VSL

National Metrology Institute

Metrology for biomethane conformity assessment

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EMN Energy Gases Workshop “Measurement Solutions for Energy Gases”

21-22 March 2023, IPQ, Monte de Caparica, Portugal

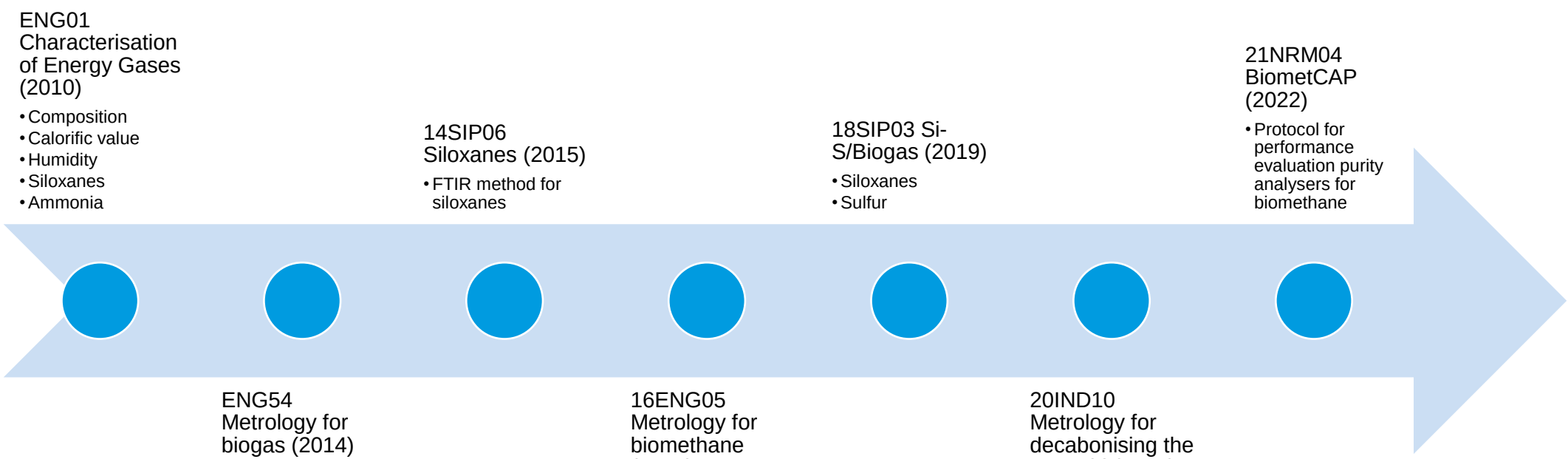
Biomethane

- “biogas, upgraded to natural gas quality”
- Direct renewable substitute for natural gas, unlike hydrogen (which requires many more adaptations)
- Specification (EN 16723) developed, for
  1. Injection into the natural gas grid (2016)
  2. Use at refuelling stations (2017)
- Specification supplements EN 16726 for high-calorific natural gas

Rationale

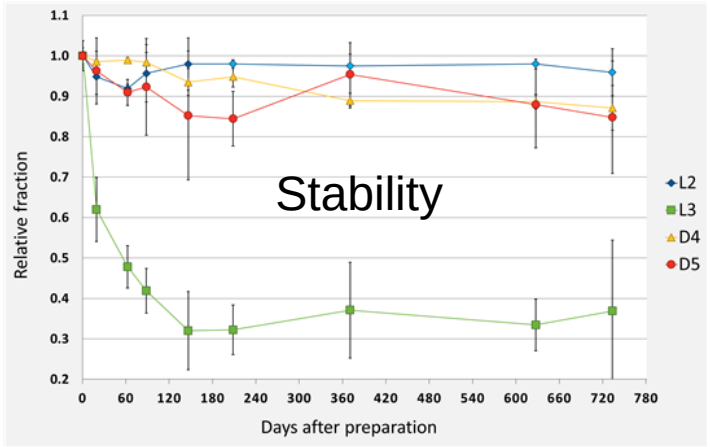
- Urgent need to diversify the supply of natural gas
  - Environmental (carbon dioxide emission reduction)
  - Economical (EU resources for natural gas are declining)
  - Geopolitical (lesser dependence on imported gas)
- Biomethane and upgraded biogas and need to fulfil certain criteria to be compatible with appliances of end users (households, industry)
- Demonstrating conformity requires
  - Setting criteria
  - Reliable measurement methods
  - Measurement standards and certified reference materials
  - Laboratories with competence in determining properties of biomethane and biogas
  - Conformity assessment

EURAMET's response to the introduction of biomethane

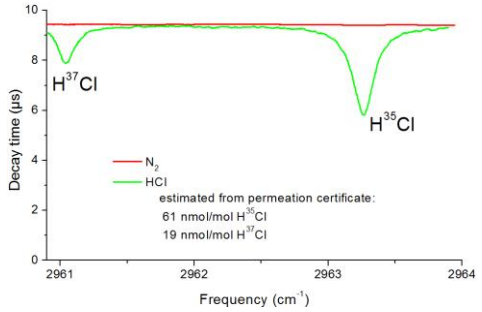


What were (are) the challenges?

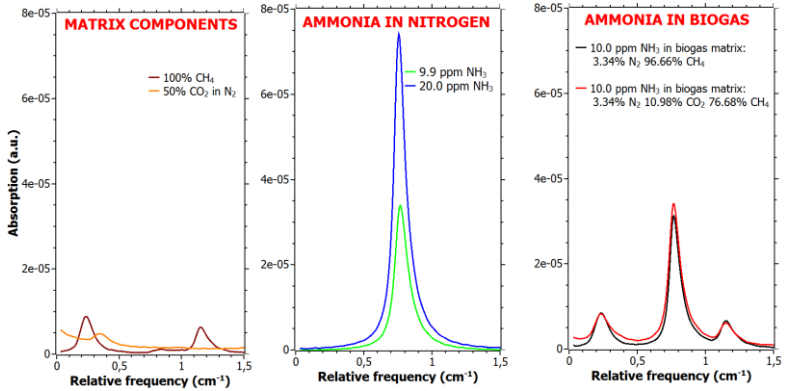
Stability



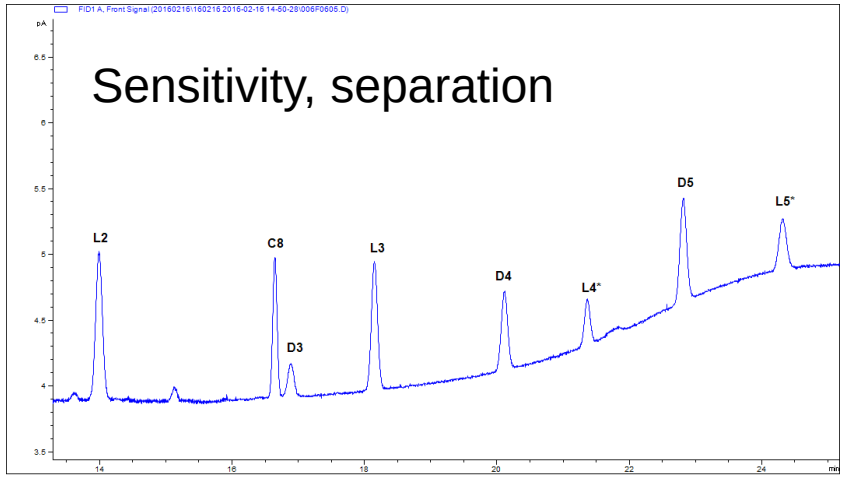
Isotopic composition



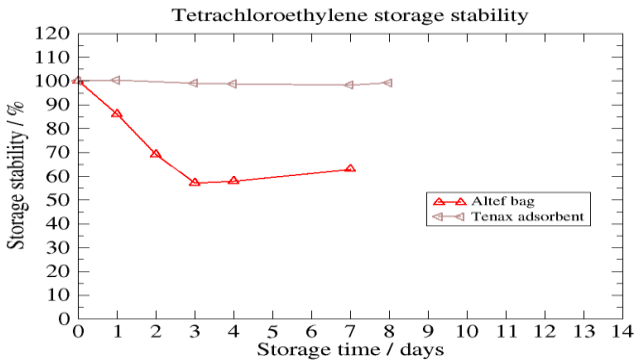
Spectral interferences

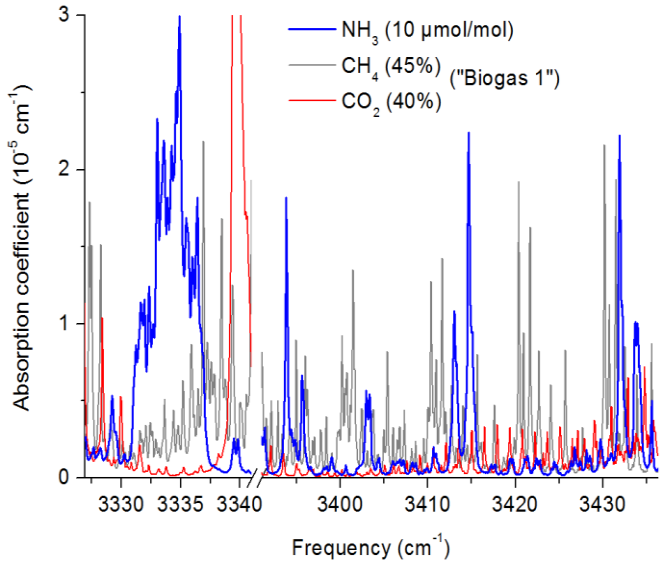


Sensitivity, separation



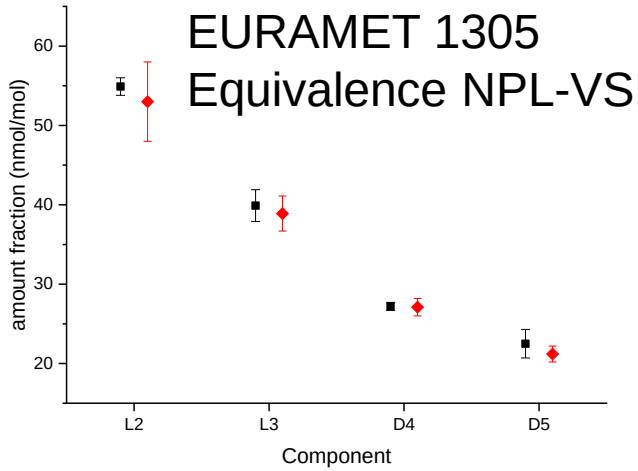
Sampling

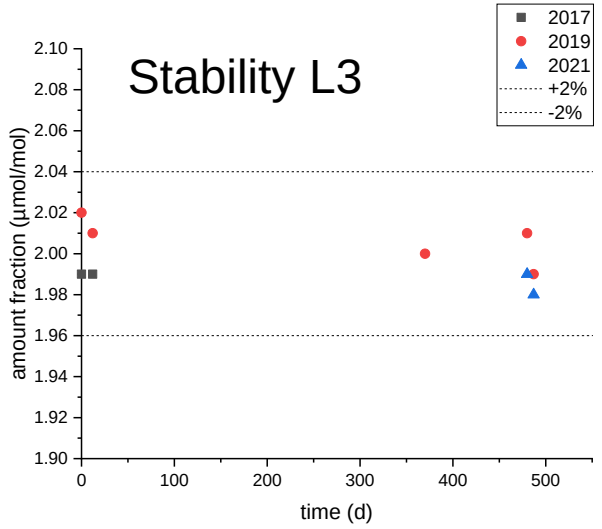




Siloxanes and silicon content

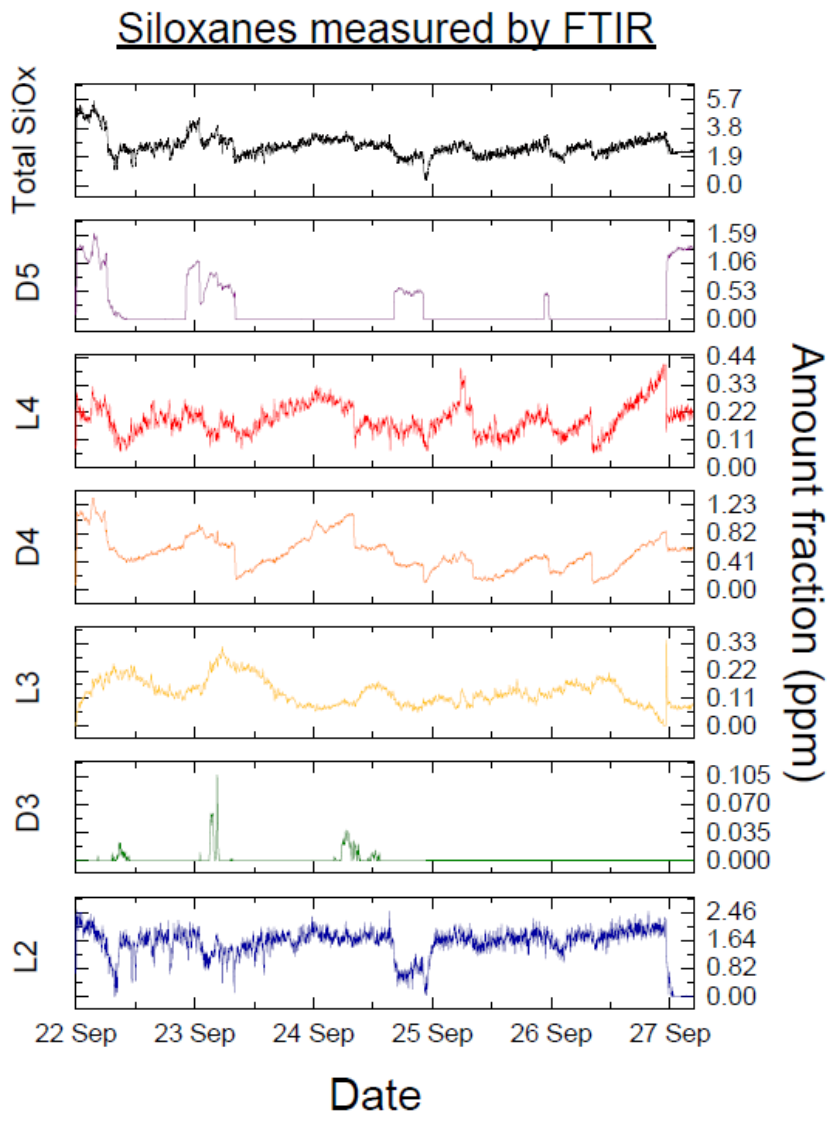
- Methods developed for
  - Total silicon content (ICP-AES, GC-ICP-MS)
  - Siloxane content (GC-MS, TD-GC-MS/FID, GC-FID, GC-TOF-MS)
- Repeatability and reproducibility of methods acceptable
- Gravimetrically prepared gas mixtures
  - Down to levels relevant for the biomethane specification
  - Successful introduction of a solid (D3)
  - Initial losses substantial (between -5% down to -70%)
- Proficiency tests organised with SI-traceable reference values





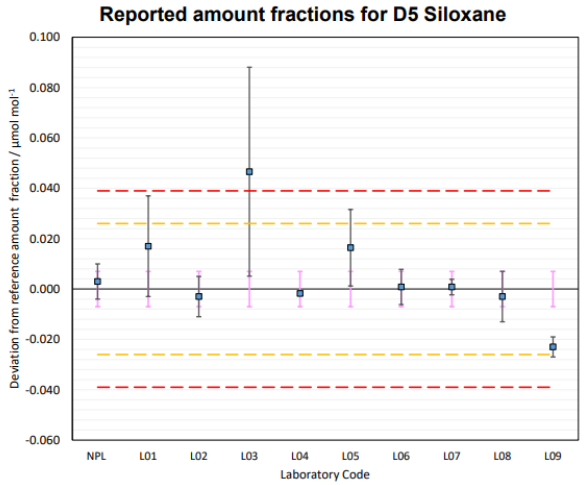
EMPIR 14SIP06 Siloxanes

- Comparison of on-line and laboratory based measurement of siloxanes in biogas.
- Laboratory-based method validation using traceable gas reference standards
- Results showed it was possible to achieve live monitoring of siloxanes breakthrough in filters to with 5% uncertainty

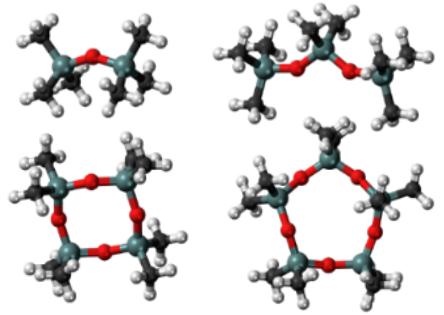


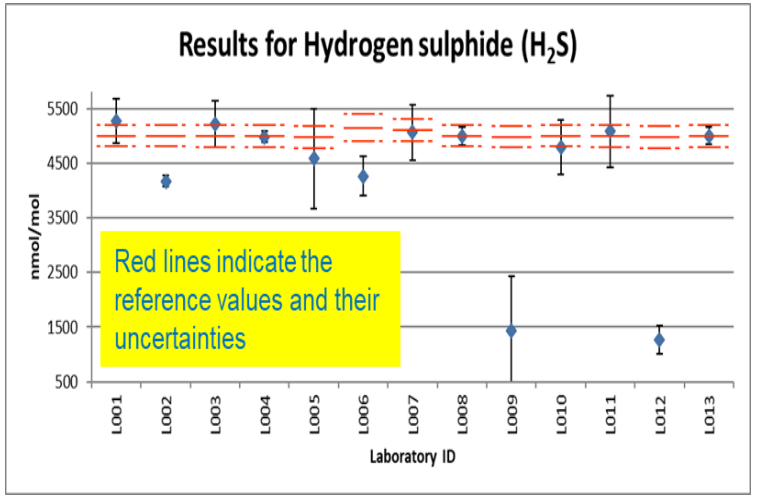
Interlaboratory comparisons on siloxanes and sulfur (18SIP03)

- Different labs with different calibration, sampling and measurement methods contributed to the comparisons
- Generally good agreement between participants
- Traceable and stable gas mixtures are important for a successful comparison. Pay attention to instability due to reactions, adsorptions, etc.

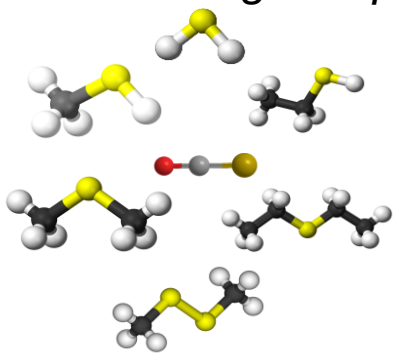


Siloxanes



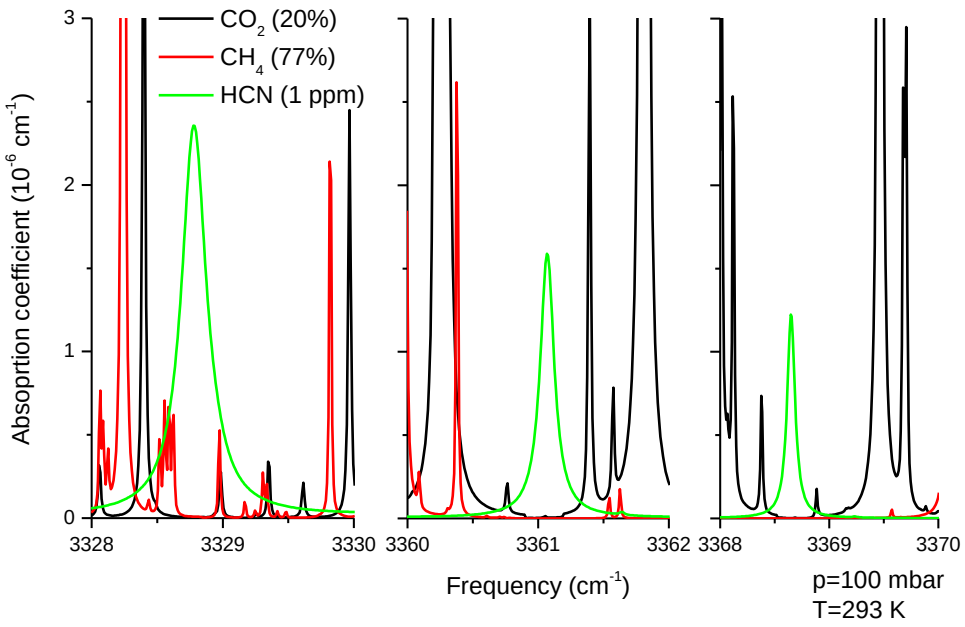


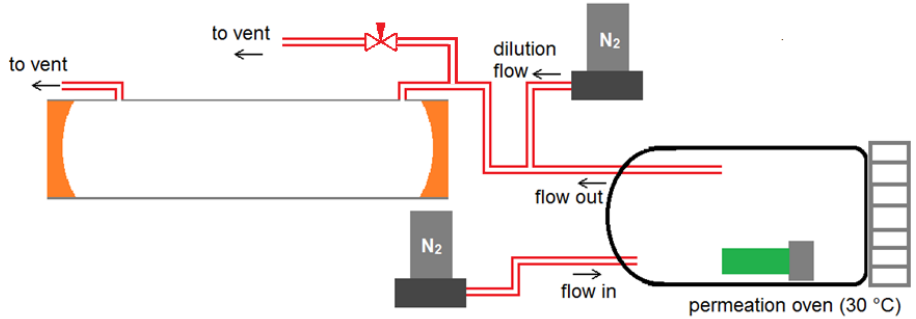
S-containing comp.



Hydrogen cyanide content

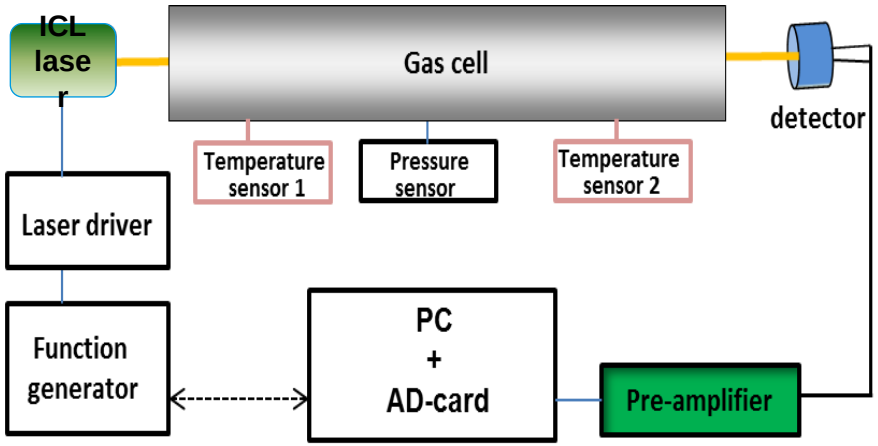
- Method developed based on CRDS
- Gas mixture preparation using permeation method (ISO 6145-10)
- Some issues with current implementation of the gas mixture preparation method
  - Temperature stability of the oven
  - Manual weighing of the tube
  - Dilution system using mass flow controllers
- Detection limit in the low-ppb range, even for a biomethane matrix

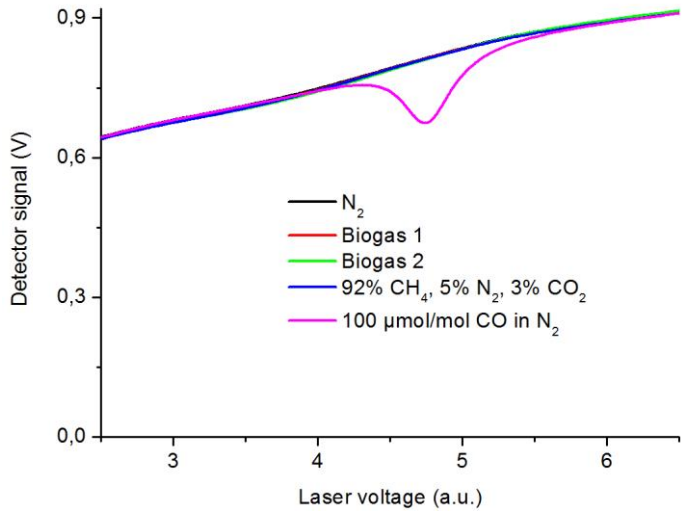


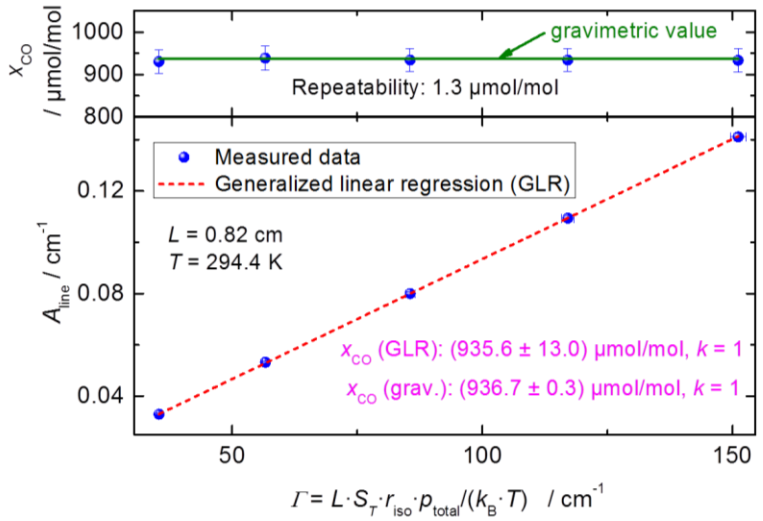


Carbon monoxide content

- Development of static reference gas mixtures unproblematic down to the ppm level
- GC/TCD and GC-FID(Nicat) methods developed for high- and low ranges
- Laser adsorption method developed, with little effect of the biogas/biomethane matrix
- Portable analyser developed for CO, CH_4 and HCl

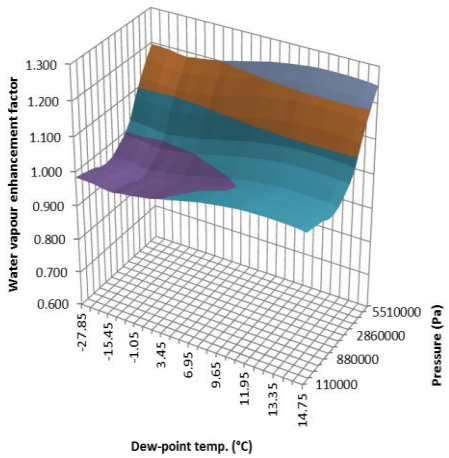


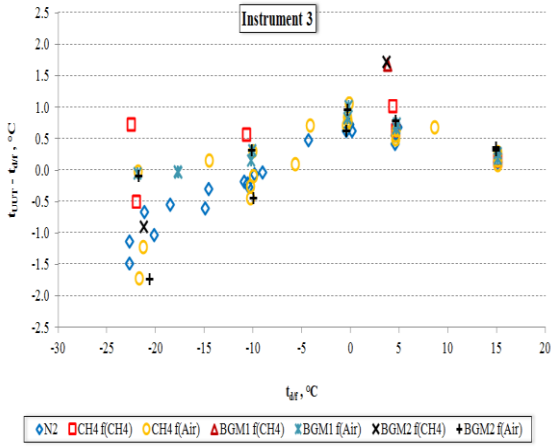




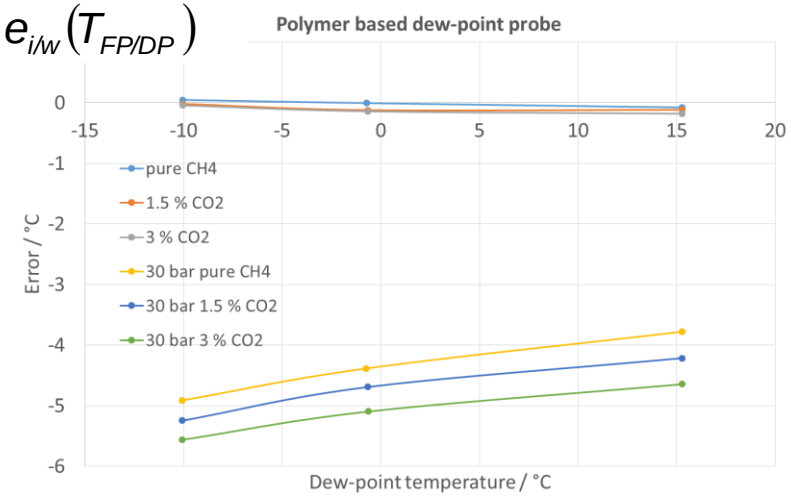
Moisture content

- Facilities for water dewpoint measurement further developed to measure water enhancement factor
- First results confirm models for natural gas for biomethane compositions
- Several common moisture sensors assessed for matrix and pressure sensitivity
- Best practice guide developed



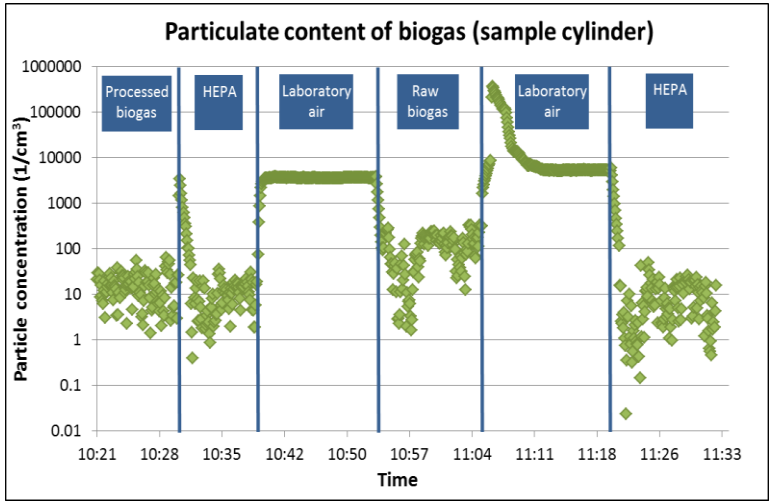


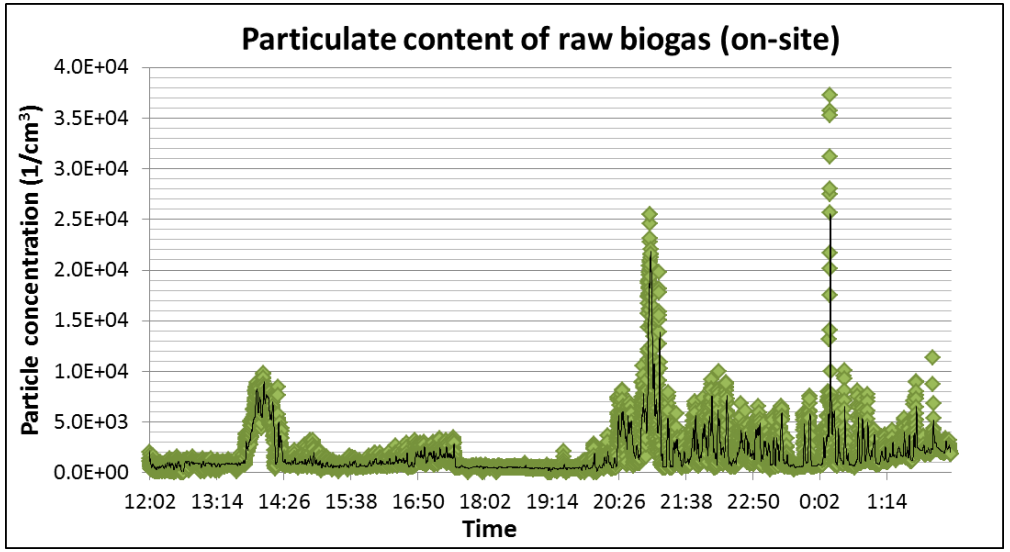
$$f(p,T_{FP/DP}) = \frac{x_{i/w} \cdot p}{e_{i/w}(T_{FP/DP})}$$

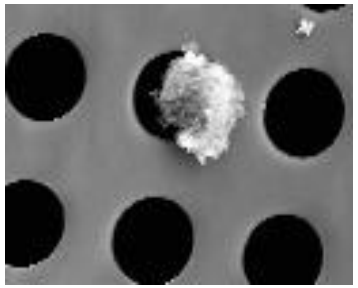


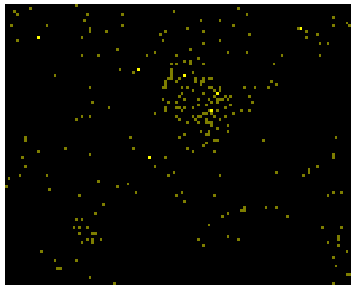
Particulate content

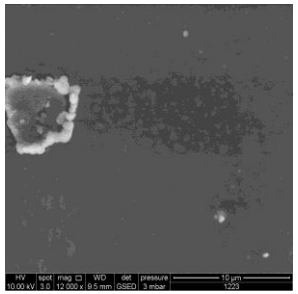
- Method developed for measuring particulate concentration in biomethane and biogas
- Offsite analysis of particulate concentration not feasible (particles stick to the walls of the sample collection vessel)
- Particulate concentration generally lower than in indoor air
- Recommendation developed for measuring particulate concentration and offered to standardisation





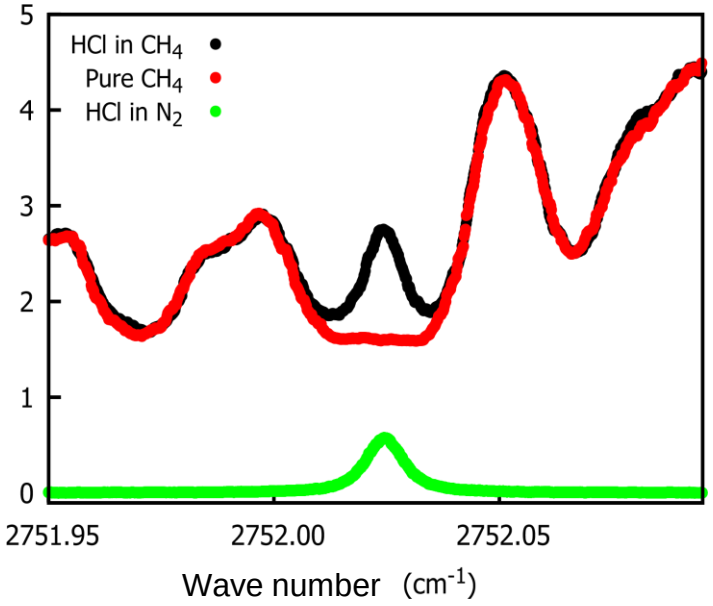


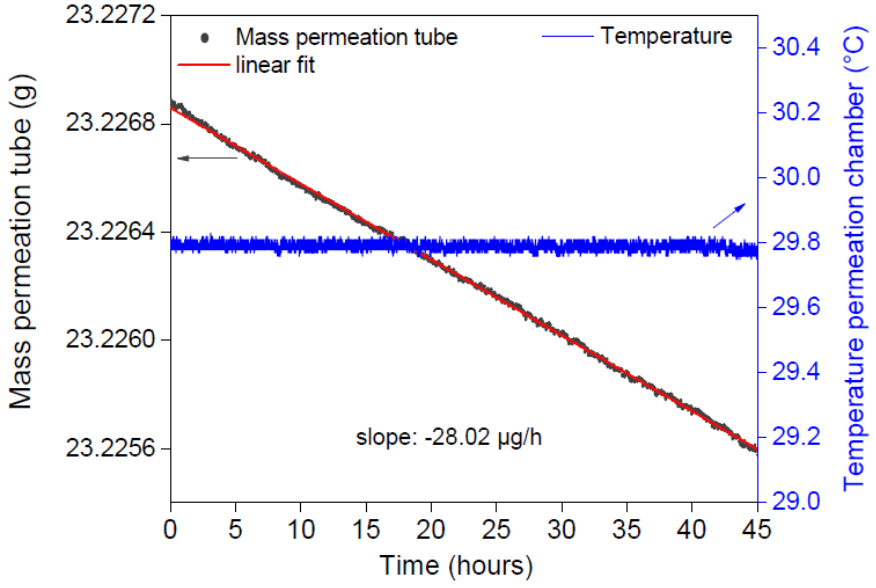


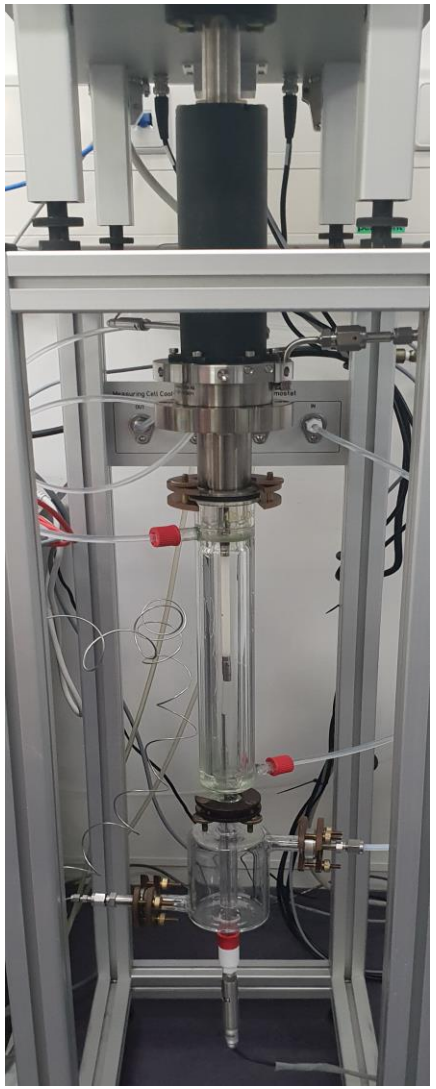


Gas standards and test methods for HCl

- Dynamic gas standards: permeation method using magnetic suspension balance
- Test method using CRDS improved but still suffers from matrix interference
- Dedicated direct absorption (DDA) method on-going
- Target relative expanded uncertainty (3 %)



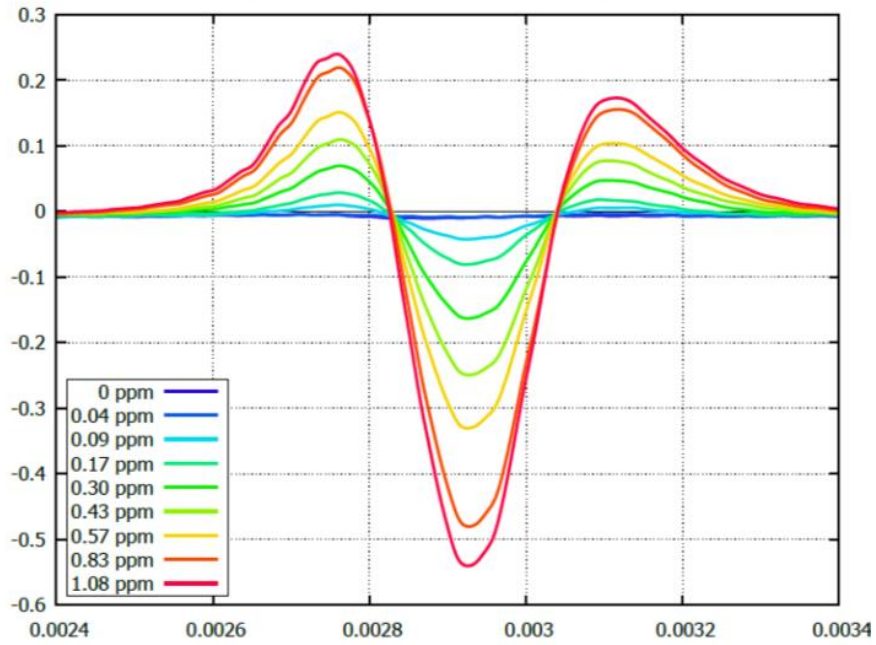




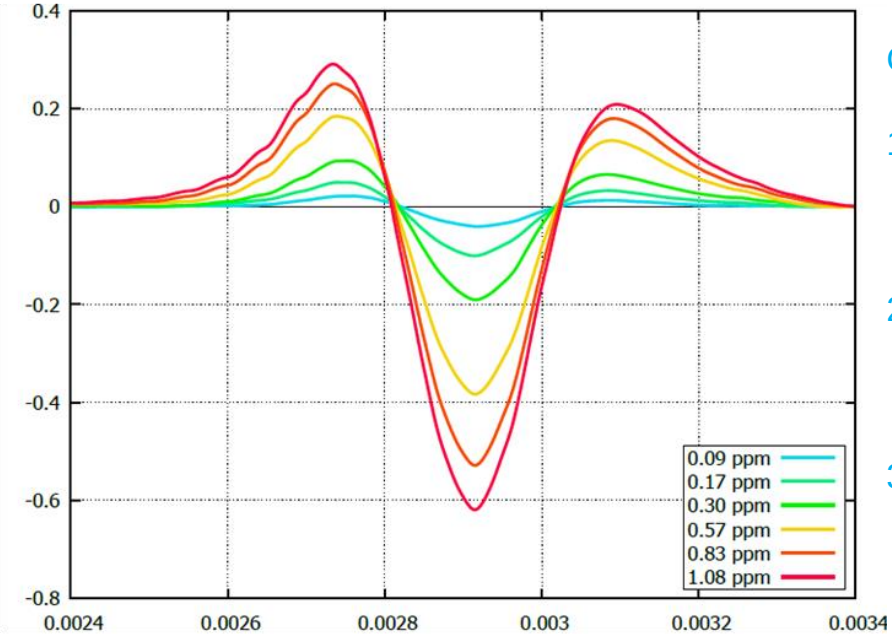
Gas standards and test methods for HF

- Dynamic gas standards: permeation method using magnetic suspension balance
- Test method using direct absorption and wavelength modulation spectroscopy
- Target relative expanded uncertainty (10 %)

HF in N_2 matrix



HF in CH_4 matrix (CH_4 background subtracted)

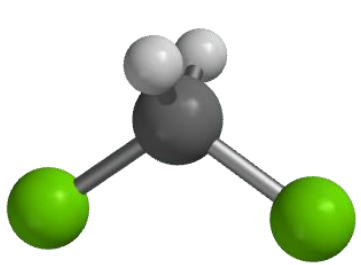


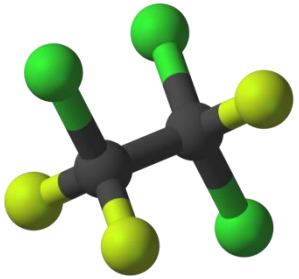
Conclusions:

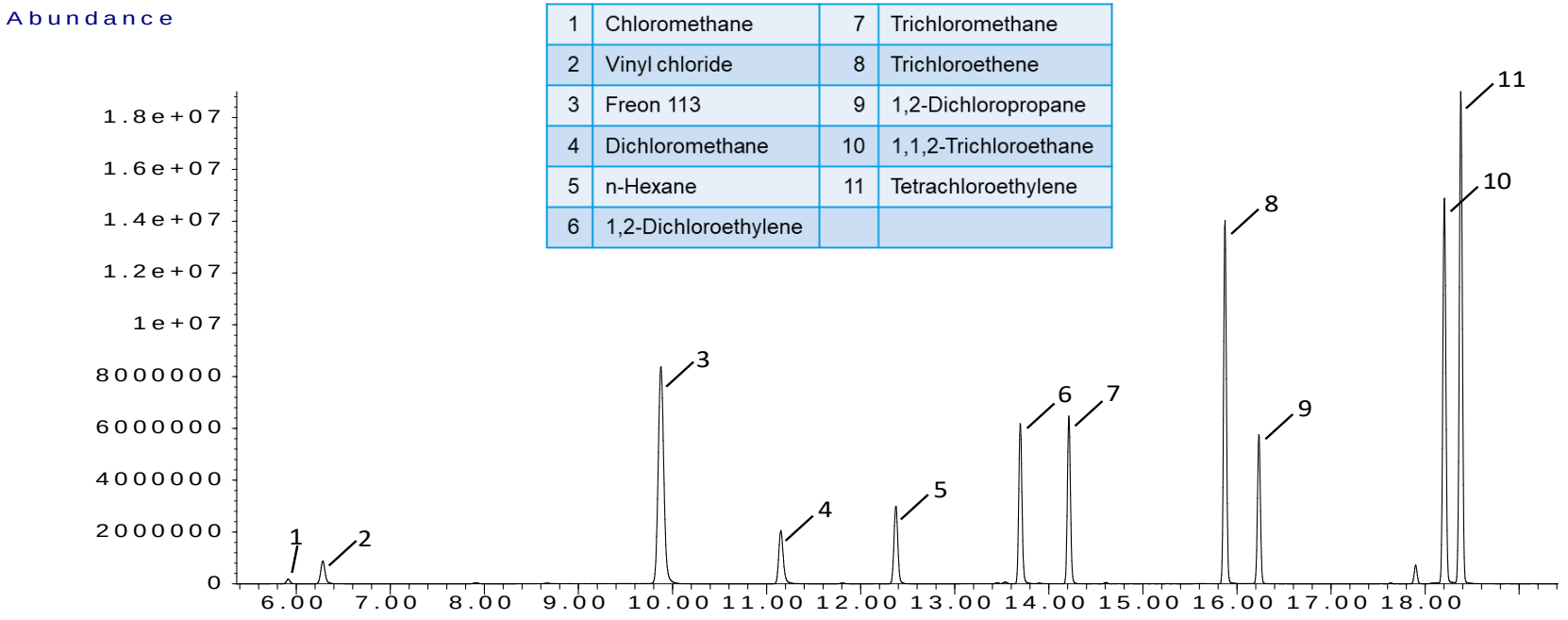
1. HF in CH_4 can be analyzed in the ppb and lower ppm range
2. Interference by CH_4 is relatively low at a cell pressure of 100 mbar
3. Coated materials are used due to highly reactive nature of HF

Gas standards and test methods for halogenated VOCs

- Static gas standards developed
  - 50 nmol/mol
- Test method using GC-FID/MS developed
- Long-term stability on-going
- Target relative expanded uncertainty (3 %)





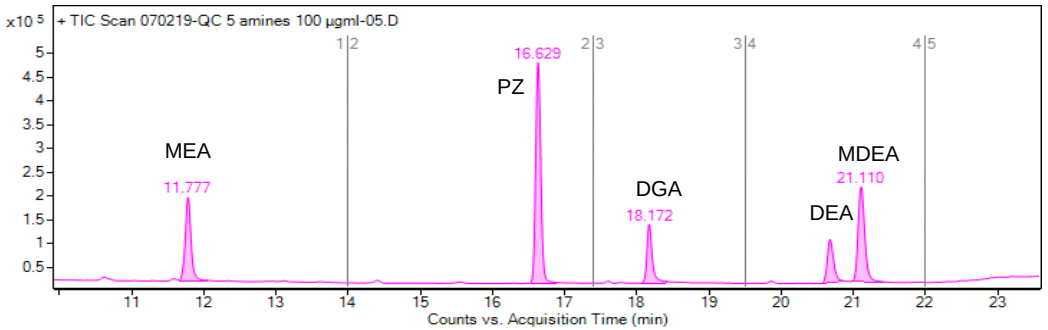


1	Chloromethane	7	Trichloromethane
2	Vinyl chloride	8	Trichloroethene
3	Freon 113	9	1,2-Dichloropropane
4	Dichloromethane	10	1,1,2-Trichloroethane
5	n-Hexane	11	Tetrachloroethylene
6	1,2-Dichloroethylene		

Compound	Stdev (%)
Vinyl chloride	0.5
Chloromethane	0.6
Freon 113	0.4
Dichloromethane	0.3
n-Hexane	0.3
1,2-dichloroethylene	0.5
Trichloromethane	0.7
Trichloroethene	0.4
1,2-dichloropropane	0.3
1,1,2-trichloroethane	0.4
Tetrachloroethylene	0.4

Gas standards and test methods for alkanolamines

- Used for biogas upgrading into biomethane (to remove H_2S, COS and CO_2)
- Due to low vapor pressure and high viscosity of some selected amines, gas mixtures are not prepared in cylinders
- Instead, five amines are spiked on sorbent tubes
  - Methyldiethanolamine (MDEA)
  - Diethanolamine (DEA)
  - Monoethanolamine (MEA)
  - Piperazine (PZ)
  - Diglycolamine (DGA)
- Method using TD-GC-MS/FID
- Acceptable repeatability and reproducibility

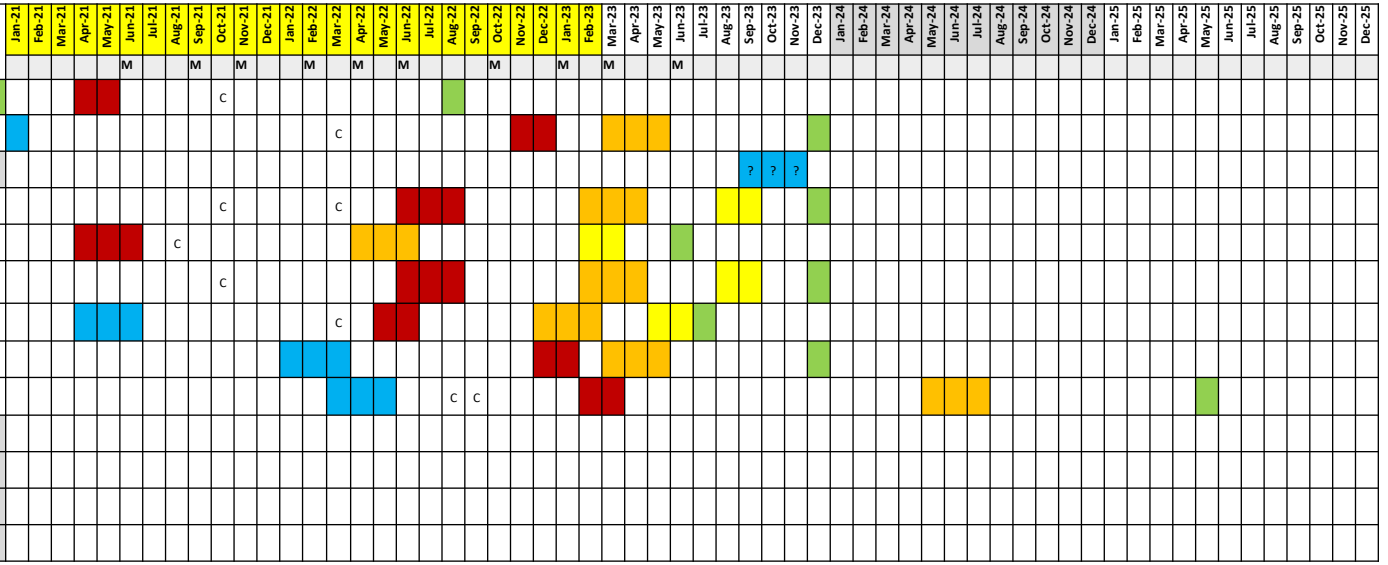


Standardisation

- Much of the work done in the EURAMET projects is taken up in standardisation
- Key committees:
  - CEN/TC408 Biomethane → specifications
  - ISO/TC193/SC1/WG25 Biomethane → test methods
  - ISO/TC193/SC1/WG20 Sampling
- State of play:
  - EN 16723 underwent a systematic review and will be updated
  - First generation of dedicated test methods well underway

Standardisation of methods (ISO/TC193/SC1/WG25)

Number	Title/subject	SDT	Status
ISO/DTS 2610	Analysis of natural gas - Biomethane — Determination of amines content	24	published
ISO/CD 2611-1	Analysis of natural gas — Biomethane determination of halogenated compounds — Part 1: HCl and HF content by ion chromatography	36	registered
ISO/NWIP 2611-2	Analysis of natural gas – Biomethane - Measurement of halogenated VOCs		not yet circulated
ISO/DIS 2612	Analysis of natural gas — Biomethane - Determination of ammonia content by Tuneable Diode Laser Absorption Spectroscopy	36	registered
ISO/FDIS 2613-1	Analysis of natural gas — Silicon content of biomethane — Part 1: Determination of total silicon content by AES	36	registered
ISO/DIS 2613-2	Analysis of natural gas — Silicon content of biomethane — Part 2: Determination of siloxane content by Gas Chromatography Ion Mobility Spectrometry	36	registered
ISO/CD 2614	Analysis of natural gas — Biomethane — Determination of terpenes' content by micro gas chromatography	24	registered
ISO/CD 2615	Analysis of natural gas — Biomethane — Determination of the content of compressor oil	24	registered
ISO/CD 2620	Analysis of natural gas — Biomethane — Determination of VOCs by thermal desorption gas chromatography with flame ionization and/or mass spectrometry detectors	36	registered
	Analysis of natural gas – Determination of the biogenic carbonfraction - Radiocarbon (14C) method		not yet circulated
	Carbon monoxide content		not yet circulated
	Particulates' content		not yet circulated
	Ketones		not yet circulated



Concluding remarks

- EURAMET has responded adequately to the introduction of biomethane
- A measurement infrastructure has been established, covering
  - Calibration
  - Analysis
  - Physical properties (calorific value, density etc.)
  - Sampling
- Input provided to CEN/TC408, ISO/TC193/SC1/WG20 (Sampling) and …/WG25
- EMN Energy Gases lists many of the services developed by the NMIs/DIs
- Basis for CCQM-K112 Composition of biogas

Acknowledgements

Coordinators, WP leads and partners in the named projects

Members of ISO/TC193/SC1 and the experts in ISO/TC193/SC1/WG20 and /WG25

Got interested? Contact me at avdveen@vsl.nl

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European Metrology Research Programme
Programme of EURAMET

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EMPIR EURAMET

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