



**Dutch
Metrology
Institute**

Welcome to session 3: halogenated VOC content

Joint Workshop of the consortium of “Metrology for biomethane” and ISO/TC193/SC1/WG25 Biomethane

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Topics

1. NWIP for total silicon concentration (IMBiH)
2. NWIP for siloxanes (NPL)
3. NWIP for halogenated VOCs (VSL + INERIS + RISE)
4. NWIP for HCl + HF (wet chemistry) (INERIS + ISSI)
5. NWIP for ammonia (NPL + VSL + RICE)
6. NWIP for terpenes (RICE + RISE + NPL)
7. NWIP for compressor oil concentration (RISE + INERIS)
8. NWIP for amines concentration (RICE + VSL)
9. NWIP for biogenic methane fraction (RUG)

Workshop objectives

- Presentation of the methods developed in “Metrology for Biomethane” (EMPIR, 16ENG05) in support of the biomethane specification EN 16723
- Presentation of the validation performed on the methods
- Q&A on the project outcomes
 - Ask questions using the “chat” function in MS Teams
 - You can post your questions any time during the presentation
 - After the presentation, the questions will be addressed
- Sessions are recorded for developing records from the meeting; they will not be made public
- Presentations will be made available on the workshop website



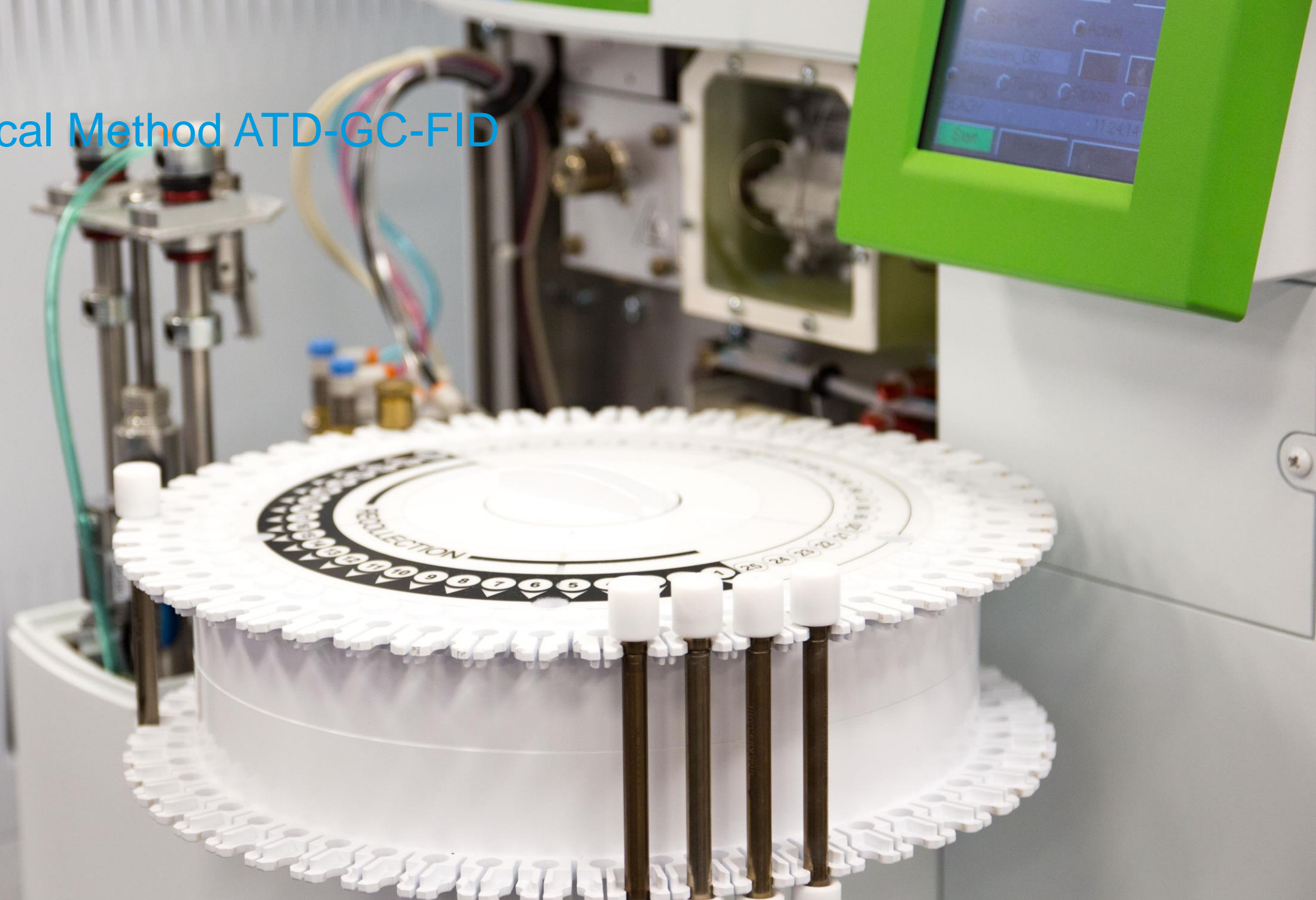
VSL Halogenated VOC measurement standard

- 10 halogenated VOCs often encountered in upgraded biogas or biomethane
- ~ 50 nmol mol⁻¹ in methane
- ISO 6142-1:2015

Component	CAS
chloromethane	74-87-3
dichloromethane	75-09-2
cis-1,2-dichloroethane	156-59-2
Trichloromethane	67-66-3
n-hexane (internal standard)	110-54-3
trichloroethylene	79-01-6
1,2-dichloropropane	78-87-5
1,1,2-trichloroethane	79-00-5
tetrachloroethylene	127-18-4
trichloro trifluoroethane (freon 113)	76-13-1
vinyl chloride	75-01-4

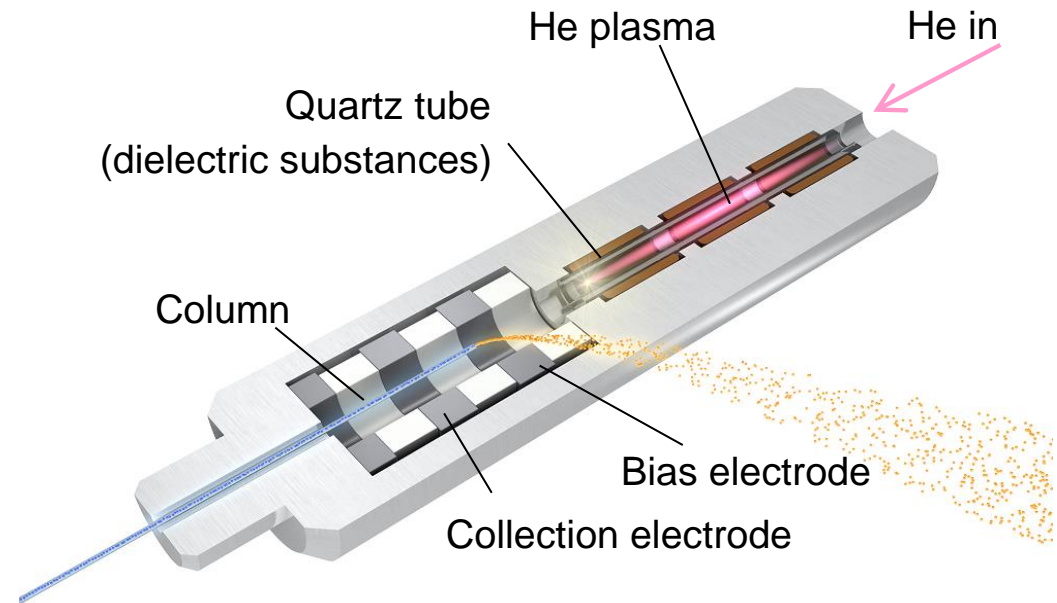
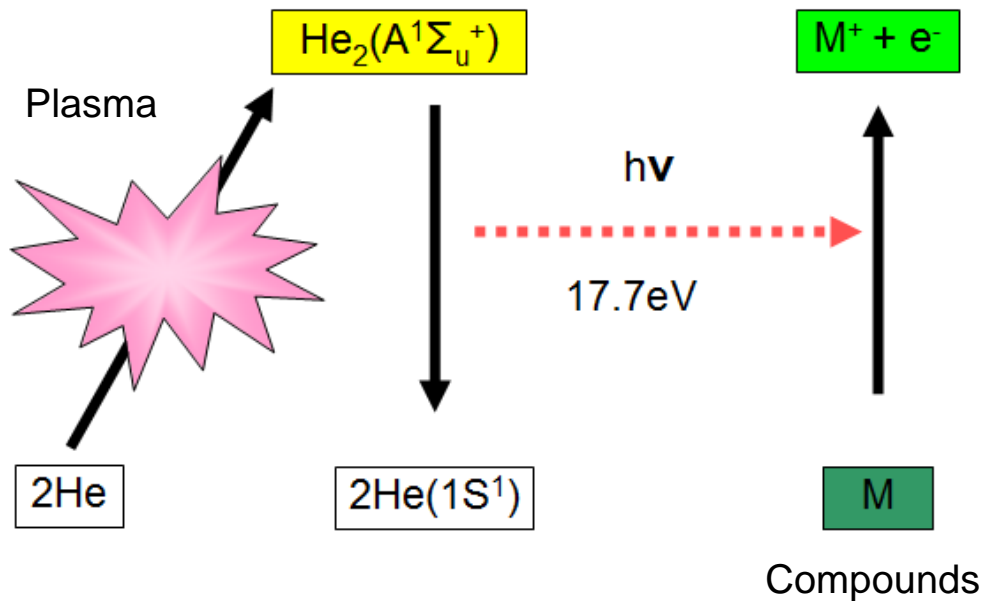


Analytical Method ATD-GC-FID



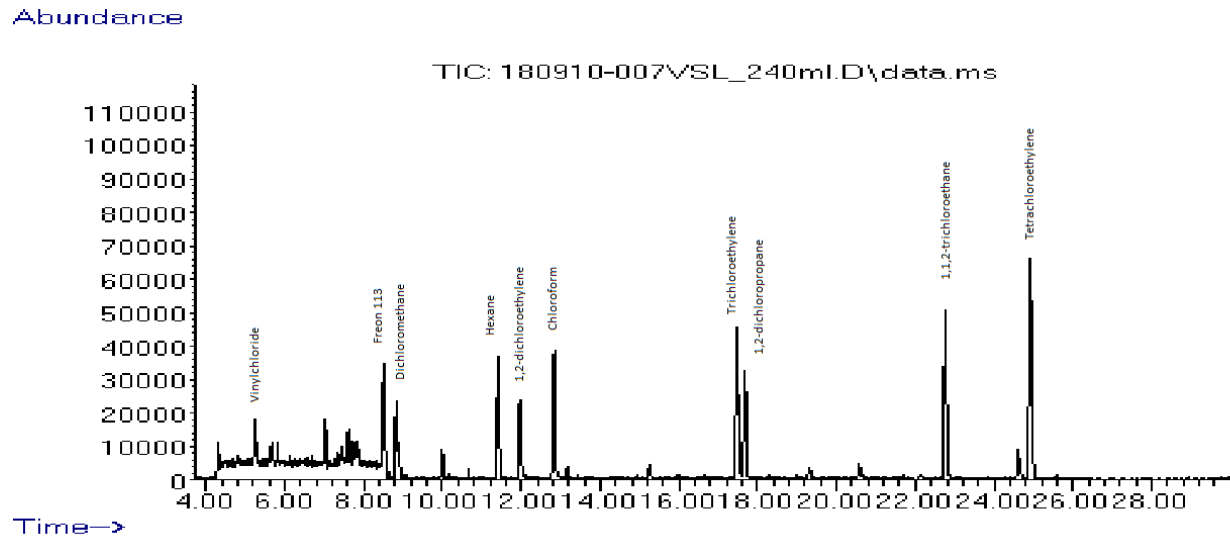
Analytical Method GC-BID

- Barrier ionization discharge (BID) detector



Method 1 – using sorbent tubes

- Three different sorbents were tested:
 - Tenax TA
 - Multi-bed sorbents: Tenax TA (weak), Carboxen 1003 (medium), Carbograph 1 (strong)
 - Train of 2 sorbents (medium/weak): Chromosorb + Tenax TA: used in series



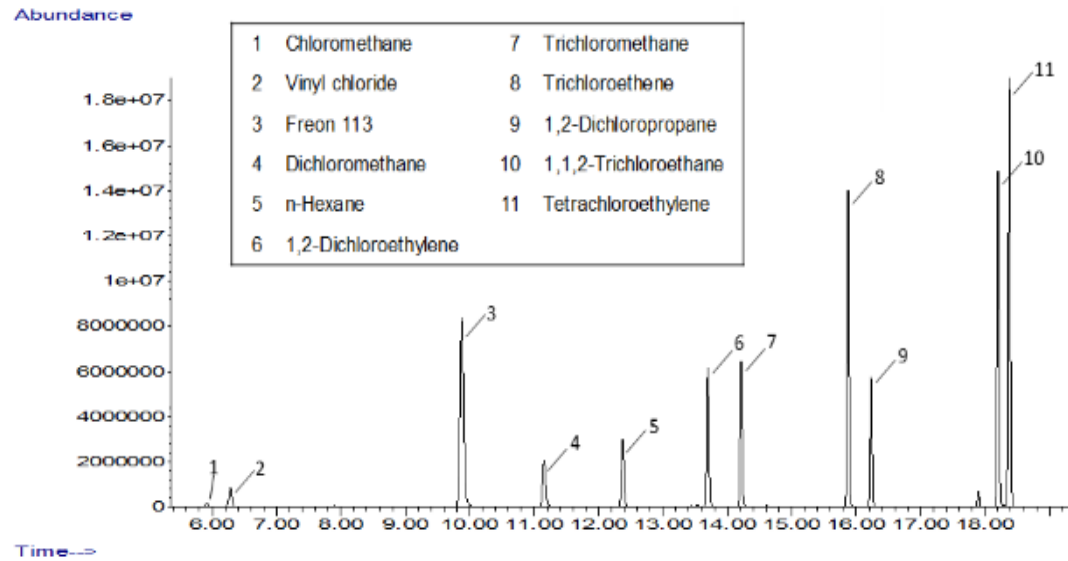
Method 1 – using sorbent tubes

- Performance characteristics
 - Limit of detection (LOD) → ≤ 12 ng/tube and ≤ 10 nmol mol⁻¹
 - Working range → linear between 2 and 100 ng/tube
 - Trueness (bias, recovery) → ≤ 4 %
 - Precision (repeatability, intermediate precision and reproducibility) → ≤ 4 %
 - Ruggedness (robustness) → no effects of flow and pressure during sampling of the tubes
- Measurement uncertainty

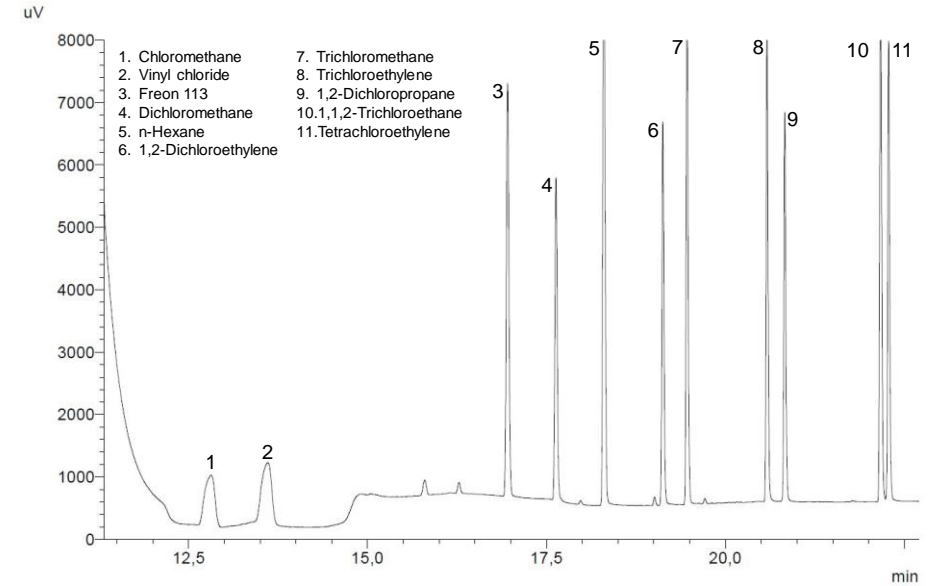
	U (%) samples on Tenax TA	U (%) samples on Tenax TA/Carboxen 1003/ Carbograph 1
Chloroform	11	8
Dichloromethane	32	13
Tetrachloroethylene	10	8

Method 2 – direct analysis

- ATD-GC-FID/MSD

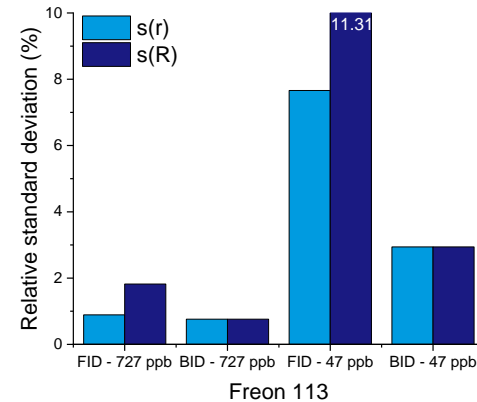
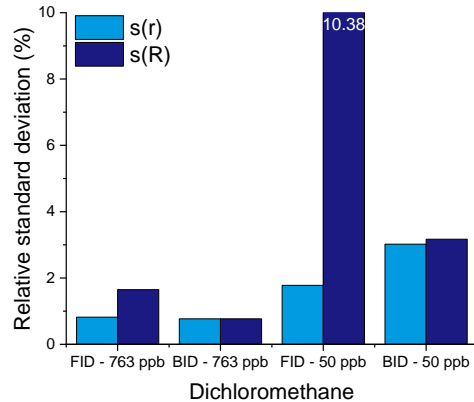
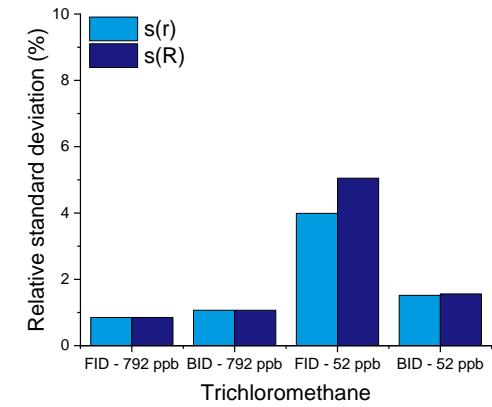
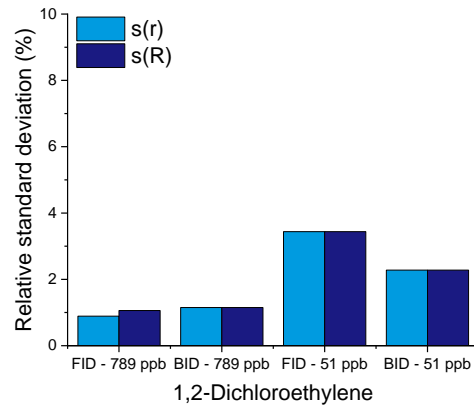
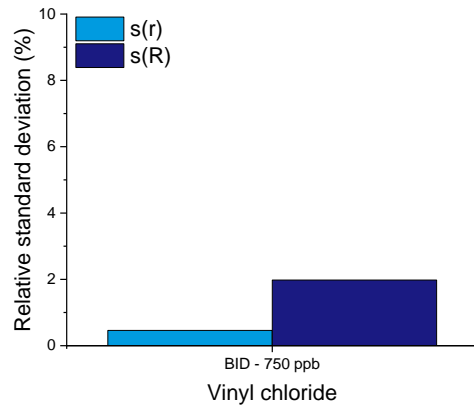


- GC-BID



Method 2 – direct analysis

- Repeatability (s(r)) and reproducibility (s(R)) standard deviation from the analysis of the halogenated VOCs in methane at approximately 750 ppb and 50 ppb
- ANOVA calculations according to ISO 5725-2



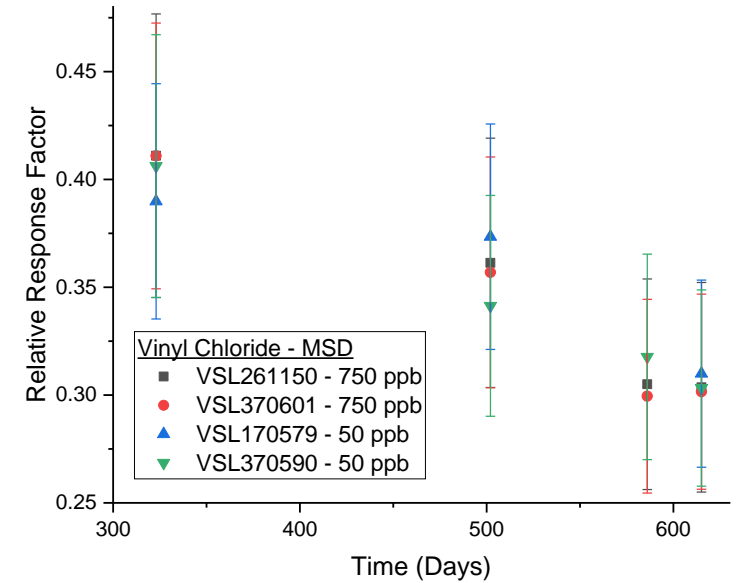
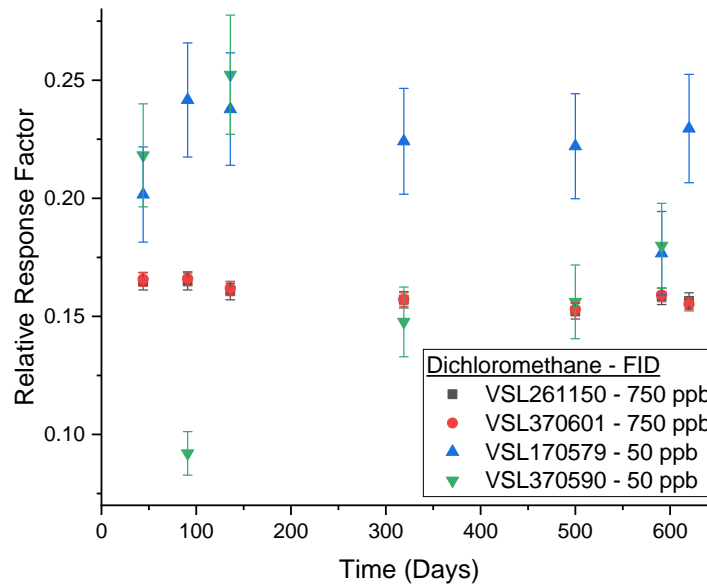
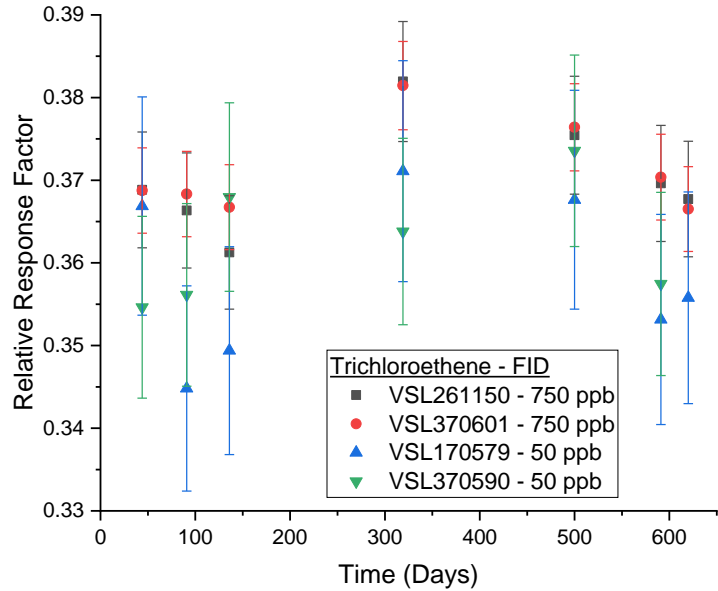
Method 2 – direct analysis

Measurement uncertainty ($k = 1$)

- ATD-GC-MSD
 - 6 % - 18 %
- ATD-GC-FID
 - 750 ppb → 1.0 % - 2.5 %
 - 50 ppb → 1.6% - 10 %
- GC-BID
 - 750 ppb → 0.8 % - 2.0 %
 - 50 ppb → 1.6 % - 3.2 %



Stability halogenated VOC measurement standard



Using sorbent tubes

- Measurement uncertainty $\leq 13\%$ ($k = 2$)

Direct analysis

- With preconcentration $\leq 20\%$ ($k = 2$)
- Without preconcentration $\leq 6\%$ ($k = 2$)