.2
Formic acid (HCOOH)	0.2
Ammonia (NH ₃)	0.1
Total halogenated compounds (Halogenate ion basis)	0.05
	mg/kg
Maximum particulates concentration	1

Application 1: Hydrogen Purity (ISO 14687)

Possibility to assess detection limits :

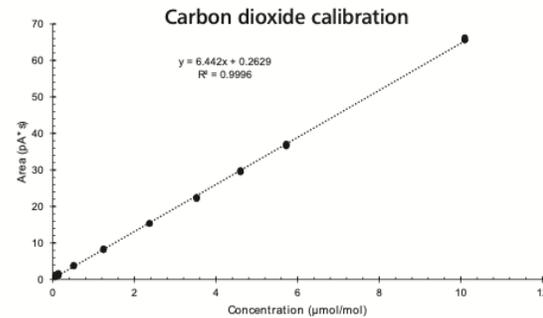
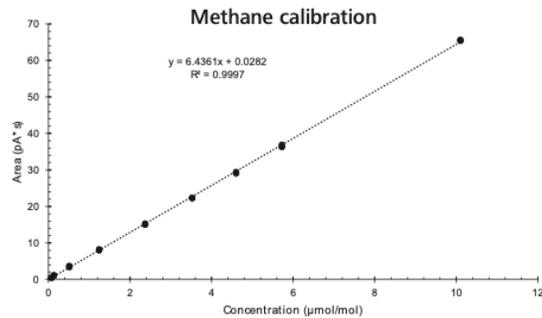
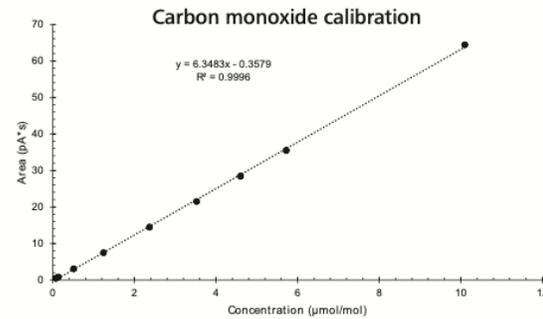
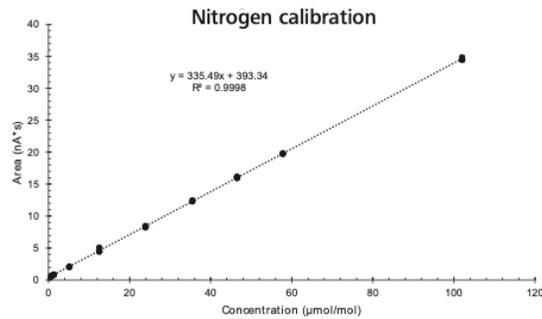
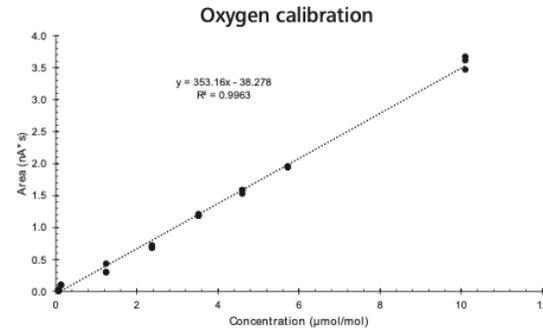
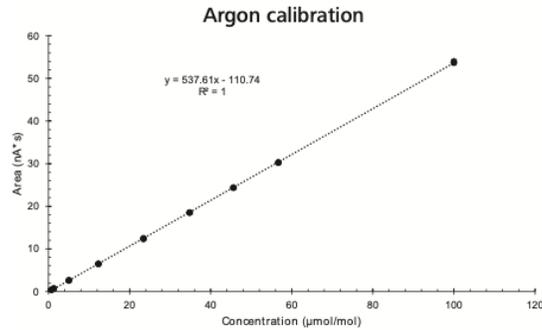
Compound	ISO Specification ($\mu\text{mol/mol}$)	Detection limit ($\mu\text{mol/mol}$)
Argon	300	<0.1
Oxygen	5	<0.1
Nitrogen	300	<0.1
Carbon monoxide	0.2	0.1
Methane	100	<1
Carbon dioxide	2	<1
Heavy hydrocarbons	2	<1
Helium	300	<50

Chromatogram under ISO specification on the FID



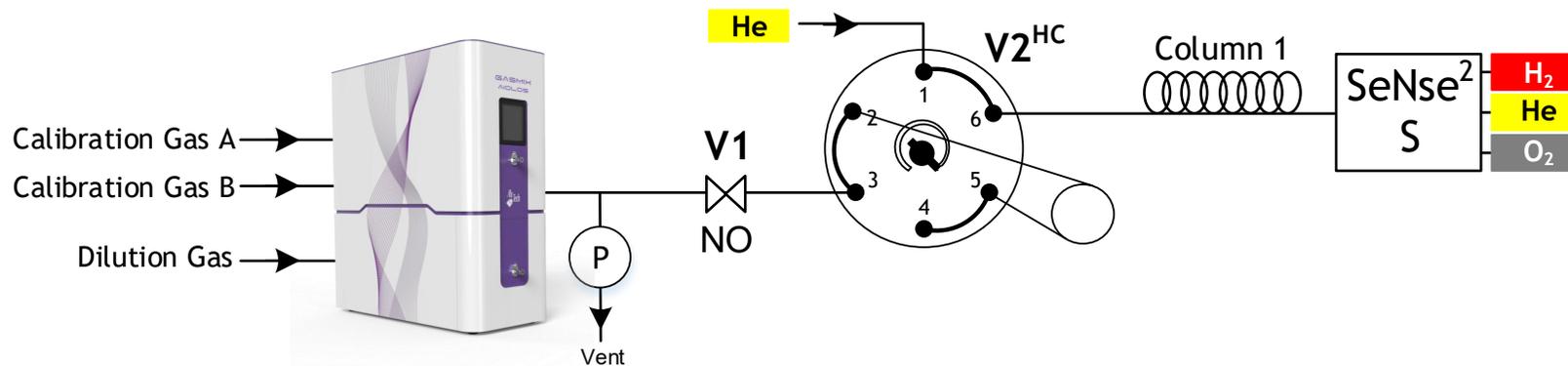


Application 1: Hydrogen Purity (ISO 14687)



Application 2: Sulfur & Ammonia

Instrument Setup

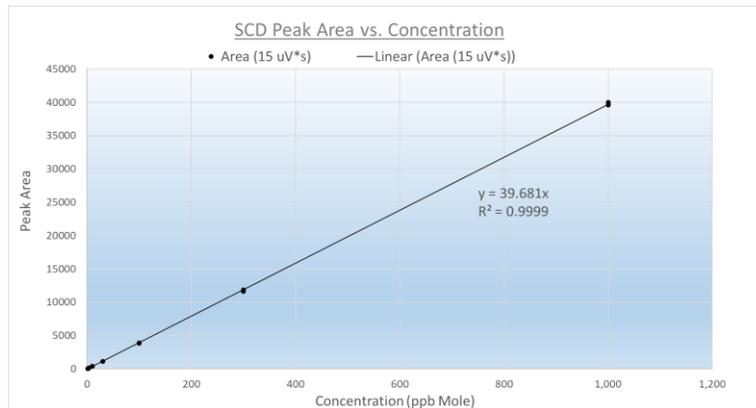


Standard gas used :

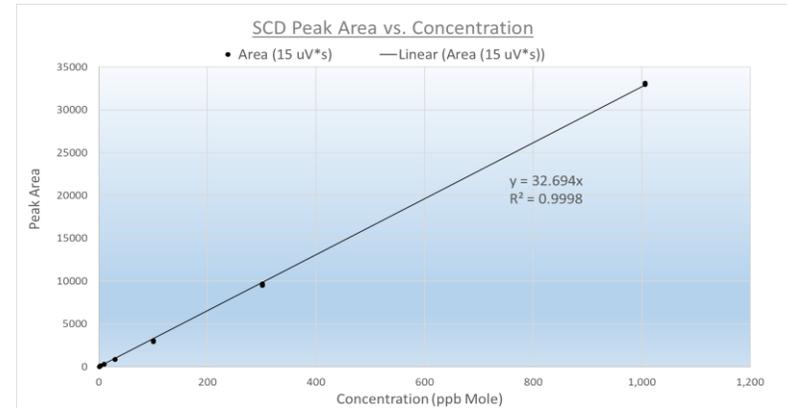
- Several sulfur compounds at around 1ppm Mole (H₂ matrix)
- NH₃ at 10ppm Mole (H₂ matrix)

Application 2: Sulfur & Ammonia

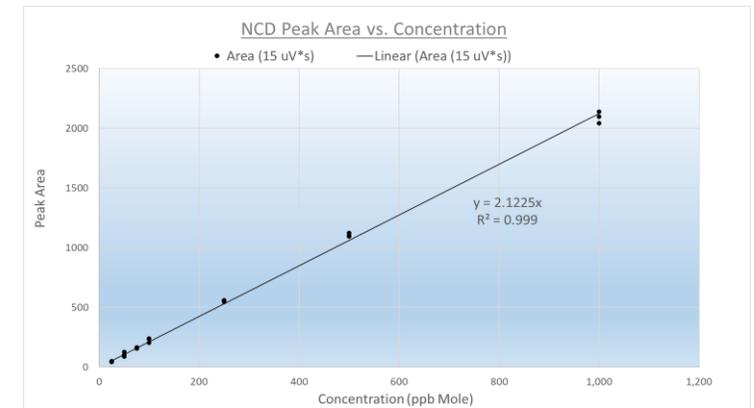
Linearity COS



Linearity H₂S



Linearity NH₃

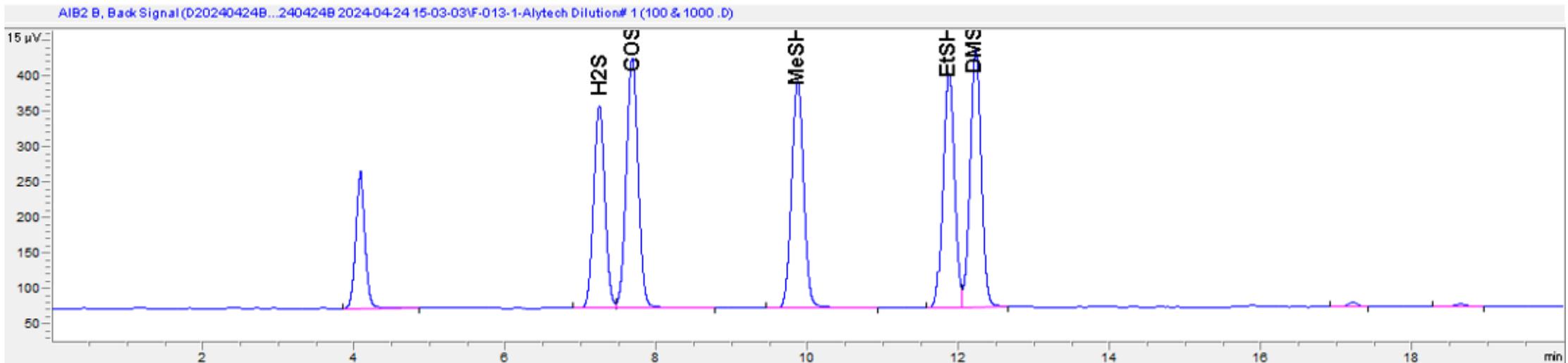


Application 2: Sulfur

Calibration Gas dilution to 100ppb level:

- 100.57 ppb Mole H₂S => RSD% (n=3) = 1.9 %
- 100.00 ppb Mole COS => RSD% (n=3) = 0.8 %
- 100.57 ppb Mole MeSH => RSD% (n=3) = 0.3 %
- 94.82 ppb Mole EtSH => RSD% (n=3) = 0.6 %
- 101.14 ppb Mole DMS => RSD% (n=3) = 1.0 %

Sub-ppm Analysis

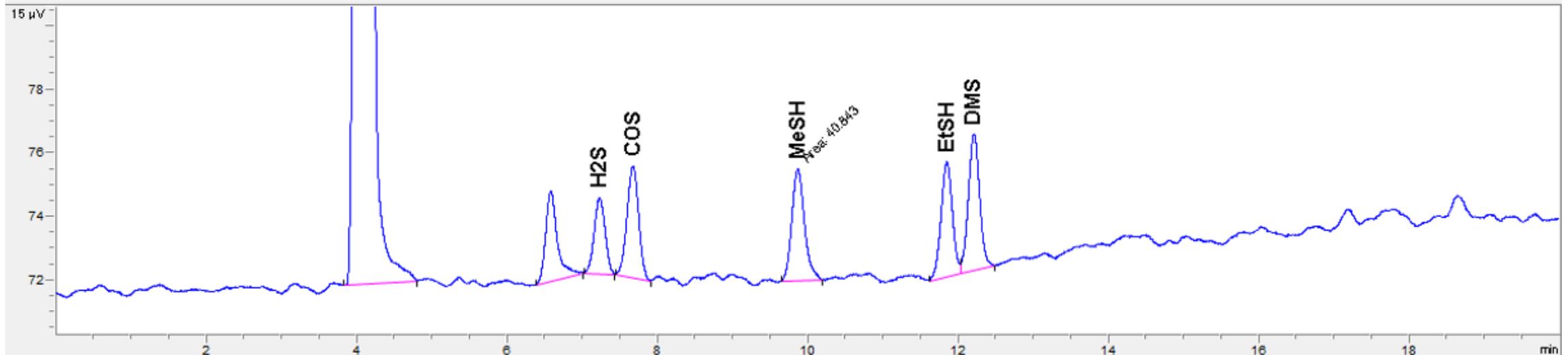


Application 2: Sulfur

Calibration Gas dilution level:

- 1.00 ppb Mole H₂S => RSD% (n=3) = 7.9 %
- 1.00 ppb Mole COS => RSD% (n=3) = 0.5 %
- 1.00 ppb Mole MeSH => RSD% (n=3) = 13.8 %
- 0.94 ppb Mole EtSH => RSD% (n=3) = 5.9 %
- 1.01 ppb Mole DMS => RSD% (n=3) = 3.3 %

Low-ppb Analysis



Application 2: Ammonia

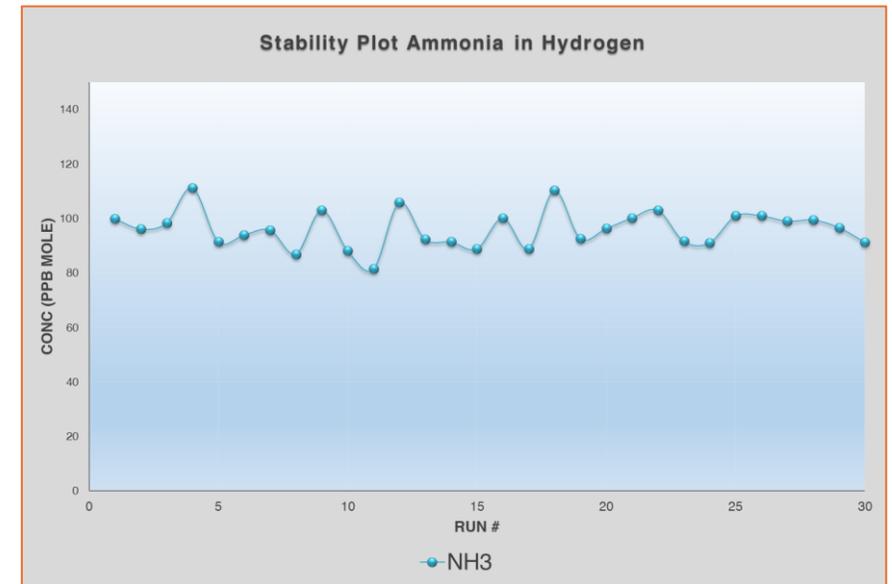
Methodology :

- Starting concentration : 10 ppm Mole NH₃ in H₂
- Sampling line purged 6 minutes at 200ppb Mole NH₃
- Stabilization time: 2 minutes

Gas dilution level:

- 100 ppb Mole NH₃ => RSD% (n=30) = 7.1 %
- 50 ppb Mole NH₃ => RSD% (n=30) = 19.4 %

-> Even for NH₃, which is very adsorptive, the results show stable and repeatable measurement at 100ppb, and controlled performance down to 50 ppb.



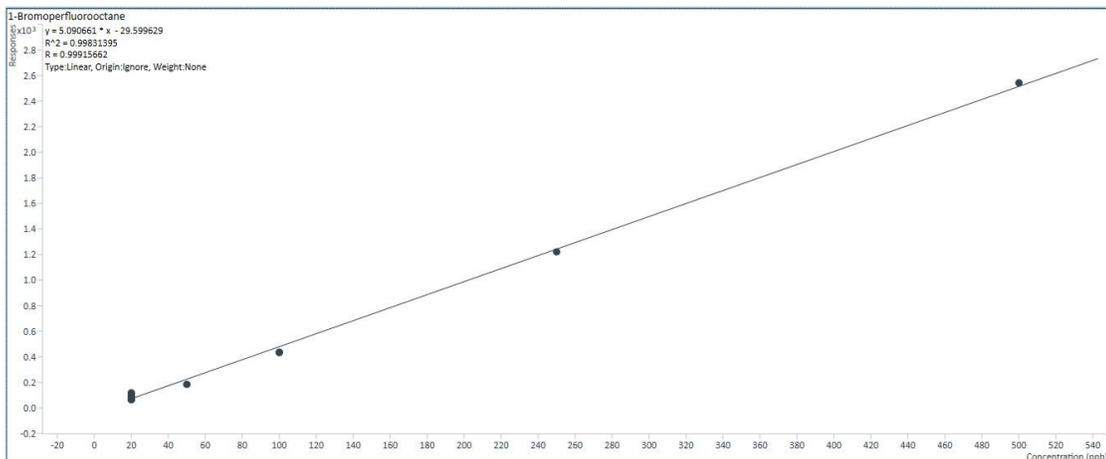
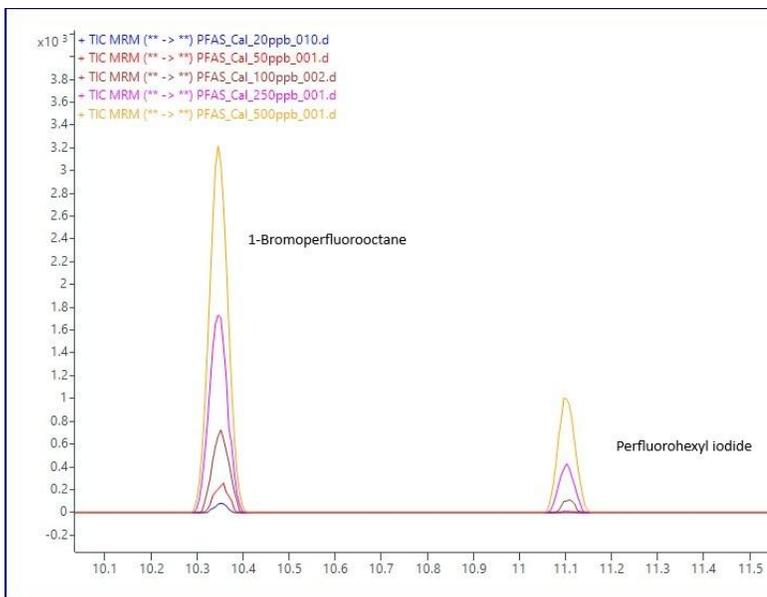
Application 3: PFAS

CERTIFIED STANDARD MIXTURE

	Component	cas #	Nominal	Actual
5	PERFLUORO-2-METHYLPENTANE	355-04-04	1.00 ppm	1.02 ppm
	PERFLUORO-2-METHYL-2-PENTENE	1584-03-08	1.00 ppm	1.02 ppm
8	PERFLUOROHEXANE	355-42-0	1.00 ppm	1.02 ppm
2	CHLOROPENTAFLUOROBENZENE	344-07-0	1.00 ppm	1.03 ppm
1	BROMOPENTAFLUOROBENZENE	344-04-07	1.00 ppm	1.05 ppm
	(PERFLUORO-N-HEXYL) ETHANE	80793-17-5	1.00 ppm	1.02 ppm
3	PERFLUOROHEXYL IODIDE	355-43-1	1.00 ppm	1.04 ppm
7	2-IODOHEPTAFLUOROPROPANE	677-69-0	1.00 ppm	1.03 ppm
	1H-PERFLUOROOCANE	335-65-9	1.00 ppm	1.01 ppm
6	1-BROMOPERFLUOROOCANE	423-55-2	1.00 ppm	1.05 ppm
	PERFLUOROHEPTANE	335-57-9	1.00 ppm	1.02 ppm
4	PERFLUOROBUTYL IODIDE	423-39-2	1.00 ppm	1.04 ppm
	PERFLUORO-4-METHYL-2-PENTANE	2070-70-4	1.00 ppm	1.06 ppm
	NITROGEN	N2	Balance	Balance

Blend Tolerance: +/- 5 %
Analytical Tolerance: +/- 2%

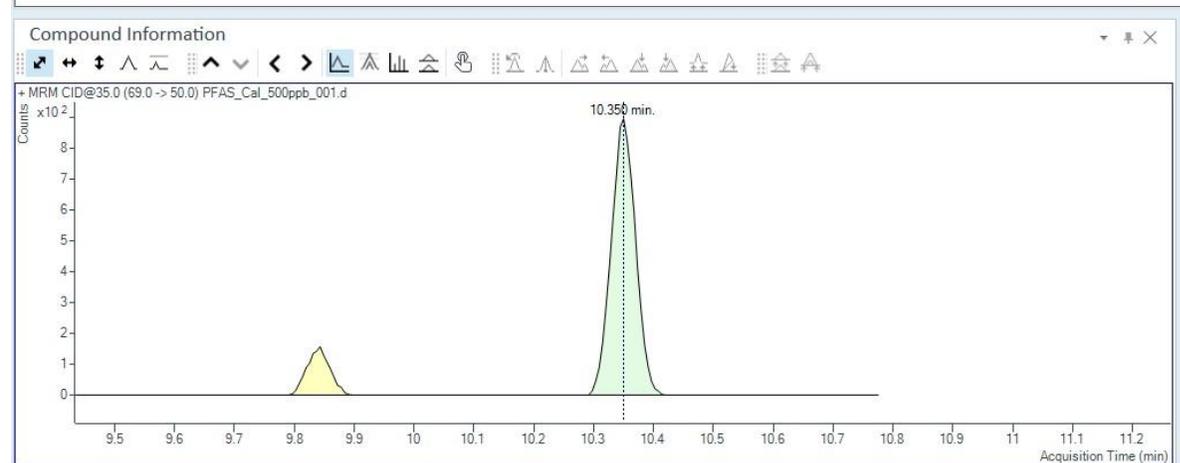
Application 3: PFAS



Batch Table

Sample: PFAS_Cal_500ppb_001.d Sample Type: <All> Compound: 1-Bromoperfluorooctane

Sample							1-Bromop...		1-Bromoperfluorooctane Results					
?	▼	Name	Data File	Type	Level	Acq. Date-Time	Exp. Conc.	Δ	RT	Resp.	Calc. Conc.	Final Conc.	Accuracy	Area
1	▼	PFAS_Cal_20ppb_001.d	Cal	1	12/10/2025 4:02 PM	20.0000	10.350	64	18.4620	18.4620	92.3	64		
2	▼	PFAS_Cal_20ppb_002.d	Cal	1	12/10/2025 4:28 PM	20.0000	10.350	118	29.0474	29.0474	145.2	118		
3	▼	PFAS_Cal_20ppb_003.d	Cal	1	12/10/2025 5:20 PM	20.0000	10.350	87	22.8697	22.8697	114.3	87		
4	▼	PFAS_Cal_20ppb_004.d	Cal	1	12/10/2025 5:45 PM	20.0000	10.356	66	18.7807	18.7807	93.9	66		
5	▼	PFAS_Cal_20ppb_005.d	Cal	1	12/10/2025 6:10 PM	20.0000	10.350	87	22.8485	22.8485	114.2	87		
6	▼	PFAS_Cal_20ppb_006.d	Cal	1	12/10/2025 6:35 PM	20.0000	10.361	97	24.8037	24.8037	124.0	97		
7	▼	PFAS_Cal_20ppb_007.d	Cal	1	12/10/2025 7:01 PM	20.0000	10.350	81	21.7673	21.7673	108.8	81		
8	▼	PFAS_Cal_20ppb_008.d	Cal	1	12/10/2025 7:25 PM	20.0000	10.356	87	22.8094	22.8094	114.0	87		
9	▼	PFAS_Cal_20ppb_009.d	Cal	1	12/10/2025 7:51 PM	20.0000	10.361	89	23.3791	23.3791	116.9	89		
10	▼	PFAS_Cal_20ppb_010.d	Cal	1	12/10/2025 8:17 PM	20.0000	10.356	69	19.4028	19.4028	97.0	69		
11	▼	PFAS_Cal_50ppb_001.d	Cal	2	12/11/2025 10:10 AM	50.0000	10.356	185	42.0607	42.0607	84.1	185		
12	▼	PFAS_Cal_100ppb_001.d	Cal	3	12/11/2025 9:16 AM	100.0000	10.350	437	91.5864	91.5864	91.6	437		
13	▼	PFAS_Cal_100ppb_002.d	Cal	3	12/11/2025 9:43 AM	100.0000	10.356	434	90.9936	90.9936	91.0	434		
14	▼	PFAS_Cal_250ppb_001.d	Cal	4	12/11/2025 11:47 AM	250.0000	10.350	1221	245.7552	245.7552	98.3	12...		
15	▼	PFAS_Cal_500ppb_001.d	Cal	5	12/11/2025 12:32 PM	500.0000	10.350	2543	505.4335	505.4335	101.1	25...		



Conclusion

- At trace levels, confidence is everything
- Accurate gas generation at sub-ppm and low ppb levels can be achieved via ISO 6145-7
- Dynamic dilution with GasMix devices transforms calibration into a traceable, flexible, and reliable process, ensuring trustable quantification in every measurement.

MEET US AT BOOTH B31



Thank you

MEET US AT BOOTH B31

