EMN for Energy Gases

Annarita Baldan, VSL

ENERGY GASES

METCCUS

VSL

MET4H2

BiometCAP

Working together with the EMN for Energy Gases

Annarita Baldan
Chair of the EMN for Energy Gases

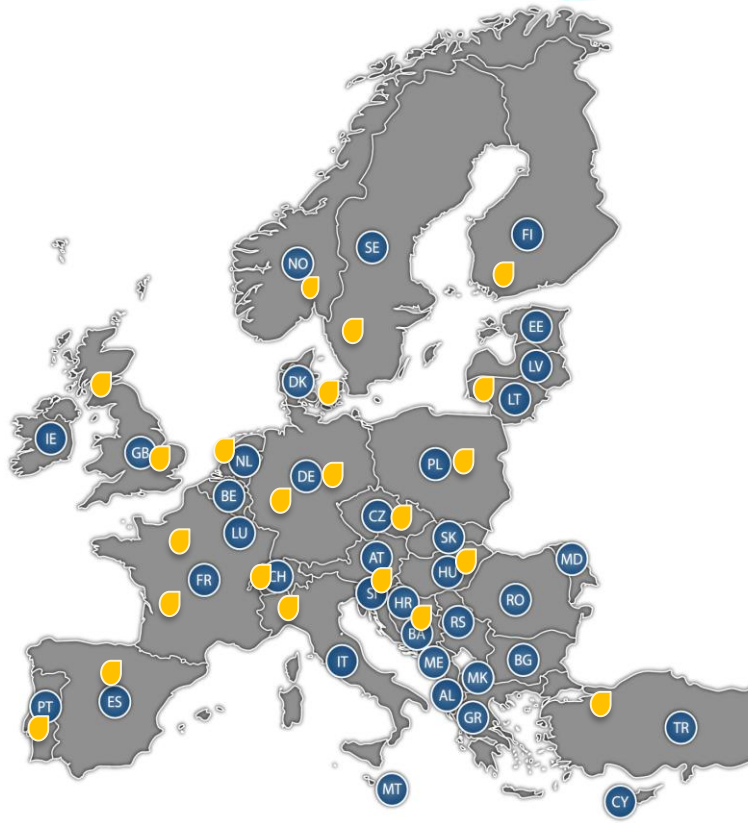
26 March 2025
EMN joint workshop

ENERGY GASES

Organisation

- Part of EURAMET
- 21 NMI/DI members and 1 Partner
- Focus on metering and use of energy gases: conventional fluids and fluids related to (emerging) renewable/ sustainable energy sources, including CCUS

"Improving reliability in the measurement of energy gases"



ENERGY GASES

EMN for Energy Gases Fact Sheet

- **Engage** with industry, regulation, standardization, policy (e.g. HE/HER, GERG, MARCOGAZ, DG Energy, CEN/CENELEC, ISO)
- **Act** as **European metrology knowledge center** for energy gases
- **Facilitate energy transition** by coordinating measurement research based on stakeholder needs
- **Boost access** to metrological services and calibration facilities

Cross-cutting character:

Methods & physical standards	
Chemical composition	**Humidity**
Flow	**Particles**
Pressure, Temperature, Density	**Material data & Material testing**
Calorimetry	**Leakage and emission measurements**

www.euramet.org/energy-gases

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Service platform

A freely accessible online measurement service platform regrouping metrological services in the energy gases field is available on the website: www.euramet.org/european-metrology-networks/energy-gases/service

The platform advertises all measurement and calibration services, including those developed in the EMRP and EMPIR Programmes and has for objective to help the industry to easily find the right measurement service or proficiency testing scheme.

- Training courses
- Sampling (for gas analysis)
- Interlaboratory comparisons
- Speed of sound
- Material data
- Material testing
- Calorimetry
- Density (direct)
- Flow
- Certified Reference Materials
- Gas analysis
- Humidity
- Temperature
- Flow

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Service platform

Search for a service

Choose what you want to see on the map:

Gases

- CO2
- Hydrogen
- H2NG
- Biogas / Biomethane
- LNG/LBG
- Natural Gas

Services

- Training courses
- Sampling for gas analysis
- Interlaboratory comparisons
- Speed of sound
- Material data
- Material testing
- Calorimetry
- Density (direct)
- Flow
- CRM
- Gas Analysis
- Humidity
- Temperature

20 Ergebnisse

List with filter

All gases | All services | All sub services | Individual service

Filters

Interactive map

Three methods to find services

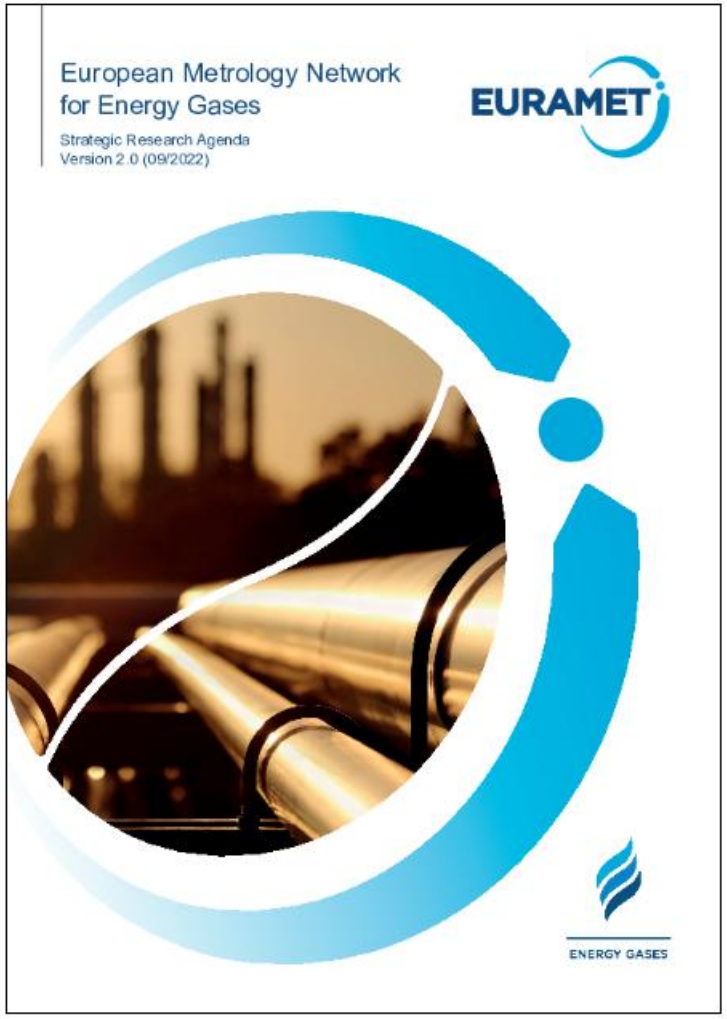
A table for each institute

Services / Gases	CO2	Hydrogen	H2NG	Biogas / Biomethane	LNG/LBG	Natural Gas
+ Training courses						
+ Sampling for gas analysis	✓	✓	✓	✓	✓	✓
+ Interlaboratory comparisons						
› Speed of sound						
› Material data				✓		
+ Material testing						
+ Calorimetry						
› Density (direct)						
+ Flow						
+ CRM						
+ Gas Analysis	✓	✓	✓	✓	✓	✓
+ Humidity						
› Temperature						

ENERGY GASES

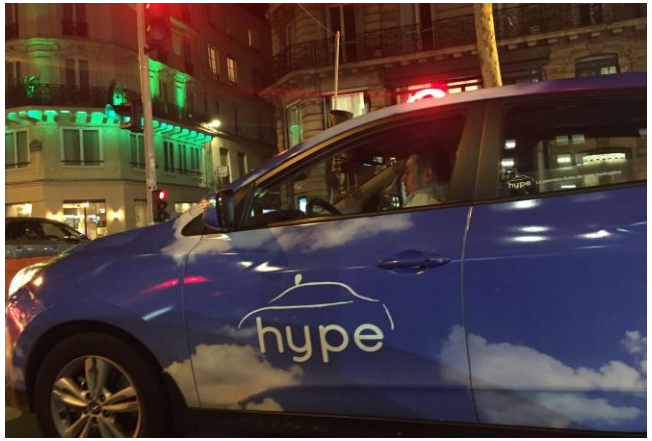
EMN Strategic Research Agenda

- Developed in collaboration with stakeholders and revised regularly
- Focused on measurement needs covering:
  - Energy gases value chain (natural gas, LNG and LBG, biogas and biomethane, hydrogen, energy carriers (e.g. NH_3))
  - CCUS (CO_2)
- Focus application areas
  - **Decarbonising natural gas**
  - **Decarbonising industry**
  - **Energy transport and storage**
  - **Cleaner fuel for mobility**
- Objective:
  - **Collaborate with industry and other research parties**
  - **Facilitate new projects in Research & Innovation**



Available at
https://www.euramet.org/european-metrology-networks/energy-gases/strategy/strategic-research-agenda

European Metrological Research in Energy Gases – Portfolio of more than 20 projects



GAS
MultiFlowMet

NEWGASMET
Decarb
MetCCUS
MaritimeMET

LNG
I, II, III

EMRP/EMPIR/
EPM
2010 - 2024

MetHyInfra
Met4H2
MetHyTrucks
H2FlowTrace

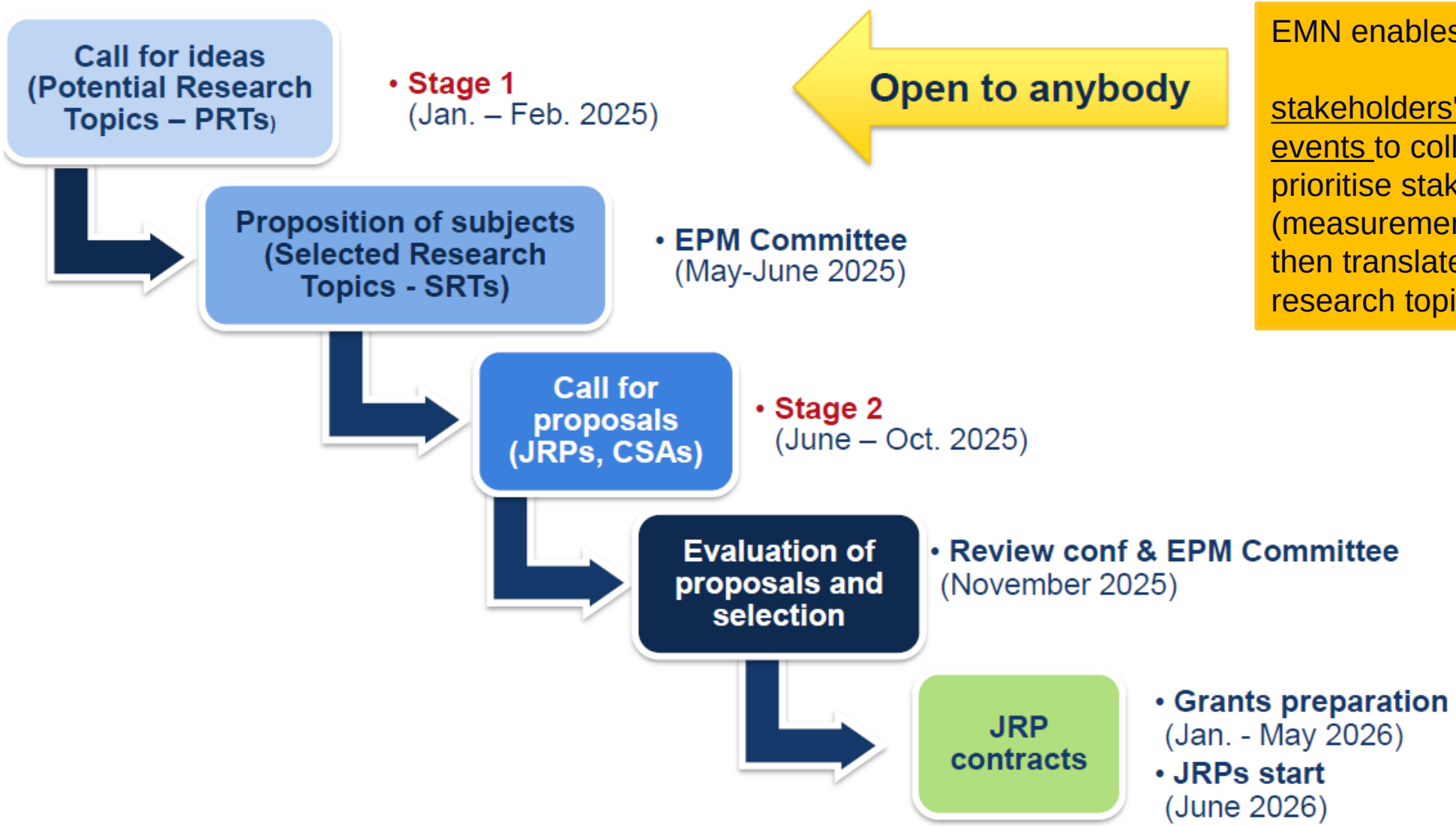
BIOGAS
BIO-
METHANE
Si-S/Biogas
BiometCAP

HYDROGEN
MetroHyVe 1,
2
MefHySto

European Partnership on Metrology

- Metrology, the science of measurement, is a building block for an industrialised and increasingly globalised and digital society: Reliable measurements are essential for innovation in industry, research, trade and regulation
- Bring together the measurement science community and stakeholders to deliver on global challenges including health and climate, support the European Green Deal, and underpin innovation in industry through collaborative research
- Co-funded by Member States and the European Union
- **https://www.metpart.eu**

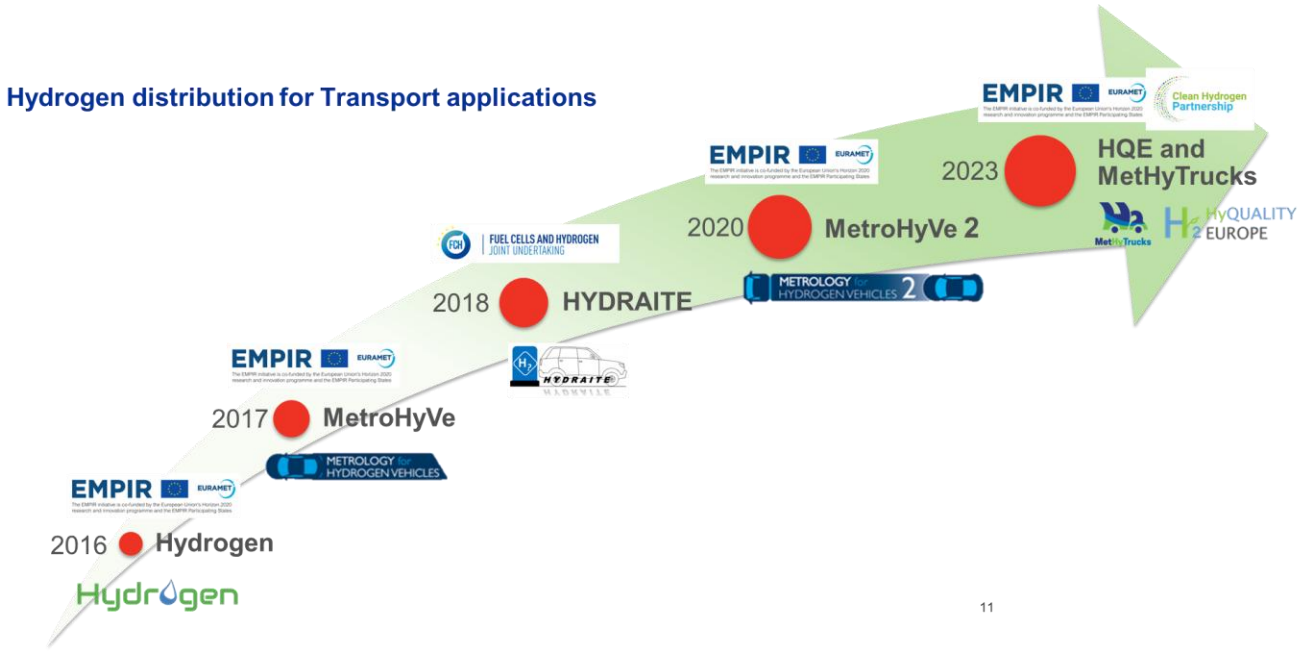
The Metrology Partnership call process

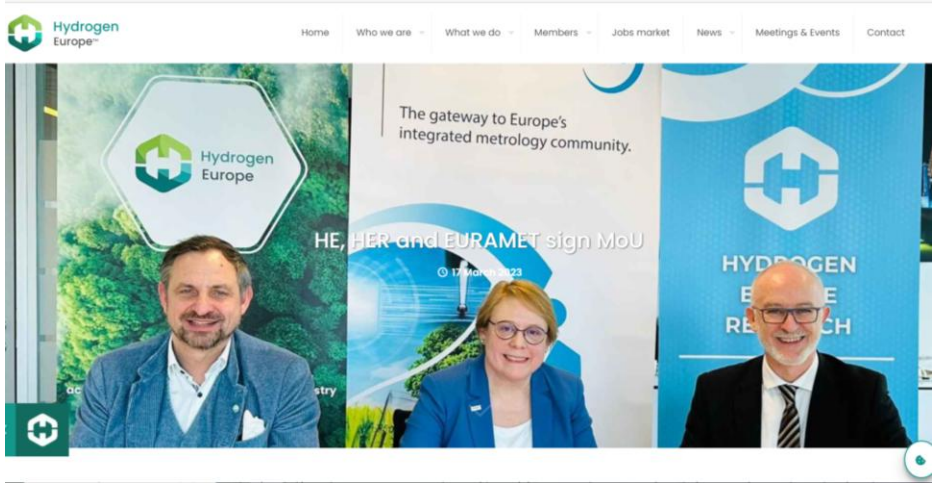


EMN enables this stage by:

stakeholders' brainstorms and events to collect and to prioritise stakeholders (measurement) needs to be then translated into proposed research topics

Example of cooperation with Hydrogen Europe and Hydrogen Europe Research associations





MoU HE/HER/EURAMET signed in March 2023

- Organisation of annual brainstorming sessions
- Feed measurement needs into Potential Research Topics
- Support in Potential Research Topics applications

Support to Standardisation

- Contribution to the European Clean Hydrogen Alliance Standardisation Roadmap (published in March 2023)

Topic	Measurement - challenge	Rationale
- Non-conventional gas injected in grid - H2NG	• Traceable standards for flow metering • Determination of calorific value (and gas composition) • Online measurement of hydrogen	Injection of hydrogen and gases in variable amount/composition in the gas grid need to be monitored → safety, trade and billing
Hydrogen for transport/mobility	• High pressure mass flow metering for vehicles at HRS (light and heavy duty/maritime)	Comply with regulation (e.g. OIML R139)
Hydrogen quality along supply chain	• Inline hydrogen analyser/sensor with suitable high sensitivity for impurities • Gas reference materials and intercomparisons • Validated online analysers • Validated sampling methods	Guarantee safety, quality and sample integrity in offline/online measurement techniques to measure hydrogen quality and guarantee comparability → support to testing laboratories
Quality control and quality assurance (fuel cells, electrolysers, material compatibility)	• Novel measurement and modelling techniques for characterisation of performance • Online techniques for real-time quality control of manufactured components	Support to development of next generation materials for industry → Innovation
Energy gases quality assurance (hydrogen, liquified hydrogen, LOHC)	• Validated temperature and pressure measuring equipment • Validated flow meters	Guarantee reliability and robustness of quantitative measurements along the hydrogen supply chain from import/production to end use → support to industry/trade/billing
Hydrogen leakage and release	• Detection/quantification/modelling • Testing and modelling pipeline corrosion	Prevent or monitor leaks for hydrogen manufacturing and transport/ storage and release in the atmosphere as indirect GHG gas. Understanding how pipeline materials behave with different gas composition/conditions, for safety and to prevent leaks
Hydrogen odorisation	• Odorants measurement methods	Evaluate the impact of odorant in hydrogen applications (fuel cell/ pipeline transport)

European Clean Hydrogen Alliance

ROADMAP ON HYDROGEN STANDARDISATION

Example of R&D in support of standardisation:

H2FlowTrace project (2024)

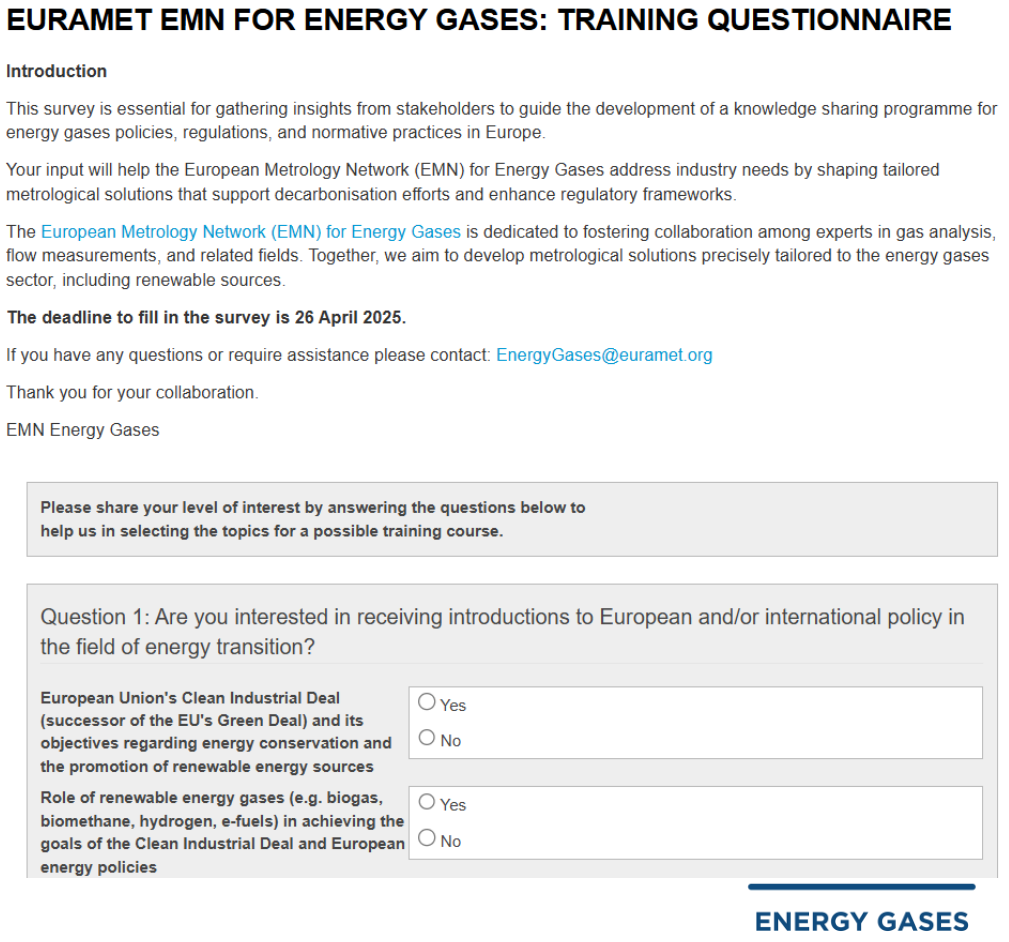
H2FLOWTRACE

in support of CEN TC234 and CEN TC237 request for pre-normative work

We need your help! Survey launched

- Goal: **organise an online and/or on-site training on energy gases**
- Define the training topics and priorities based on stakeholder needs:
  - Policy & Regulation, Standardisation, Metrology, etc.
  - Energy gases
  - Metrological aspects: high-accurate methods, calibration, traceability and uncertainty

- Link to the survey:
  https://www.euramet.org/european-metrology-networks/emn-energy-gases-training-questionnaire-2024



EURAMET EMN FOR ENERGY GASES: TRAINING QUESTIONNAIRE

Introduction

This survey is essential for gathering insights from stakeholders to guide the development of a knowledge sharing programme for energy gases policies, regulations, and normative practices in Europe.

Your input will help the European Metrology Network (EMN) for Energy Gases address industry needs by shaping tailored metrological solutions that support decarbonisation efforts and enhance regulatory frameworks.

The European Metrology Network (EMN) for Energy Gases is dedicated to fostering collaboration among experts in gas analysis, flow measurements, and related fields. Together, we aim to develop metrological solutions precisely tailored to the energy gases sector, including renewable sources.

The deadline to fill in the survey is 26 April 2025.

If you have any questions or require assistance please contact: EnergyGases@euramet.org

Thank you for your collaboration.

EMN Energy Gases

Please share your level of interest by answering the questions below to help us in selecting the topics for a possible training course.

Question 1: Are you interested in receiving introductions to European and/or international policy in the field of energy transition?

European Union's Clean Industrial Deal (successor of the EU's Green Deal) and its objectives regarding energy conservation and the promotion of renewable energy sources	○ Yes ○ No
Role of renewable energy gases (e.g. biogas, biomethane, hydrogen, e-fuels) in achieving the goals of the Clean Industrial Deal and European energy policies	○ Yes ○ No

ENERGY GASES

Thank you!
More info:

EnergyGases@euramet.org

a.baldan@vsl.nl

Website:

www.euramet.org/european-metrology-networks/energy-gases/

ENERGY GASES

MetCCUS achievements after 2.5 years

Iris de Krom, VSL

ENERGY GASES

METCCUS

VSL

MET4H2

BiometCAP

VSL

National Metrology Institute

Metrology Support for Carbon Capture Utilization and Storage

MetCCUS achievements after 2.5 years

Joint workshop EMN for Energy Gases

Iris de Krom

26 March 2025

VSL Delft, the Netherlands

METCCUS

Metrology support for CCUS

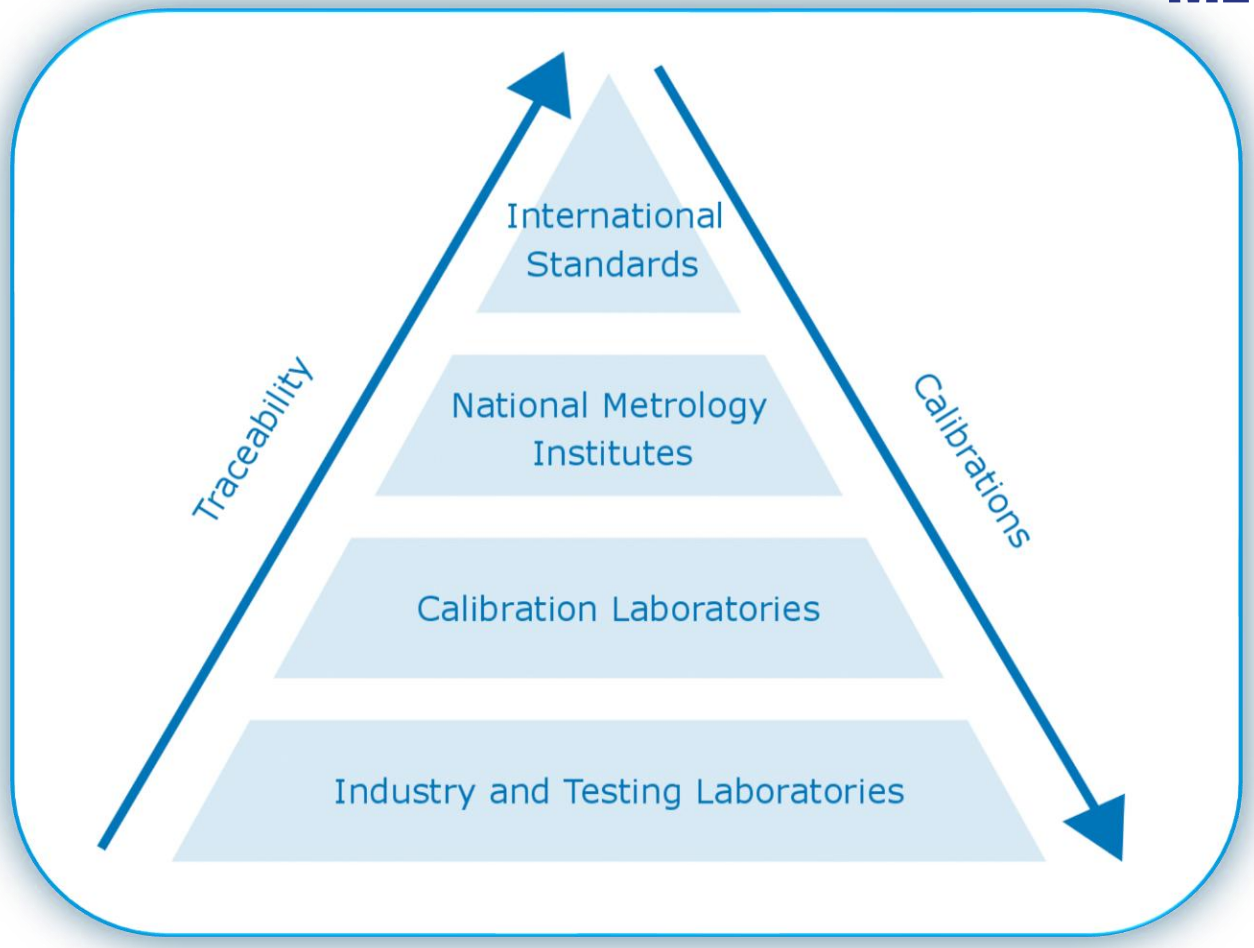
- 1 October 2022 – 30 September 2025

- 21 participants

"The project has received funding from the European Partnership on Metrology, co-financed by European Union Horizon Europe Research and Innovation Programme and from the Participating States."

Metrology


kg
m
s
A
K
mol
cd
SI


International Standards
National Metrology Institutes
Calibration Laboratories
Industry and Testing Laboratories
Traceability
Calibrations

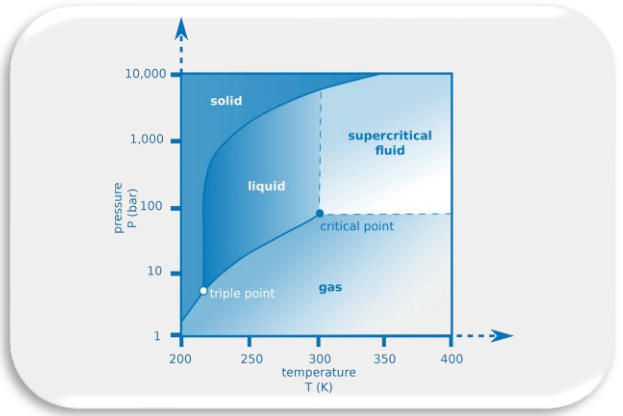
CCUS measurement challenges

Flow metering

Emission monitoring

Chemical metrology

Physical properties



Flow metering

Gas-flow

- Metrology infrastructure for monitoring CO_2 flow developed
  - < 50 m^3/h and low pressure
  - Up to 400 m^3/h and higher pressure
- Primary and transfer standards
  - Transferability tests
  - Intercomparison
  - Uncertainty <1.5 %

Liquid flow

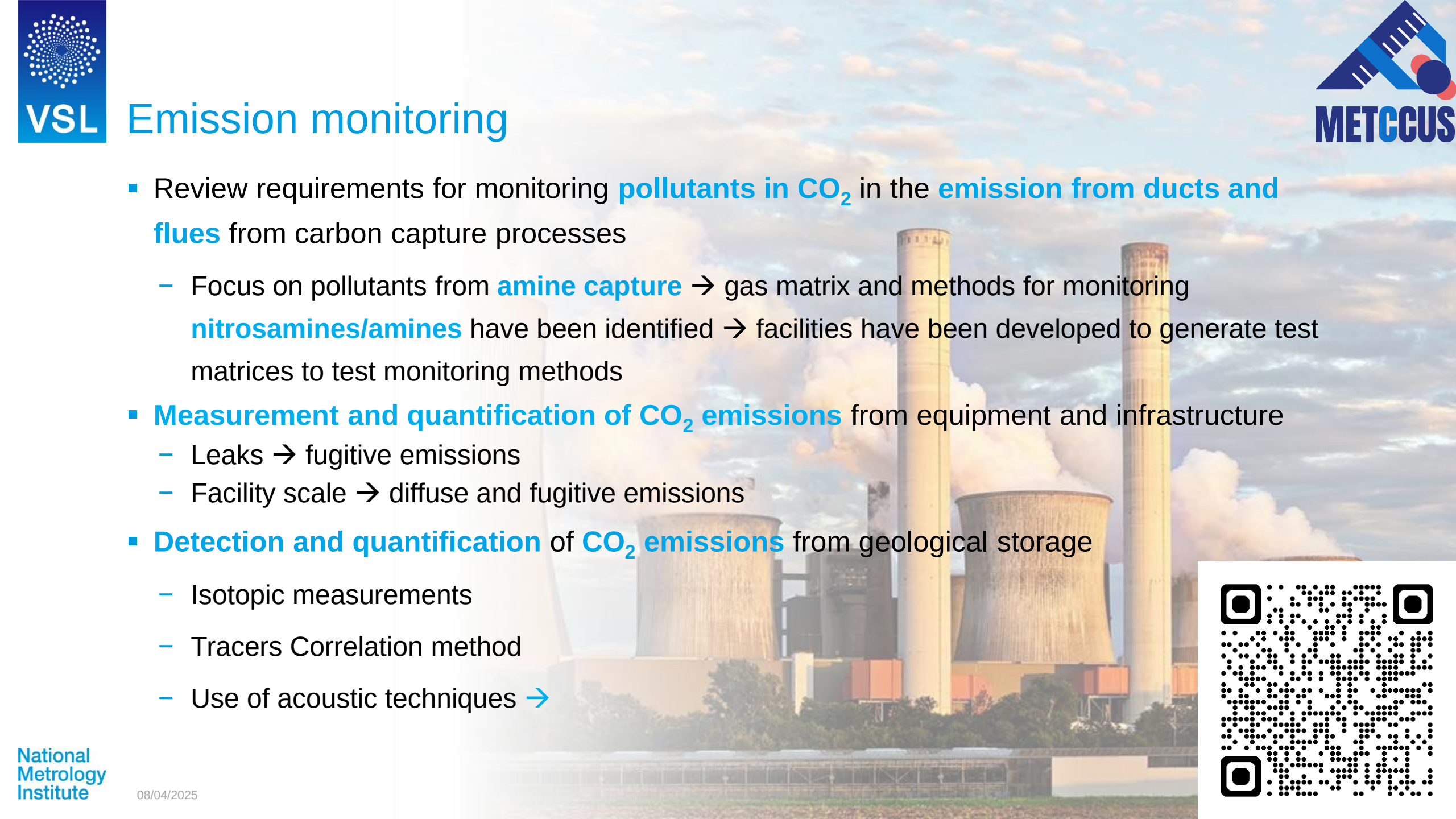
- Report: Current state of the art of traceable liquid CO_2 flow measurement and liquid CO_2 primary standard requirements →

CCS fiscal metering

- Good practice guide

Emission monitoring

- Review requirements for monitoring **pollutants in CO_2** in the **emission from ducts and flues** from carbon capture processes
  - Focus on pollutants from **amine capture** → gas matrix and methods for monitoring **nitrosamines/amines** have been identified → facilities have been developed to generate test matrices to test monitoring methods
- **Measurement and quantification of CO_2 emissions** from equipment and infrastructure
  - Leaks → fugitive emissions
  - Facility scale → diffuse and fugitive emissions
- **Detection and quantification** of **CO_2 emissions** from geological storage
  - Isotopic measurements
  - Tracers Correlation method
  - Use of acoustic techniques →



Chemical metrology

- **Primary reference materials** for impurities in CO_2
  - Literature review: commercially available cylinders for CCUS PRMs →
  - Key impurities e.g.; H_2O, NO_x, sulphur compounds, hydrocarbons, alcohols and amines
  - Permanent gases: O_2, Ar, N_2, CH_4, CO, H_2
- **Online CO_2 monitoring**
  - Development and validation of online methods
  - Round Robin Test for the measurement of impurities in CO_2
- **Offline analytical methods** for CO_2 quality
  - CO_2 capture, transport and storage
  - CO_2 conversion, utilisation and recycling →

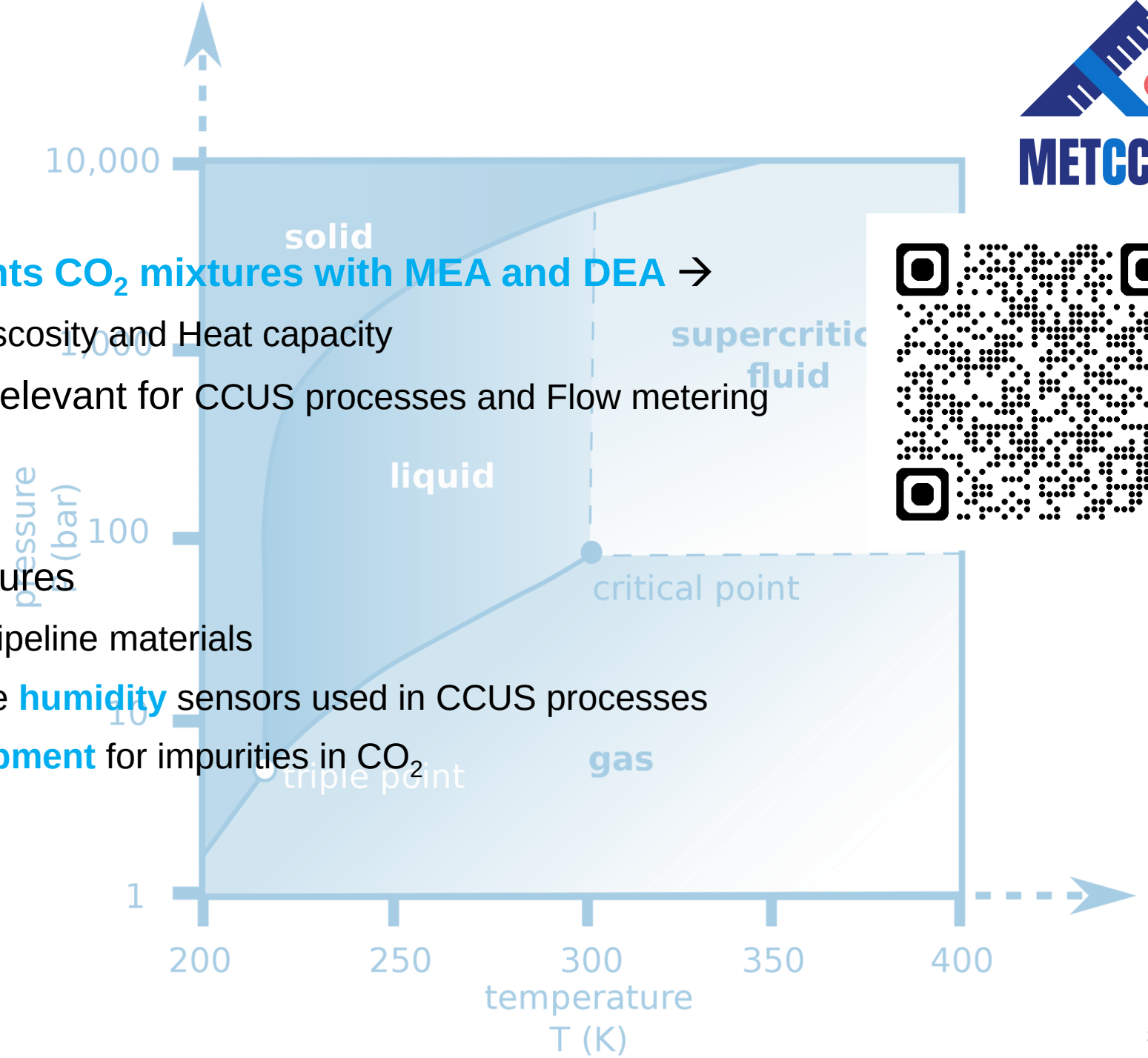
Chemical metrology – material compatibility for CO_2 sampling

- Literature review current state-of-the-art of vessels for sampling CO_2 →
- Report: Experiments to test the sampling of impurities →
- Good practice guide for the sampling of CO_2 for CCUS →

Component	Amount fraction (µmol/mol)	Restek (Silonite)	Restek (Silco)	Calibrated Instruments Inc Cali5Bond	Airborne Labs True Blue 2LT
Methanol	4-8	Stable at least 30 days (loss < 20% after D50)	Concentration decreases quickly with time	25-35% loss D1, then stable	Concentration decreases wit
	10-15	Stable at least 30 days (loss < 20% after D50)	Concentration decreases quickly with time	25-35% loss D1, then stable	Concentration decreases wit
Acetaldehyde	0.5	Stable at least D30			More than 20% loss D30
	1	Stable at least D30			15% loss D30
	4-8	Stable at least D30			
	10-15	Stable at least D30			
Ethanol	4-8	20-25% loss D50. Analysis before D10	Concentration decreases quickly with time	35% los	0. Analysis be
	10-15	20-25% loss D50. Analysis before D10		35% los	
Acetone	4-8	Max 15% loss D50	Concentration decreases quickly with time	Stable	50
	10-20	Max 15% loss D50		Stable	050
Benzene	0.3 – 2	Not compatible as benzene adsorbs on the walls	Stable at least D4		D20 but recovery at D0
	7	Not compatible as benzene adsorbs on the walls			
Hydrogen sulphide	Ca 2			100% loss D30. Analysis before D5	
	Ca 10			50% loss D30. Analysis before D5	
	Ca 20			35% loss D30. Analysis before D5	
	Ca 40			20% loss D30	
	Ca 60			15% loss D30	
	Ca 100			Less than 10% loss D30	

Physical properties

- **Experimental measurements CO_2 mixtures with MEA and DEA** →
  - Density, Speed of sound, Viscosity and Heat capacity
- **Equation of state models** relevant for CCUS processes and Flow metering
  - EoS-CG 2019
  - GERG-2008
- Monitoring CCUS infrastructures
  - **Corrosion testing** of CO_2 pipeline materials
  - Calibration method for online **humidity** sensors used in CCUS processes
  - **Online measurement equipment** for impurities in CO_2



Impact MetCCUS

- Development of
  - Primary standards and reference materials
  - Calibration and measurement methods
  - Good practice guides → www.metccus.eu
  - Literature reviews & peer reviewed articles → www.metccus.eu

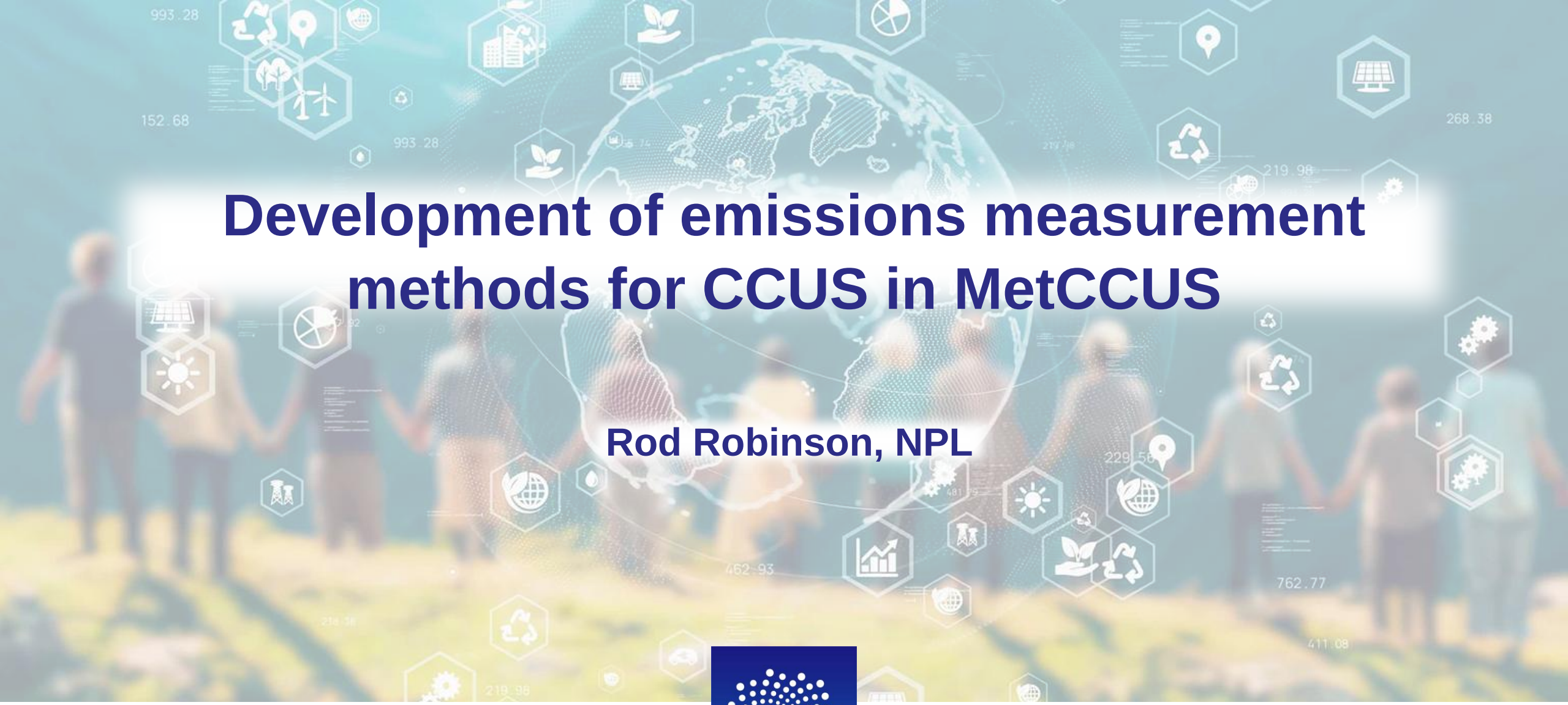
- Support
  - Development of key documentary standards, specifications and regulation
    - CEN/TC 474 & ISO/TC 265
    - EU Emissions Trading System
  - Safe and efficient CCUS operation
  - Industry to become carbon neutral and overcome climate change

Thank you for your attention

- Visit
  - www.metccus.eu
  - MetCCUS: Overview | LinkedIn

- Contact

Project coordinator
Iris de Krom
idekrom@vsl.nl



Development of emissions measurement methods for CCUS in MetCCUS

Rod Robinson, NPL

ENERGY GASES

METCCUS

VSL

MET4H2

BiometCAP

NPL
National Physical Laboratory

Update on emissions activities in METCCUS

Workshop
26 March 2025

Rod Robinson,

WP2 Lead

Rod.Robinson@npl.co.uk

WP2 Emissions

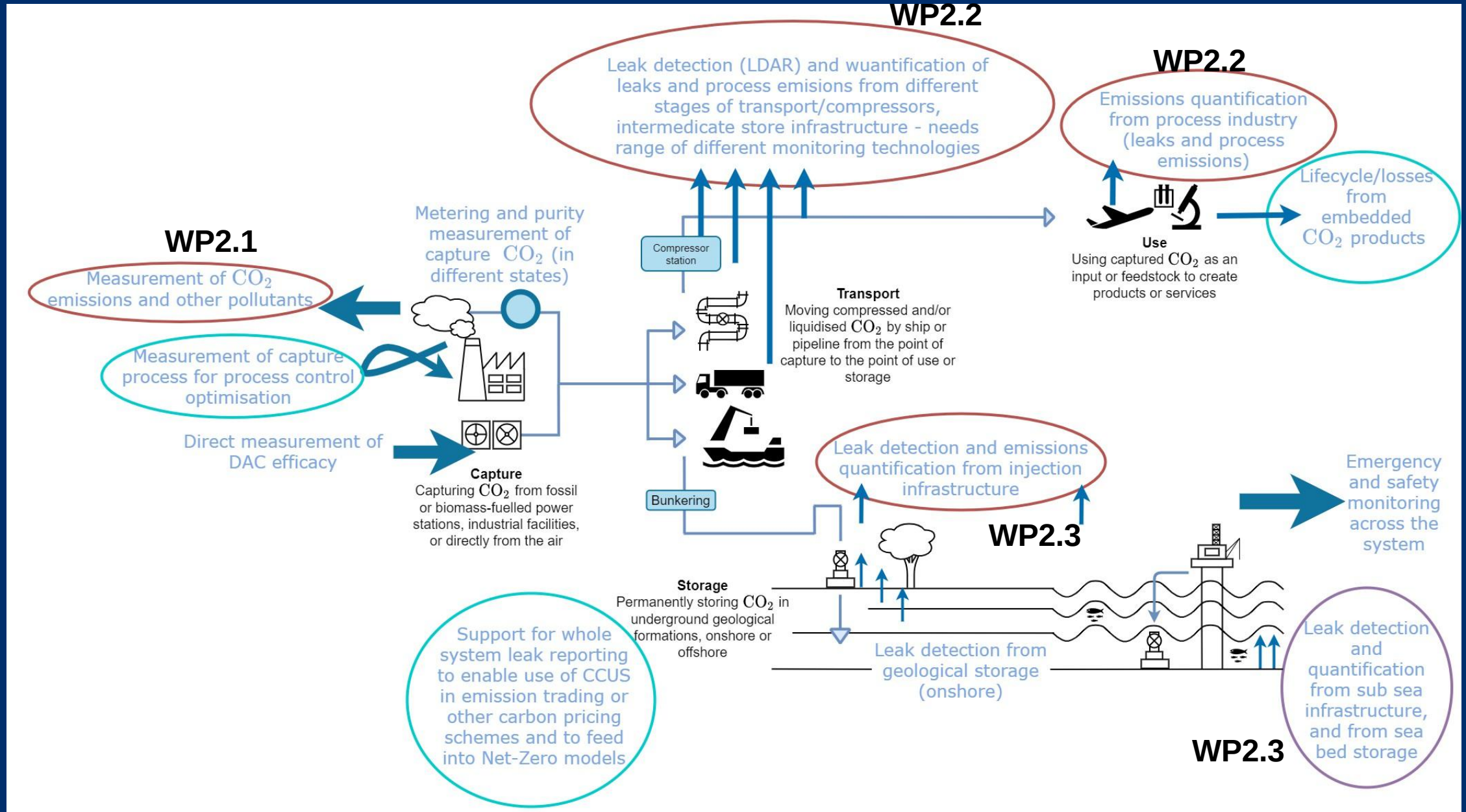
- The aim of this work package is to provide the metrological support needed to enable the measurement and reporting of emissions to air from different stages of the CCUS process

Partners:

WP Lead

Partners

Monitoring the CCUS System



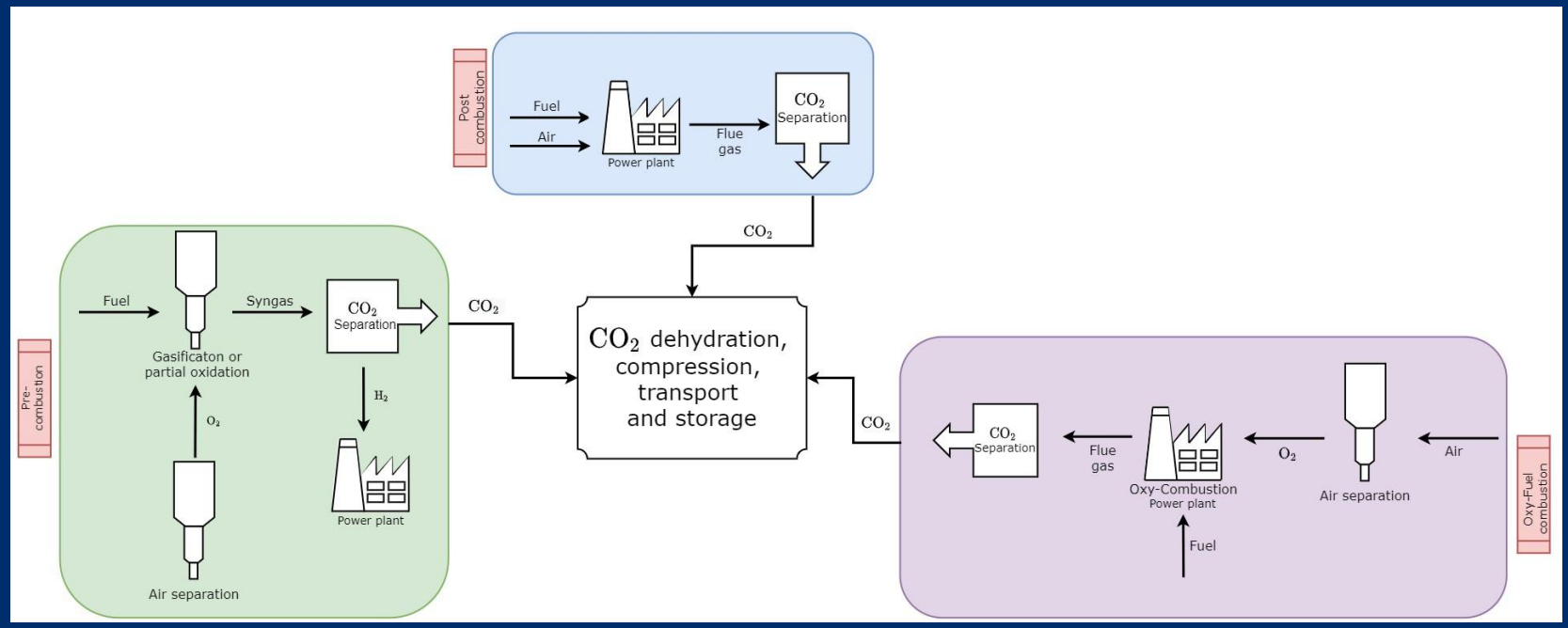
WP2 Metrological support for the measurement and reporting of CO_2 emissions to air

- Three tasks
  - Task 2.1 will develop novel methods to determine emissions of CO_2 and pollutants including amines/nitrosamines to the atmosphere from carbon capture processes. (**NPL**, **FORCE**, PTB)
  - Task 2.2 will develop the metrological capability needed for the measurement and quantification of emissions of CO_2 from CCUS equipment and infrastructure. (**NOVA**,**NPL**,**FORCE**,SINTEF, GERG)
  - Task 2.3 will assess the potential approaches needed to enable the detection and quantification of emissions of CO_2 into the environment from geological storage. (**PTB**,**NPL**,**VTT**,GERG,NOVA)

	D3	Good practice guide for the measurement of nitrosamines in post-combustion flue gas in order to enable the direct determination of emissions of CO_2 and to address the measurement of air pollutants resulting from the capture process, such as degradation products from capture solvents	Good practice guide	NPL, Force	Jul 2025 (M34)
	D4	Report on the options for the measurement and reporting of emissions to air from different stages of the CCUS process and the performance and capabilities of techniques to monitor emissions into the environment through carbon capture processes, infrastructure (leaks), or geological storage	Report	PTB, VTT, NPL, NOVA, GERG	Sep 2025 (M36)

Carbon capture

- There are three main approaches to capture CO_2 from combustion processes
- Post combustion
  - Retrofittable
  - Usually amine based capture
  -
- Pre-combustion carbon capture
  - Gasification of fossil fuel,
  - Generally linked to hydrogen production
- Oxy-fuel combustion
  - Combustion in oxygen
  - Nearly pure CO2 exhaust gas – easier to capture



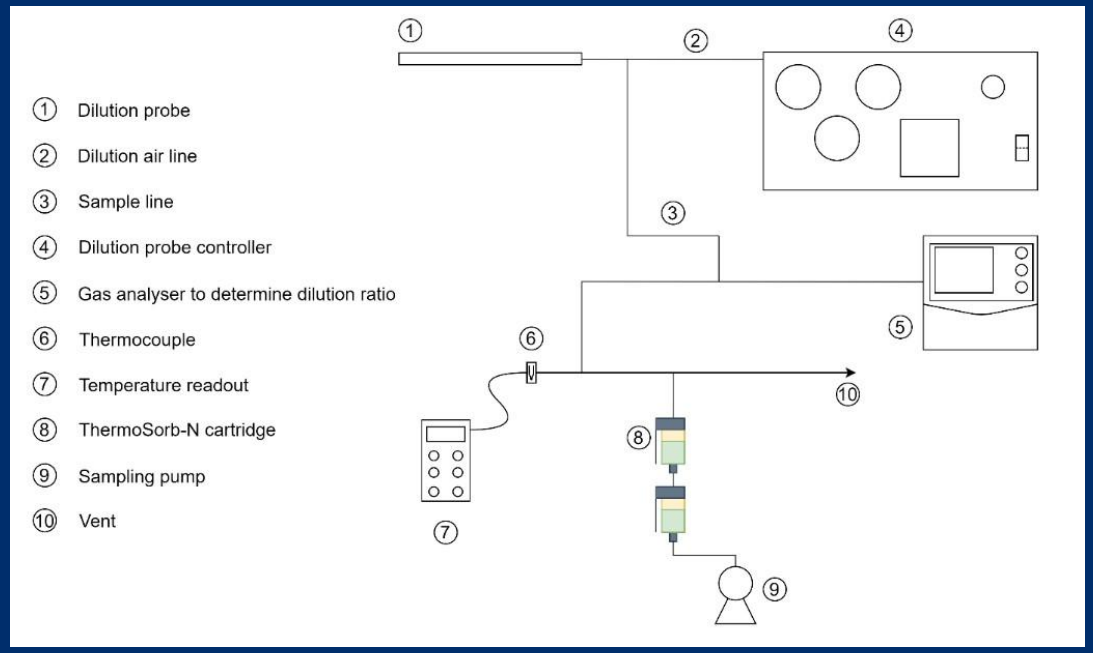
Potential methods for nitrosamines

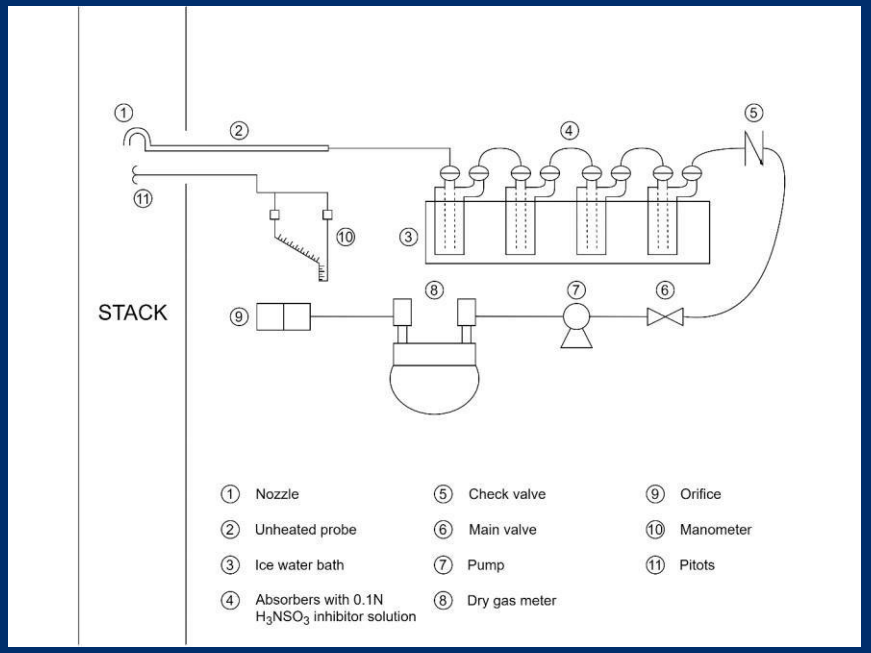
Manual Methods

- Proposed methods –
  - Sorbent trap
  - Thermosorb – dilution to dry sample

Wet chemistry based on EN14791

sulfamic acid

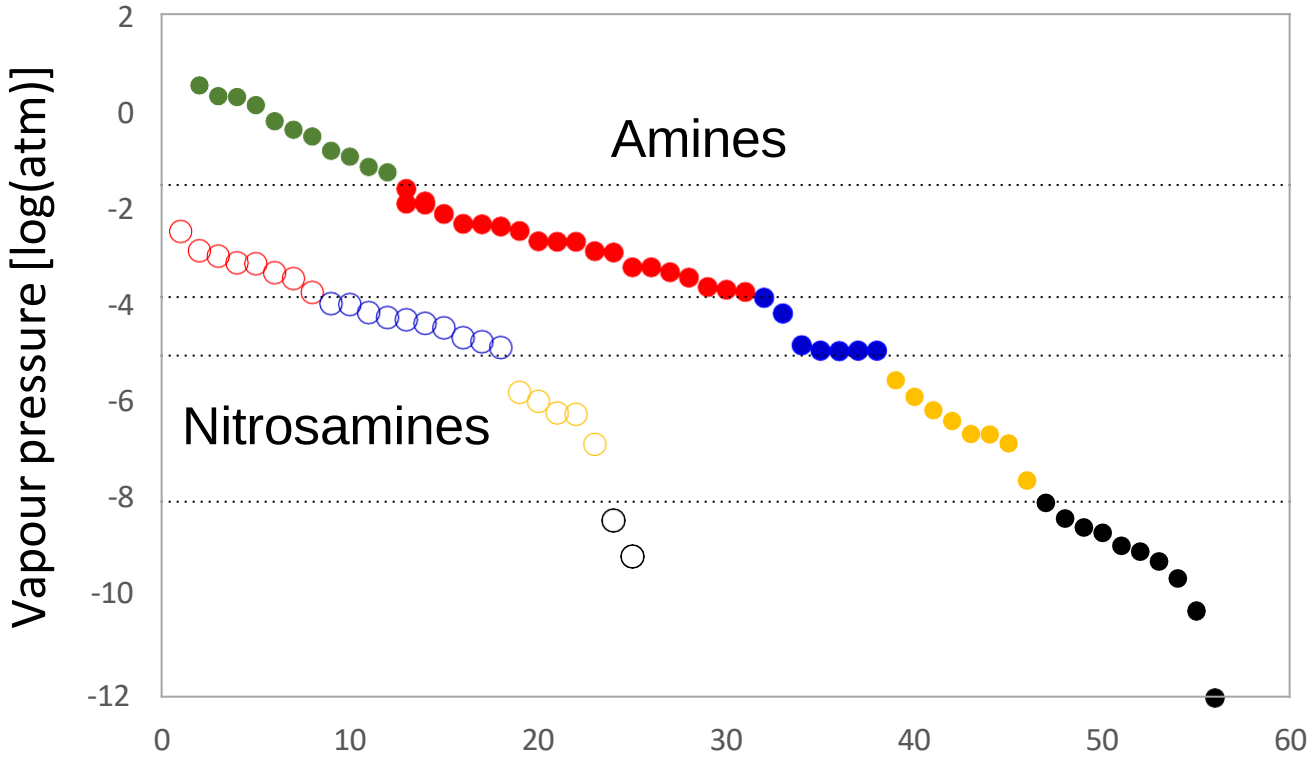




Proposed list of relevant compounds

Amines and Nitrosamines identified in CCUS (Pilot plants and lab-scale tests)

- Identified comprehensive list of compounds (which includes the regulators priority list)
- Classification in operationally defined groups attending their volatility (indicated by the vapour pressure)
- Identified potential list of standard reference material covering the range of interest (representative species)

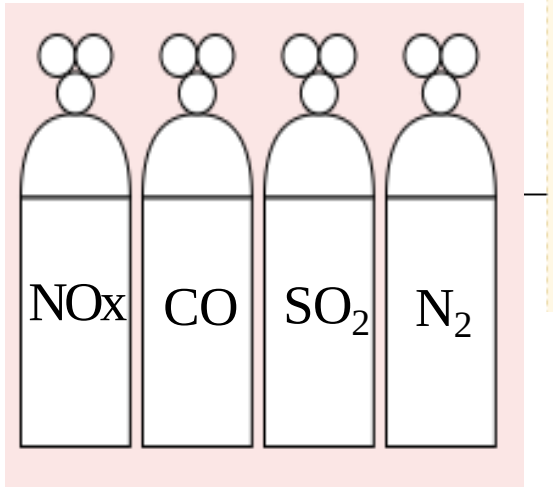


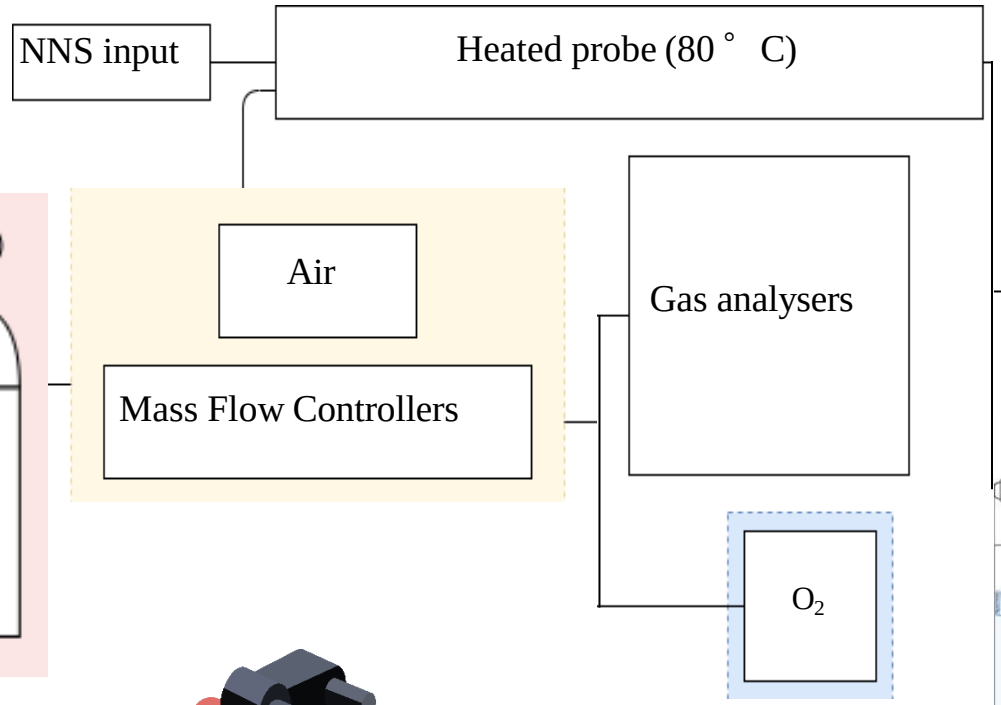
Preliminary grouping of amines and nitrosamines

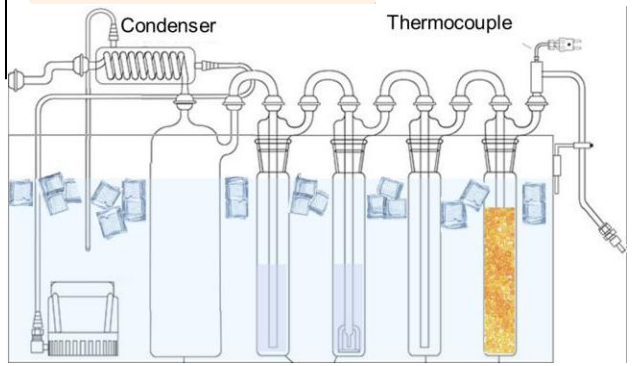
Amines/Nitrosamines test bench at NPL

Test bench, cooled liquid impingers and dry cartridges

- Testing at lab scale
- Controlled conditions and amine/nitrosamine concentrations
- Certified gas simulated media
- Safe isokinetic sampling

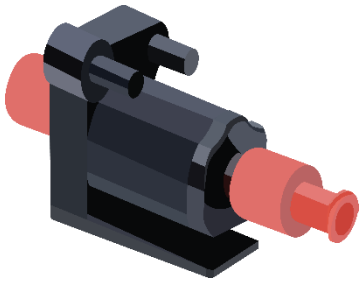






Sample's storage and shipping in ice packs

1 back dry cartridge (ThermoSorb)



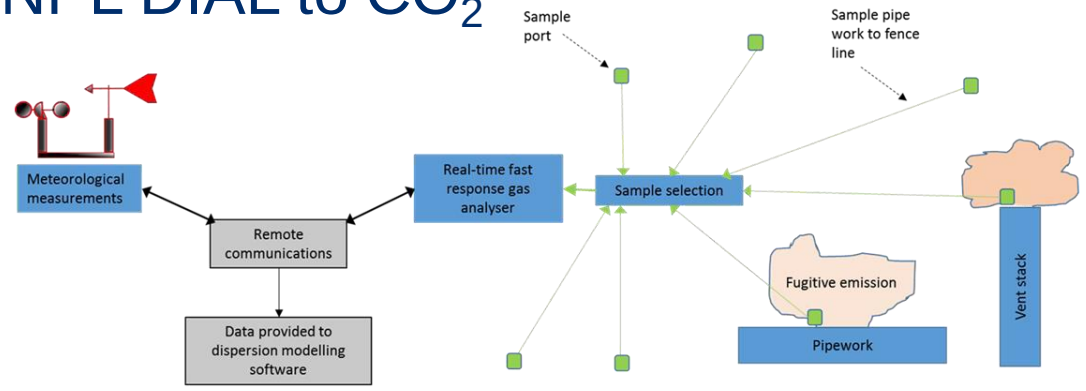
Cold sampling impingers ($0.1\ M\ H_3NSO_3$)

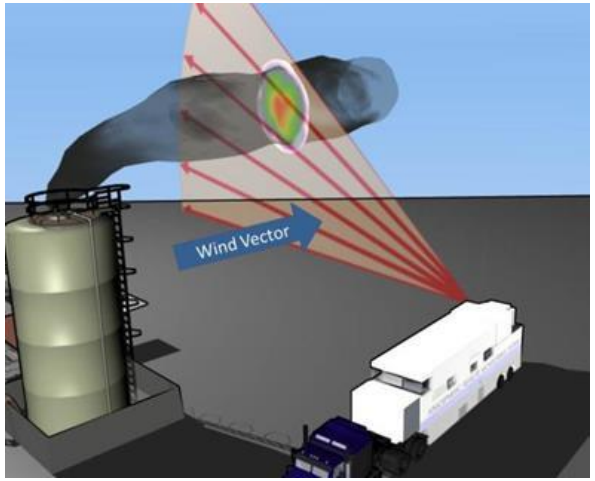
Measurement of emissions of CO_2

- Sources similar in a CCUS system as in the natural gas system
  - Fugitive leaks from components/seals/etc
    - LDAR programmes, optical gas imagining (OGI)
  - Process related vents/releases
    - Lower emission designs, OGI
  - Maintenance and repair operations
    - Engineering, design
- Measurement requirements
  - LDAR – leak detection and repair
  - Source level quantification
  - Site/area scale quantification
- CCUS specific issues
  - Requirements very challenging to meet CCS Directive
  - Ambient background levels of CO2
  - Dispersion characteristics
  - Phase of contained fluid
  - Similar techniques to methane are available

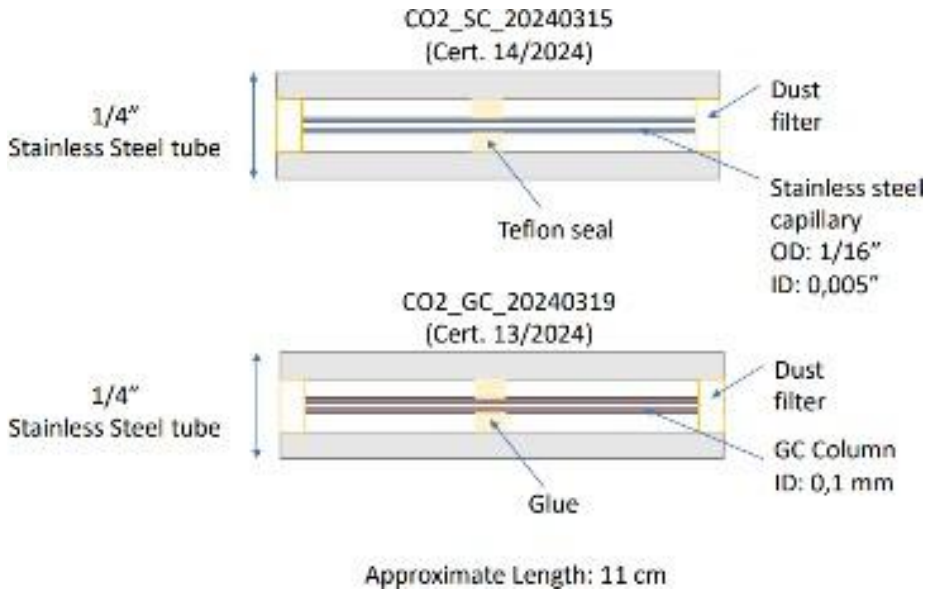
Extend measurement capabilities

- Extend hi-flow
- In internal project also looking at OGI and NPL FEDS
- In EMPIR Decarb – extending NPL DIAL to CO_2

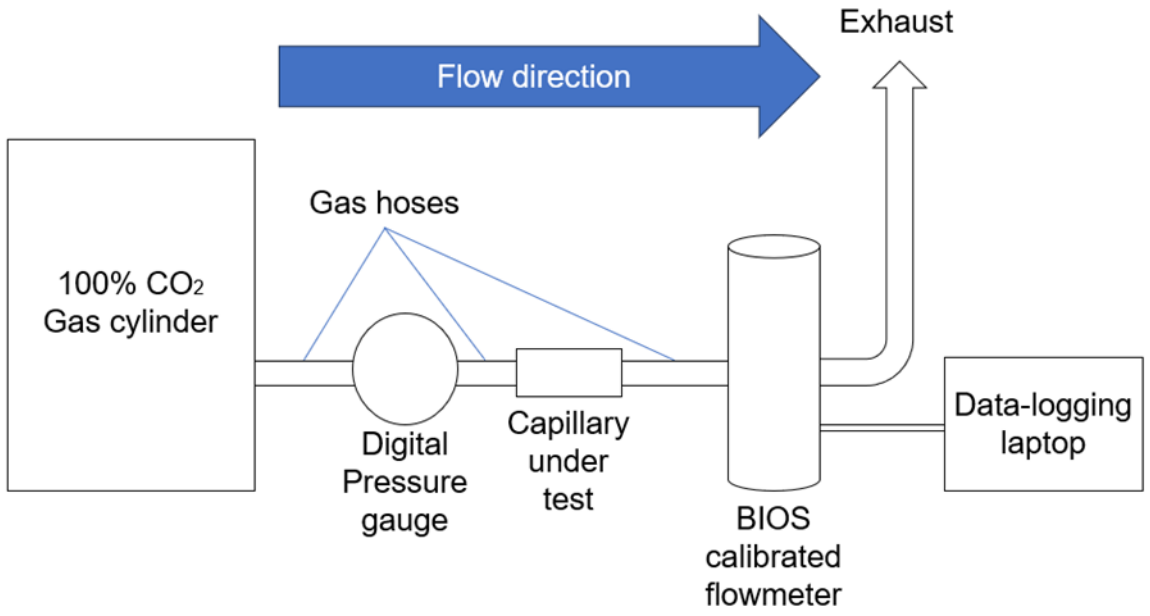


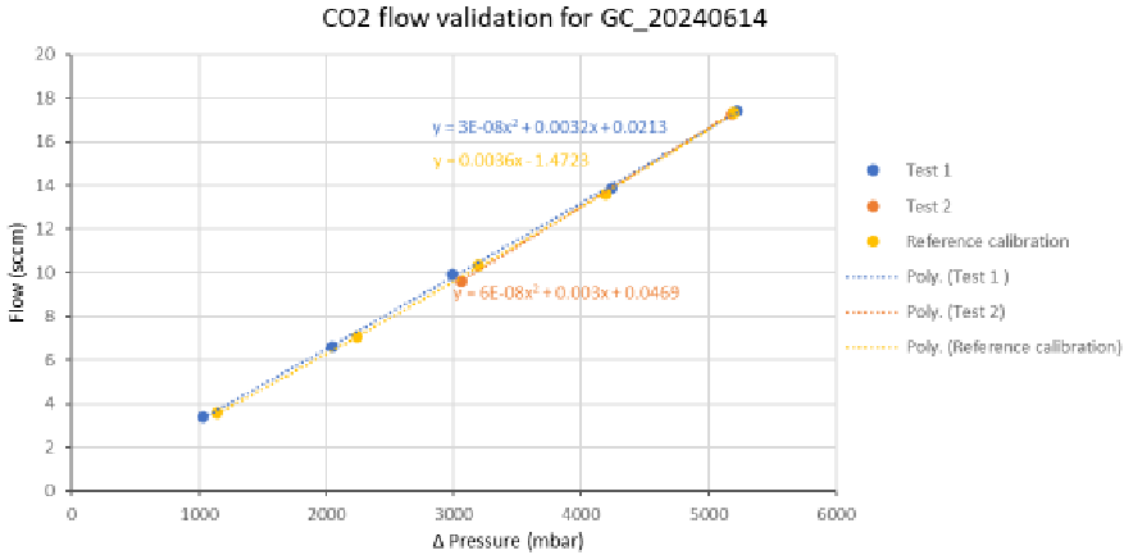


- NOVA produced and delivered three calibrated orifices to NPL, to simulate leak rates between 0,01 and 1 scc/s.
- Calibration results between NOVA and NPL were consistent.



- The calibrated orifice that presented more consisting results was sent to PTB in order to validate the leak rates on their diffuse leak system.





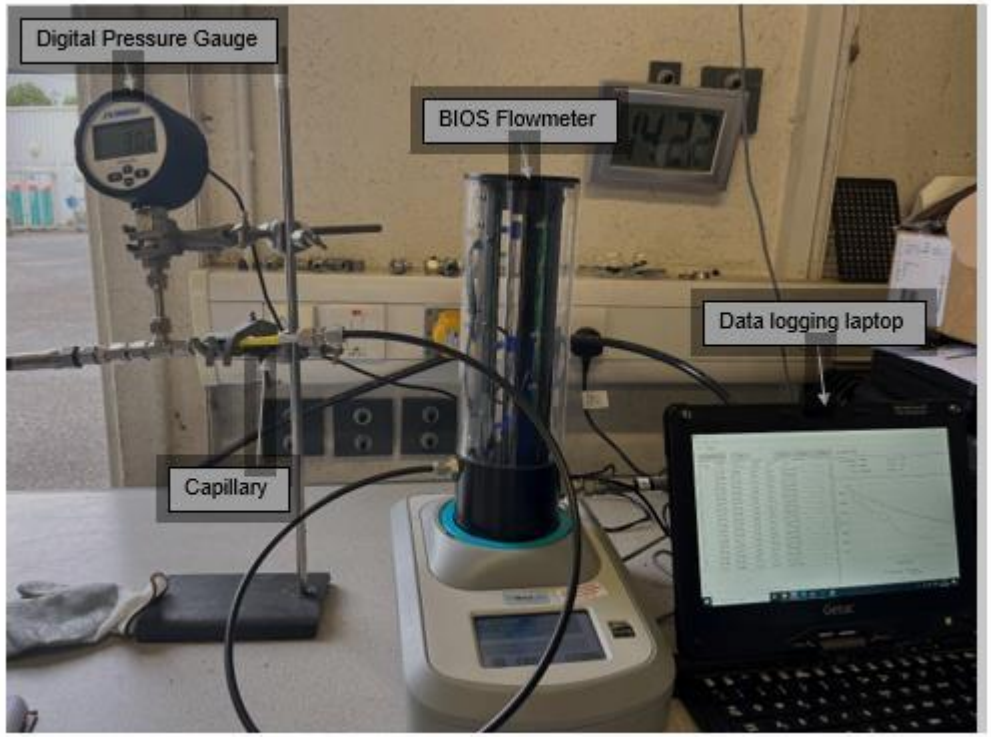
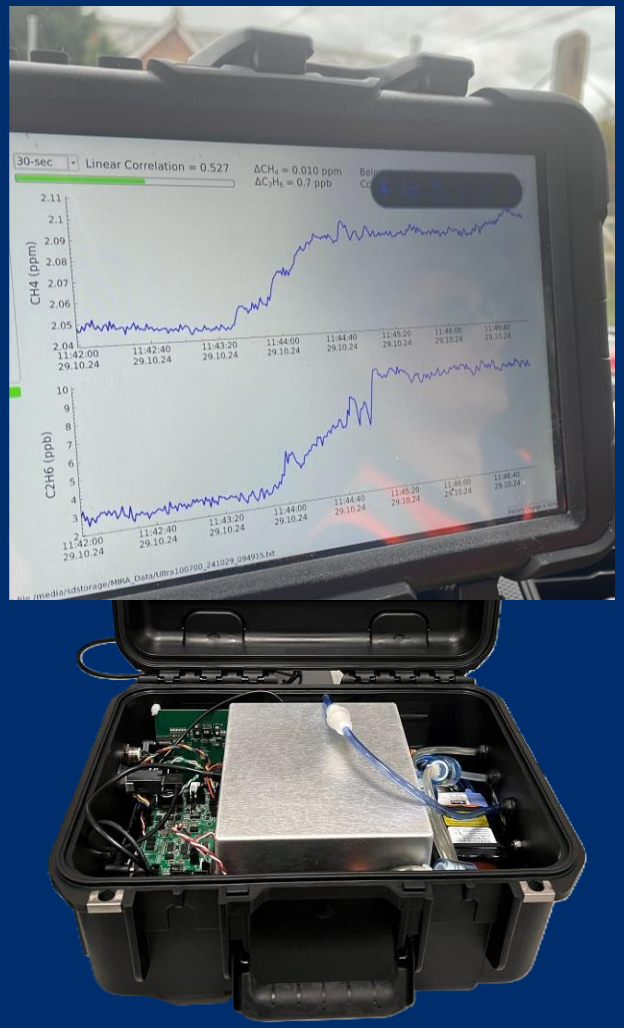


Figure 3: Equipment set up during validation.

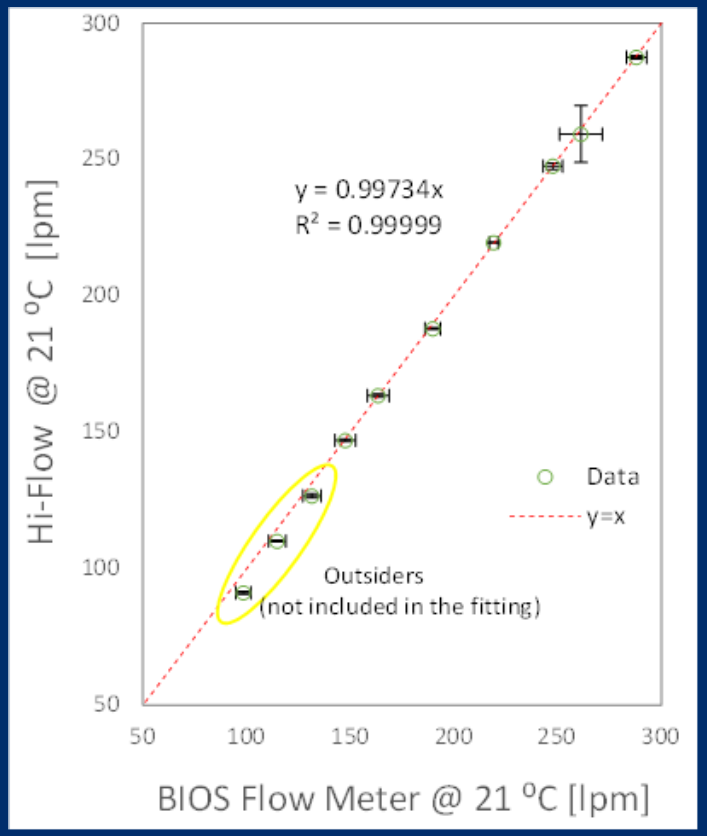
Leak Quantification

Developing a method for quantifying CO_2 leaks from individual components based on the hi-flow technology for leak quantification

- Utilise NPL's hi-flow instrument adapted with a CO_2 sensor on the exhaust port & validate d CO_2 release with the CRF
- 3-point linearity performed on AERIS MIRA CO2/N2O analyser, range 400 ppm to 2.5% CO2
- Controlled release validation with AERIS instrument mounted to hi-flow



- Determining uncertainty
  - Assessed flow uncertainty of hi-flow approach



NPL controlled release capabilities

- Range of configurable systems able to replicate various emission scenarios
- Adapted to address CO_2 emissions
- Traceable mass emissions
- Different leak types
- Challenge different measurement technologies and needs
- Provide
  - Method validation and performance data
  - Support for new techniques
  - Training
  - PT schemes

MetCCUS, Subsea leakage from storage

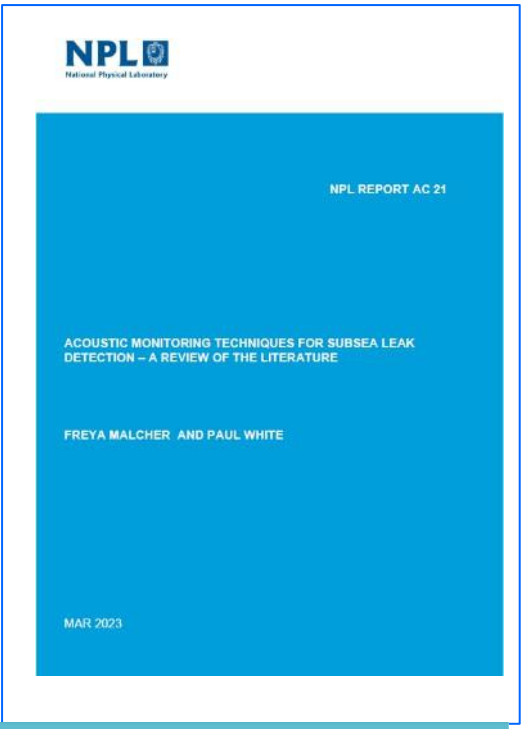
- **NPL review of acoustic techniques**

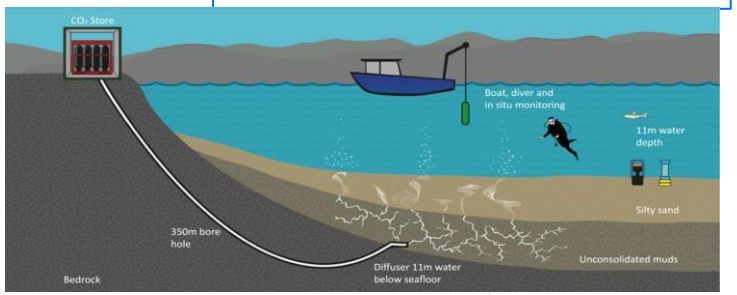
- **NPL report AC21 published**
- reviews physics of sound-bubble interaction, active and passive techniques, and existing offshore projects

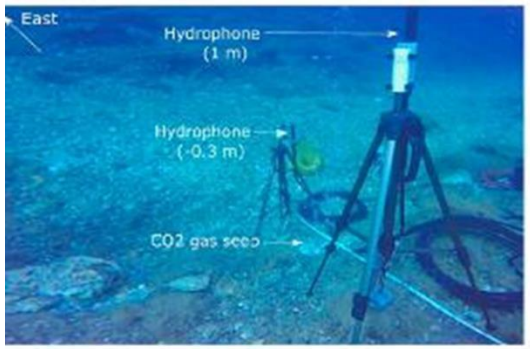
- **Active and passive acoustic techniques**
- passive uses only hydrophones to listen for leaks
- active insonifies target and detects sound scattered by bubbles

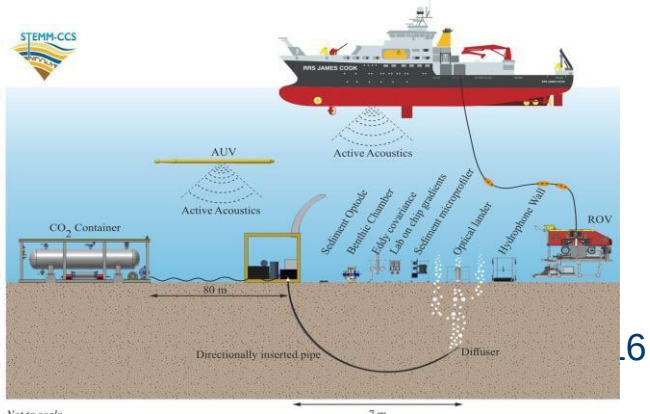
- **Review of existing in-situ offshore projects**
- ECO2 (2011-2015)
- QICS (2012)
- STEMMS-CCS (2016-2020)

- **Knowledge gaps**
- re-evaluation of existing datasets using new models
- better understanding of depth dependence
- Greensands new active acoustics project (Denmark)



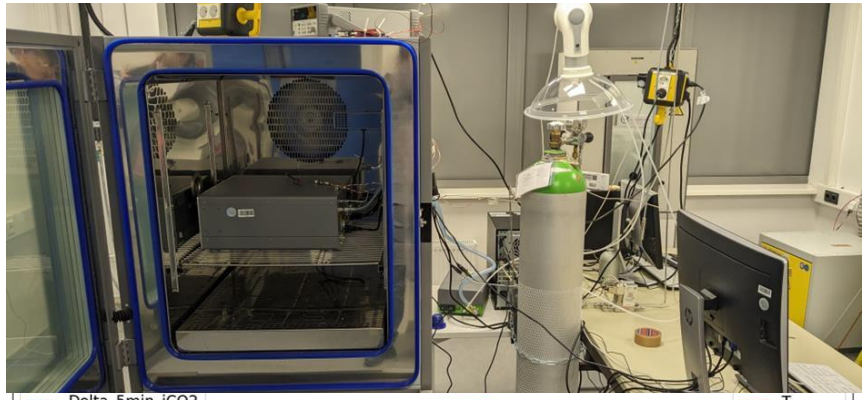


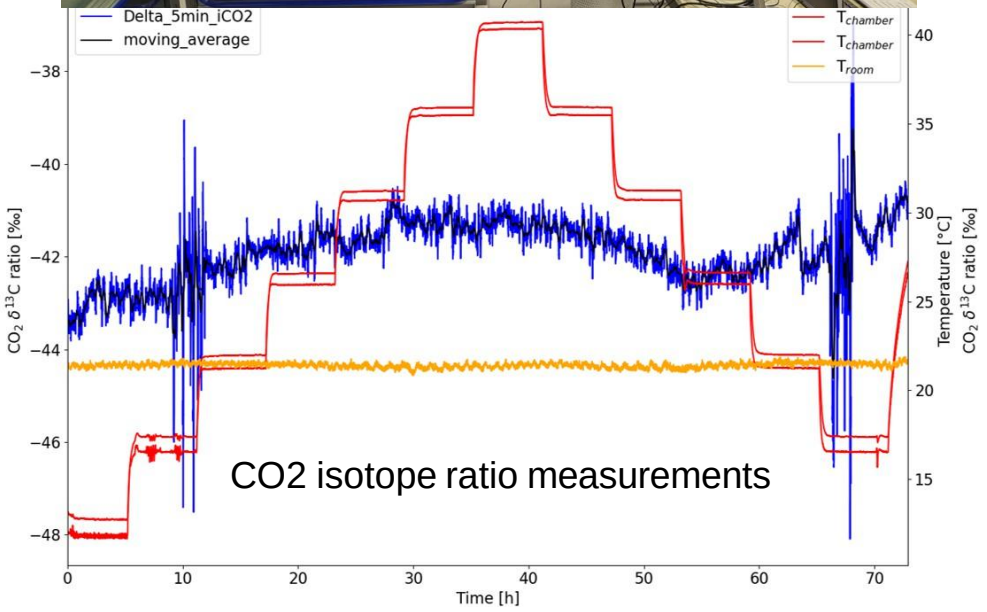




Update on isotopic detection

- Lab testing
  - measurement set-up assembled,
  - instrument tested in a climate chamber in preparation for open air measurements
  - auto sampler tested.



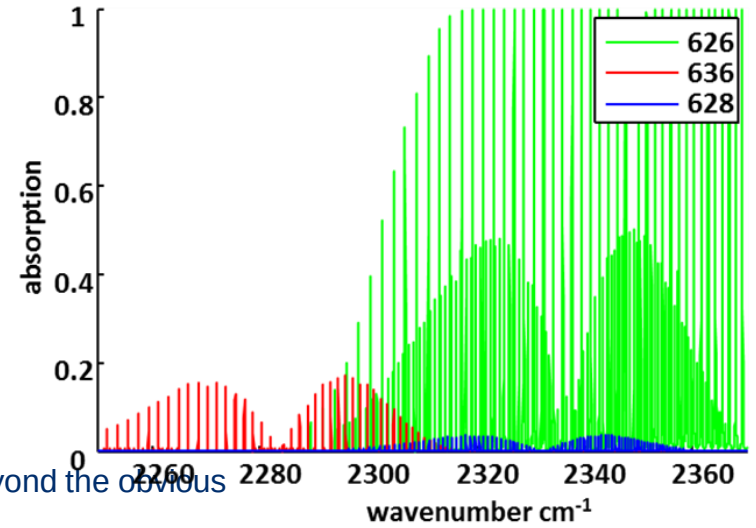


Overview of PTB's activities

- Field test site: components for the open air testing facility
- Linear surface level emissions
- Measurement campaign, measurements with VTT and PTB instruments

Isotopic measurements

- VTT deploy Isomed to measure stable isotopes at 100% of CO_2. PTB use their Picarro to measure isotopes at atmospheric level of CO_2.
- Modified Isomed (measuring at 100% of CO_2), stability etc. some basic functionality tests. Simulated leak test at "field experiments" at PTB.
- VTT will monitor delta value of the released CO_2 (at 100% level). PTB will use their Picarro assess how big the leak has to be in order to detect it with Picarro.



Summary

- METCCUS Emissions work delivering a suite of outputs to support monitoring emissions from CCUS
  - Pollutant emissions from capture plant
    - Nitrosamine measurement method
    - Review of direct monitoring approaches
  - CO_2 emission from infrastructure
    - Leak detection merhos assessment
    - Leak quantification method development
    - Site level quantification assessment of tracer approach
  - Emissions from storage
    - Review of sub sea methods
    - Potential for use of isotopic methods to detect emission from storage

Initial results from field assessment of the Tracer Corelation method for determining site level CO_2 emissions

Jacob Monster, FORCE Technology
Fabrizio Innocenti, NPL

ENERGY GASES

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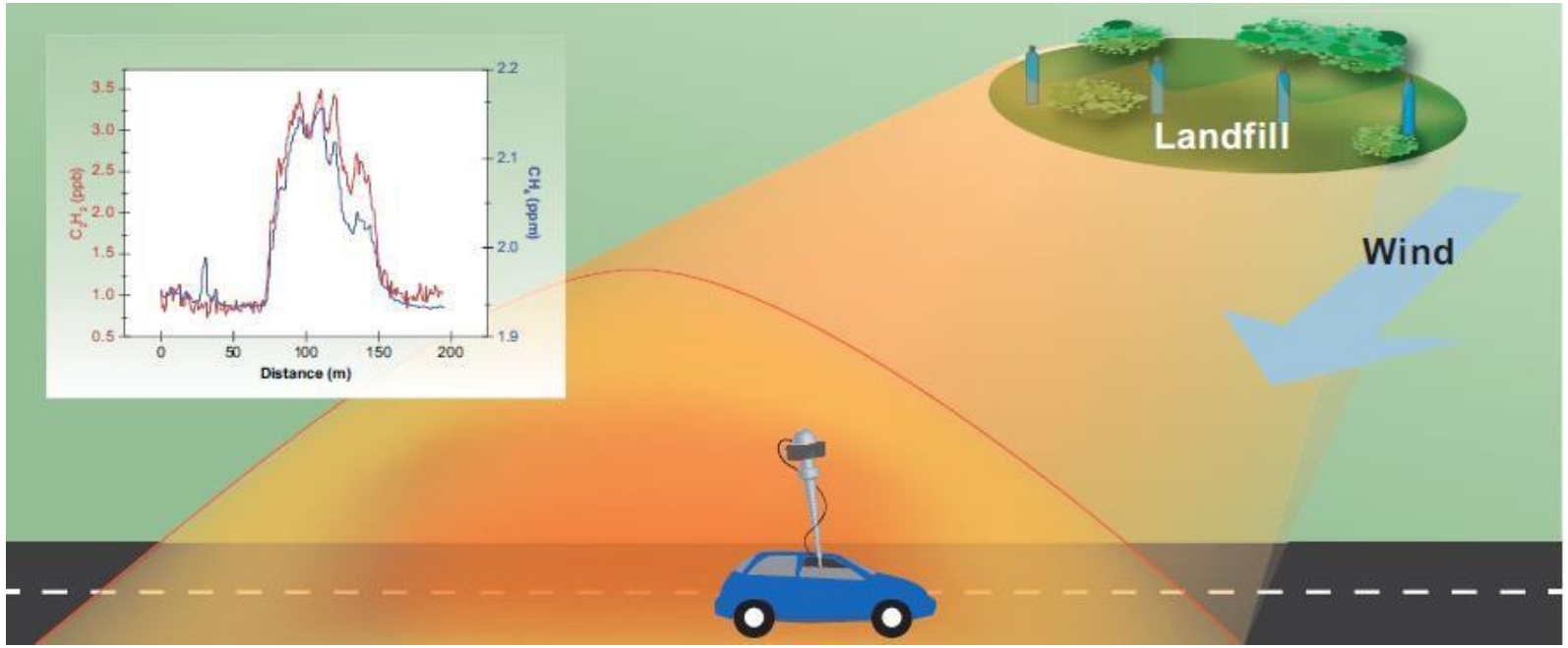
MET4H2

BiometCAP

Tracer correlation method



- Often used for large (area), diffuse sources
- Can also be used smaller (area) sources

- Tracer gas with long atmospheric lifetime
- Good/stable wind & road conditions
- Sensitive analytical instrument
- No interfering sources

Tracer correlation method, application

Examples of application:

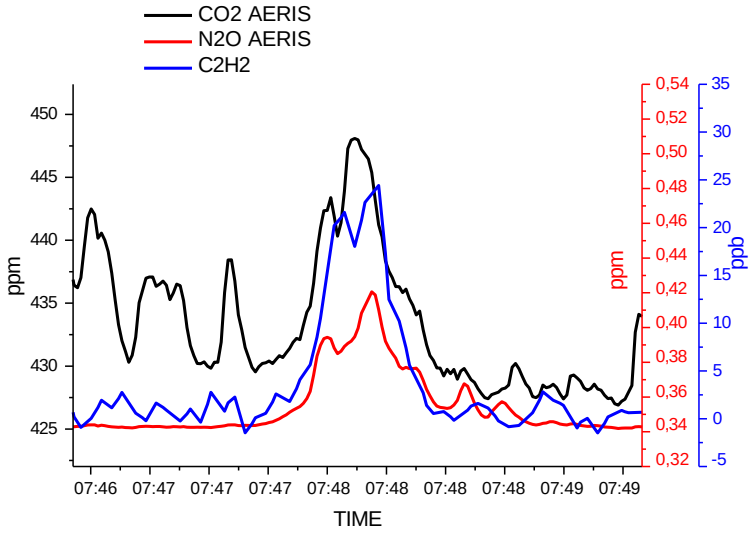
- Methane from landfills
- Methane from biogas production
- Nitrous oxide from waste water treatment
- Methane from extraction/handling natural gas
- CO_2 from CCUS?

CO_2 and tracer correlation method

First tests and results:

Waste water treatment, aeration tanks (CO_2 strip off)

Measurement road (red)

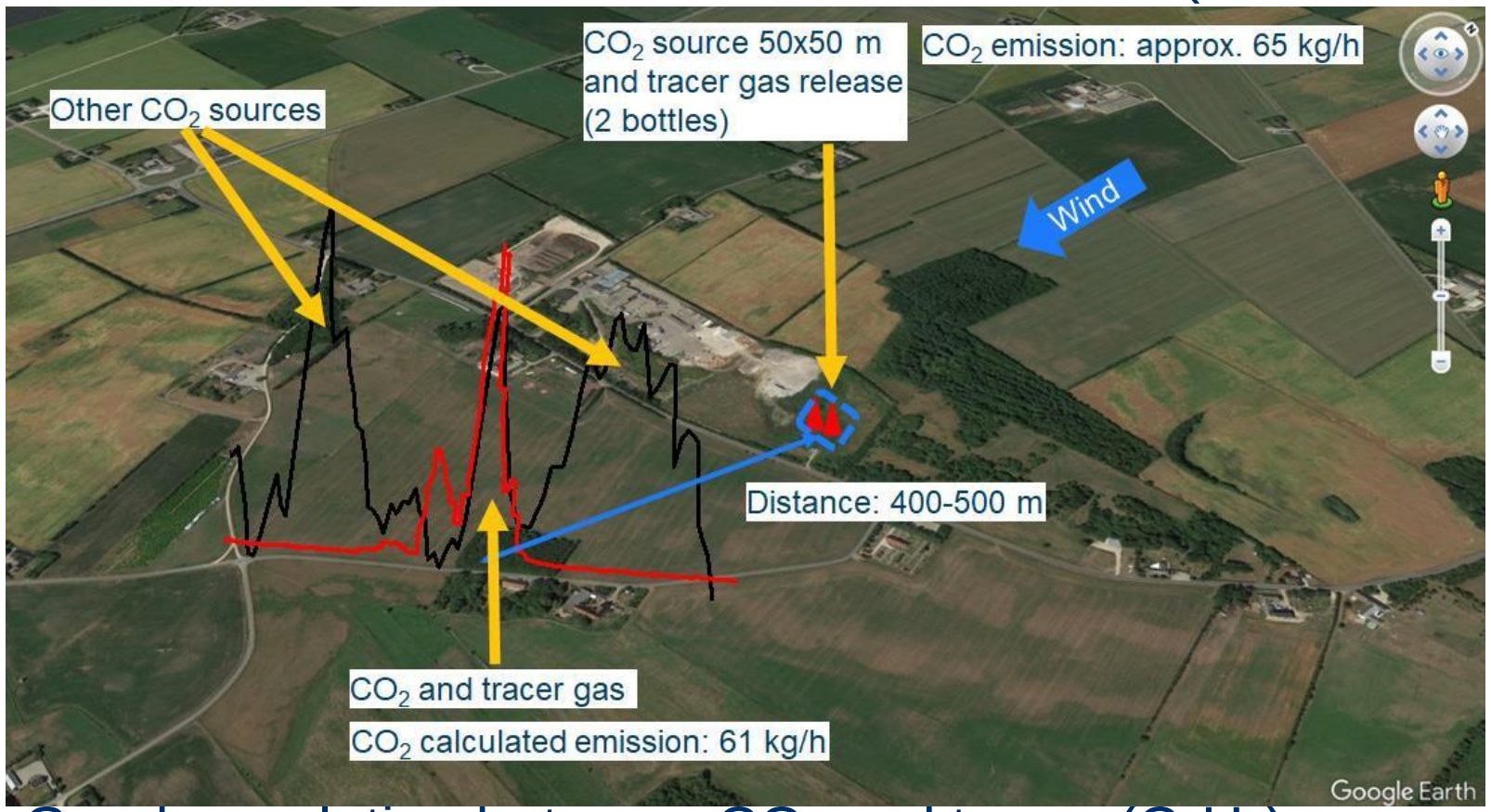


Good correlation between CO_2, N_2O and tracer (C_2H_2)

CO_2 “noise” observed

CO_2 and tracer correlation method

First tests and results: Landfill with biocover (oxidation of CH_4 to CO_2)



Good correlation between CO_2 and tracer (C_2H_2)

CO_2 “noise” observed

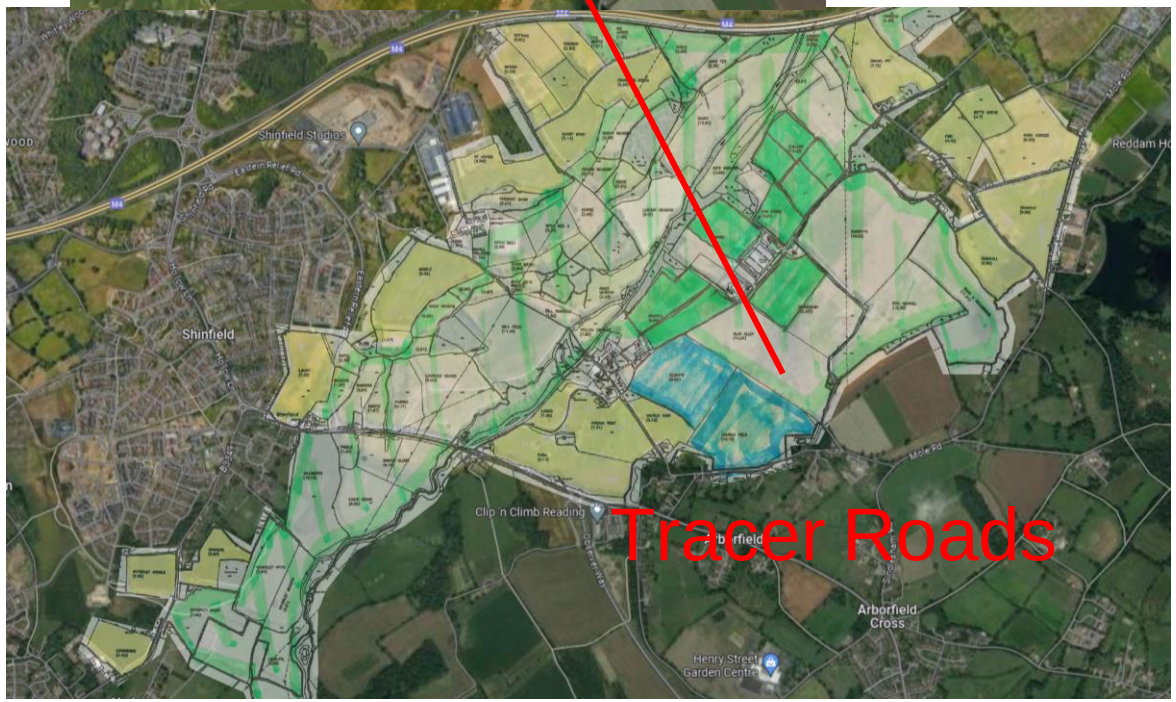
NPL
National Physical Laboratory

CEDAR Agricultural Campaign

November 2024

Centre for Dairy Research

- Just south of Reading.
- Part of The University of Reading.
- Lots of fields, multiple barns, several hundred cows.
- Conducts their own research into emissions, sustainability etc.



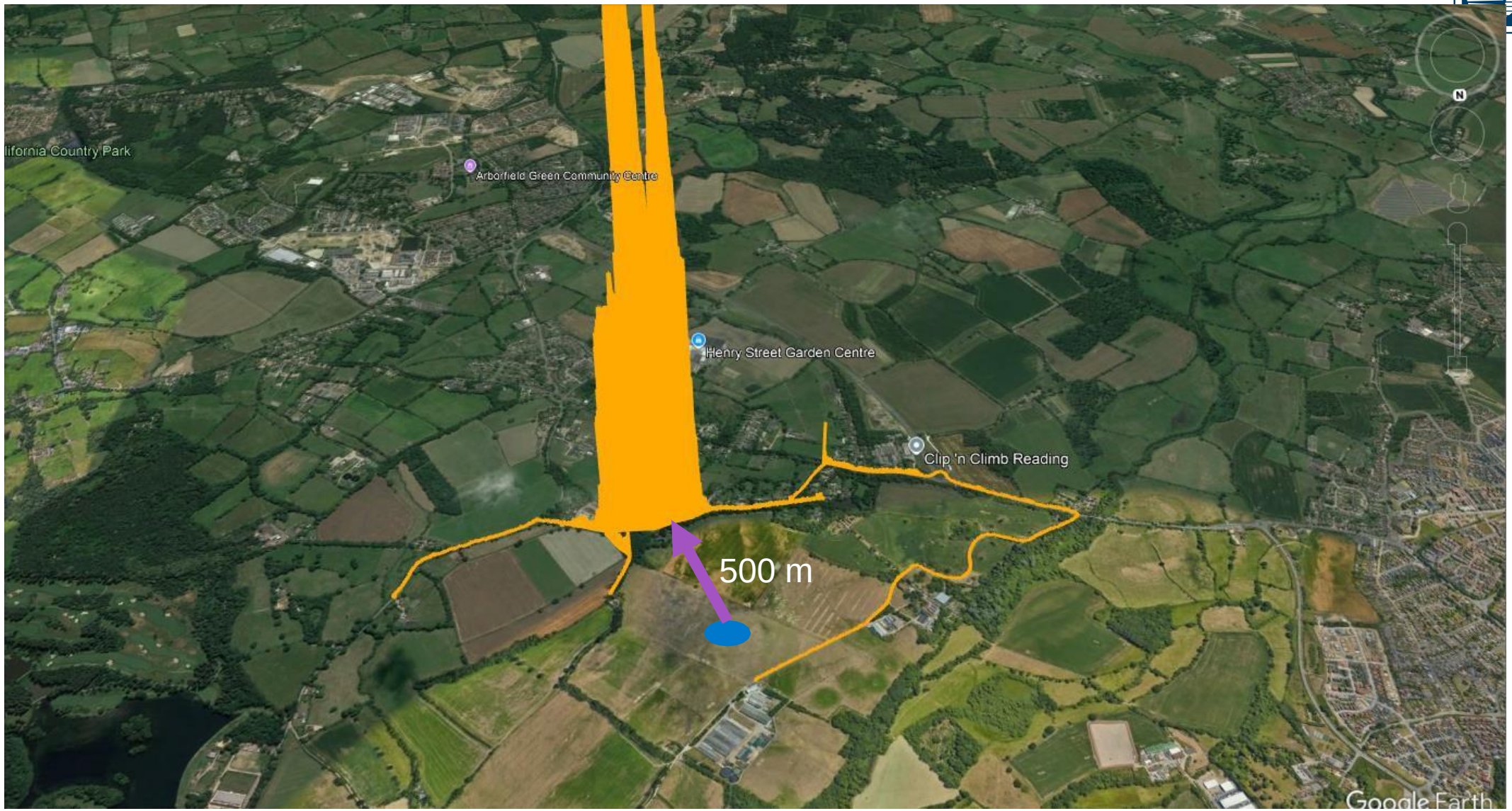
Controlled Release Set-up

CO_2 Releases

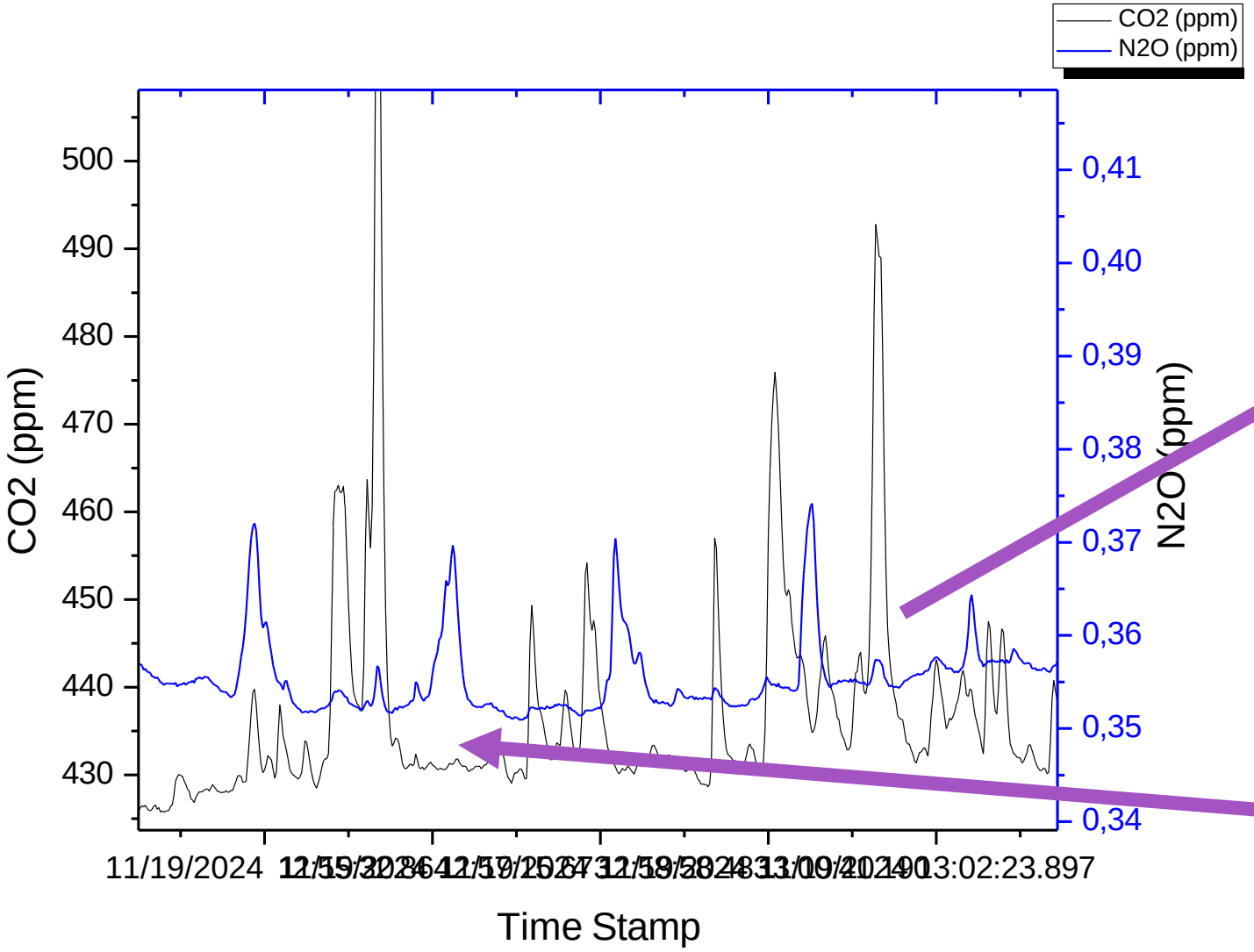
3 CO_2 releases of ~ 1 hour and ½ each with release rates from ~15 kg/h to ~ 25 kg/h

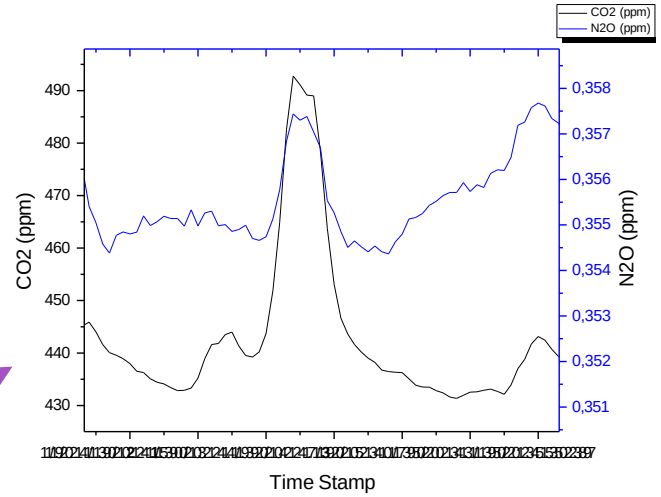
Co-release af N_2O
Acetylene released a few meters away

Results from the campaign



Results from the campaign





Plume from car exhaust

Plume from release

Results from the campaign

Conclussion:

With the conditions in Reading and the current instrumentation:

- Measurements need to be performed (much) closer to the source

and/or

- The diffuse emission must be larger emission rate (> 100 kg/h)

and/or

- Measurements need to be performed at very stable atmospheric conditions (e.g. at night)

- Measurements should be performed without traffic
- EV an advantage (or UAV)

- At optimized conditions: detection limit approx. 10 kg/h (maybe less)
- At Reading conditions: detection limit approx. 100 kg/h

- Limiting factor: concentration resolution of CO_2 instrumentation

Extra info:
FORCE measurement car emits approx. 30.000 x more CO_2 than N_2O (GWP approx. 300)

Flow metering technologies and calibration transferability in CCUS

Ara Abdulrahman, VSL

ENERGY GASES

METCCUS

VSL

MET4H2

BiometCAP

CCUS METERING TECHNOLOGIES AND TRANSFERABILITY

ARA ABDULRAHMAN

MARCH 26, 2025

The project has received funding from the European Partnership on Metrology, co-financed by European Union Horizon Europe Research and Innovation Programme and from the Participating States.

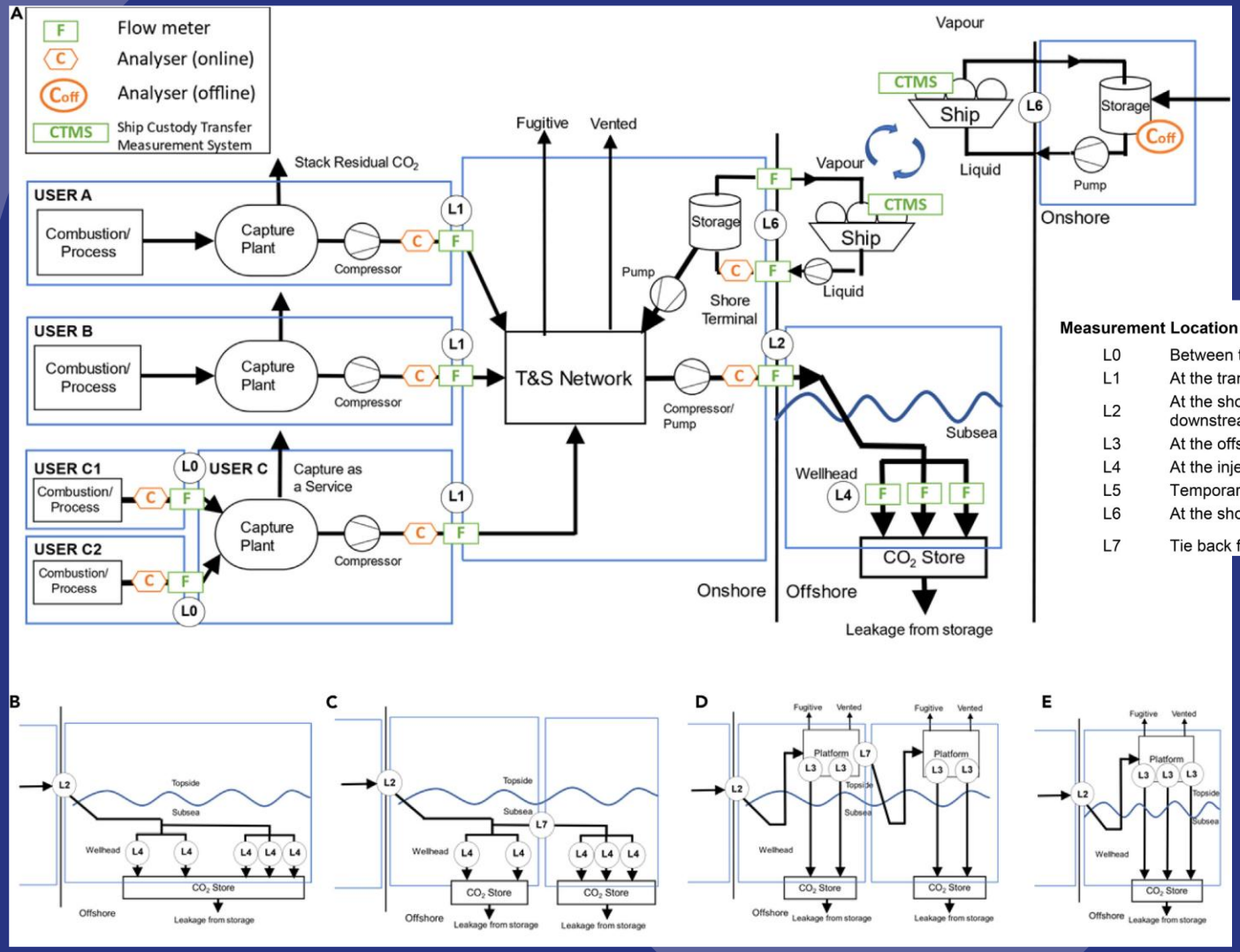
EURAMET

METCCUS

OVERVIEW

- Flow Measurement along the CCUS chain
- Accuracy Requirements
- Flow metering technologies and transferability
- Results and achievements in MetCCUS

FLOW MEASUREMENT ALONG THE CCUS CHAIN



Measurement Location

L0	Between the emitter and the capture plant inlet
L1	At the transportation and storage network onshore entry point
L2	At the shore facility before entering the offshore transportation and storage network (it can be upstream or downstream of compression/pumping station)
L3	At the offshore platform topside
L4	At the injection point into geological storage
L5	Temporary storage tanks along the transport network (not shown in this figure)
L6	At the shore terminal for ship loading and off-loading
L7	Tie back from another offshore platform and/or another geological storage (see diagrams (c) and (d))

ACCURACY REQUIREMENTS

EU ETS 2018/2066 & 2018/2067:

2.5% on mass

Based on CEMS, less suitable for large scale CCUS

UK/Norway (ETS), Canada and Australia:

1.5% vol

ISO: No explicit statements on accuracy requirements for CO_2

OIML R117 & R137:

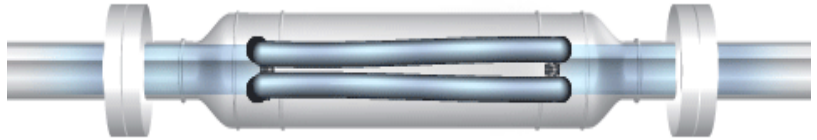
- Liquid CO_2: accuracy class 1.5 (1% meter)
- Gas CO_2: meter should be qualified on gas type of application

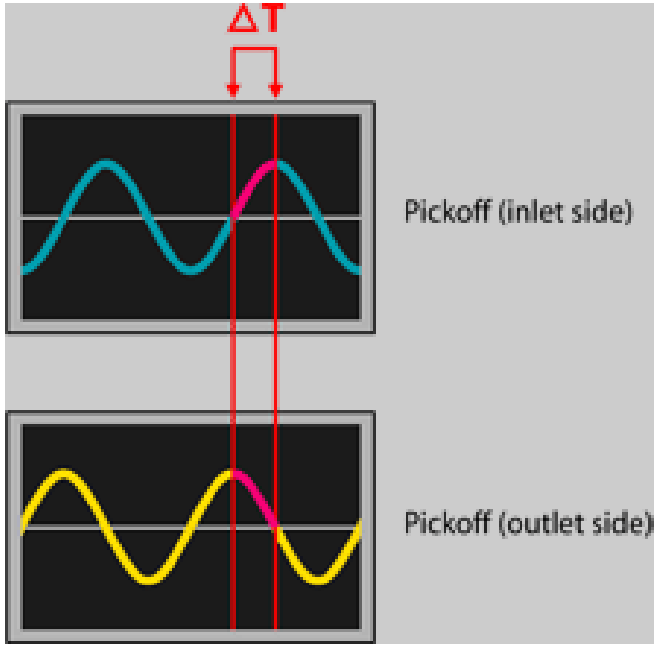
NIST Handbook 44:

- Liquid CO_2: accuracy class 2.5 (1.5% meter)

CORIOLIS METERS

- Direct mass flow measurement (mass balance)
- Inline density measurement (Indirect volume flow) - diagnostics
- Accuracy on mass as low as 0.25% (gases) and 0.05% (water)
- Always measuring → zero-flow, mounting and pipe support (zero procedure)
- Negligible installation effects, no conditioning required





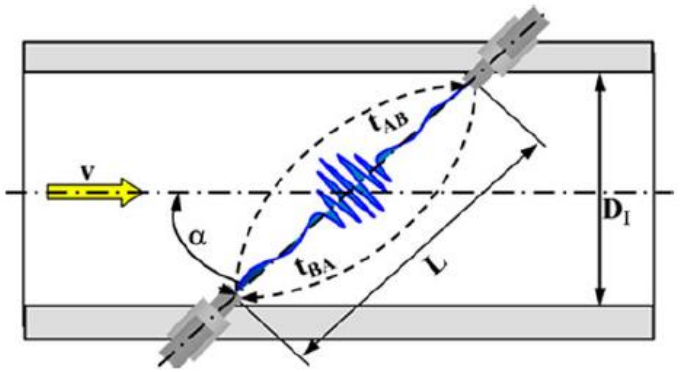
CORIOLIS METER TRANSFERABILITY

- Pressure Effect (as high as 0.02%/bar)
- Temperature Effect
- Viscosity Effect
- Speed of Sound Effect (larger sizes and frequency dependent)
- Effects are published by manufacturers
- Reynolds number dependency
- Limited testing against dP meter has shown promising transferability between water and Liquid CO_2

ULTRASONIC METERS

- Measures fluid velocity throughout pipe cross section
- Volume flow measurement → Mass flowrate through density
- Inline Speed of Sound measurement - diagnostics
- Always measuring → zero-flow
- No obstruction or moving parts → Low ΔP
- Many D's upstream pipe length required if no conditioning is used
- Minimum pipe size 4" due to ΔT

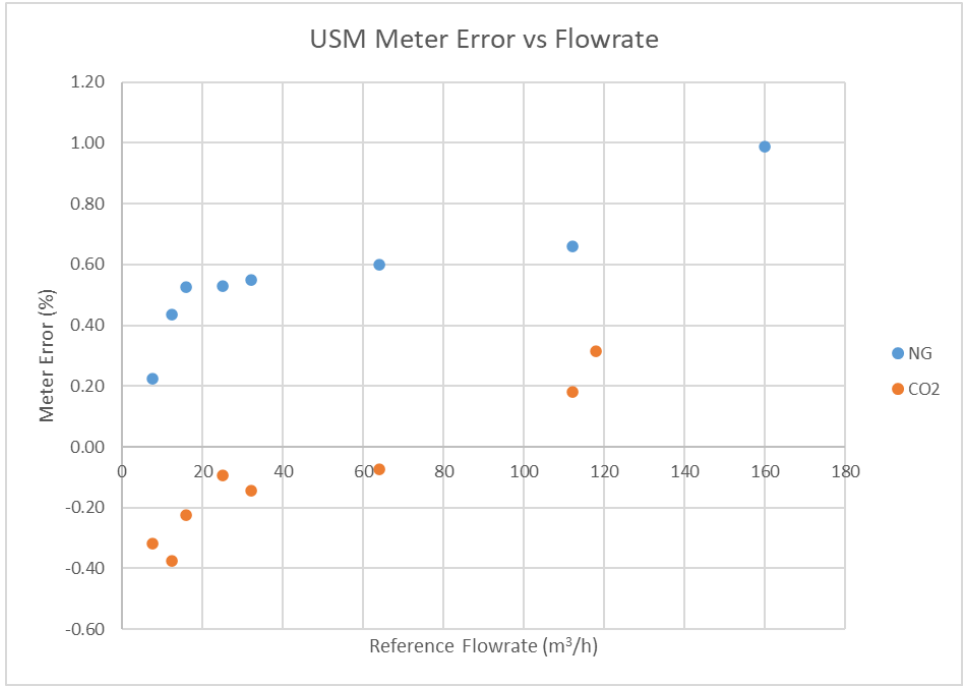
$$Q = \frac{\pi}{4} D_I^2 \cdot \frac{L}{2\cos\alpha} \cdot \frac{t_{BA} - t_{AB}}{t_{AB} \cdot t_{BA}}$$



v = Gas velocity
L = Measuring path
α = Angle of inclination in °
t_{AB} = Sound transit time in flow direction
t_{BA} = Sound transit time against flow direction
D_I = Pipe inner diameter
Q = Volume flow

ULTRASONIC METER TRANSFERABILITY

- Reynolds number dependency
- Pressure, Temperature, Viscosity Effects
- Difference in sound attenuation between fluids
- Composition and Equation of State very important for correct settings



TURBINE METERS

- Common in oil and gas industry with lots of experience
- They measure **volume** flowrate → Composition and EoS become very important for mass flow measurement
- Accuracy around 1% have been claimed, not verified with traceable CO_2 reference
- Reynolds number dependency vs. flowrate
- Transferability also possible using the PTB turbine meter model
- One phase meter, large risk of mechanical failure in 2 phase
- Typically require 10D upstream pipe length if no conditioning is used

DIFFERENTIAL PRESSURE METERS

- Orifice Plates are the most common type of DP meters
- Differential pressure measurement across orifice plate→ Mass and volume flowrate through density (composition, pressure and temperature)
- Very dependent on composition measurement and Equation of State
- Discharge coefficient and flow calculated with ISO 5167 standard
- Accuracy around 1% have been claimed, not verified with CO_2
- Reynolds number dependency with Discharge Coefficient
- Always measuring → zero-flow
- Large obstruction → High ΔP → Possible pressure drop induced phase change
- Many D's upstream pipe length required if no conditioning is used

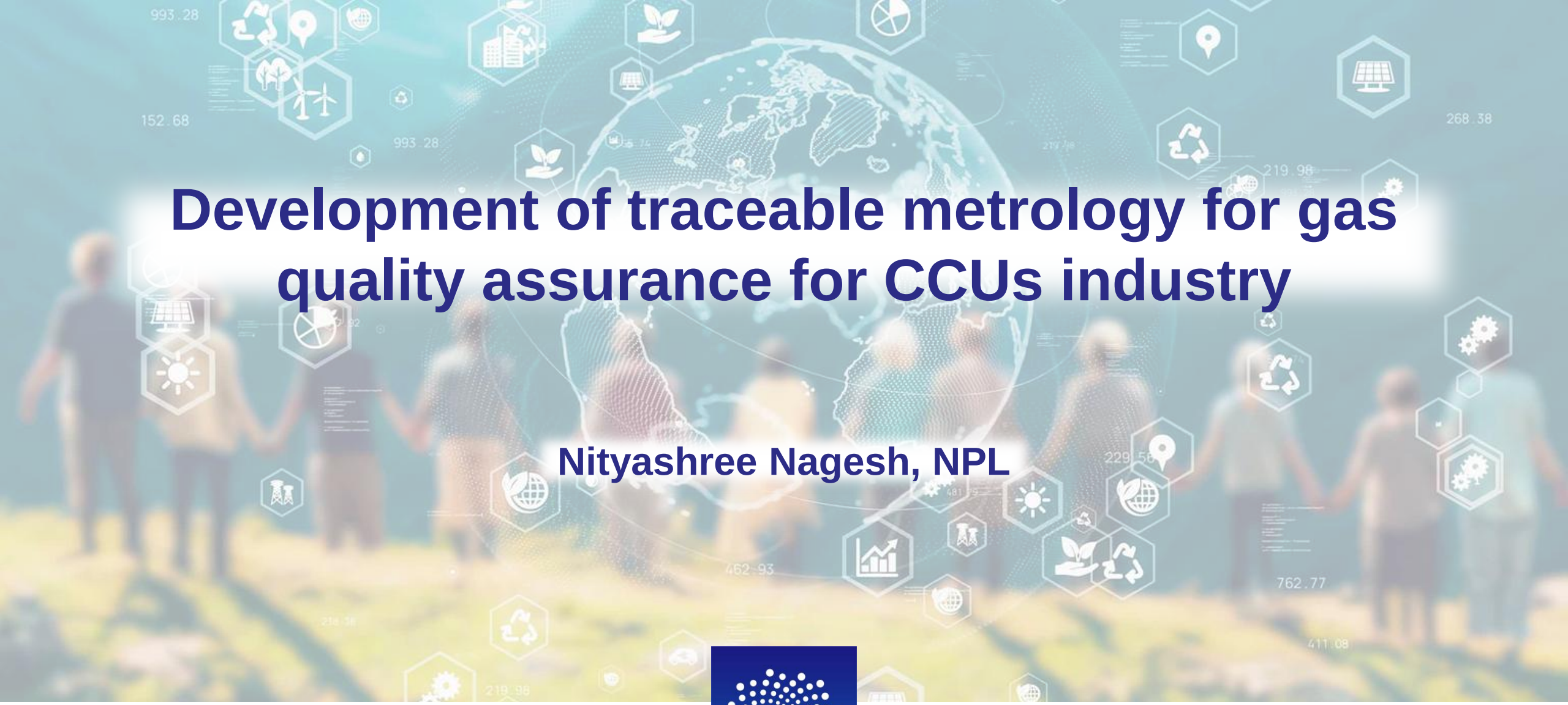
ACHIEVEMENTS IN METCCUS

- Established SI-traceable primary standards for high and low pressure CO_2 gas flow
- Investigate transferability of several flow metering technologies to Natural Gas and Nitrogen Calibrations
- Interlaboratory comparisons to determine the equivalency between the laboratories

THANK YOU!

AABDULRAHMAN@VSL.NL

HTTPS://METCCUS.EU/



Development of traceable metrology for gas quality assurance for CCUs industry

Nityashree Nagesh, NPL

ENERGY GASES

METCCUS

VSL

MET4H2

BiometCAP

Development of traceable metrology for gas quality assurance for CCUS industry

Image: https://blog.se.com/sustainability/2020/12/21/carbon-capture-utilization-and-storage-ccus-what-we-need-to-know/ (accessed 20/3/24)

Nityashree Nagesh, Manohara G. V. and Josh Hamilton

National Physical Laboratory, Hampton Road, Teddington, TW11 0LW, United Kingdom

Outline

- CCUS Measurement Challenges and Importance of CO_2 Quality
- Building CO_2 Purity Infrastructure
- Metrology Development for Trace-Level Reactive Impurities in CO_2
- PRMs and Methods developed under MetCCUS Project
- Metrology Development for Dense Phase CO_2
- Performance Testing of Carbon Capture Materials
- Conclusions

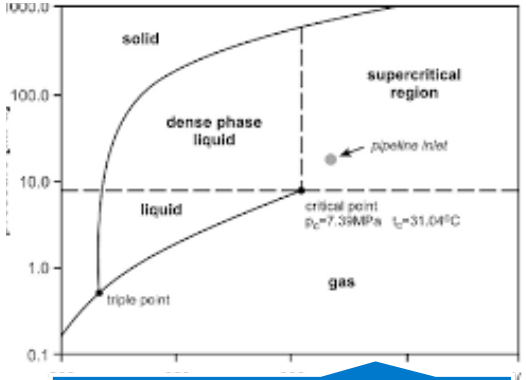
CCUS Measurement Challenges

NPL

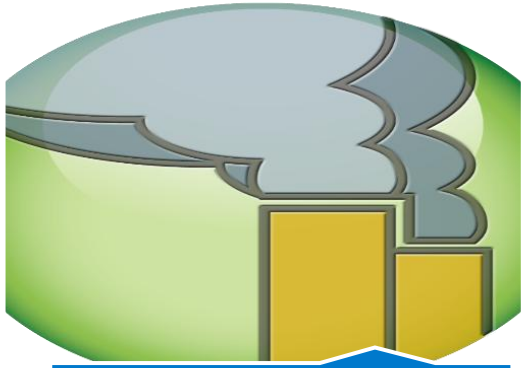
Gas quality

Humidity

Flow metering



Equations of state



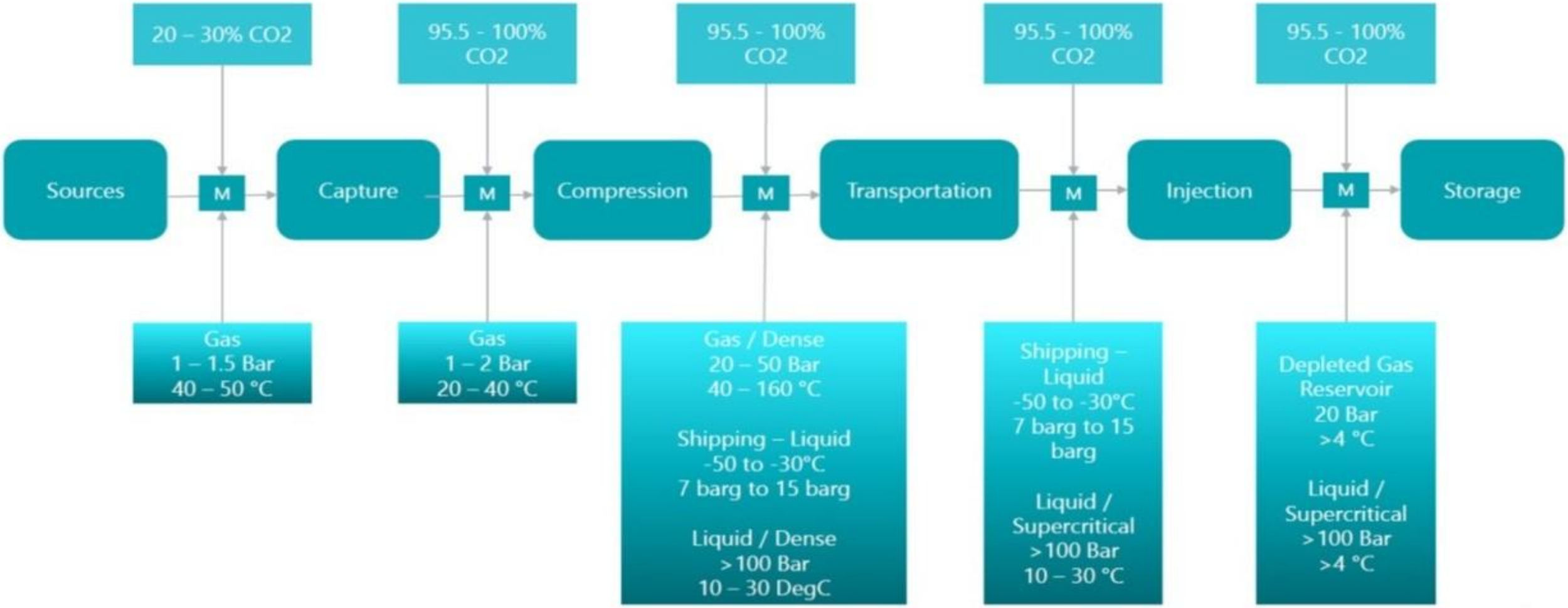
Emissions monitoring

Corrosion

Materials testing

Leak detection

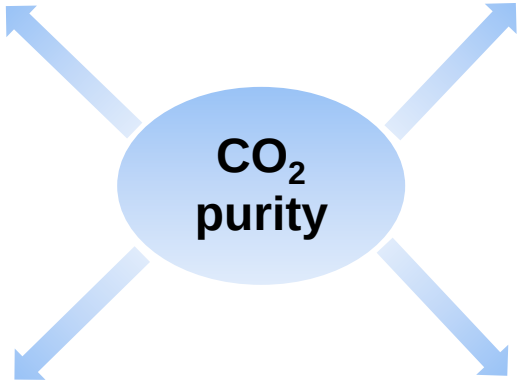
CO_2 Specification across CCUS Value Chain



Importance of CO_2 Quality for CCUS

Capture performance:
Can provide information to allow for process optimisation and more efficient capture. MEA impurities can indicate degradation of sorbent beds

Transport infrastructure:
H_2O and H_2S impurities can react to form sulphuric acid which is corrosive and can damage pipelines. Glycol can also damage seals and other components



Storage integrity:
Non-condensable gases such as O_2, N_2, Ar, CH_4 and H_2 can reduce possible amount of CO_2 storage capacity. This can cause pipeline ductility issues and lower oil recovery

Utilisation:
The many different uses of CO_2 within industry have varying quality requirements, e.g. C_6H_6 requires analysis for food/beverage grade CO_2 as it spoils the flavour

NPL have provided recommendations on CO_2 purity for CCS processes:

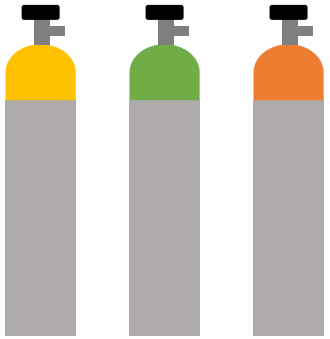
	Rationale	Pipeline	Storage		
			Saline reservoir sequestration	*Unmineable coal seams*	*Oil and gas recovery*
H_2O[a]	Reacts with sulphur to produce sulphuric acid which is corrosive	Use same maximum limits as storage method	300 µmol mol^{-1}	300 µmol mol^{-1}	300 µmol mol^{-1}
H_2S[b]	Toxic		5 µmol mol^{-1}	5 µmol mol^{-1}	5 µmol mol^{-1}
CO[b]	Toxic		20 µmol mol^{-1}	20 µmol mol^{-1}	20 µmol mol^{-1}
O_2	Non-condensable gas, thinning of pipeline, reacts with hydrocarbons, enhances growth of aerobic bacteria		4 cmol mol^{-1}	4 cmol mol^{-1}	100 µmol mol^{-1}
CH_4[c]	Non-condensable gas, pipeline ductility issues, flammable		4 cmol mol^{-1}	4 cmol mol^{-1}	1 cmol mol^{-1}
N_2[c]	Non-condensable gas		4 cmol mol^{-1}	4 cmol mol^{-1}	1 cmol mol^{-1}
Ar[c]	Non-condensable gas		4 cmol mol^{-1}	4 cmol mol^{-1}	1 cmol mol^{-1}
H_2[c]	Non-condensable gas, lower recovery of oil		4 cmol mol^{-1}	4 cmol mol^{-1}	1 cmol mol^{-1}
SO_x[b]	Toxic		0.5 µmol mol^{-1}	0.5 µmol mol^{-1}	0.5 µmol mol^{-1}
NO_x[b]	Toxic		0.5 µmol mol^{-1}	0.5 µmol mol^{-1}	0.5 µmol mol^{-1}
NH_3[b]	Toxic		25 µmol mol^{-1}	25 µmol mol^{-1}	25 µmol mol^{-1}
C_2H_6	Flammable, might cause asphyxiation at high temperatures		1 cmol mol^{-1}	1 cmol mol^{-1}	1 cmol mol^{-1}
C3[+]	Flammable, might cause asphyxiation at high temperatures		1 cmol mol^{-1}	1 cmol mol^{-1}	1 cmol mol^{-1}
Particulates	Not specified		1 µmol mol^{-1}	1 µmol mol^{-1}	1 µmol mol^{-1}
HCl[b]	Toxic		1 µmol mol^{-1}	1 µmol mol^{-1}	1 µmol mol^{-1}
HF[b]	Toxic		1.8 µmol mol^{-1}	1.8 µmol mol^{-1}	1.8 µmol mol^{-1}
HCN[b]	Toxic		0.9 µmol mol^{-1}	0.9 µmol mol^{-1}	0.9 µmol mol^{-1}
Hg[b]	Toxic		0.02 mg m^{-3}	0.02 mg m^{-3}	0.02 mg m^{-3}
Glycol	Damage to seals and other components		46 nmol mol^{-1}	46 nmol mol^{-1}	46 nmol mol^{-1}
MEA[b]	Toxic		1 µmol mol^{-1}	1 µmol mol^{-1}	1 µmol mol^{-1}

Purity requirements of carbon dioxide for carbon capture and storage, A. Murugan, et al., npl REPORT CSSC 0001

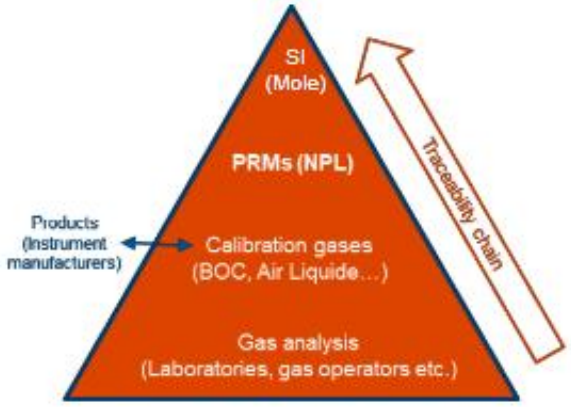
Building CO_2 Purity Infrastructure

Traceable PRMs and Accurate Purity Analysis Methods

Preparation of Primary Reference Materials (PRMs)



- ❑ PRMs are prepared gravimetrically following ISO 6142-1:2015
- ❑ Traceable to SI
- ❑ PRMs ensure measurements are traceable and accurate



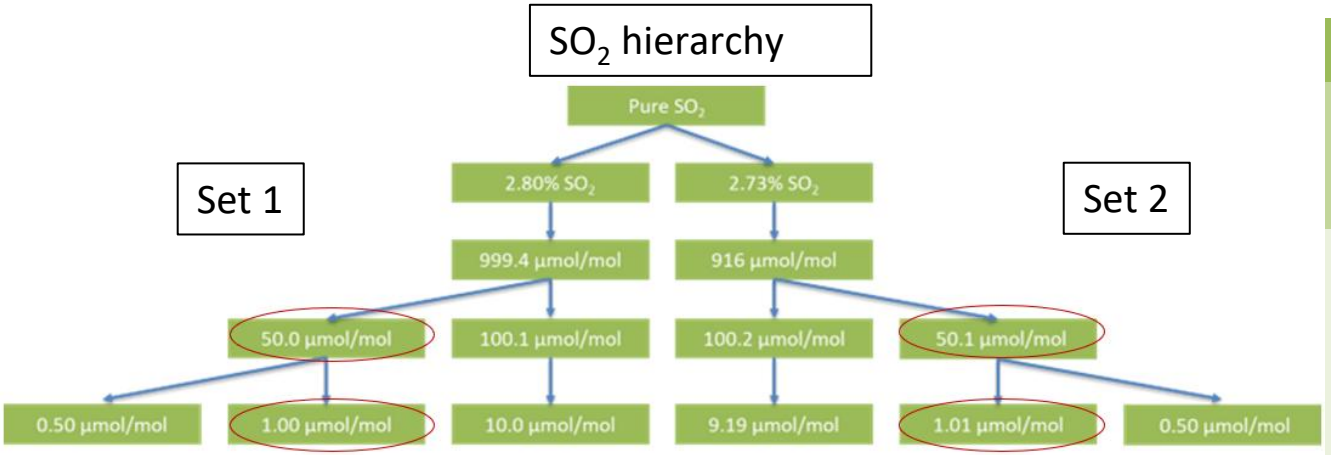
Gas Measurement Hierarchy

Development of Accurate Analytical Methods

- ❑ Traceable PRMs will be employed for method development
- ❑ Various analytical parameters will be assessed:
  - LOD/LOQ
  - Linearity & working range
  - Trueness
  - Selectivity & interferences
  - Precision: Repeatability & intermediate precision
  - Robustness
- ❑ Develop uncertainty budget: Following GUM
- ❑ Method validation according to ISO/IEC 17025

Metrology Development for Trace-level Reactive Impurities in CO_2

Preparation and Validation of SO_2 in CO_2 PRMs



PRM Hierarchy for SO_2 in CO_2 mixtures

Set 1			Set 2		
PRM	Gravimetric Amount Fraction of SO_2 (µmol/mol)	Gravimetric Uncertainty (%, *k=2*)	PRM	Gravimetric Amount Fraction of SO_2 (µmol/mol)	Gravimetric Uncertainty (%, *k=2*)
D180420	27967.66	0.138	D180421	27295.16	0.142
D180724	999.45	0.228	D049952	916.79	0.246
D180717	100.09	0.232	D180719	100.20	0.250
D180698	50.04	0.246	D180720	50.058	0.260
D180493	10.00	0.550	D180435	9.19	0.154
D180428	1.00	0.298	D180362	1.01	0.358
D180324	0.50	0.550	D180487	0.50	0.532

Gravimetric amount fractions with combined uncertainty *(k=2)* of SO_2 in the PRMs

SO_2 in CO_2 Acquisition Method (GC-SCD)	
Method Parameter	**Details**
Gas Chromatograph Model	Agilent 8890 (G3545A)
Detector Model	Agilent 8255 Sulfur Chemiluminescence Detector
Column	Agilent 19095Z-626:HP-1
Carrier Gas	He
Oven Temperature	30 °C

Method Parameters for SO_2 Quantification

	D180698	D180720	D180428	D180362
Gravimetric Amount Fraction of SO_2 (µmol/mol)	50.04	50.06	1.00	1.01
Analytical Amount Fraction of SO_2 (µmol/mol)	49.67	50.81	0.88	1.14
Expanded combined uncertainty (%, *k=2*)	2.90	2.92	3.64	3.47

Validation results of 1 µmol/mol and 50 µmol/mol SO_2 in CO_2 PRMs

Commercial Project (2024-2025)

Similarly, traceable PRMs & accurate methods developed for supporting analysis of

- NO (0.5 to 500 µmol/mol) → GC-NCD
- NO_2 (1.0 to 250 µmol/mol) → GC-NCD
- O_2 (5.0 to 100 µmol/mol) → GC-PDHID
- H_2O (1.0 to 500 µmol/mol) → QMA
- H_2S (0.02 to 100 µmol/mol) → GC-SCD

- Extending PRMs preparation and Analysis Methods to multicomponent mixtures

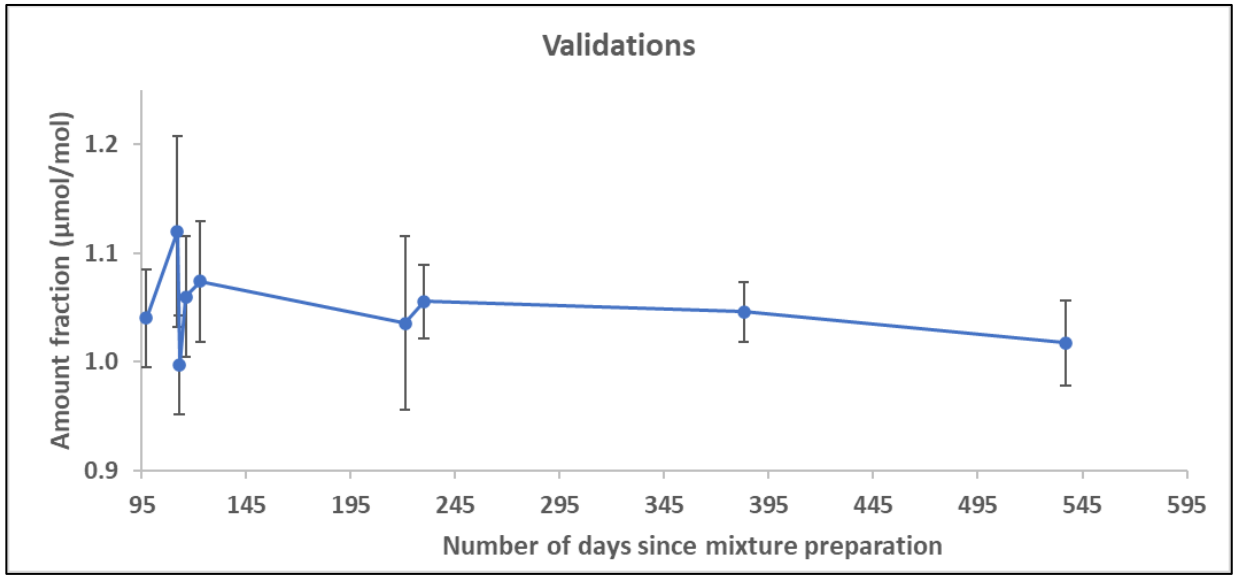
PRMs and Methods Developed under MetCCUS Project

MetCCUS Project Updates WP3- A3.1.3

Binary PRMs

Validation of DMS in CO_2

- Validation of 1 µmol/mol DMS in CO_2 was carried out 3 times on a GC-SCD using a calibration curve of DMS in CO_2 standards from 10-0.5 µmol/mol
- DMS amount fraction remains stable after 6, 12, and 18 months



Cylinder ID	Mixture type	Gravimetric amount fraction (µmol/mol)	Gravimetric u/c, *k*=2 (µmol/mol)
D049938	Standard	9.99	0.018
D050052	Standard	5.09	0.018
D049955	Standard	1.00	0.004
D610430	Unknown	1.03	0.004
D755047	Standard	0.53	0.004

Gravimetric amount fractions with combined uncertainty *(k=2)* of DMS

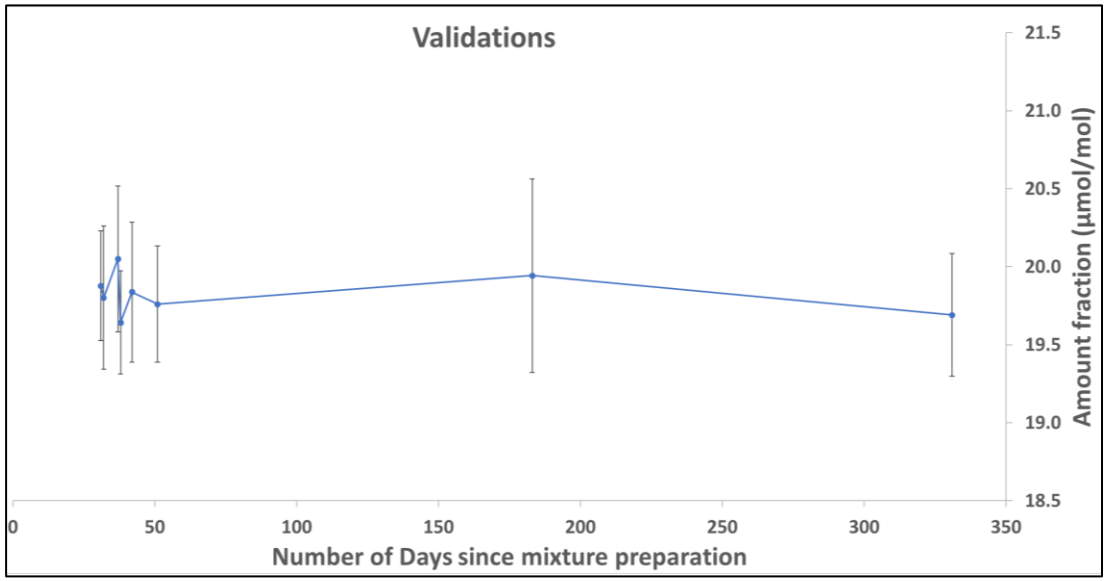
Validation results of 1 µmol/mol of DMS in CO_2 PRMs and stability studies

D610430	Validation 1	Validation 2	Validation 3	Robustness (24 ml/min)	6 month stability	Robustness (36 ml/min)	12 month stability	18 month stability
Analytical amount fraction (µmol/mol)	1.04	1.00	1.06	1.07	1.04	1.06	1.05	1.02
Analytical uncertainty, *k*=2 (%)	3.91	4.55	5.23	5.28	7.71	3.20	2.62	3.85

MetCCUS Project Updates WP3- A3.1.3 – Binary PRMs

Validation of EtOH in CO_2

- Validation of 20 µmol/mol EtOH in CO_2 was carried out 4 times on a GC-MS/FID using a calibration curve of EtOH in CO_2 standards from 1000-5 µmol/mol
- EtOH amount fraction remains stable after 6, 12 months



Cylinder ID	Mixture type	Gravimetric amount fraction (µmol/mol)	Gravimetric u/c, *k*=2 (µmol/mol)
D049959	Standard	1002	0.24
D180567	Standard	250	0.07
D180254	Standard	50	0.05
D050229	Unknown	20.0	0.04
D180264	Standard	4.5	0.01

Gravimetric amount fractions with combined uncertainty *(k=2)* of EtOH

Validation results of 20 µmol/mol of EtOH in CO_2 PRMs and stability studies

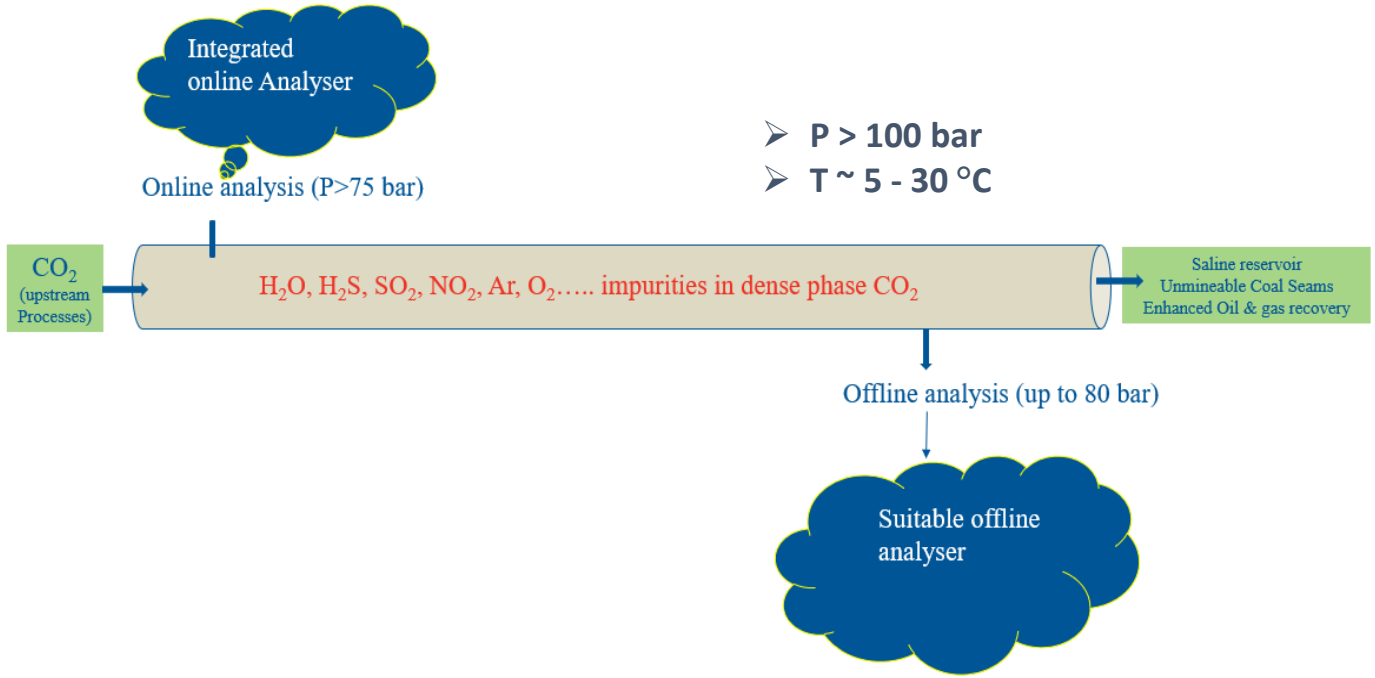
D050229	Validation 1	Validation 2	Validation 3	Robustness (15 ml/min)	Validation 4	Robustness (45 ml/min)	6 month stability	12 month stability
Analytical amount fraction (µmol/mol)	19.88	19.80	20.05	19.64	19.84	19.76	19.94	19.69
Analytical uncertainty, *k*=2 (%)	1.76	2.32	2.33	1.69	2.26	1.88	3.12	1.99

Other mixtures and methods developed under MetCCUS project – WP3

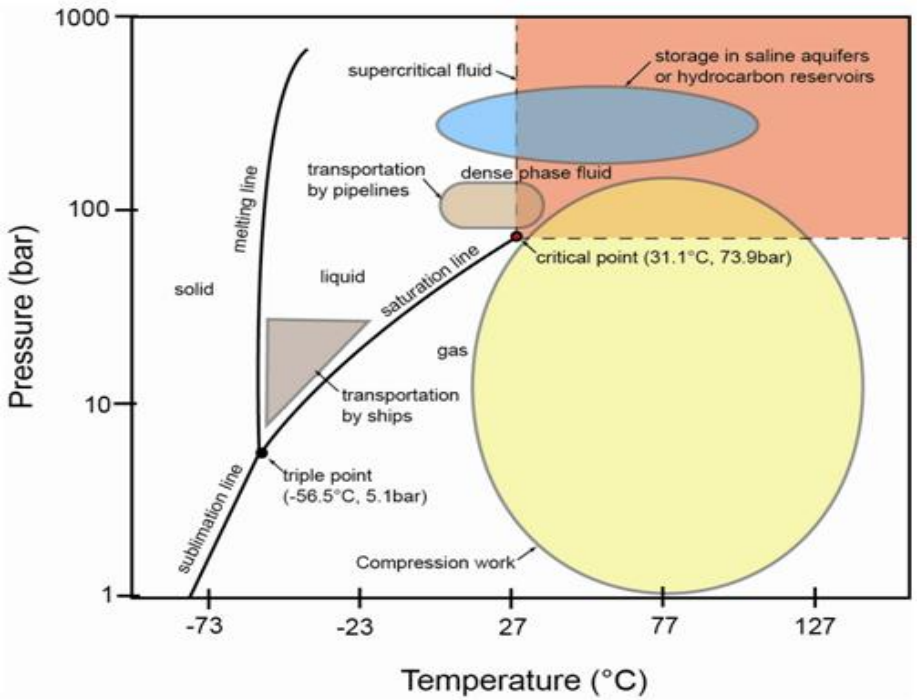
	Mixture 1			Mixture 2			Mixture 3
Participants	Impurity	Amount fraction	Cylinder type	Impurity	Amount fraction	Cylinder type	Impurity
VSL	H_2O	10 ppm	Aculife IV/-	NO_2	1 ppm	Alphatech /-	SO_2, ≤20 ppm
NPL	C_2H_5OH	≤20 ppm	Spectra-seal	DMS	≤1 ppm	Spectra-seal	-
CMI	NO_2	≤ 100 ppm	AL/ Aculife	N_2O	≤ 10 ppm	AL/ Aculife	-
IPQ	H_2S	10 ppm	Aculife III/ IV	SO_2	≤20 ppm	Aculife III/ IV	-

Metrology Development for dense phase CO_2

Can gas phase metrology can be extended to dense phase CO_2?



Schematic of Pipeline transport and need for dense phase CO_2 purity analysis



Phase diagram of CO_2

- CO_2 <u>shows anomalous properties</u> as supercritical fluid.
- Pressure variation studies – effect on the analysed impurities in CO_2

Commercial Project (2024-2025)
Ongoing work under NMS (2024-2029)

NPL Current Capability

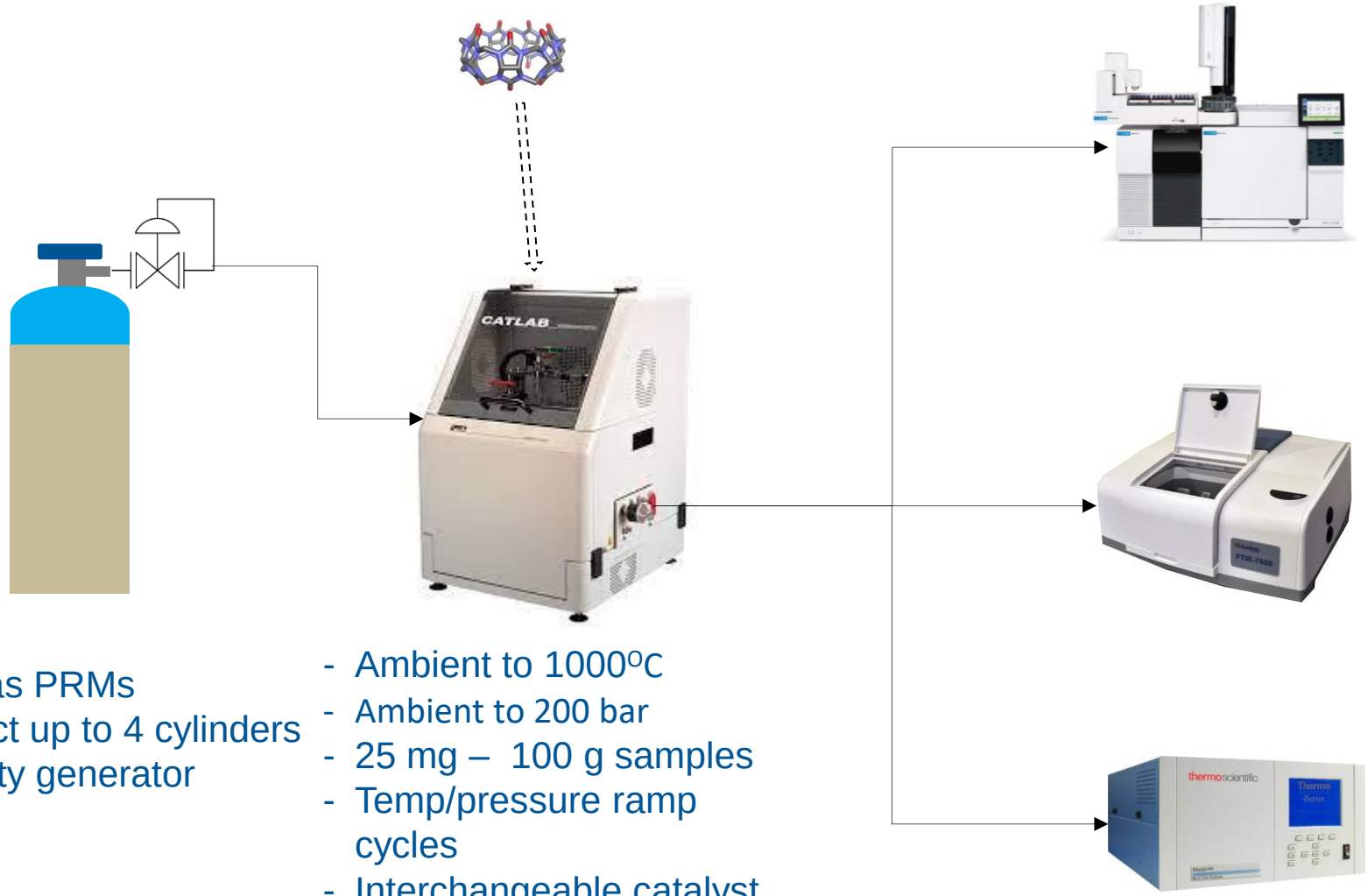
Component	ISO 27913		UK CCUS projects specifications Summary			NPL measurement capability		
	Units	Limit	Units	Limit (Min)	Limit (Max)	Units	Lower limit	Upper limit
CO_2	mol%	≥ 95.0						
N_2 (1)	mol%	4	mol%	1	4	mol%	0.03	4
H_2 (1)	mol%	1	mol%	0.05	2	mol%	0.04	2.0
Ar (1)	mol%	4	mol%	1	4	mol%	0.005	4
CO (1)	mol%	0.2	mol%	0.01	0.2	mol%	0.0003	0.1
Methane (1)	mol%	4	mol%	1	4	mol%	0.023	4
Ethane (1)	mol%	4	mol%	1	4	mol%	0.005	0.5
Propane & Other Aliphatic Hydrocarbons (2)	mol%	0.15 in total	mol%	0.15	2	mol%	0.005	0.01
H_2O	ppm mol	50	ppm mol	20	50	ppm mol	1	500
O_2	ppm mol	10	ppm mol	10	20	ppm mol	5	1000
NOx (NO, NO_2) (3)	ppm mol	10	ppm mol	1	100	ppm mol	0.5	500
SOx (SO, SO_2, SO_3) (4)	ppm mol	10	ppm mol	0.1	50	ppm mol	0.5	100
H_2S	ppm mol	5	ppm mol	5	20	ppm mol	0.02	100
COS	ppm mol	100	ppm mol	0.02	10	ppm mol	0.01	100
CS_2	ppm mol	20	ppm mol	0.2	10			
NH_3	ppm mol	10	ppm mol	10	1500	ppm mol	10	1000
BTEX (5)	ppm mol	15 in total	ppm mol	0.001	50	ppm mol	1.4	80
Methanol	ppm mol	350	ppm mol	10	500	ppm mol	50	350
VOCs (8) - DMS	mg/Nm^3	48 in total	ppm mol	20	60	ppm mol	0.5	10
VOCs (8) - Ethanol	mg/Nm^3	48 in total	ppm mol	20	60	ppm mol	4.5	1000
Amines (10,11)	ppb mol	100 in total	ppm mol	0.08	10			
Nitrosamines and Nitramines (13)	µg/Nm^3	3 in total	µg/Nm^3	0.1	5			
Naphthalene (14)	ppb mol	100	ppb mol	5	250			

NPL measurement capability covers ISO 27913 threshold limit

NPL measurement capability exists but doesn't cover ISO 27913 threshold limit. Additional work required to extend working range

NPL measurement capability development in progress 25/26

Performance Testing of Carbon Capture Materials



- Flue gas PRMs
- Connect up to 4 cylinders
- Humidity generator

- Ambient to 1000^{o}C
- Ambient to 200 bar
- 25 mg – 100 g samples
- Temp/pressure ramp cycles
- Interchangeable catalyst cartridge

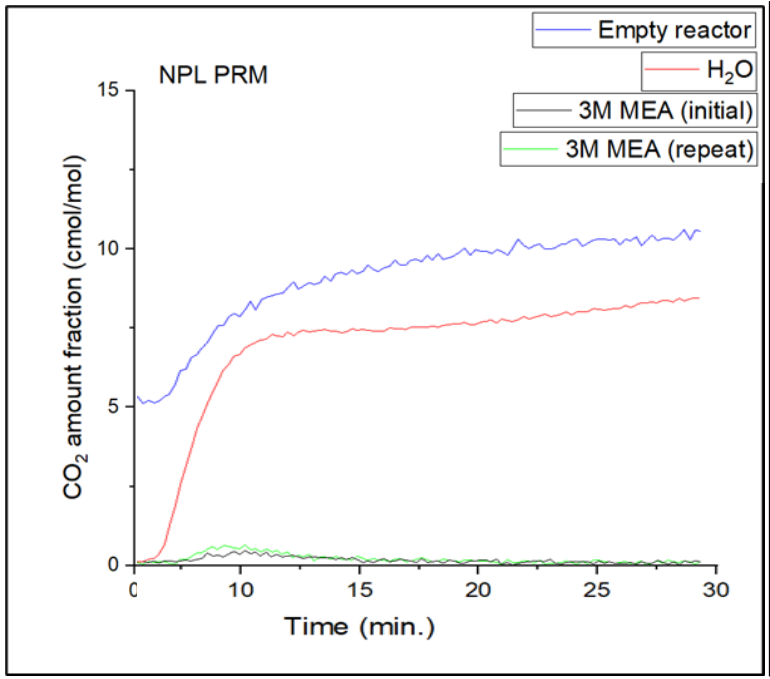
Materials Testing Platform

Assessment Criteria

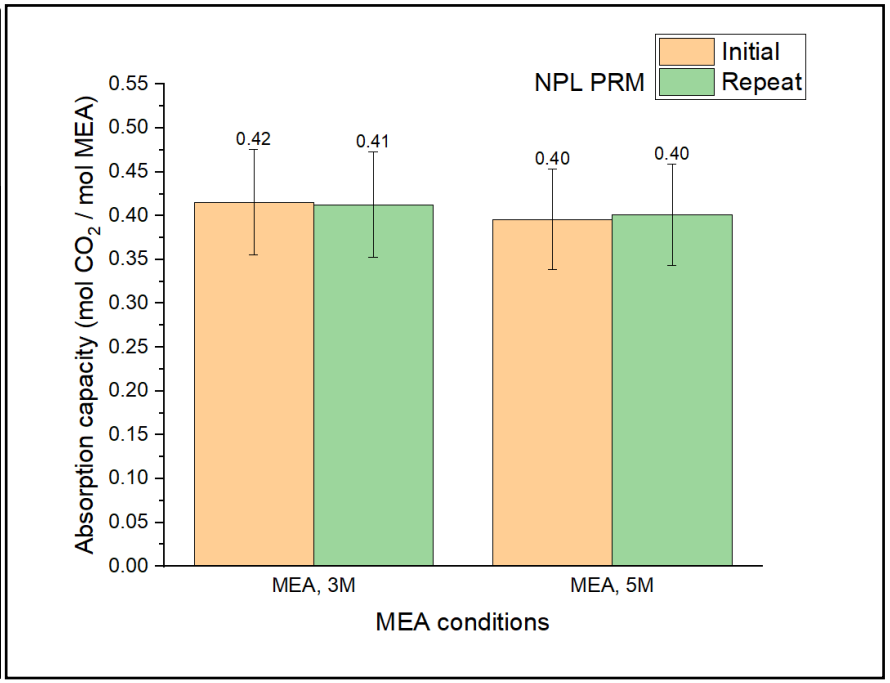
- **CO_2 capture efficiency**
- **Degradation products**
- **Material stability**
- **CO_2 purity**

Method Development for liquid solvent testing

High pressure reactor vessel with a temperature controller and stirrer



CO_2 amount fraction against time, 3M MEA with NPL PRM.



CO_2 absorption capacity for 3M and 5M MEA solution on interaction with NPL PRM.

- Method development and uncertainty budget calculations.
- Advanced industrial solvents are being tested.
- Effect of impurities on capture capacity and stability is assessed.

Work funded through NMSCCUS Net-Zero Uplift project (2022-2025)

Conclusions

❑ **Supporting CCUS industry by Developing Traceable Metrology for CO_2 Gas Quality and by offering;**

✓ **Bespoke Primary Reference Materials (PRMs)**

✓ **Instrument Calibration**

✓ **Sampling and Purity Analysis of CO_2**

✓ **Assessment/Benchmarking of Capture solvents/sorbents for efficiency, stability and CO_2 purity.**

✓ **Qualify and quantify degradation products/impurities specific to a CCUS technology.**

✓ **Proficiency Testing**

Research Funded by…

NPL

EMPIR

EURAMET

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

Department for Science, Innovati & Technology

Origen

bp

C-Capture

METCCUS

Metrology for decarbonising the gas grid

Thank you for your attention

Any Questions?

Department for Science, Innovation & Technology

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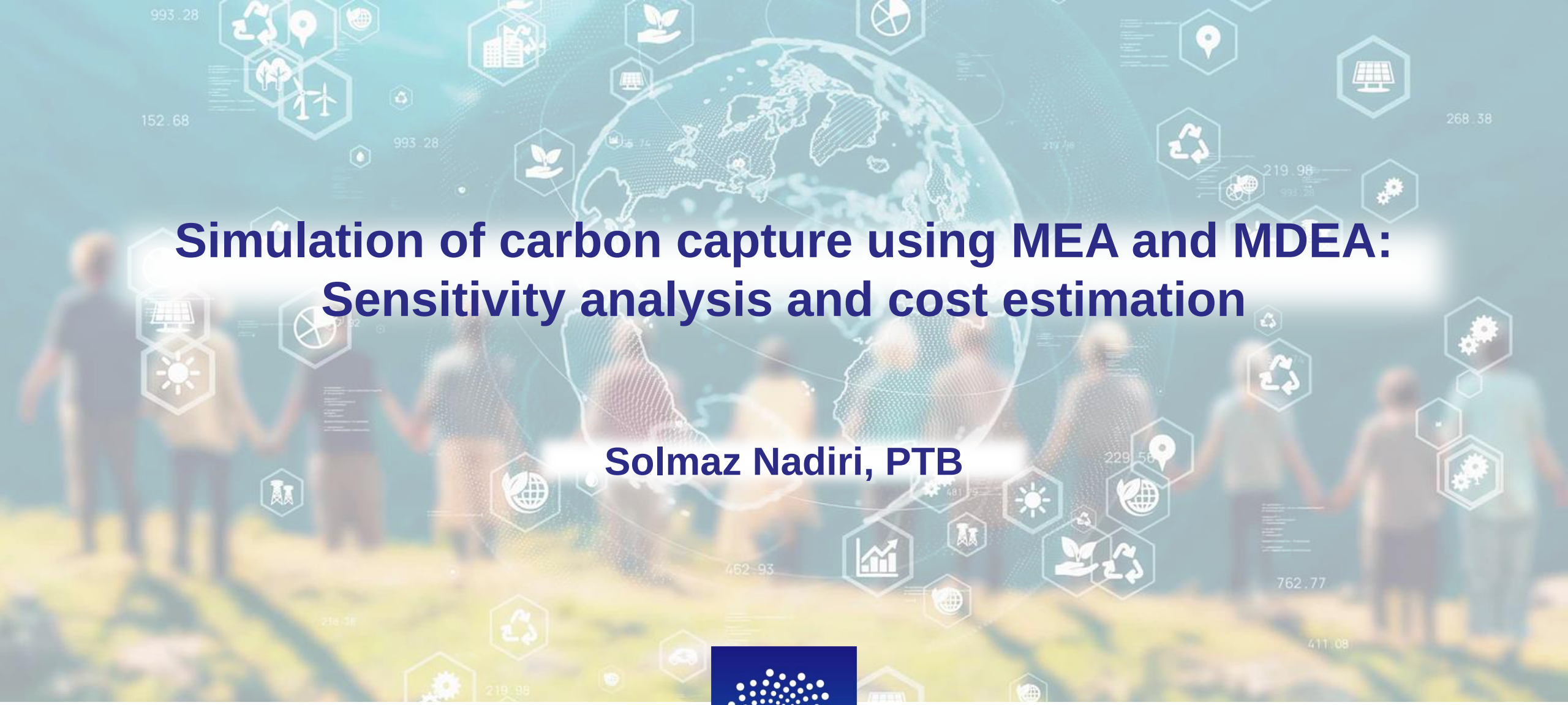


Simulation of carbon capture using MEA and MDEA: Sensitivity analysis and cost estimation

Solmaz Nadiri, PTB

ENERGY GASES

METCCUS

VSL

MET4H2

BiometCAP

Physikalisch-Technische Bundesanstalt
Braunschweig and Berlin
National Metrology Institute

Simulation of carbon capture using MEA and MDEA:

Sensitivity analysis and cost estimation

MetCCUS, 26th March 2025

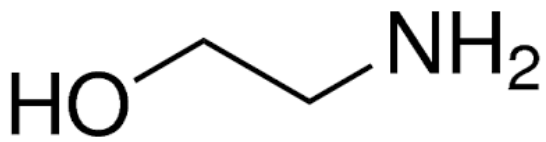
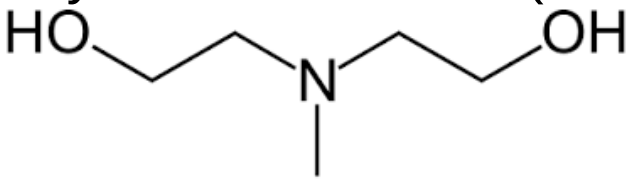
Solmaz Nadiri

Where simulation meets measurement in CCUS

- ✓ Even the best simulation relies on accurate input data.
- ✓ Metrology ensures the simulation reflects reality.

Predict CO_2 capture efficiency, reboiler duty	Accurate CO_2 concentration measurement
Model solvent circulation and process dynamics	Flow, temperature, pressure sensors
Sensitivity analysis	Calibration of analyzers and instruments
Cost and energy estimates	Real data from flue gas & utility systems

Solvents

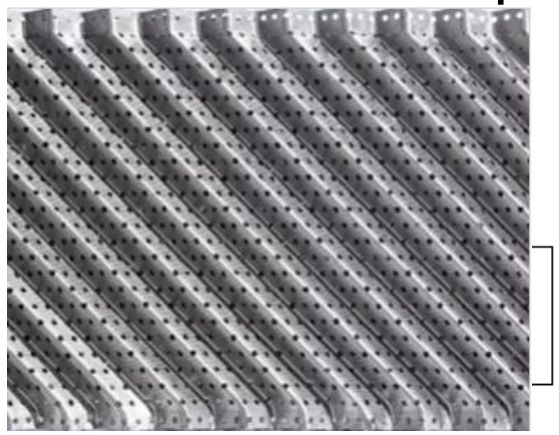
	Monoethanolamine (MEA)	Methyl diethanolamine (MDEA)
		
Boiling Point (°C)	~170°C	~247°C
Viscosity (solution)	High	Low
CO_2 Capacity	(~0.4–0.5 mol CO_2/mol amine)	(~1 mol CO_2/mol amine)
Reaction Rate	Very fast	Very slow
Heat of Reaction with CO_2	~85 kJ/mol CO_2	~65 kJ/mol CO_2
Corrosiveness	High	Low
Thermal Stability	Low	High
Solvent Cost	Low	High
Regeneration Energy	High	Low

Simulation Setup

	MEA	MDEA
Flue gas	72 kg/hr CO_2: 8.5 %wt H_2O: 7.1 %wt N_2 & O_2: 84.4 %wt	
Property method	ENRTL-RK	
Solvent total flow	201.3 kg/hr	499.42 kg/hr
Solvent concentrations	27.5 %wt	40 %wt
Absorber	D=0.125 m, H=4.62 m	D=0.2 m, H=20.42 m
Stripper	D=0.125 m, H=2.92 m	D=0.125 m, H=3.42 m

Process Flow Diagram

FLEXIPAC structured packing



MDEA and MEA comparison

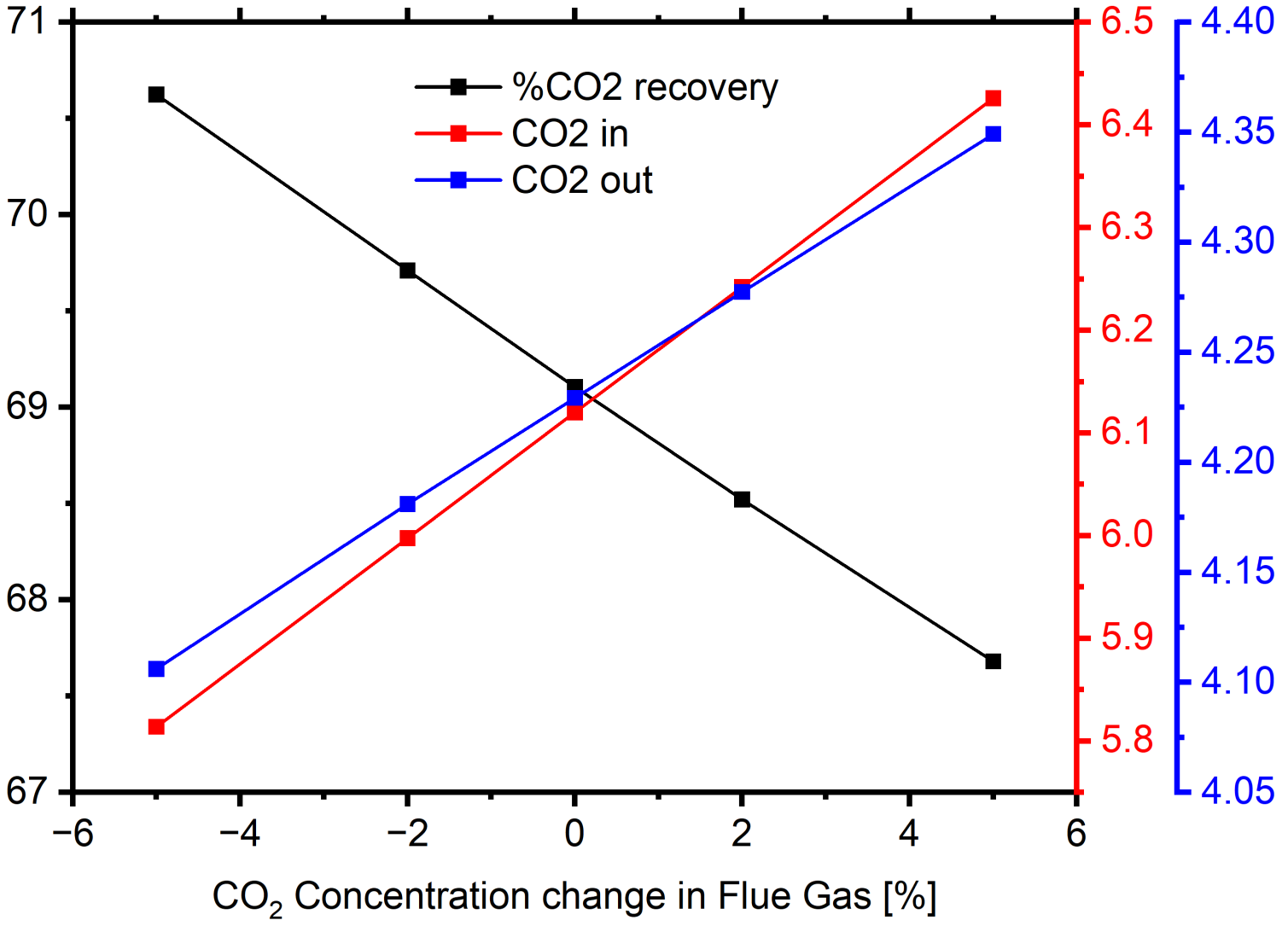
	MEA	MDEA
% CO_2 removal	72.6	69
Reboiler heat duty [kW]	7.05	6.75
Electricity [kW]	61.5	52.4
Cooling Water [m^3/h]	0.012	0.015
Steam @100PSI* [kg/h]	12.27	11.75

*100 PSI ≅ 6.9 bar

Impact of measurement uncertainty on CO_2 Capture Efficiency

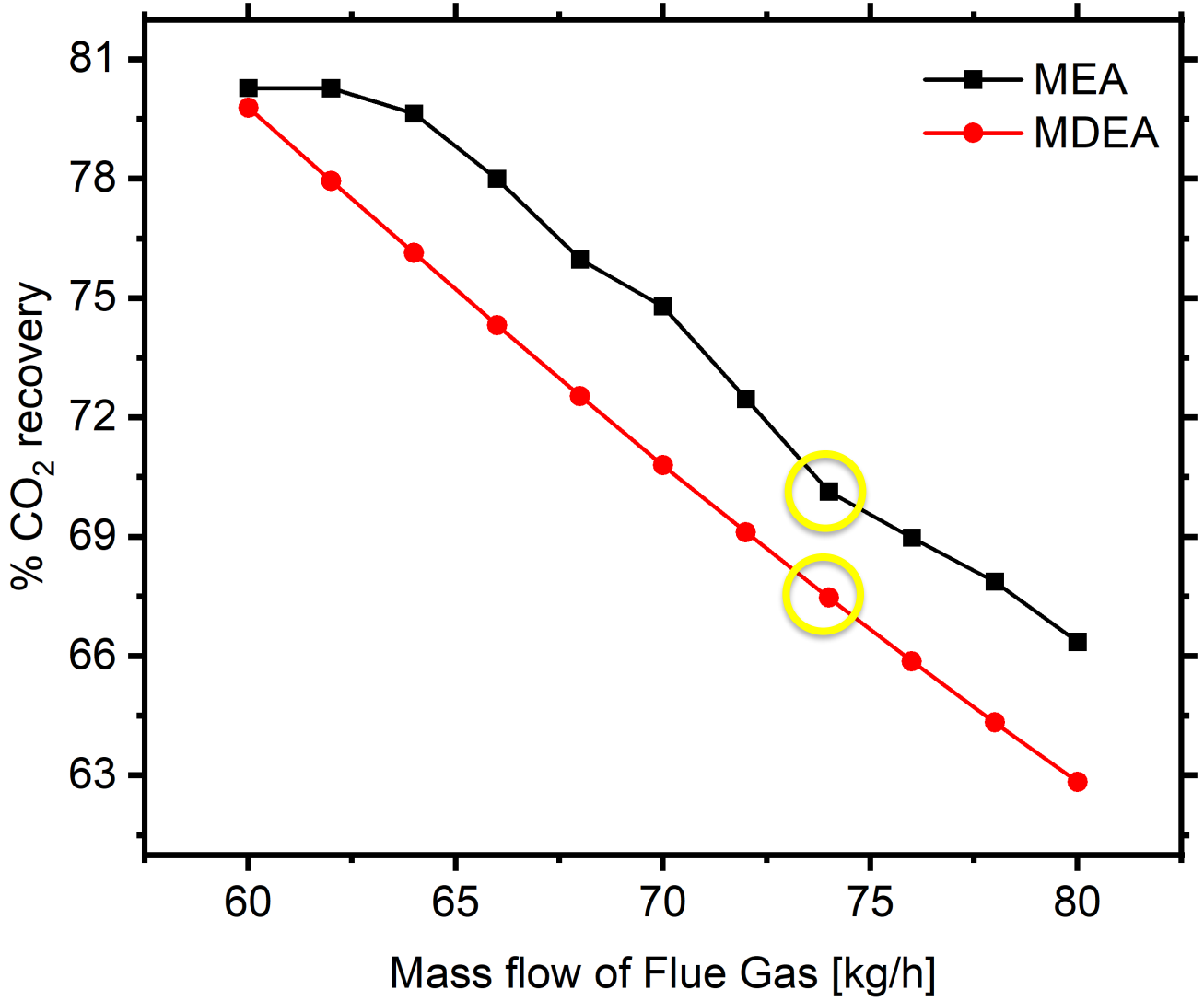
- A ±5% error in CO_2 concentration measurement can cause a ±3% shift in calculated removal efficiency.

- This could lead to incorrect decisions in:
  - Process optimization
  - Economic evaluation
  - Regulatory reporting
  - Lifecycle assessments



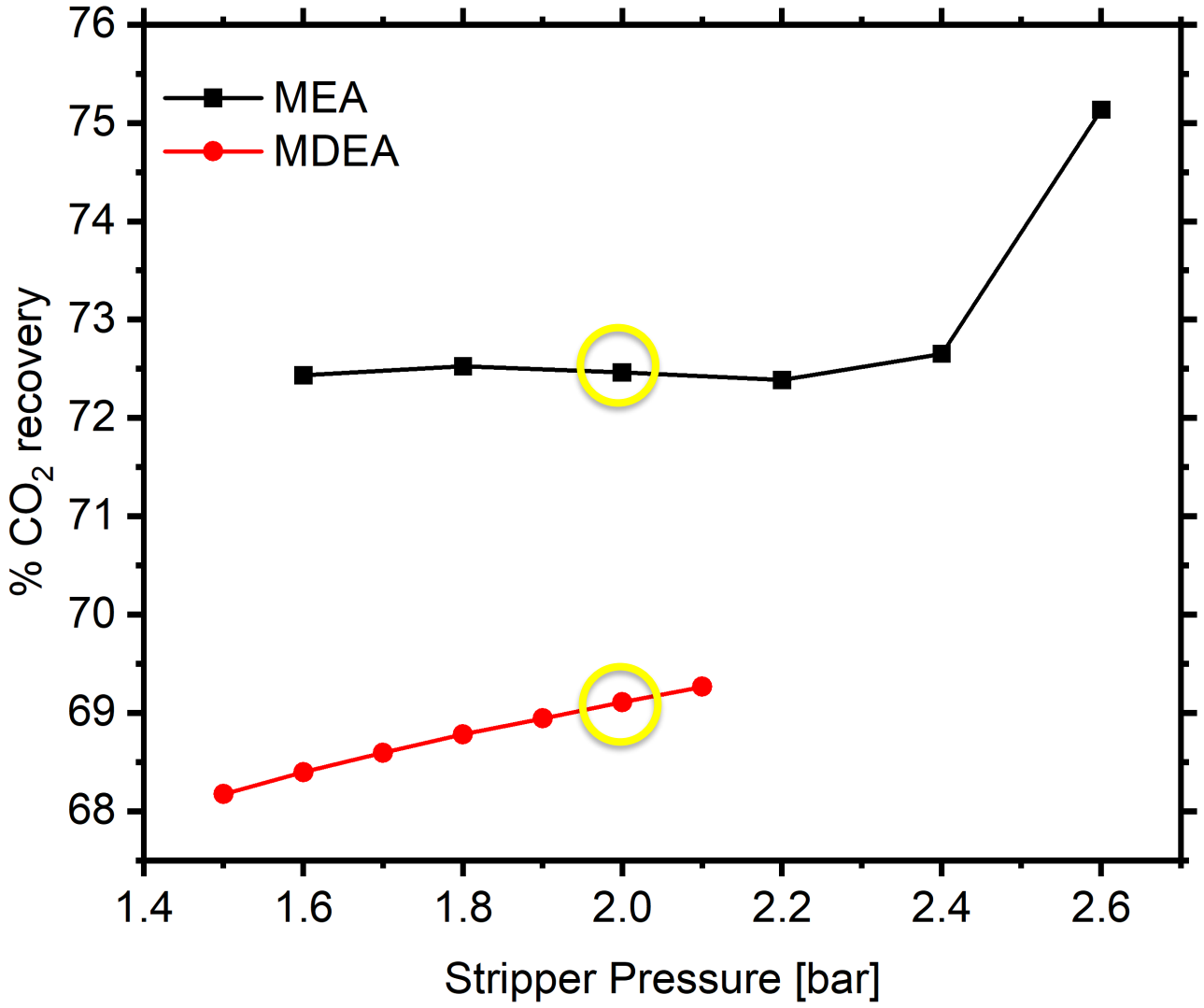
Effect of Flue Gas Flowrate on CO_2 Recovery

- As flue gas flow increases, CO_2 recovery declines for both solvents due to reduced contact time.
- MDEA's performance drops off faster than MEA, showing lower absorption capacity at high gas loads.
- Useful for designing systems under fluctuating flue gas loads.
- Highlights importance of precise flue gas metering and flow measurement.



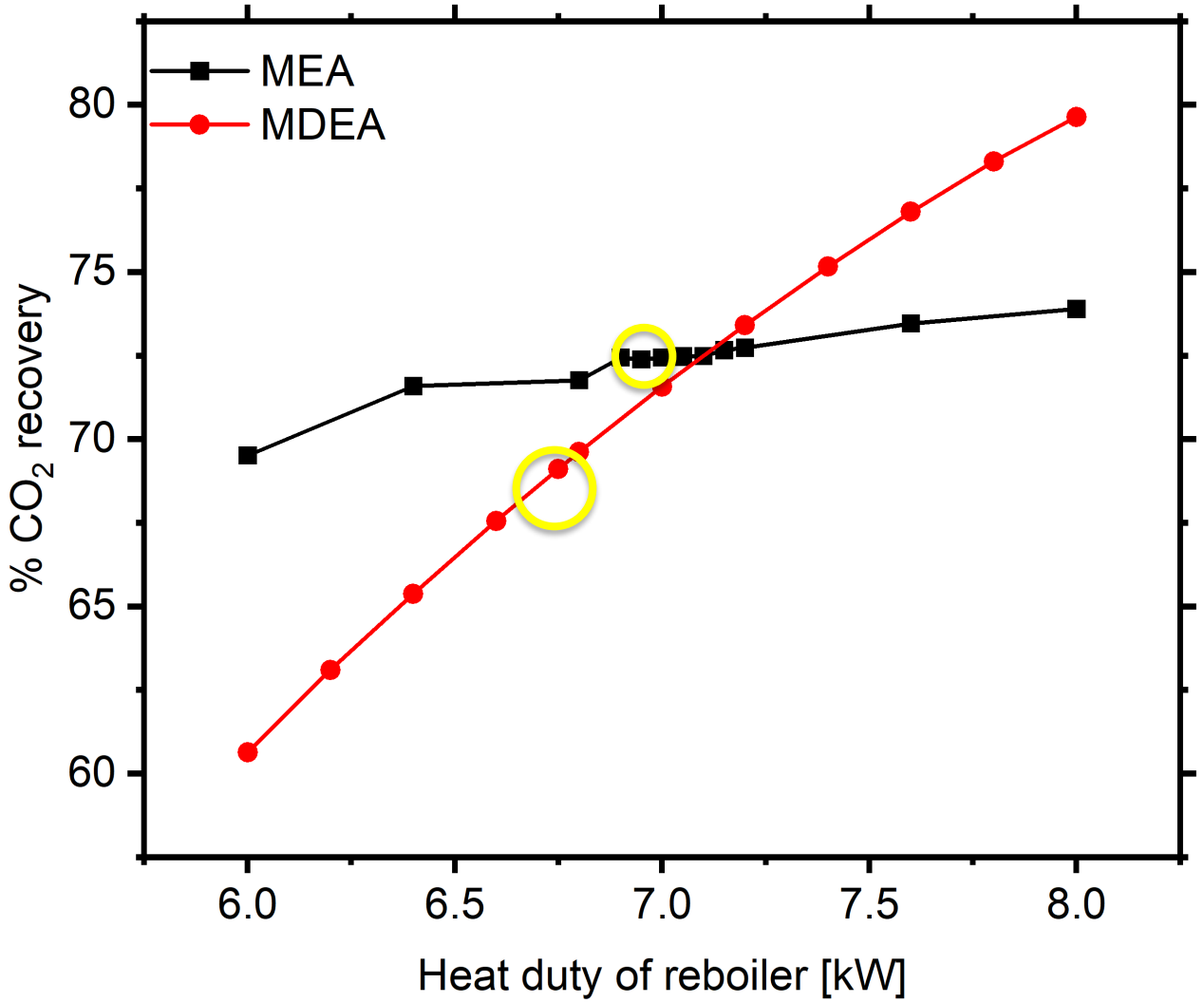
Effect of **Stripper Pressure** on CO_2 Recovery

- CO_2 recovery for MEA remains stable until a sudden jump, likely due to improved driving force.
- MDEA responds more linearly but stays less efficient overall.



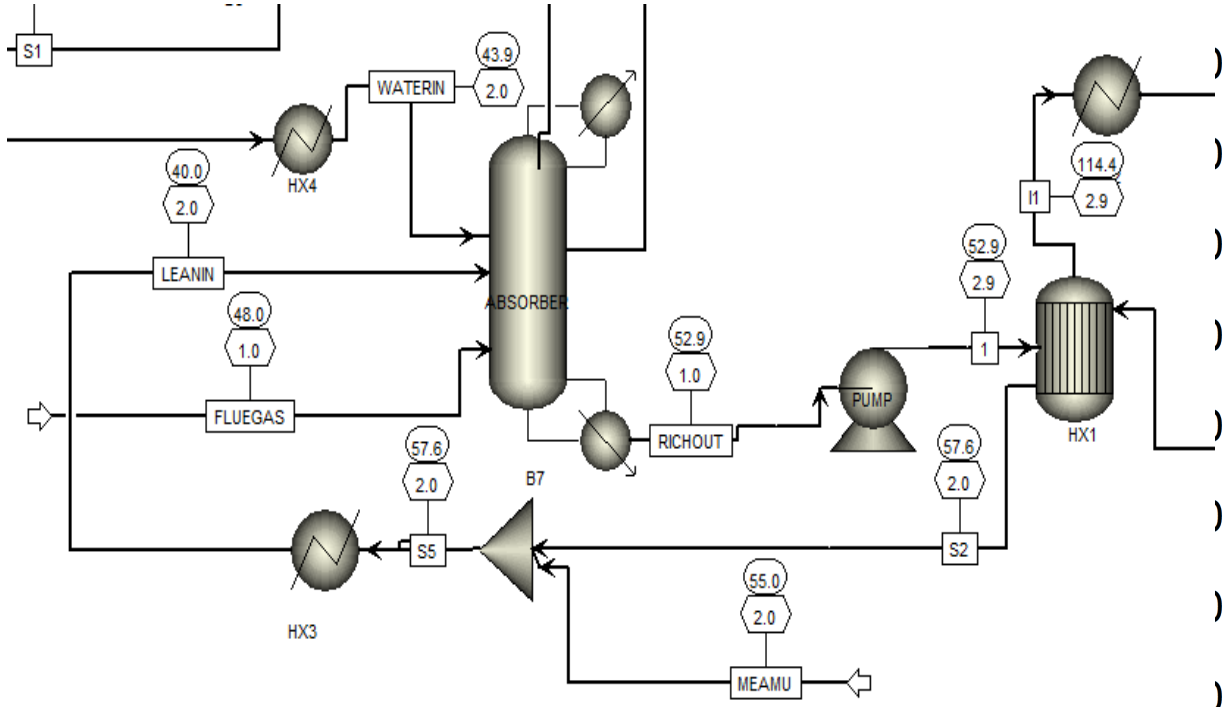
CO_2 Recovery vs. Reboiler Duty

- MEA achieves high recovery with less energy increase, making it more efficient up to ~7.2 kW.
- MDEA's higher regeneration energy yields higher CO_2 capture only at high duty.

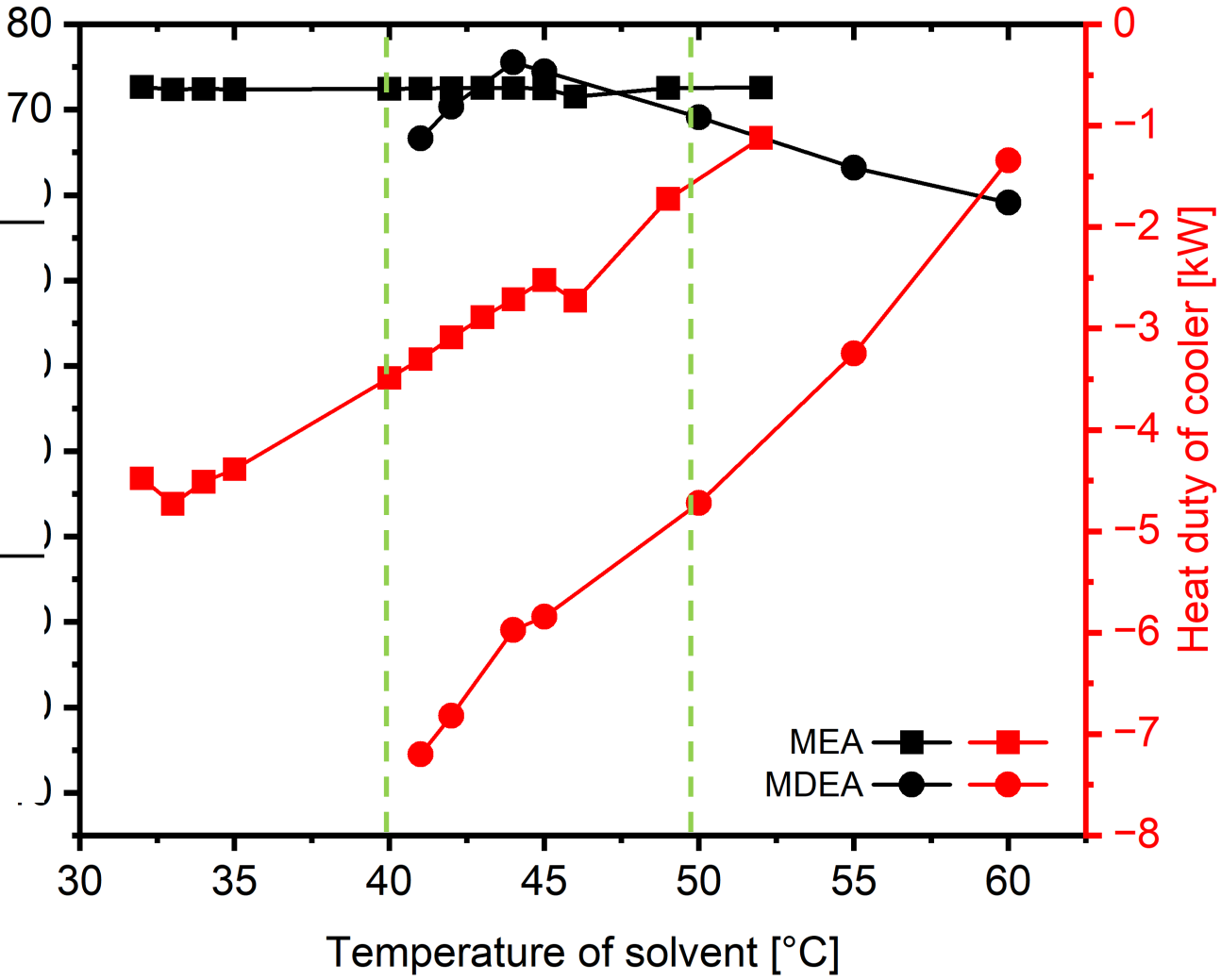


Impact of Lean Solvent Temperature on CO_2 Recovery and Cooling Duty

- MEA is cooled from 58°C, and MDEA from 60°C before entering



between thermal energy use and absorption efficiency.



Conclusion and Outlook:

- **MEA** performs better in terms of CO_2 recovery, especially at low flue gas flowrates and moderate energy input.
- **MDEA** is more energy-efficient at higher duties but is sensitive to temperature and less effective at low CO_2 partial pressures.

- Sensitivity analysis shows that: Small changes in operating parameters (like pressure, flowrate, temperature) can significantly affect CO_2 capture performance.
- Accurate measurements of CO_2 concentrations, flowrates, and temperatures are crucial, even small errors (±5%) can distort key performance indicators.

🔍 Metrology Insight:

- Reliable CCUS system design depends on trusted data inputs, and this is where metrology makes the invisible impact visible.

🔮 Outlook:

- Integrate uncertainty quantification into simulations.
- Use simulation as a tool to guide measurement priorities.
- Strengthen collaboration between process modeling and measurement science in future MetCCUS work.

Thank you for your attention!

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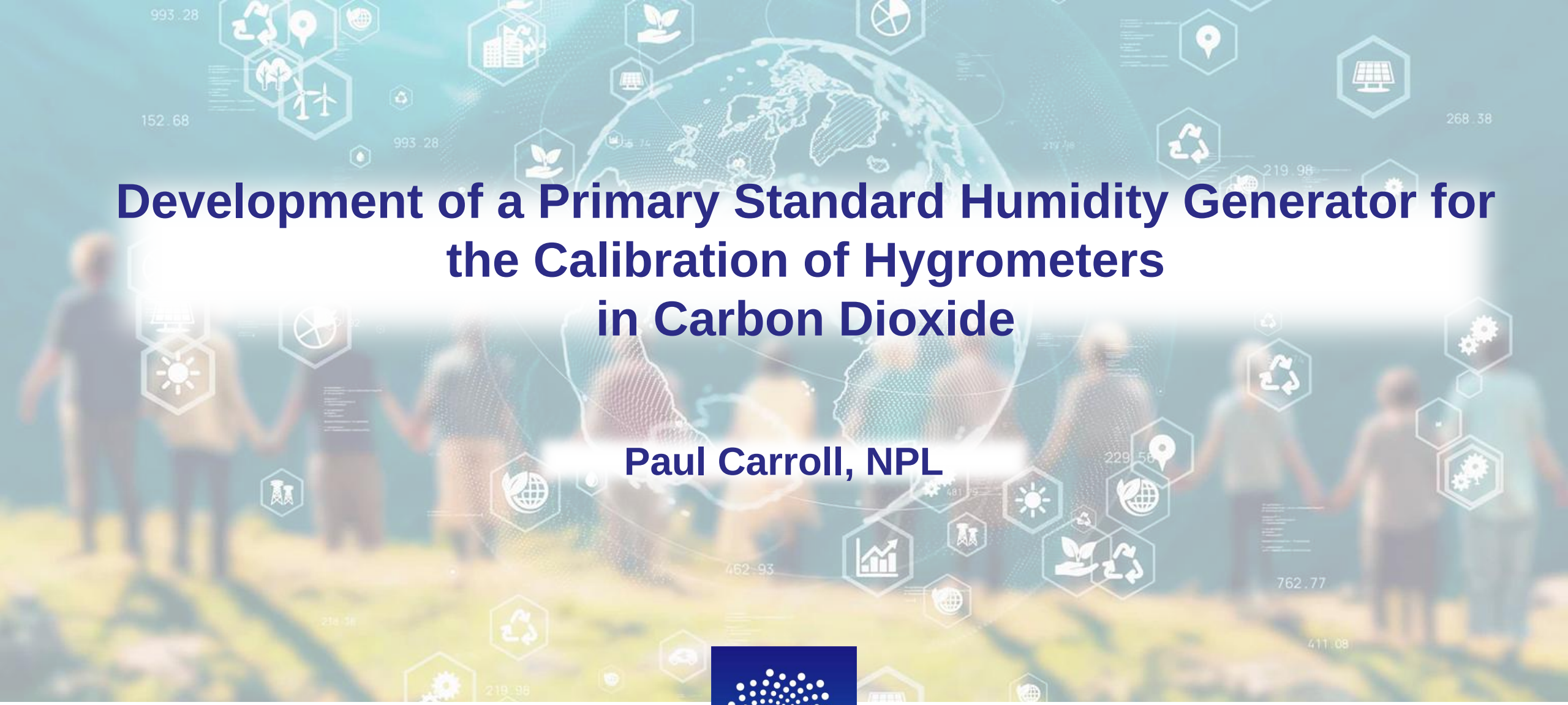


Development of a Primary Standard Humidity Generator for the Calibration of Hygrometers in Carbon Dioxide

Paul Carroll, NPL

ENERGY GASES

METCCUS

VSL

MET4H2

BiometCAP

METCCUS

A PRIMARY STANDARD HUMIDITY GENERATOR FOR THE CALIBRATION OF HYGROMETERS IN CARBON DIOXIDE

PAUL CARROLL - NPL

METROLOGY SUPPORT FOR CARBON CAPTURE UTILISATION AND STORAGE

The project has received funding from the European Partnership on Metrology, co-financed by European Union Horizon Europe Research and Innovation Programme and from the Participating States.

NPL

EURAMET

METCCUS

A PRIMARY STANDARD HUMIDITY GENERATOR FOR THE CALIBRATION OF HYGROMETERS IN CARBON DIOXIDE

- The need for humidity calibration capabilities in carbon dioxide.
- Adaptation of existing humidity generator to be compatible with CO_2 operation.
- Primary traceability to dew-point temperature units (°C) via reference PRT calibrated against NPL Temperature Standards.
- Example of first trial single-pressure dew-point temperature calibration.
- Further trial calibration of in-house water vapour spectrometer also performed.
- Discussion on conversion of reference value to other humidity units e.g amount fraction of water vapour.

THE NEED FOR HUMIDITY CALIBRATION CAPABILITIES IN CARBON DIOXIDE

- In carbon capture usage and storage (CCUS), monitoring of the quality of carbon dioxide (CO_2) is important during transportation, processing and storage.

- Water vapour is particularly important in order to prevent corrosion of system pipework and components.

- Traceable humidity measurements of suitable accuracy required to ensure that regulatory limits are not exceeded.

NPL

THE NEED FOR HUMIDITY CALIBRATION CAPABILITIES IN CARBON DIOXIDE

- The provision of primary dew-point calibration standards for air at atmospheric pressure is well established.
- But hygrometers are used industrially in CCUS applications to make humidity measurements of CO_2 at a wide range of pressures.
- Some hygrometer types are affected by the background gas species or pressure -need to calibrate hygrometers in the conditions of use.
- To address this, a capability for humidity calibration in CO_2 has been developed at the UK National Physical Laboratory.

ADAPTATION AND VALIDATION OF AN EXISTING PRIMARY HUMIDITY STANDARD

- Thunder 3900 Low Humidity Generation System successfully adapted for use with CO_2.
- Primary traceability to dew-point temperature units (°C) via reference PRT calibrated against NPL Temperature Standards.
- Frost-point temperature range -60 °C to -10 °C
- Water vapour amount fraction range 10 µmol·mol^{-1} to 0.25 %

Int J Thermophys (2015) 36:3453–3465
DOI 10.1007/s10765-015-1984-2

A Calibration Facility for Dew Point in Air up to 1 MPa

P. A. Carroll[1] · S. A. Bell[1] · M. Stevens[2]

Identification Number/DOI:
10.1007/s10765-015-1984-2

ADAPTATION AND VALIDATION OF AN EXISTING PRIMARY HUMIDITY STANDARD

Adaptation details:

- Confirmed with manufacturer compatibility of existing components with CO_2
- Modified dry gas bleed pipework connections of generator so that CO_2 not venting into laboratory.
- Added exhaust lines routed to extraction to avoid risk of build-up of CO_2 in the laboratory.

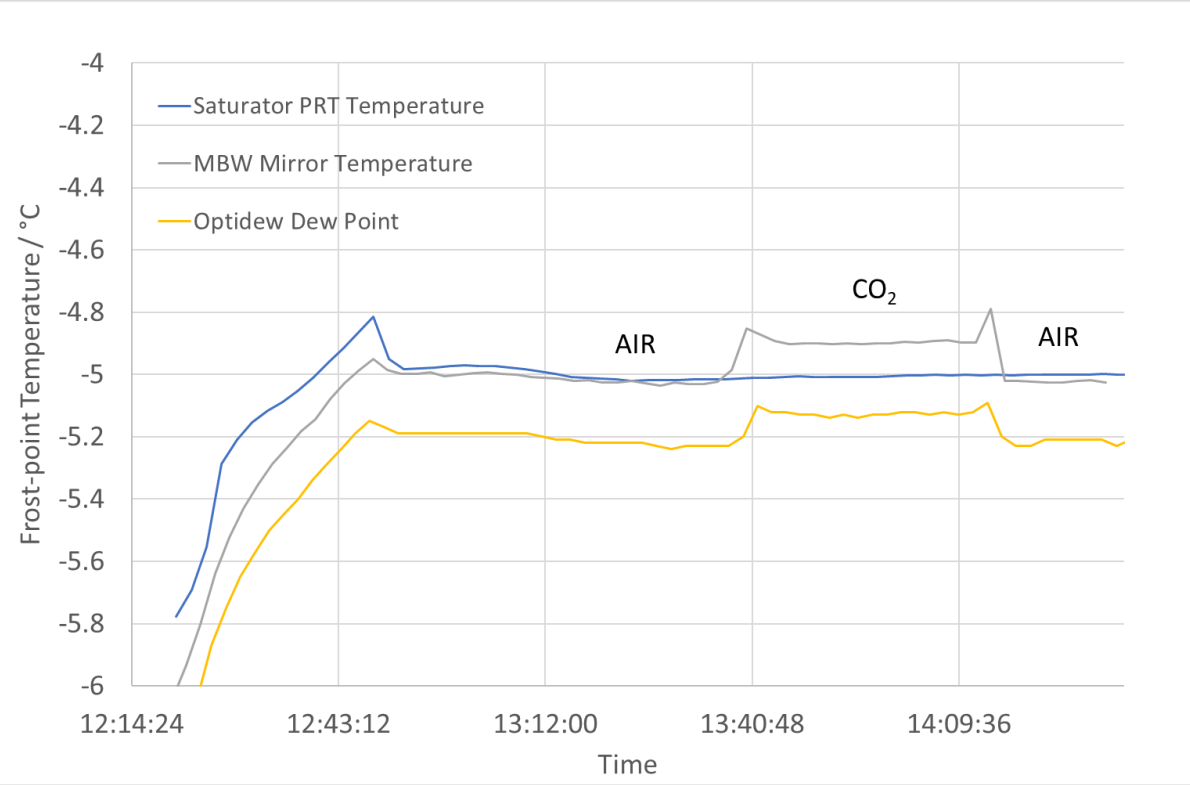
ADAPTATION AND VALIDATION OF AN EXISTING PRIMARY HUMIDITY STANDARD

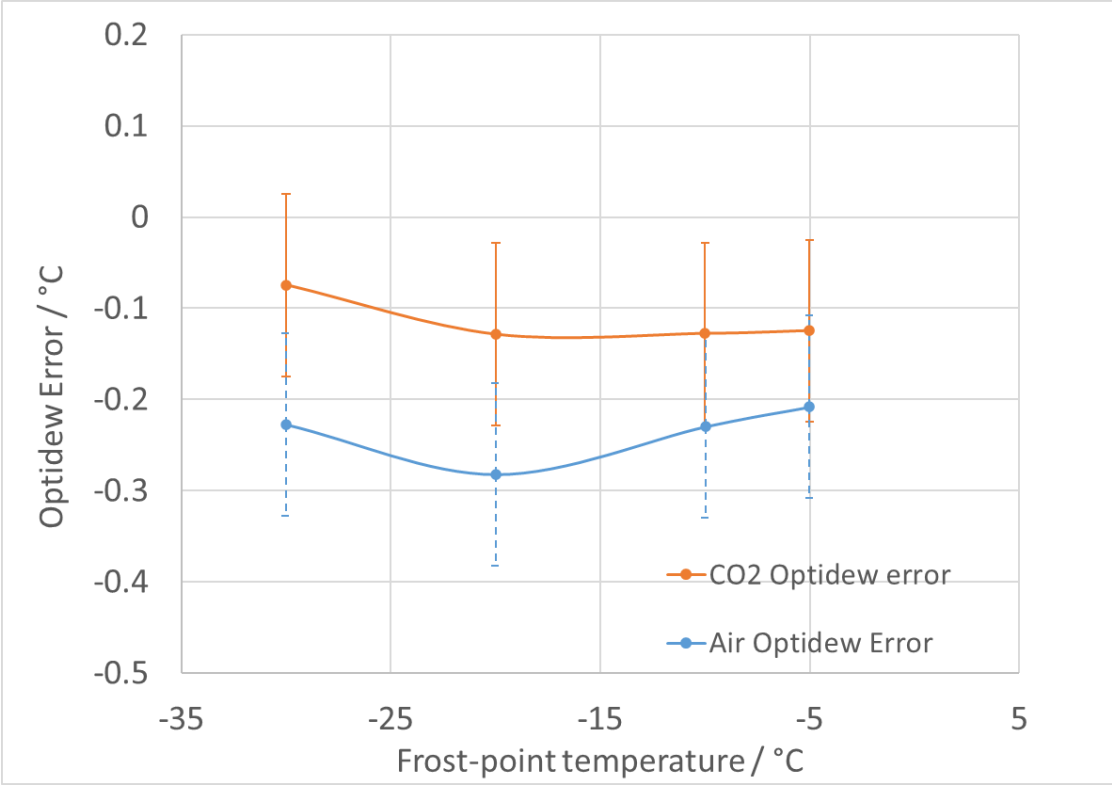
Validation details. Uncertainty components evaluated for:

- Reference temperature measurement effects: PRT calibration, self-heating, drift, resistance bridge
- Temperature gradient profiling of fluid bath surrounding saturator
- Temperature conditioning of test gas
- Saturator efficiency
- Pressure effects
- Contamination, desorption
- Vapour pressure and water vapour enhancement factor
- Unit under test contributions

FIRST TRIAL DEW-POINT TEMPERATURE CALIBRATION OF A HYGROMETER

- Single-pressure dew-point temperature calibration of Michell Optidew chilled-mirror hygrometer



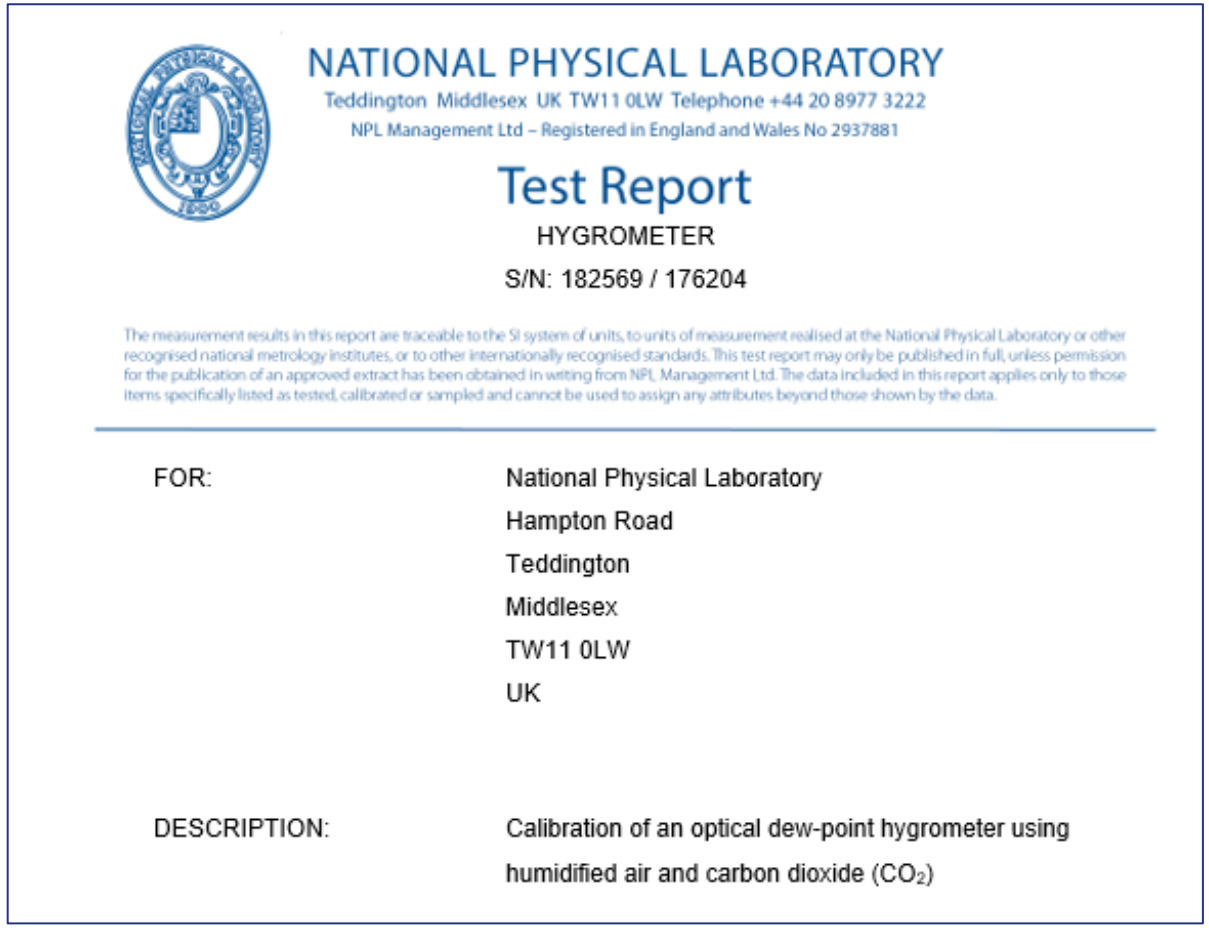


FIRST TRIAL DEW-POINT TEMPERATURE CALIBRATION OF A HYGROMETER IN CO_2

- Test report for Michell Optidew instrument with calibration data in the range -30 °C to -5 °C Frost-point Temperature.

- Key Exploitable Result in MetCCUS **(A4.3.5)**

- Will be available to download from project website.



NATIONAL PHYSICAL LABORATORY

Teddington Middlesex UK TW11 0LW Telephone +44 20 8977 3222

NPL Management Ltd – Registered in England and Wales No 2937881

Test Report

HYGROMETER

S/N: 182569 / 176204

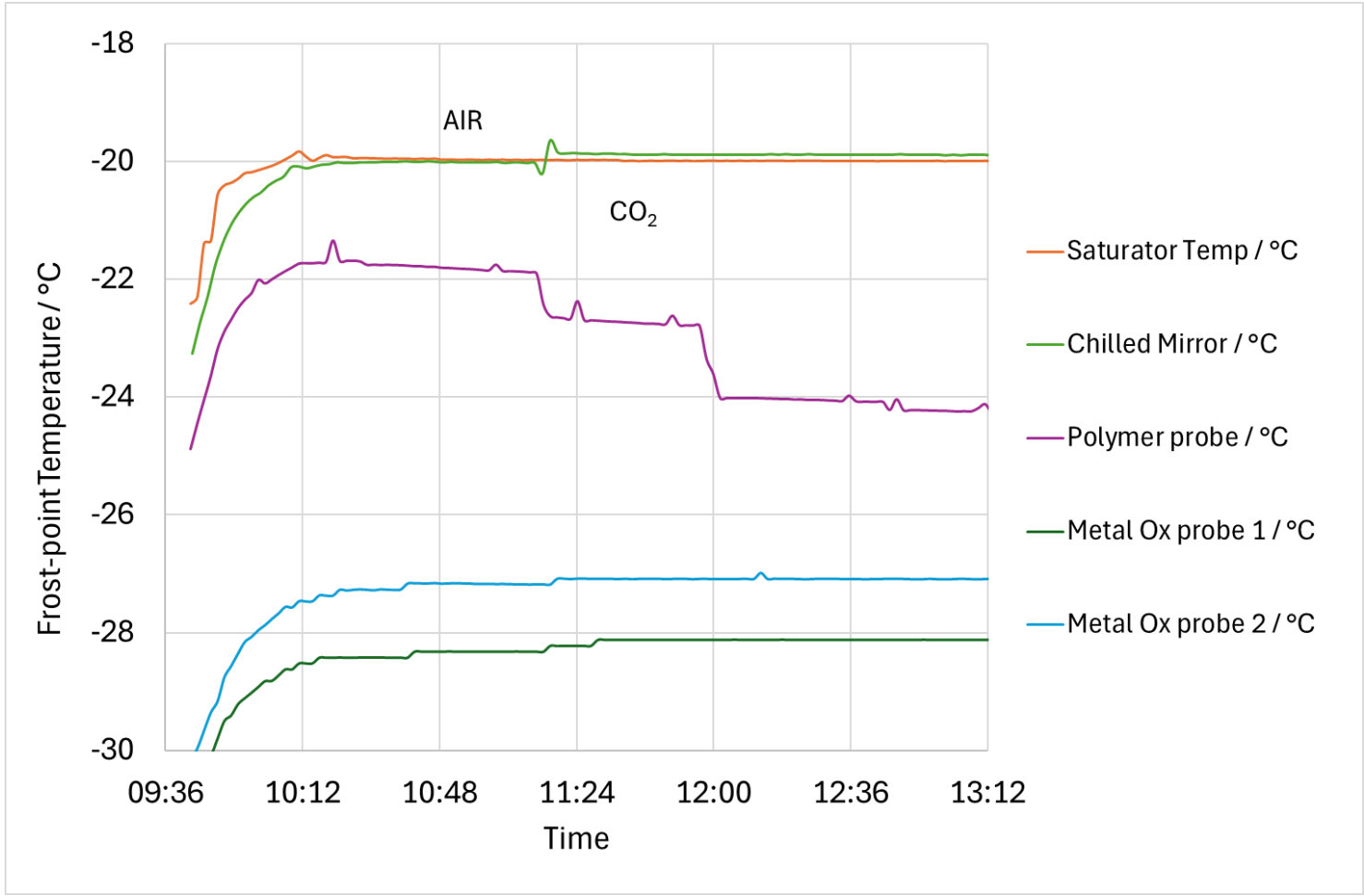
The measurement results in this report are traceable to the SI system of units, to units of measurement realised at the National Physical Laboratory or other recognised national metrology institutes, or to other internationally recognised standards. This test report may only be published in full, unless permission for the publication of an approved extract has been obtained in writing from NPL Management Ltd. The data included in this report applies only to those items specifically listed as tested, calibrated or sampled and cannot be used to assign any attributes beyond those shown by the data.

FOR:	National Physical Laboratory Hampton Road Teddington Middlesex TW11 0LW UK
DESCRIPTION:	Calibration of an optical dew-point hygrometer using humidified air and carbon dioxide (CO_2)

FIRST TRIAL DEW-POINT TEMPERATURE CALIBRATION OF A HYGROMETER IN CO_2

Recent testing shows other instrument types can also:

- Significantly switch to under-reading in CO_2 compared to air.
- Or remain unaffected by background gas species change



FURTHER TRIAL CALIBRATION IN CO_2 OF IN-HOUSE WATER VAPOUR SPECTROMETER

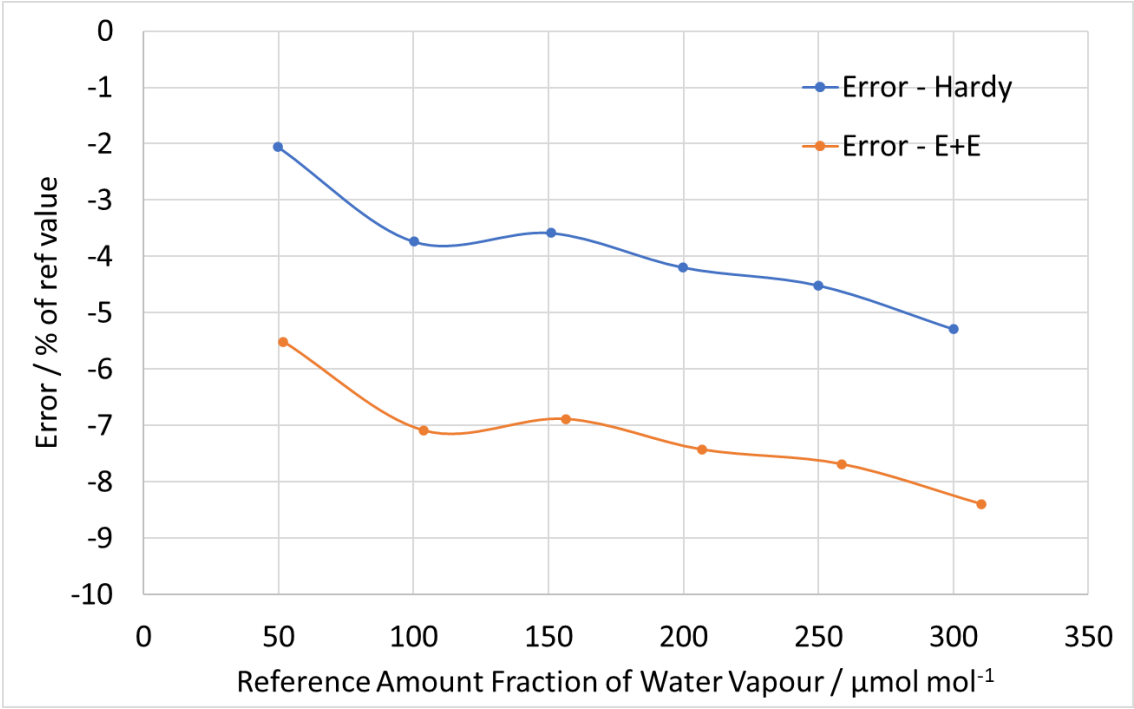
- Further trial calibration of water vapour spectrometer has also been completed in range 20 µmol mol^{-1} to 300 µmol mol^{-1}
- Reference value depends on *f* (P,T) formula used:
- Experimentally derived formulae for CO_2 from E+E

Determination of Water Vapor Enhancement Factors in Carbon Dioxide

E+E Elektronik Ges.m.b.H., Langwiesen 7, 4209 Engerwitzdorf, Austria | T +43 7235 605-0, F +43 7235 605-8
Maintaining the Austrian national standard for humidity on behalf of BEV – Bundesamt für Eich und Vermessungswesen – Austria

Patrick Raab | Helmut Mitter
patrick.raab@epluse.com

- Compared to use of accepted *f* (P,T) formulae for air [1]



[1] B Hardy (1998) *"ITS-90 formulations for vapor pressure, frost point temperature, dewpoint temperature, and enhancement factors in the range –100 to +100 C."* Proceedings of the Third International Symposium on Humidity and Moisture, Teddington, London, England.

CONVERSION OF REFERENCE VALUE TO OTHER HUMIDITY UNITS E.G AMOUNT FRACTION OF WATER VAPOUR AND FUTURE WORK.

- Further consider uncertainty components for amount fraction calibration mode of operation.
- Limited experimental data available for water vapour enhancement factor for CO_2 in range of interest.
- Non-ideality of CO_2 and water-vapour mixtures can be experimentally investigated for CO_2 at pressures up to 2 MPa (T3900 saturator maximum working limit).
- Would increase experimental data available water vapour enhancement factors in CO_2 – reducing uncertainty in humidity quantity conversions.

THANK YOU!

PAUL.CARROLL@NPL.CO.UK

WWW.NPL.CO.UK/TEMPERATURE-HUMIDITY

BiometCAP project, overview and progresses so far

Lucy Culleton, NPL

ENERGY GASES

METCCUS

VSL

MET4H2

BiometCAP

21NRM04 BiometCAP

Protocol for SI-traceable validation of methods for biomethane conformity assessment

Overview and progress so far

Lucy Culleton, NPL

26th March 2025, BiometCAP workshop, VSL, Delft

Project introduction - objectives

BiometCAP

NPL National Physical Laboratory

1. To develop cost-effective gas transfer standards, for the impurities specified in EN 16723 for use in biomethane conformity assessment with uncertainties of 1 % - 10 %.

2. To develop a protocol for the sampling, analysis and performance evaluation of the gas analysers that are used for biomethane conformity assessment.

3. To use the protocol, developed in objective 2, to evaluate the performance of different types of relevant industrial gas analysers

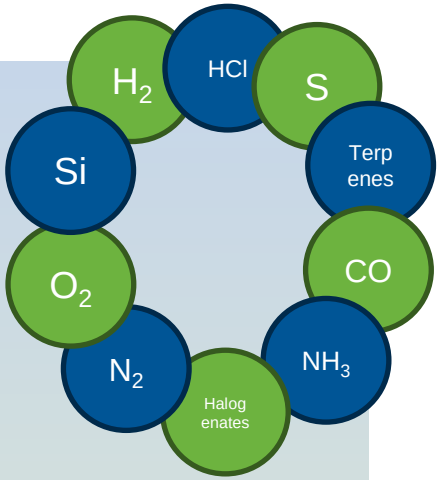
4. To collaborate with the technical committee ISO/TC193/SC1/WG25 “Biomethane”, and the users of the standards they develop

WP1: Development of gas transfer standards for SI-traceable performance evaluation

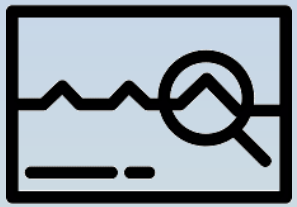
NPL National Physical Laboratory

BiometCAP

1.1:
Preparation and validation of static reference gas standards for performance evaluation



1.2:
Development of methods for the preparation of traceable gas transfer standards



Laboratory

Biomethane site

1.3:
Validation of methods for the preparation of gas transfer standards

Inter-labaratory comparison

+ D1

WP2: Protocol for SI-traceable performance evaluation

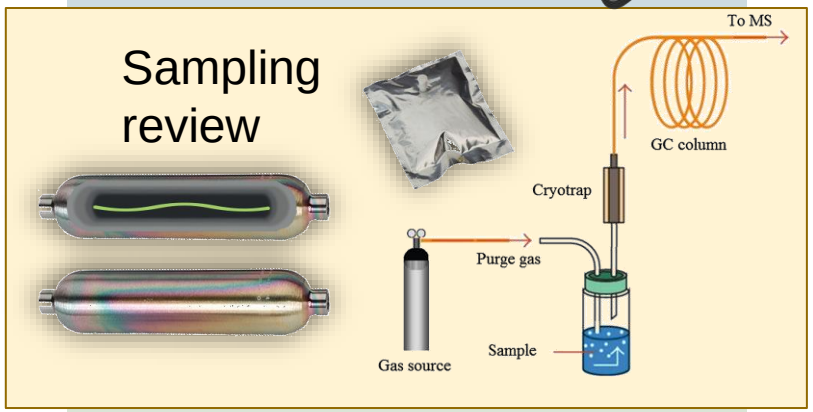
NPL National Physical Laboratory

BiometCAP

2.1: Development of validation protocol

Technology review

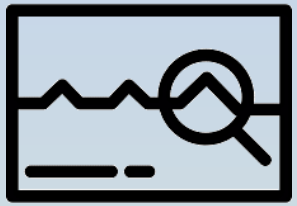
Sampling review



Parameters

- Limit of detection
- Limit of quantification
- Repeatability
- Reproducibility
- Linearity
- Cross interference
- Selectivity
- Matrix effects

2.2: Validation of the protocol



- ***Total silicon***
- ***Siloxanes***
- ***Ammonia***
- ***HCl***
- ***Halogenated VOCs***
- ***Sulphur***
- ***Terpenes***
- ***Hydrogen***
- ***Carbon monoxide***
- ***Oxygen***
- ***Nitrogen***

Summary report

+ D2

2.3: New work item proposal

"Protocol for performance evaluation of gas analysers used in biomethane conformity assessment"

NWIP + ISO text

+ D3

WP3: Performance evaluation of industrial analysers and reference instrumentation

NPL National Physical Laboratory

BiometCAP

3.1: Selection of industrial analysers and reference instrumentation

+ many more…

Reporting procedure & template

+ D4

3.2: Laboratory and field trials for performance evaluation of industrial analysers and reference instrumentation

Laboratory

Biomethane site

Summary report

+ D5

3.3: Comparison of performance evaluation results

- Location
- Technique
- Analyte

Summary report + D6

Good practice guide + D7

WP4: Creating impact

Dissemination & communication

4.1: Contribution to standardisation and metrology committees

- **ISO/TC158/WG3**
- **ISO/TC158/WG4**
- **ISO/TC158/WG5**
- **ISO/TC193/SC1/WG25**
- **CEN/TC408**
- **CCQM-GAWG**
- **EURAMET TC-MC**

4.2: Knowledge transfer

- **Stakeholder committee**
- **Website**
- **Conference presentations**
- **Peer reviewed journal papers**
- **Trade journal articles**
- **EMN for energy gases**
- **GERG networks**
- **Social media**
- **Partner knowledge transfer**

4.3: Training

Webinars

Workshops

4.4: Uptake and exploitation

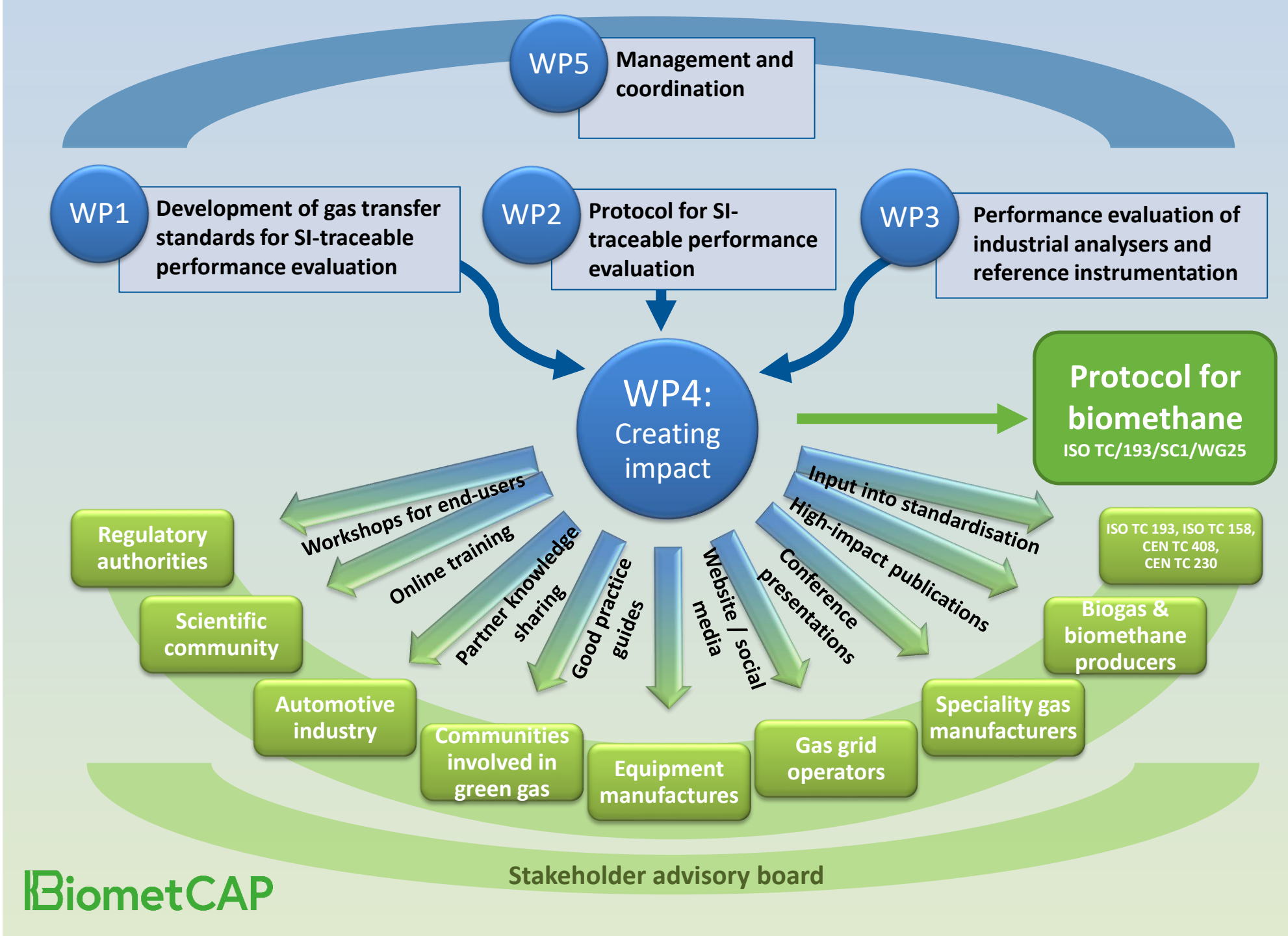
Services

- Validated standards & methods
- Validated protocol
- Measurement services

Promotion to stakeholders

- Laboratories
- Research institutes
- Industry

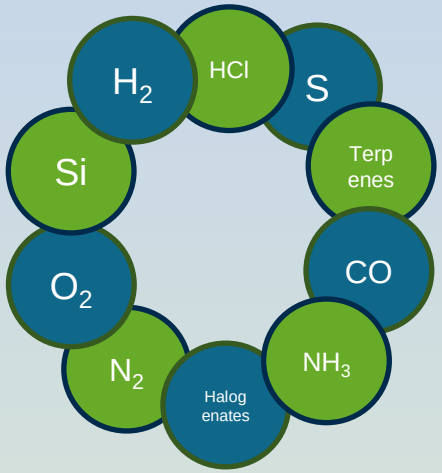
Project overview



BiometCAP

Progress overview

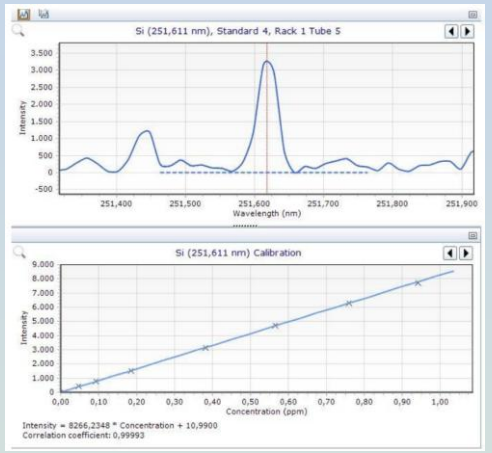
- Reference standards and dynamic systems successfully developed

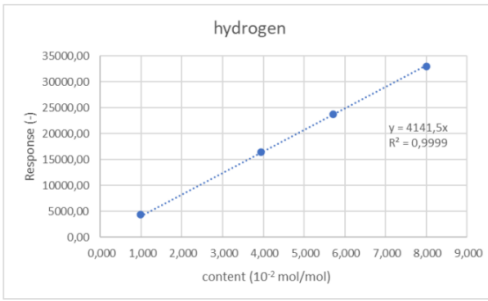


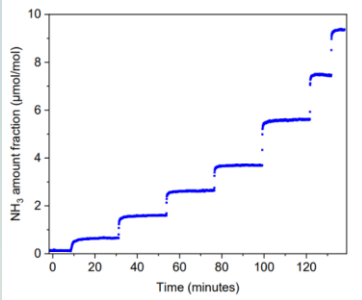
Progress overview

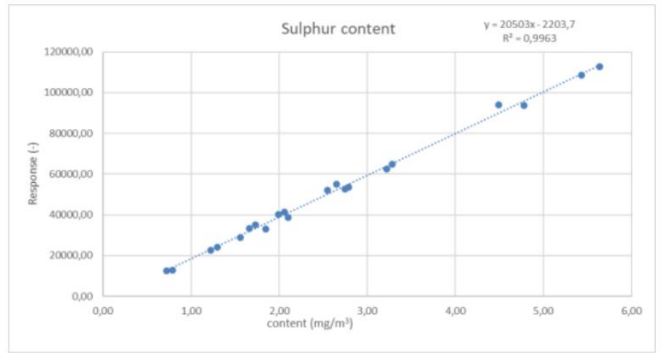
- Validation protocol successfully applied to a variety of measurement methods

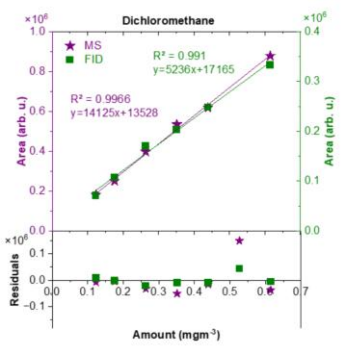
Partner	Targeted compounds	Analytial method	Measurement uncertainties
IMBiH	Total silicon	AES	2%
RISE	Siloxanes (L2, L3, D3, D4, D5)	TD-GC-MS/FID	11%
VSL			4-11%
NPL		GC-IMS	3-8%
VSL	Ammonia	Laser spectroscopy	6%
NPL		GC-NCD	-
VSL	Hydrogen chloride	Laser spectroscopy	7%
RISE	Halogenated VOCs	GC-MS/FID	10%
BFKH	Sulphur compounds	GC-SCD/FID	3-8%
CMI			6%
NPL			15%
NPL	Terpenes	GC-MS/FID	2-14%
RISE		TD-GC-MS/FID	9%
NPL	Hydrogen Carbon monoxide Oxygen Nitrogen	TG-TCD	Hydrogen 10% Carbon monoxide 0.5% Oxygen 13% Nitrogen 6%
CMI			Hydrogen 1.6% Carbon monoxide 0.8% Oxygen 1.6% Nitrogen 0.4%
Tubitak			Hydrogen 0.4% Carbon monoxide 0.6% Oxygen - Nitrogen 0.4%







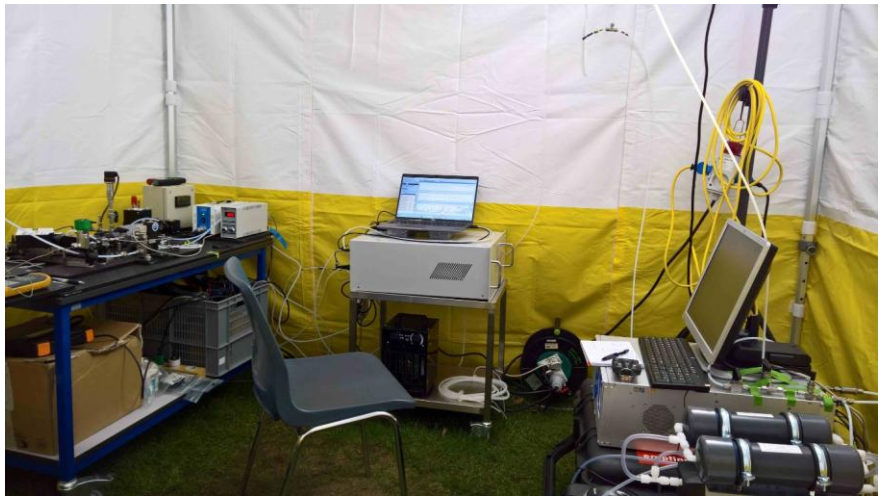




Progress overview

Field trial application in Denmark and Finland

- Comparison of results to take place



Progress overview

NPL National Physical Laboratory

Dissemination:

- Webinars
- Workshops
- Conferences
- Website (8 reports available)

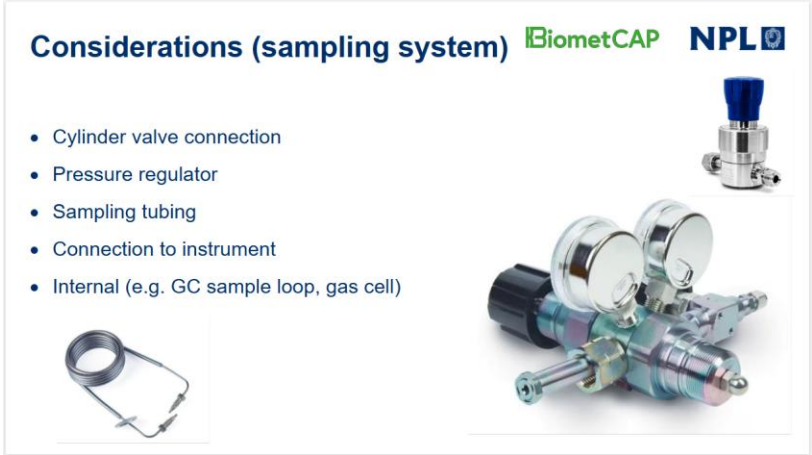


Table 3 – Material compatibility for gas cylinders

	Stainless steel				Aluminium															
	Untreated		Sulfinert®		Untreated		Aculife VII		Performax		SPECTRA-SEAL		SPECTRA-SEAL PT		Experis		Megalife		PB	
	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b	a	b
Inert compounds (N2 for ex.)	S [19]	S [19]	X	X	S [19]	S [19]	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Methane	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Carbon dioxide	S [19]	S [19]	X	X	S [19]	S [19]	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Oxygen	S [19]	S [19]	X	X	S [19]	S [19]	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Carbon monoxide	S [19]	S* [19]	X	X	S [19]	S [19]	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Siloxanes	i.d.	i.d.	S† [21]	S† [21]	i.d.	i.d.	i.d.	i.d.	S† [6]	S† [6]	S† [6]	S† [6]	S† [6]	S† [6]	S [6]	S [6]	S [6]	S [6]	S† [6]	S† [6]
Ammonia	S [19]	S [19]	S [6]	S [6]	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	S [26]	S [26]	S [26]	S [26]	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.
Hydrogen sulphide	NS [19]	S [19]	S [26]	S [26]	NS [26]	S [19]	S [26]	S [26]	X	X	S [26]	S [26]			i.d.	i.d.	i.d.	i.d.	i.d.	i.d.
Sulphur compounds	NS [26]	i.d.	S	S	N [26]	i.d.	i.d.	i.d.	i.d.	i.d.	S [26]	S [26]	S	S	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.
Halogenated compounds																				
Hydrocarbons	S [19]	S [19]	X	X	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	X	X	X	X	X	X	i.d.	i.d.		
Terpenes	i.d.	i.d.	S [27]	S [27]	i.d.	i.d.	i.d.	i.d.	i.d.	i.d.	NS [27]	i.d.	NS [27]	NS [27]	S [27]	S [27]	i.d.	i.d.	i.d.	i.d.

*According to ISO16664, stainless steel cylinders have a limited suitability for CO for mole fractions above 1 vol-%

† Suitability demonstrated for siloxanes L2, D3, D4, D5. Instability observed when L3 siloxane present.

Covering:
Sampling
Results of laboratory validations
Reporting procedure
…more to come!

Publicly available guide to biomethane sampling

Production of gas transfer standards for performance evaluation of the that are used for biomethane conformity assessment systems

Ain Nazirah, Oliver Williams, Christopher Bamforth
NPL

ENERGY GASES

METCCUS

VSL

MET4H2

BiometCAP

Production of gas standards for performance evaluation of the measurement systems that are used for biomethane conformity assessment

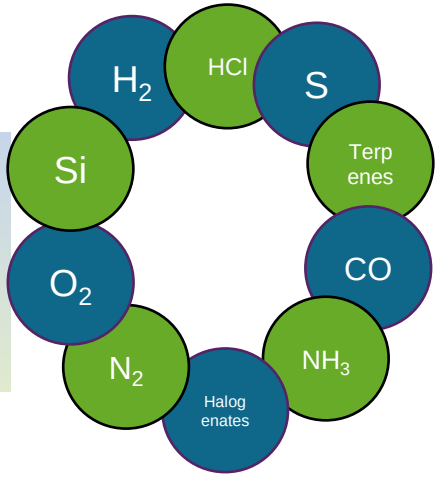
Ain Nazirah, Oliver Williams, Christopher Bamforth

BiometCAP workshop, Delft, The Netherlands

26th March 2025

Overview

1.1: Preparation and validation of static reference gas standards for the performance evaluation of the measurement systems that are used for biomethane conformity assessment

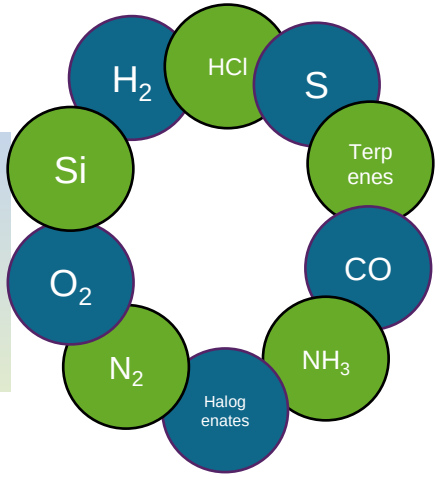


1.2: Development of lab-based or portable dynamic systems for the preparation of traceable gas transfer standards

1.3: Validation of the methods developed in Task 1.2 for the preparation of traceable gas transfer standards

Overview

1.1: Preparation and validation of static reference gas standards for the performance evaluation of the measurement systems that are used for biomethane conformity assessment



1.2: Development of lab-based or portable dynamic systems for the preparation of traceable gas transfer standards

1.3: Validation of the methods developed in Task 1.2 for the preparation of traceable gas transfer standards

1.1.1: Specification and stakeholder survey

- Reviewed existing standards and produce specification for compositions and combinations of gas standards

Component	Lower Amount Fraction			Higher Amount Fraction			Unit	Relative uncertainty target
	Pre-survey	Post-survey	Final	Pre-survey	Post-survey	Final		
total silicon	0.3	0.01	0.3	1	1	1	mg m^{-3}	6%
terpenes	0.01	0.01	0.01	10	50	10	µmol mol^{-1}	5%
hydrogen chloride	1	1	1	n/a	n/a	n/a	µmol mol^{-1}	10%
ammonia	10	0.1	10	20	20	20	µmol mol^{-1}	5%
total sulphur	5	1	1	20	50	50	mg m^{-3}	3%
halogenated VOCs	50	50	50	750	750	750	nmol mol^{-1}	3 – 10 %
hydrogen	2	0.01	0.01	10	10	10	cmol mol^{-1}	1%
nitrogen	2	0.01	0.01	10	10	10	cmol mol^{-1}	1%
oxygen	0.001	0.001	0.001	1	1	1	cmol mol^{-1}	1%
carbon monoxide	0.1	0.01	0.1	n/a	0.1	n/a	cmol mol^{-1}	1%

1.1.1: Target amount fractions

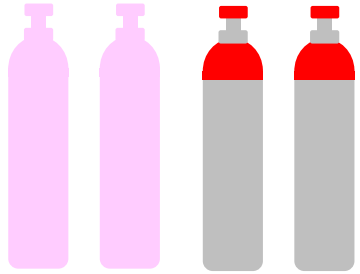
- Target amount fractions and uncertainties for components of interest

Component	Range of interest	Target amount fraction	Unit	Target uncertainty (k = 2) (%)
Total silicon	0.3 – 1	1	mg m^{-3}	6
Terpenes	0.01 – 10	10	µmol mol^{-1}	5
Total sulphur	1 – 50	20	mg m^{-3}	2
Ammonia	10 – 20	20	µmol mol^{-1}	5
Hydrogen	0.01 – 10	2	cmol mol^{-1}	1
Nitrogen	0.01 – 10	2	cmol mol^{-1}	1
Oxygen	0.001 – 1	0.04	cmol mol^{-1}	1
Carbon monoxide	1000	1000	µmol mol^{-1}	1

1.1: Reference standard preparation

- High accuracy, SI-traceable gas reference standards were prepared gravimetrically according to ISO 6142-1* using high precision techniques developed at NPL.
- Gas standards were prepared in passivated aluminium cylinders.
- Passivation selection is essential to ensure stability of gas standards.
- Cylinder passivations below were selected based on previous research (Metrology for biomethane 16ENG05**)

Cylinder passivation	Components
BOC SPECTRA-SEAL	Total sulphur, NH_3, H_2, N_2, O_2, CO
Air Products Experis	Terpenes
Air Liquide Megalong	Total silicon



*International Organization for Standardization, "ISO 6142-1 Gas analysis -Gas analysis -Preparation of calibration gas mixtures —Part 1: Gravimetric method for Class I mixtures, ISO Geneva, 2015

**EMPIR Metrology for biomethane 16ENG05 Final publishable Report. https://www.euramet.org/research-innovation/search-research-projects/details/project/metrology-for-biomethane

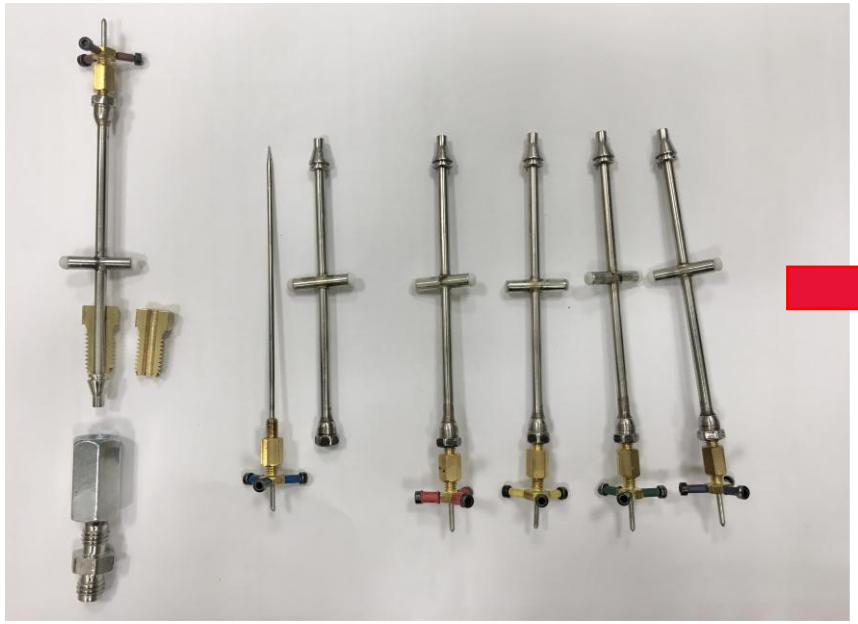
1.1: Reference standard preparation

Pure component

Transfer vessel

1.1: Reference standard preparation

- Addition of very low mass using special vessels (20-80 mg)



1.1: Reference standard preparation

- Addition of matrix gas (high purity methane)
- Homogenised by heating and rolling cylinders for 2 hours

1.1.2: Validation

- Mixtures validated using NPL Primary Reference Materials (PRM) in accordance with ISO 6143* using direct comparison method

GC with mass spectrometry

- Siloxanes
  - Hexamethyldisiloxane – L2 siloxane ($C_6H_{18}OSi_2$)
  - Octamethyltrisiloxane – L3 siloxane ($C_8H_{24}O_2Si_3$)
  - Hexamethylcyclotrisiloxane – D3 siloxane ($C_6H_{18}O_3Si_3$)
  - Octamethylcyclotetrasiloxane – D4 siloxane ($C_{10}H_{30}O_5Si_5$)
  - Decamethylcyclopentasiloxane – D5 siloxane ($C_{10}H_{30}O_5Si_5$)
- Terpenes
  - (+)-α-pinene ($C_{10}H_{16}$)
  - (+)-3-carene ($C_{10}H_{16}$)
  - R-(+)-limonene ($C_{10}H_{16}$)

*International Organization for Standardization, “ISO 6143:2001 Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures”

1.1.2 & 1.1.4: Validation

- Mixtures validated using NPL Primary Reference Materials (PRM) in accordance with ISO 6143* using direct comparison method

GC with nitrogen chemiluminescence detector

- ❖ Ammonia (NH_3)

GC with sulphur chemiluminescence detector

- ❖ Hydrogen sulphide (H_2S)
- ❖ Diethyl sulphide ($C_4H_{10}S$)
- ❖ Ethyl methyl sulphide (C_3H_8S)
- ❖ Methanethiol (CH_3SH)

*International Organization for Standardization, “ISO 6143:2001 Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures”

1.1.5: Validation

- Mixtures validated using NPL Primary Reference Materials (PRM) in accordance with ISO 6143* using direct comparison method

Gas chromatography (GC) with thermal conductivity detector

- Hydrogen (H_2)
- Nitrogen (N_2)
- Oxygen (O_2)
- Carbon monoxide (CO)

*International Organization for Standardization, “ISO 6143:2001 Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures”

1.1.2: Results

- Amount fractions achieved were within target ranges according to EN16723-1, EN16723-2 and stakeholder input:

Component	Range of interest	Target amount fraction	Achieved amount fraction	Unit	Target uncertainty ($k = 2$) (%)	Achieved uncertainty ($k = 2$) (%)
Total silicon	0.3 – 1	1	1.00	mg m^{-3}	6	**6** ✓
Terpenes	0.01 – 10	10	9.77	µmol mol^{-1}	5	**3** ✓
Ammonia	10 – 20	20	19.60	µmol mol^{-1}	5	**3.5** ✓
Total sulphur	1 – 50	20	21.31	mg m^{-3}	2	**NPL: 2** **BFKH: 4.6**
Hydrogen	0.01 – 10	2	1.97	cmol mol^{-1}	1	**NPL: 0.51** **TUBITAK: 1**
Nitrogen	0.01 – 10	2	2.00	cmol mol^{-1}	1	**NPL: 0.40** **TUBITAK: 1**
Oxygen	0.001 – 1	0.04	0.04	cmol mol^{-1}	1	**NPL: 1** **TUBITAK: -**
Carbon monoxide	1000	1000	1000	µmol mol^{-1}	1	**NPL: 0.50** **TUBITAK: 1**

1.1.4: Results

- Amount fractions achieved were within target ranges according to EN16723-1, EN16723-2 and stakeholder input:

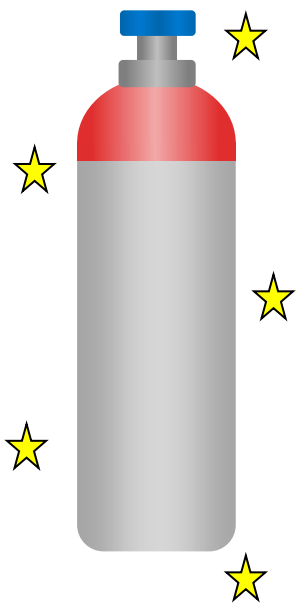
Component	Range of interest	Target amount fraction	Achieved amount fraction	Unit	Target uncertainty ($k = 2$) (%)	Achieved uncertainty ($k = 2$) (%)
Total silicon	0.3 – 1	1	1.00	mg m^{-3}	6	**6**
Terpenes	0.01 – 10	10	9.77	µmol mol^{-1}	5	**3**
Ammonia	10 – 20	20	19.60	µmol mol^{-1}	5	**3.5**
Total sulphur	1 – 50	20	21.31	mg m^{-3}	2	**NPL: 2** **BFKH: 4.6**
Hydrogen	0.01 – 10	2	1.97	cmol mol^{-1}	1	**NPL: 0.51** **TUBITAK: 1**
Nitrogen	0.01 – 10	2	2.00	cmol mol^{-1}	1	**NPL: 0.40** **TUBITAK: 1**
Oxygen	0.001 – 1	0.04	0.04	cmol mol^{-1}	1	**NPL: 1** **TUBITAK: -**
Carbon monoxide	1000	1000	1000	µmol mol^{-1}	1	**NPL: 0.50** **TUBITAK: 1**

1.1.5: Results

- Amount fractions achieved were within target ranges according to EN16723-1, EN16723-2 and stakeholder input:

Component	Range of interest	Target amount fraction	Achieved amount fraction	Unit	Target uncertainty ($k = 2$) (%)	Achieved uncertainty ($k = 2$) (%)
Total silicon	0.3 – 1	1	1.00	mg m^{-3}	6	**6**
Terpenes	0.01 – 10	10	9.77	µmol mol^{-1}	5	**3**
Ammonia	10 – 20	20	19.60	µmol mol^{-1}	5	**3.5**
Total sulphur	1 – 50	20	21.31	mg m^{-3}	2	**NPL: 2 BFKH: 4.6**
Hydrogen	0.01 – 10	2	1.97	cmol mol^{-1}	1	**NPL: 0.51 TUBITAK: 1** ✓
Nitrogen	0.01 – 10	2	2.00	cmol mol^{-1}	1	**NPL: 0.40 TUBITAK: 1** ✓
Oxygen	0.001 – 1	0.04	0.04	cmol mol^{-1}	1	**NPL: 1 TUBITAK: -** ✓
Carbon monoxide	1000	1000	1000	µmol mol^{-1}	1	**NPL: 0.50 TUBITAK: 1** ✓

1.1.6: Multi-component mixtures



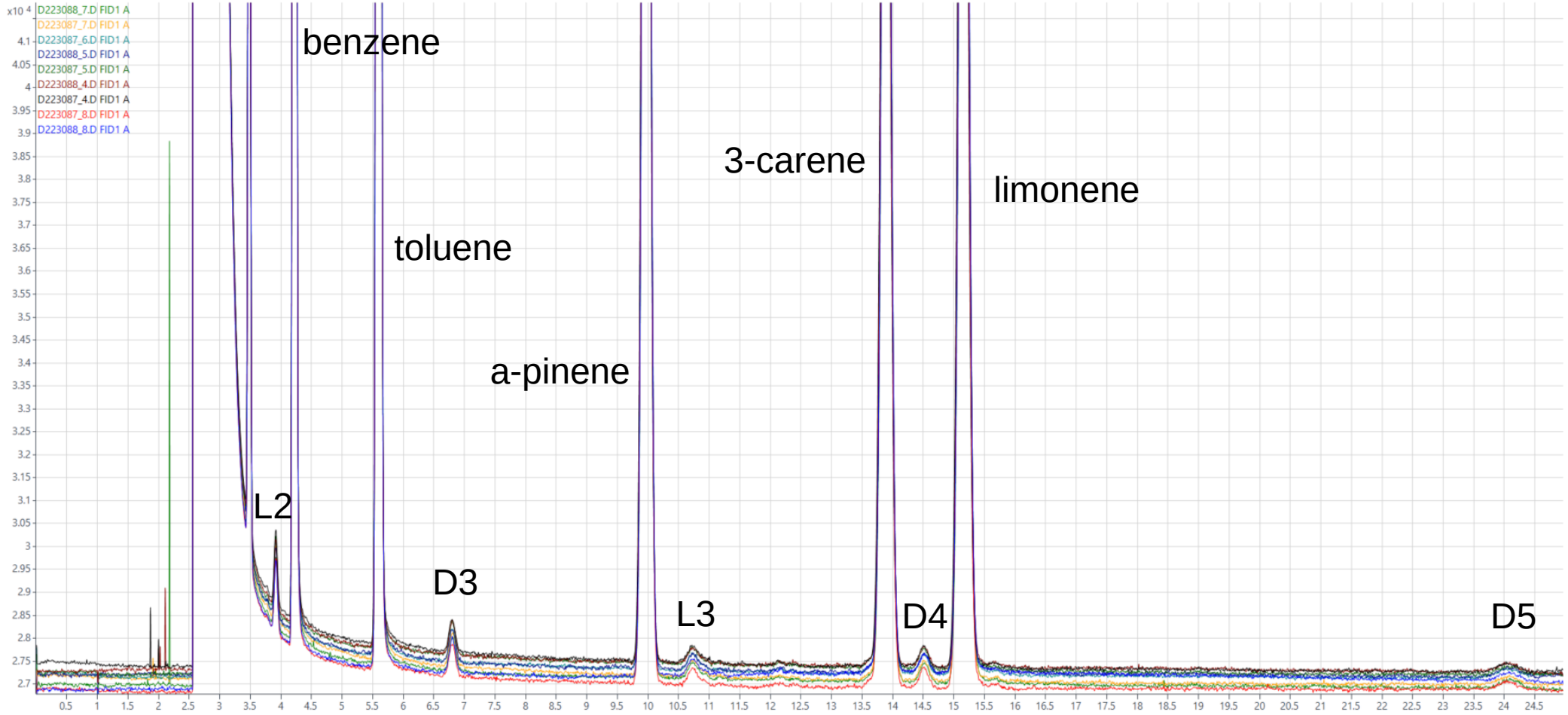
Component	Target amount fraction (μmol mol^{-1})
L2 siloxane	0.085
L3 siloxane	0.056
D3 siloxane	0.056
D4 siloxane	0.043
D5 siloxane	0.033
Benzene	10
Toluene	10
α-pinene	3.32
3-carene	3.00
limonene	3.18
Methane	Balance

*L2 siloxane - Hexamethyldisiloxane
*L3 siloxane - Octamethyltrisiloxane
*D3 siloxane - Hexamethylcyclotrisiloxane
*D4 siloxane - Octamethylcyclotetrasiloxane
*D5 siloxane - Decamethylcyclopentasiloxane

- 12-month stability study of novel all-in-one gas mixture (0, 3, 6, 12 months)
- Used for interference testing in WP2
- Summary report will be produced towards the end of the stability study

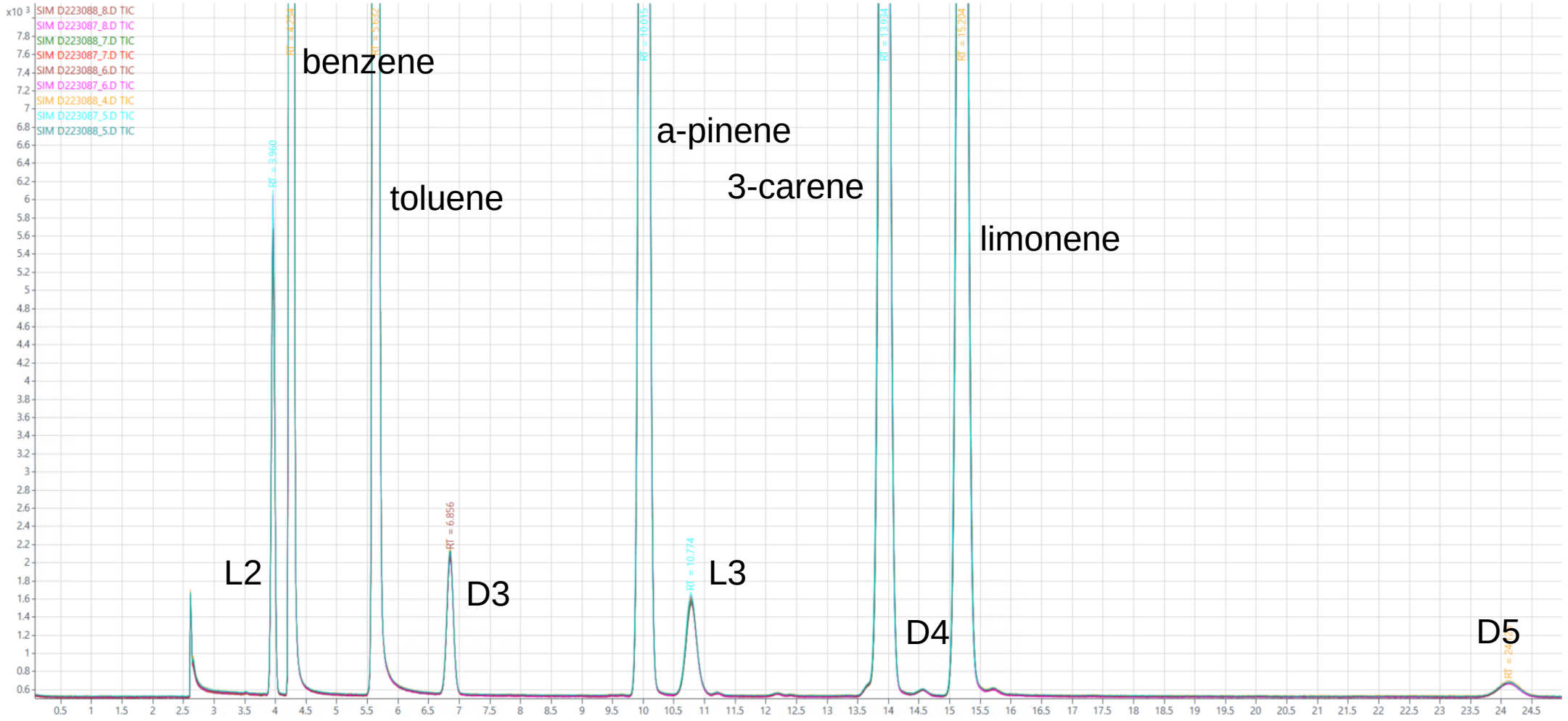
1.1.6: Multi-component mixtures

- FID



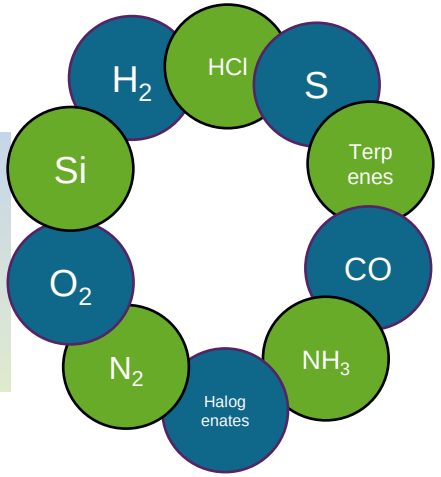
1.1.6: Multi-component mixtures

- MS (SIM)



Overview

1.1: Preparation and validation of static reference gas standards for the performance evaluation of the measurement systems that are used for biomethane conformity assessment

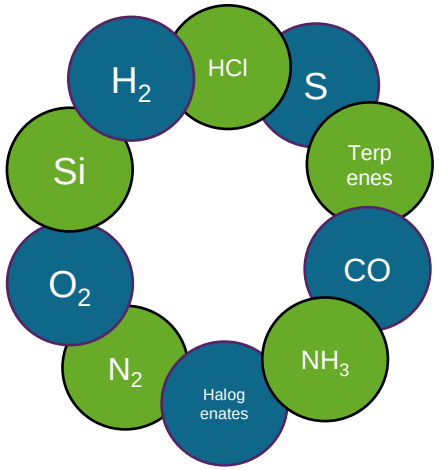


1.2: Development of lab-based or portable dynamic systems for the preparation of traceable gas transfer standards

1.3: Validation of the methods developed in Task 1.2 for the preparation of traceable gas transfer standards

1.2: Development of dynamic systems

Development of portable dynamic systems for the preparation of traceable gas transfer standards



1.2: Benefits of dynamically generated references

Static gas reference materials for biomethane conformity assessment contain low amount fractions of analytes

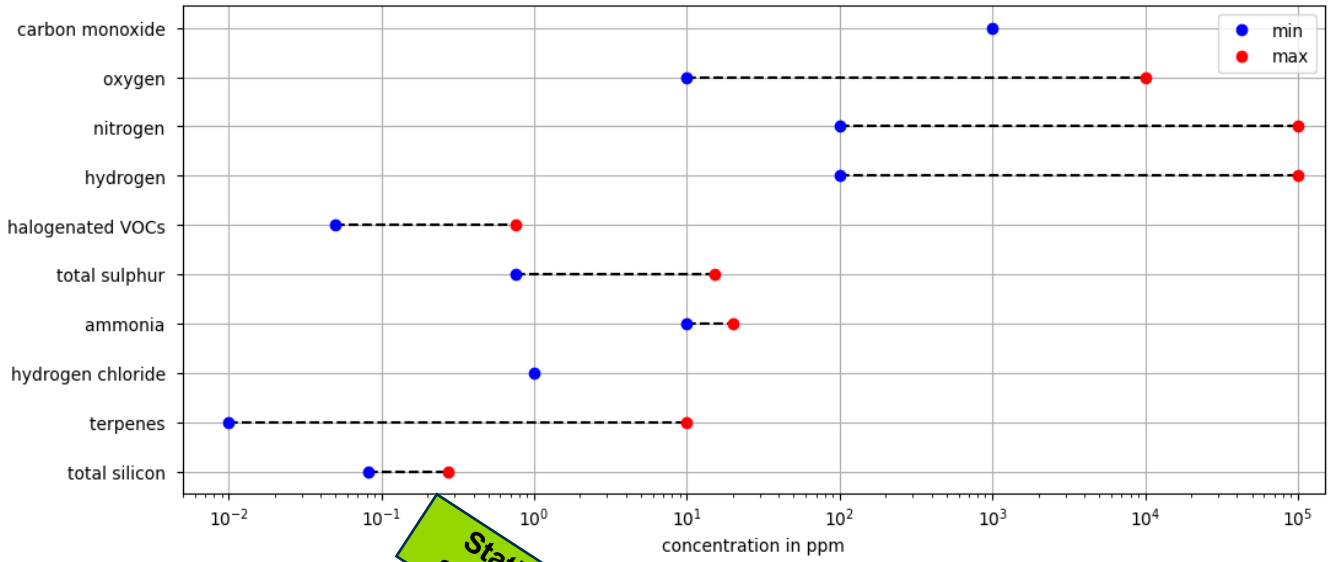
→ They may **decay quickly and need to be replaced often** 

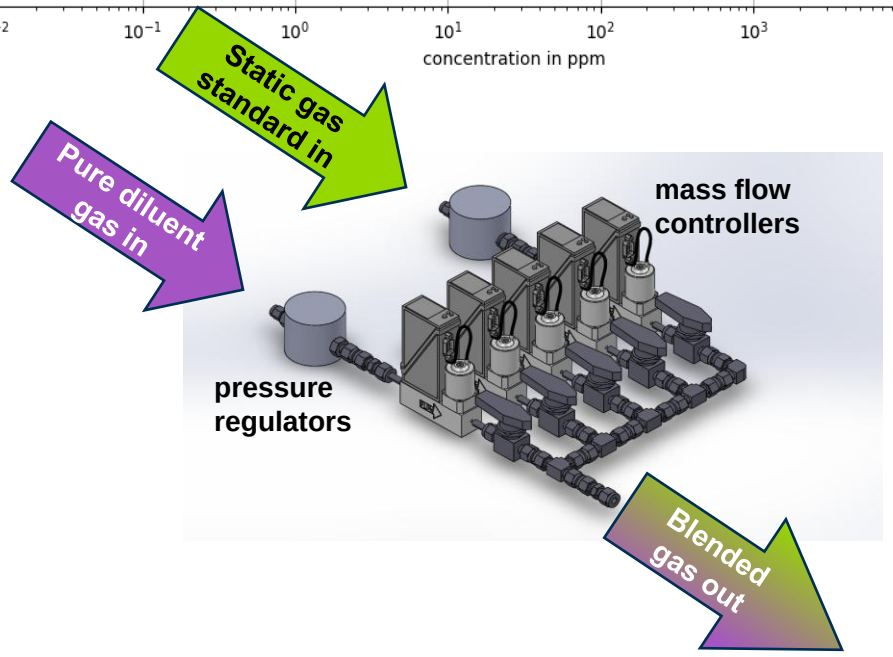
High-concentration gas mixtures tend to be more stable

→ **Dynamically diluting** provides an alternative to regularly purchasing static standards

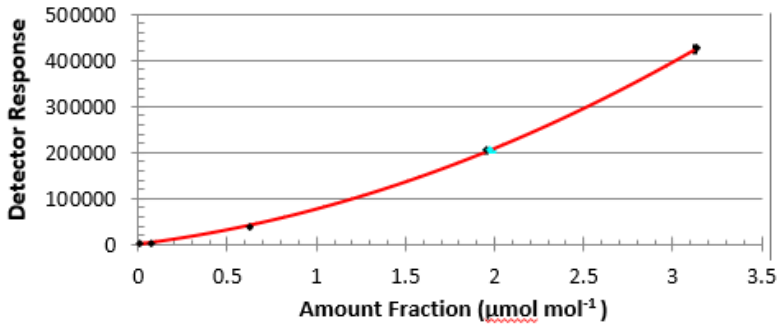
1.2.1: NPL Dynamic dilution system

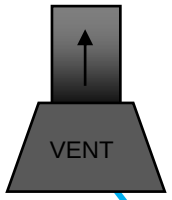
- **Requirements:**
  - Cover full range of concentrations from work package 1.1.1
  - Low flow uncertainties
  - Avoid excessive gas consumption
  - Portability
  - Minimise adsorption effects for ‘sticky’ substances (e.g. sulphur, ammonia)

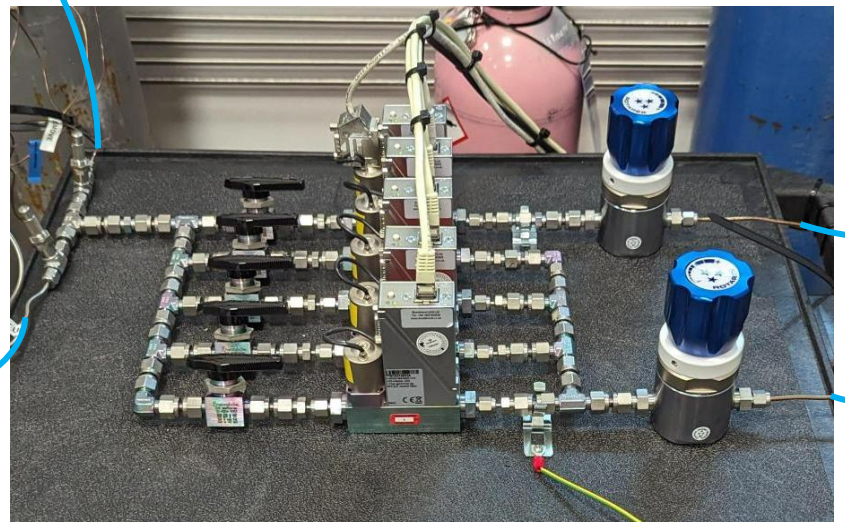


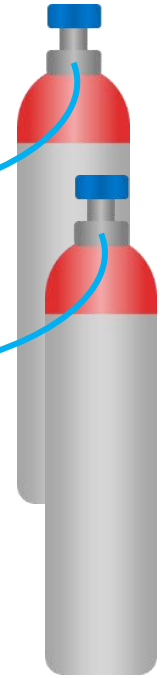


1.2.1: NPL Dynamic dilution system









1.2.2: VSL Dynamic preparation facility

VSL calibrated their dynamic preparation facility for **biomethane-related gas matrices** (methane, carbon dioxide, nitrogen and hydrogen) over the amount fractions specified in A1.1.1

1.2.3: PTB portable optical gas standard

PTB have modified an existing spectroscopic system to become a portable optical gas standard (OGS) for ammonia.

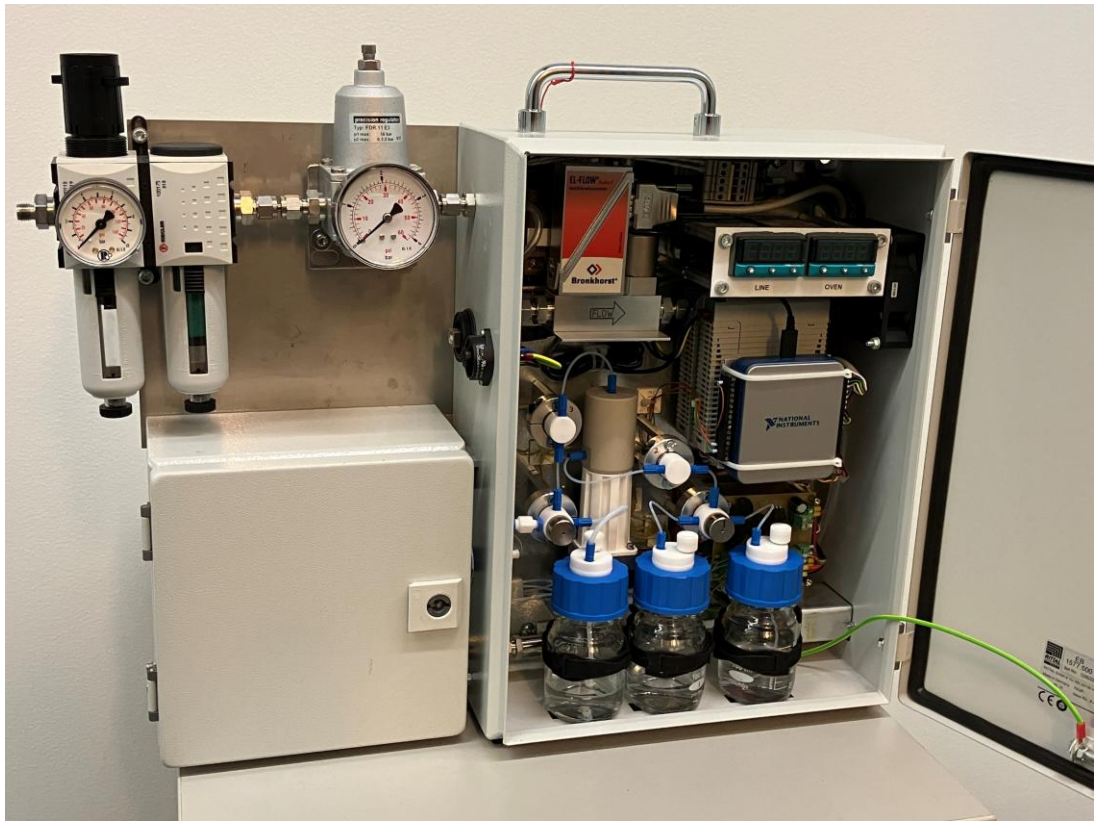
Tested in the 10 µmol mol^{-1} – 20 µmol mol^{-1} range using the ammonia standard from WP1

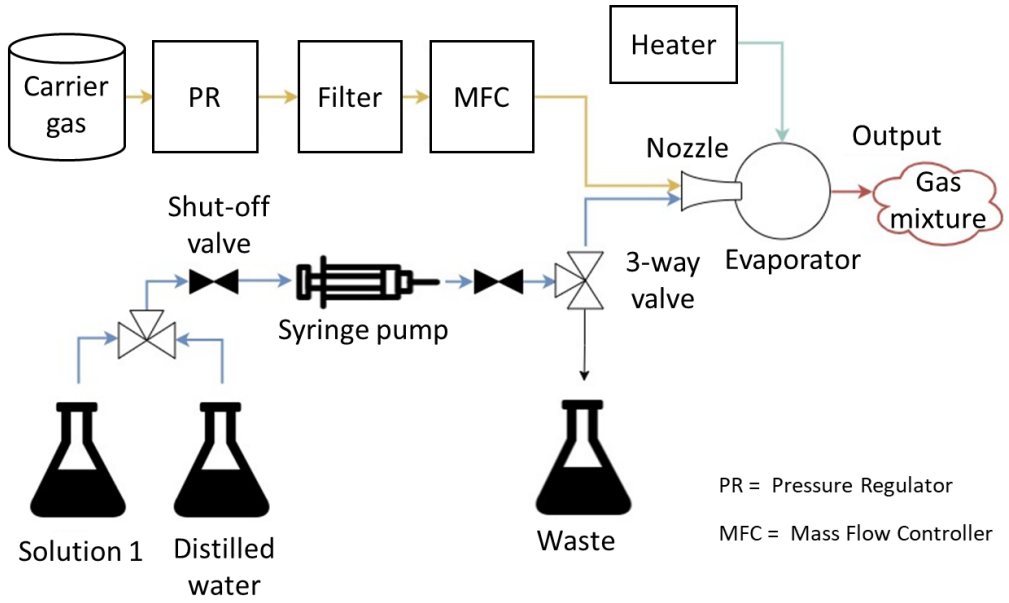
1.2.4: VTT Liquid Evaporative Generator

Generator output flow rate	up to 10 L/min
Generated gas concentration	ppm to ppb levels
Generated trace gases	Any water-soluble chemical (e.g. NH_3, HCL, HF, Hg)*
Carrier gas	Air, N_2, CH_4, H_2, CO_2*
Typical water concentration of generated gas	0.1 - 1.5 vol-%

Used to generate ppm-levels of NH3 in biomethane for BiometCAP

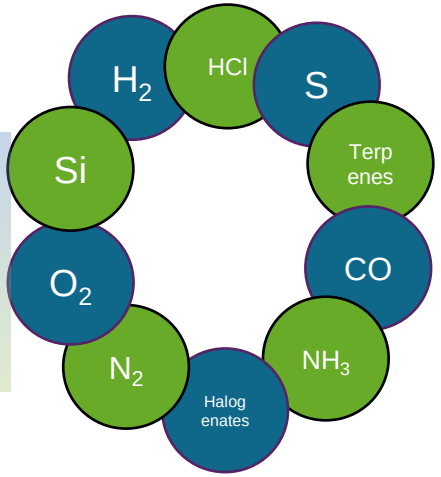
1.2.4: VTT Liquid Evaporative Generator





Overview

1.1: Preparation and validation of static reference gas standards for the performance evaluation of the measurement systems that are used for biomethane conformity assessment

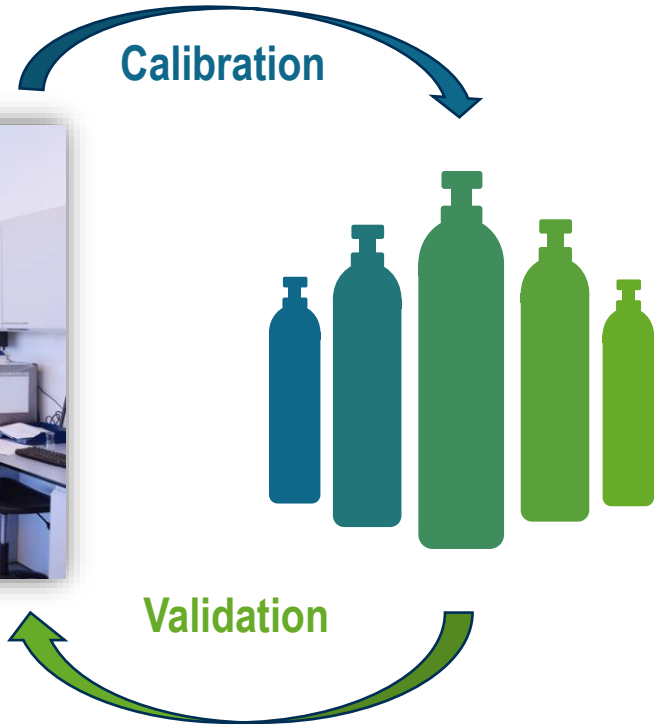


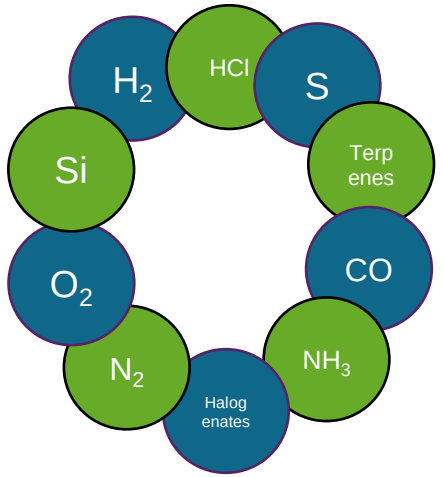
1.2: Development of lab-based or portable dynamic systems for the preparation of traceable gas transfer standards

1.3: Validation of the methods developed in Task 1.2 for the preparation of traceable gas transfer standards

1.3: Validation of methods and standards

Laboratory-based validation of the **dynamic preparation facilities** for the preparation of traceable biomethane transfer standards by calibrating the static standards.



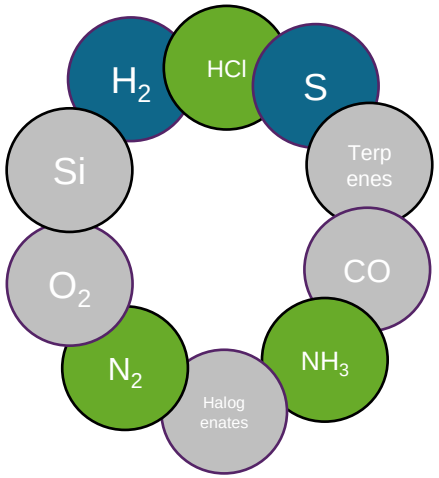


National Physical Laboratory

1.3.1: Validation of methods and standards

Laboratory-based validation of the **dynamic preparation facilities** for the preparation of traceable biomethane transfer standards by calibrating the static standards.

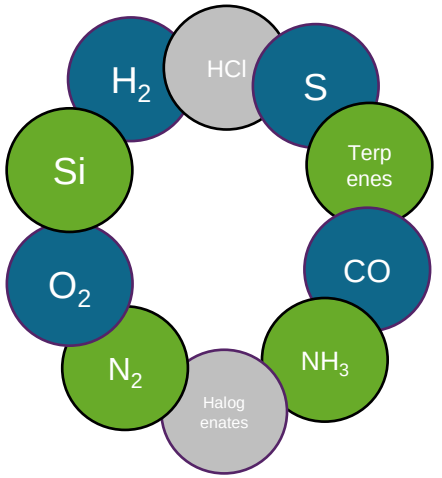
VSL validated their **dynamic preparation facility** and **dynamic permeation facility** with nitrogen, hydrogen, total sulphur, ammonia, and hydrogen chloride.



1.3.2: Validation of methods and standards

Laboratory-based validation of the **dynamic preparation facilities** for the preparation of traceable biomethane transfer standards by calibrating the static standards.

NPL validated their **dynamic preparation facility** with nitrogen, hydrogen, oxygen, total sulphur, ammonia, total siloxanes, and total terpenes.



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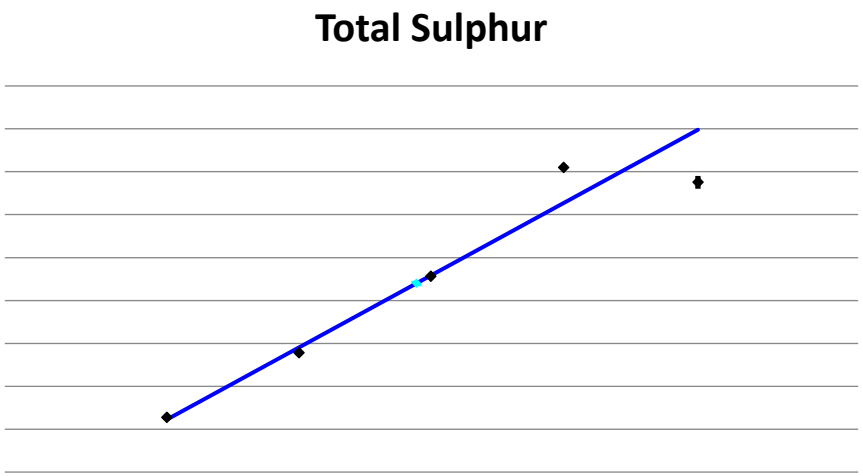

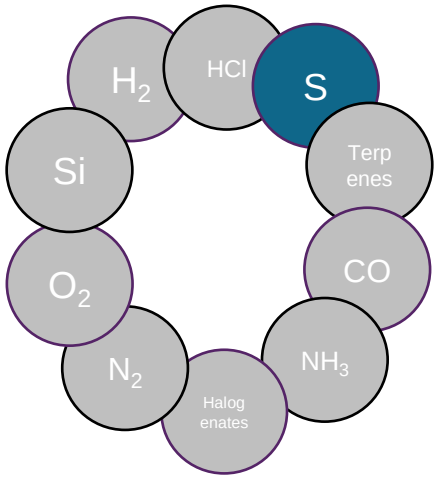

Black = dynamic standard
Cyan = BFKH PRM from 1.1.4

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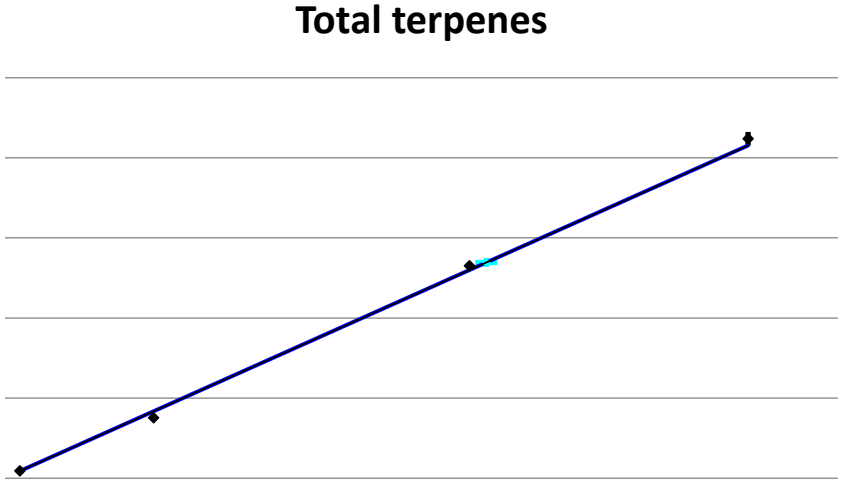
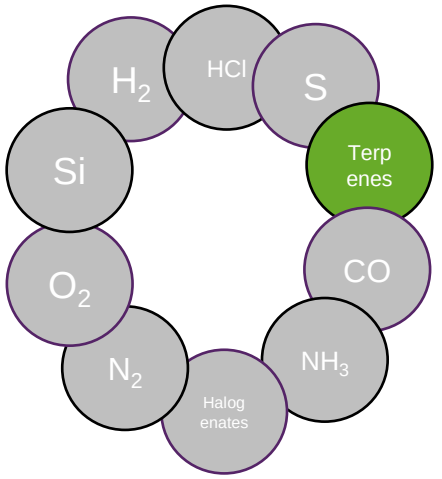
1.3.2: Validation of methods and standards

Laboratory-based validation of the **dynamic preparation facilities** for the preparation of traceable biomethane transfer standards by calibrating the static standards.

NPL validated their **dynamic preparation facility** with nitrogen, hydrogen, oxygen, total sulphur, ammonia, total siloxanes, and total terpenes.



Black = dynamic standard
Cyan = NPL PRM from 1.1.2



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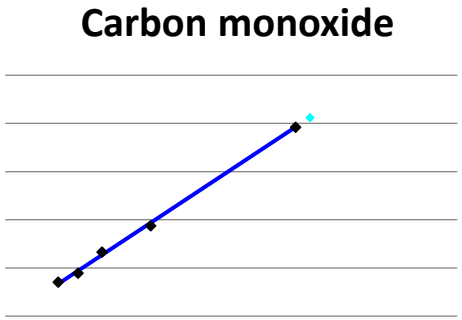

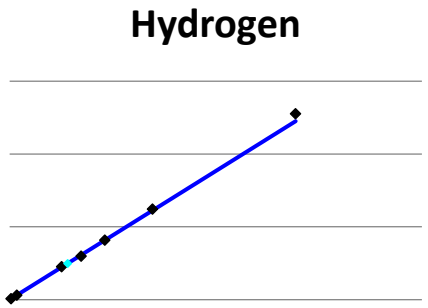

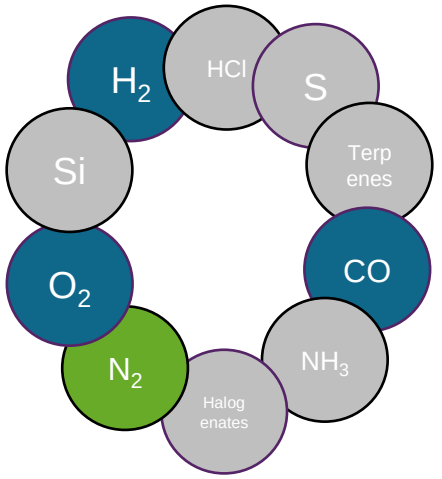

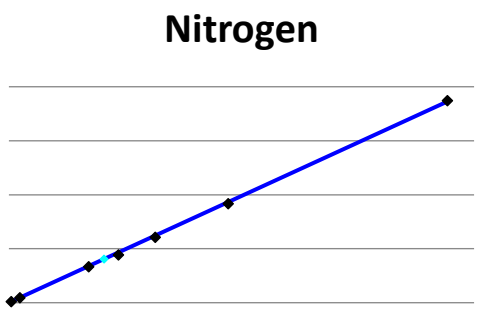

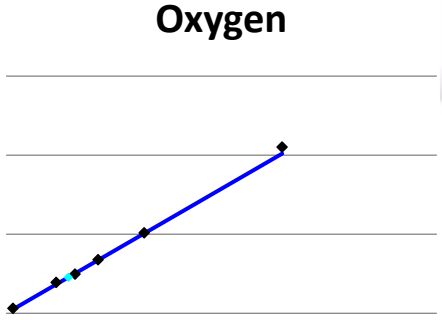

Cyan = TÜBİTAK PRM from 1.1.5

1.3.2: Validation of methods and standards

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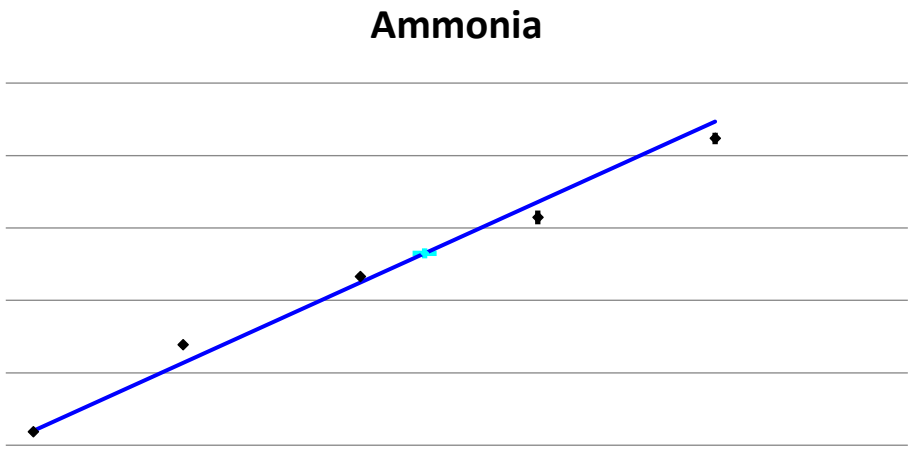

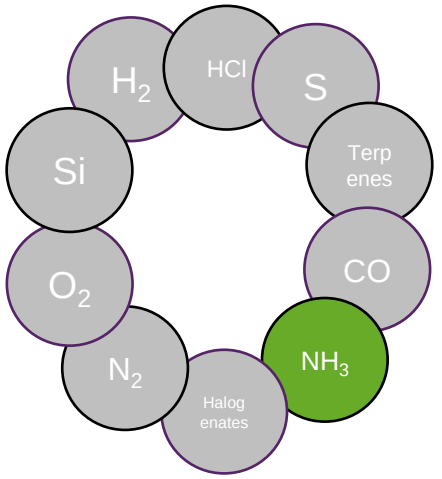

Cyan = NPL PRM from 1.1.2

1.3.2: Validation of methods and standards

Laboratory-based validation of the **dynamic preparation facilities** for the preparation of traceable biomethane transfer standards by calibrating the static standards.

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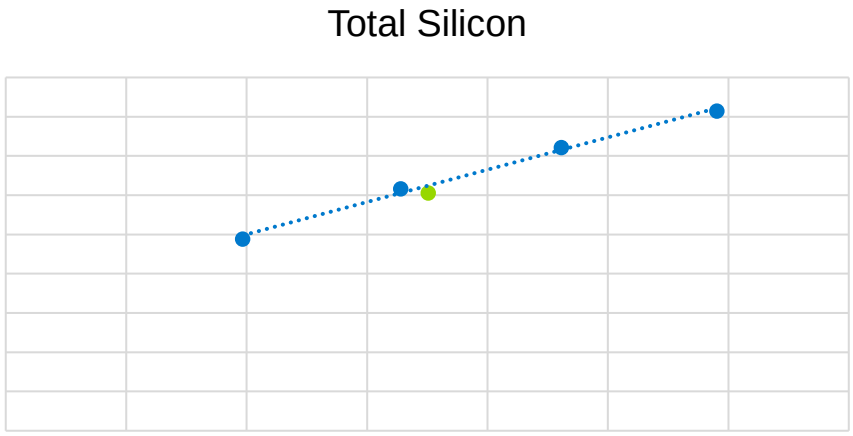
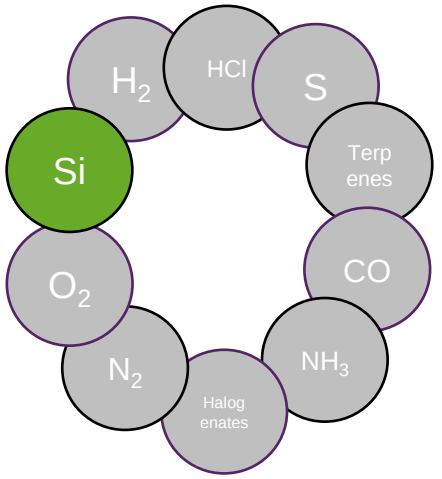


GAS



Cyan = NPL PRM from 1.1.2

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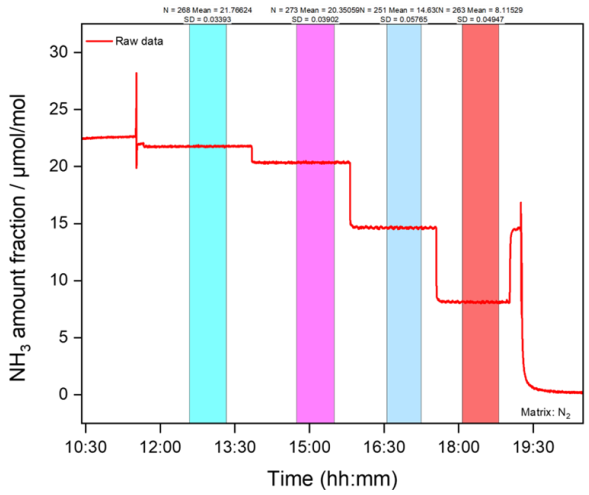
1.3.3: Validation of methods and standards

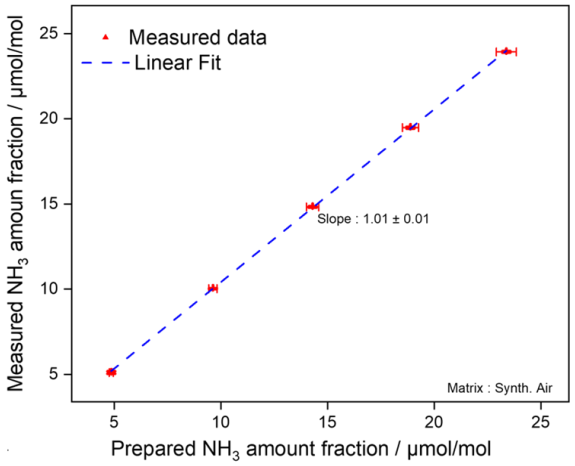
Laboratory-based validation of the **dynamic preparation facilities** for the preparation of traceable biomethane transfer standards by calibrating the static standards.

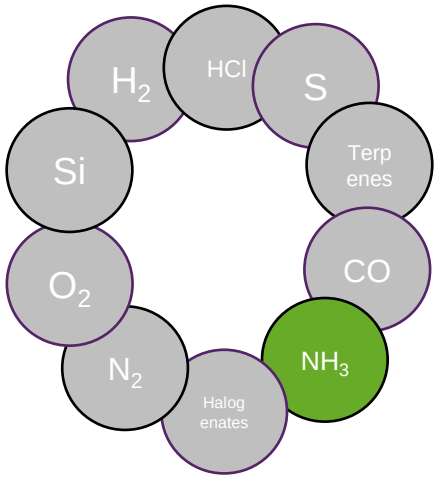
PTB validated their **Optical Gas Standard (OGS) facility** with ammonia.

Spectroscopic system on NH_3 measurements

- Spectroscopic system is based on OF-CEAS
- Examples on performance evaluation; the response time and linearity of the instrument





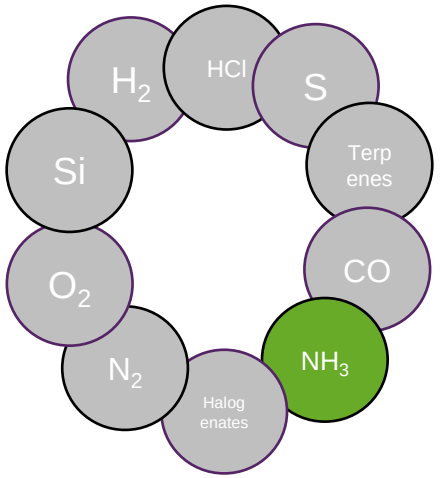


1.3.4: Validation of methods and standards

Laboratory-based validation of the **dynamic preparation facilities** for the preparation of traceable biomethane transfer standards by calibrating the static standards.

VTT and DTU validated their **liquid evaporative generator facility** with NH3.

Expanded uncertainty of 1.9% for analyte amount fraction realised.



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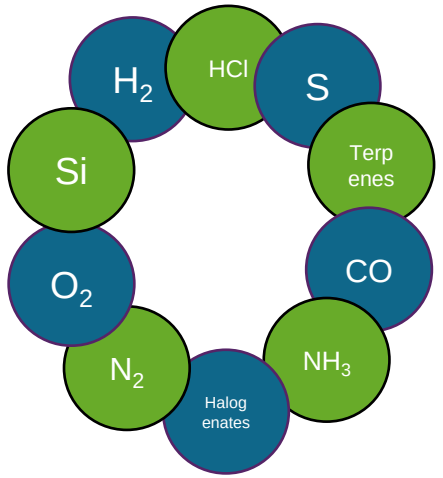
DTU

1.3.5: Validation of methods and standards

Laboratory-based validation of the **dynamic preparation facilities** for the preparation of traceable biomethane transfer standards by calibrating the static standards.

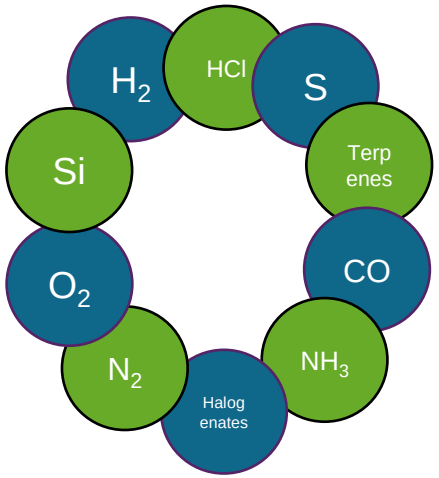
VSL are preparing a summary report on the development of dynamic systems. NPL will submit a biomethane industry trade magazine article based on this.



1.3.6: Reporting

Laboratory-based validation of the **dynamic preparation facilities** for the preparation of traceable biomethane transfer standards by calibrating the static standards.

NPL will prepare a summary report on the **development** and **validation** of **dynamic gas standard preparation facilities** and **novel multicomponent static standards** for the EN16723 impurities in biomethane. Will be submitted as a EURAMET report and a peer reviewed publication.



National Physical Laboratory

Acknowledgement

The project BiometCAP 21NRM04 has received funding from the European Partnership on Metrology, co-financed from the European Union's Horizon Europe Research and Innovation Programme and by the participating states.

Thanks for listening!

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Protocol for evaluation of lab-based instruments and methods used in biomethane conformity assessment

Sandra Hultmark, RISE

ENERGY GASES

METCCUS

VSL

MET4H2

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Protocol for evaluation of lab-based instruments and methods used in biomethane conformity assessment

Sandra Hultmark, RISE
26th of March 2025

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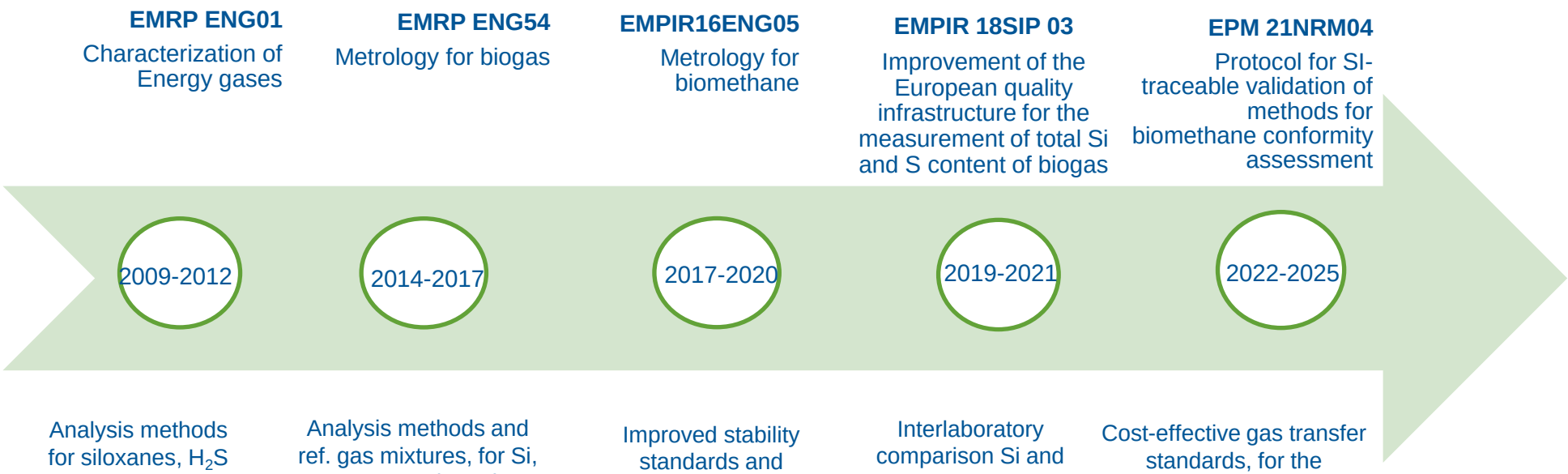
RI. SE

Development of a measurement infrastructure



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Why do we need a protocol?

Reliable and traceable purity measurements can only be obtained with equipment of known performance. Instrument manufacturers and end users therefore need a standardised protocol in order to meaningfully demonstrate instrument performance in both laboratory and field conditions.

The protocol can be used to:
a) Determine a range for each component over which the uncertainties are valid;
b) Determine uncertainties over a pre-defined range for each analyte;
c) Evaluate the performance of analyzers in the field

The protocol will be submitted to ISO/TC193/SC1/WG25 for consideration as a new ISO standard (in the form of a New Work Item Proposal (NWIP) and draft ISO standard text).

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ISO/TC193/SC1/WG25 “Biomethane” has developed a series of standards mostly based on the work done during 16ENG05 Metrology for biomethane

BiometCAP will produce a NWIP “Protocol for performance evaluation of gas analysers used in biomethane conformity assessment”

Methods developed for biomethane

Impurities	Measurement principle	ISO standard
Amines	TD-GC-MS/FID (specifically alcohol-amines and piperazines)	ISO/TS 2610:2023 ISO 2620:2024
Halogenated compounds	IC (HF and HCl)	ISO 2611-1:2024
	TD-GC-MS/FID (halogenated organic compounds)	ISO 2620:2024
Ammonia	TDLAS	ISO 2612:2023
Total silicon content or Siloxanes	GC-IMS (siloxanes)	ISO 2613-2:2023
	TD-GC-MS-FID (Siloxanes)	ISO 2620:2024
	AES (total silicon)	ISO 2613-1:2023
Terpenes	µ GC-TCD	ISO 2614:2023
	TD-GC-MS-FID	ISO 2620:2024
Compressor oil	GC-MS (or GC-FID)	ISO 2615:2024
Other VOCs (ketones, hydrocarbons, furans...)	TD-GC-MS-FID	ISO 2620:2024

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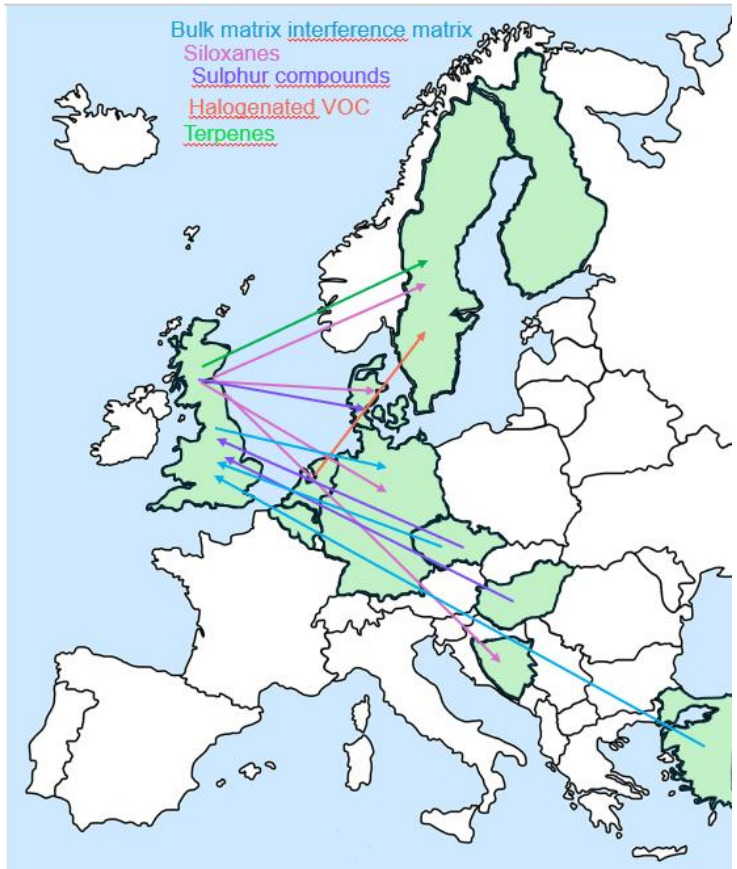
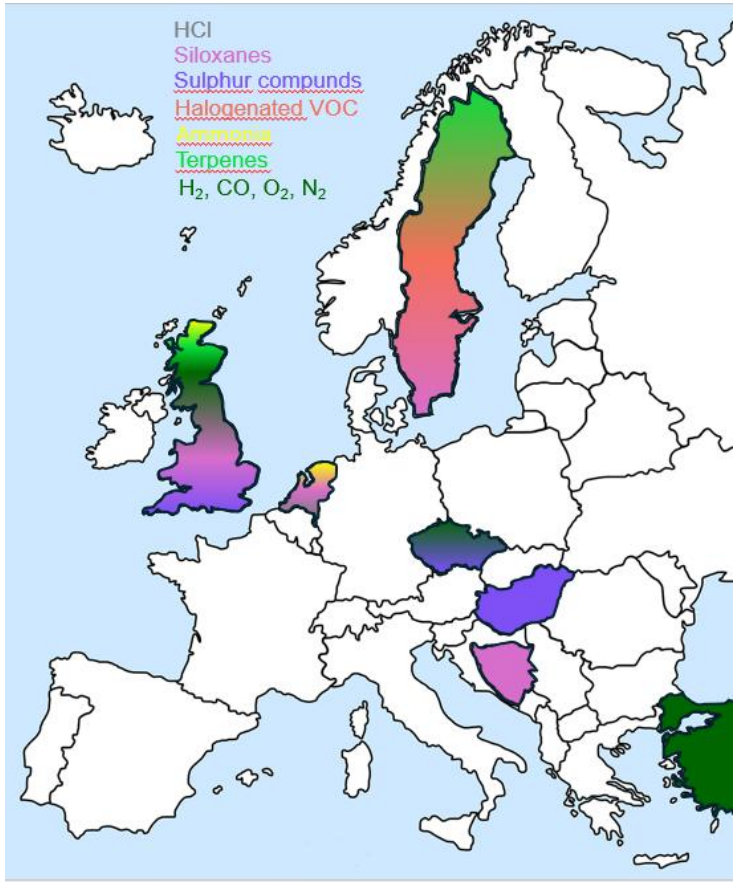


Production and exchange of gas mixtures between partners



Validation of the protocol on species at 7 NMIs

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WP2: Protocol for use in the SI-traceable performance evaluation of the measurement systems that are used for biomethane conformity assessment

RI. SE

Task 2.1: Development of a performance assessment protocol

- The aim of this task is to develop a performance assessment protocol detailing how to evaluate the gas analysers that are used for measuring key impurities in biomethane

Task 2.2: Validation of the performance assessment protocol

- The aim of this task is to demonstrate the fitness of purpose of the performance assessment protocol

Task 2.3: New work item proposal

- The aim of this task is to develop a new work item proposal (NWIP) (a proposal and draft ISO standard text, describing the protocol for performance evaluation of the gas analysers that are used in biomethane conformity assessment) for a new ISO standard for consideration by ISO/TC193/SC1/WG25.

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Task 2.1: Development of a performance assessment protocol

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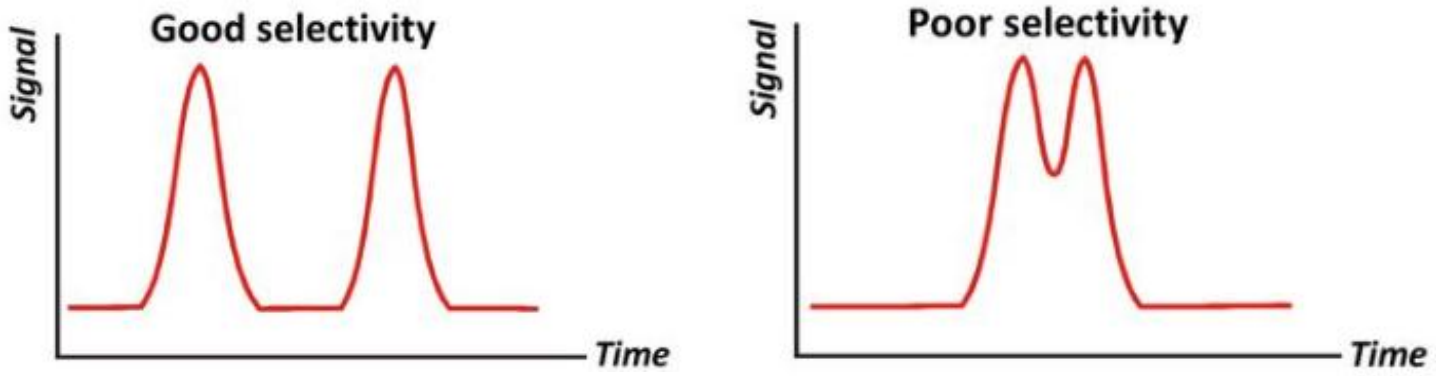
The general procedure for determining the performance characteristics of the instrument consists of eight steps (four planning steps, one experimental step and three calculation steps).

1) Specify the components to be measured and the measuring range (planning)
2) Establish the expected function of the response (for example linear response) (planning)
3) Specify the set of reference gas mixtures needed (planning)
4) Choose a gas mixture to be used for routine calibration (planning)
5) Collect data to evaluate the performance characteristics (experimental)
6) Evaluate/calculate the performance characteristics related to the range (LOQ, LOD..) (calculation)
7) Evaluate/calculate the performance characteristics related to the precision and bias (calculation)
8) Calculate the measurement uncertainties

Parameters to evaluate

- **Selectivity:**



- **Limit of detection (LOD) and limit of quantification (LOQ):**

LOD the smallest amount or concentration of the analyte in the test sample that can be reliably distinguished. Limit of quantitation (LOQ) – the lowest concentration of the analyte that can be determined with an acceptable repeatability and trueness.

- **Working range and linearity:** Defines the interval over which reliable results are obtained

- **Robustness/ruggedness:**The terms robustness and ruggedness refer to the ability of an analytical method to remain unaffected by small variations.

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Parameters to evaluate

Measurement uncertainty: Indicate how close a measurement result is to the true value

Precision:characterizes the closeness of agreement between the measured values obtained by the replicate measurements on the same or similar objects under specified conditions.

- Repeatability
- Intermediate precision
- Reproducibility

Trueness / bias:closeness of agreement between the average of an infinite number of replicate measured quantity values and a reference quantity value.

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Task 2.2: Validation of the performance assessment protocol

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NMIs	Targeted compounds	Analytical method	Standard	Measurement uncertainties
IMBiH	Total silicon	AES	ISO 2613-1:2023	2%
RISE	Siloxanes	TD-GC-MS-FID	ISO 2620:2024	11%
VSL			ISO 2620:2024	4-11%
NPL		GC-IMS	ISO 2613-2:2023	3-8%
VSL	Ammonia	TDLAS	ISO 2612:2023	6%
NPL		GC-NCD	own method	*
VSL	Hydrogen chloride	TDLAS	own method	7%
RISE	Halogenated VOC	TD-GC-MS-FID	ISO 2620:2024	10%
BFKH	Sulphur compounds	GC-SCD-FID	Modified ISO 19739	3-8%
CMI			Modified ISO 19739	6%
NPL			Modified ISO 19739	15%
NPL	Terpenes	GC-MS-FID	Modified ISO 2620:2024	2-14%
RISE		TD-GC-MS-FID	ISO 2620:2024	9%
NPL	Hydrogen, carbon monoxide, oxygen, nitrogen	GC-TCD	ISO 6974-6:2002	Hydrogen 10% Carbon monoxide 0.5% Oxygen 13% Nitrogen 6%
CMI			ISO 6974-6:2002	Hydrogen 1.6% Carbon monoxide 0.8% Oxygen 1.6% Nitrogen 0.4%
UME			ISO 6974-1:2012	Hydrogen 0.4% Carbon monoxide 0.6% Nitrogen 0.4%

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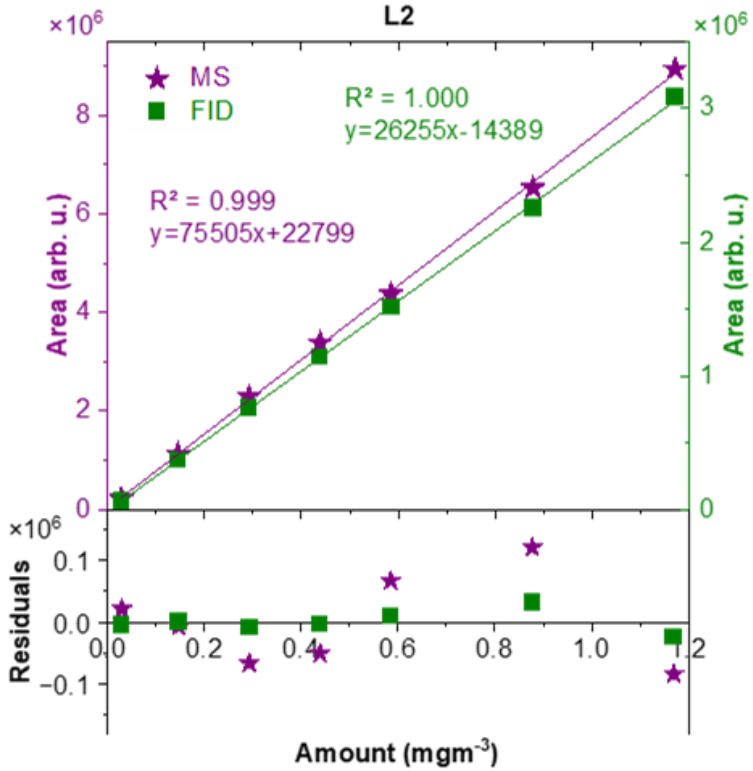
The validation of the method ISO 2620:2024 according to the performance assessment protocol

siloxanes (A2.2.1)

Compounds	$u(R_w)$ rel. %	u(bias) rel. %	$U = 2u_c$ %
Disiloxane hexamethyl	3.04	4.56	11



Compounds	LOD, $mg.m^{-3}$ (S/N = 3)	LOQ, $mg.m^{-3}$ (S/N = 10)
MS detector		
L2	0.002	0.006
FID detector		
L2	0.007	0.02

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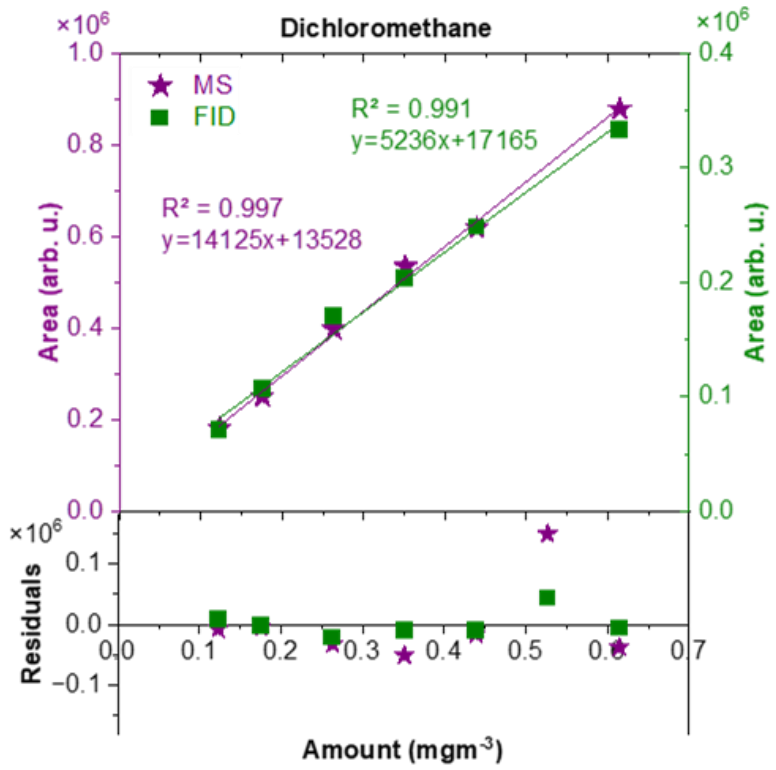
The validation of the method ISO 2620:2024 according to the performance assessment protocol

halogenated VOCs (A2.2.4)

Compounds	$u(R_w)$ rel. %	u(bias) rel. %	$U = 2u_c$ %
Dichloromethane	2.65	4.11	10



Compounds	LOD, $mg.m^{-3}$ (S/N = 3)	LOQ, $mg.m^{-3}$ (S/N = 10)
MS detector		
Dichloromethane	0.03	0.09
FID detector		
Dichloromethane	0.01	0.04

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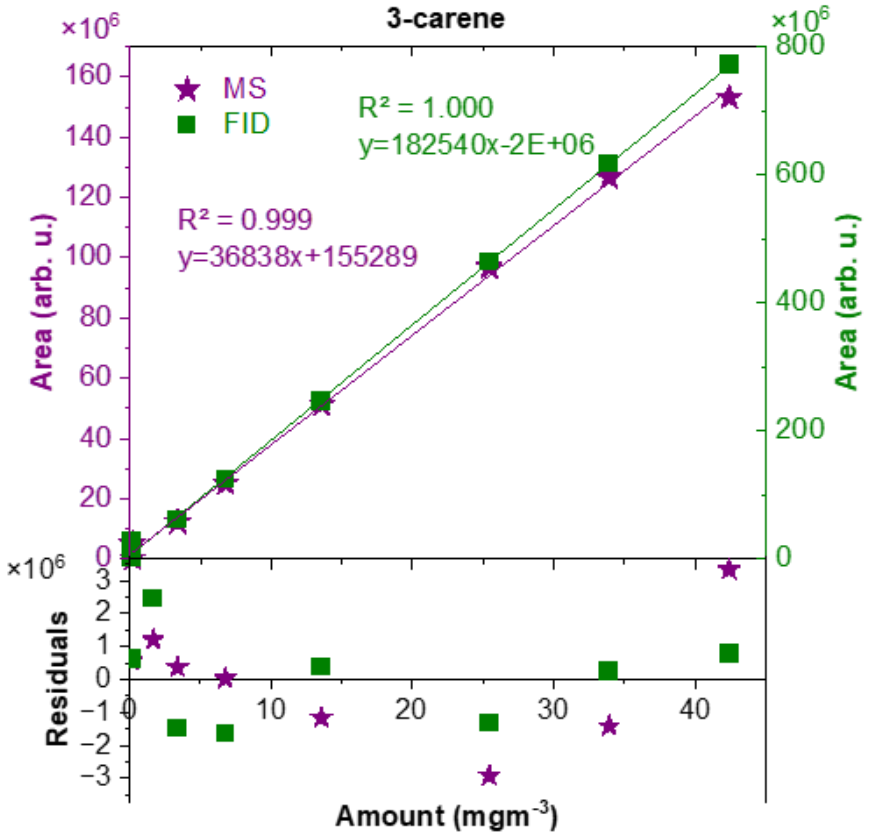
The validation of the method ISO 2620:2024 according to the performance assessment protocol

terpenes (A2.2.6)

Compounds	$u(R_w)$ rel. %	u(bias) rel. %	$U = 2u_c$ %
3-carene	2.62	3.31	9



Compounds	LOD, $mg.m^{-3}$ (S/N = 3)	LOQ, $mg.m^{-3}$ (S/N = 10)
MS detector		
3-carene	0.008	0.03
FID detector		
3-carene	0.002	0.007

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Task 2.3: New work item proposal

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Halogenated compounds	IC (HF and HCl)	ISO 2611-1:2024
	TD-GC-MS/FID (halogenated organic compounds)	ISO 2620:2024
Ammonia	TDLAS	ISO 2612:2023
Total silicon content or Siloxanes	GC-IMS (siloxanes)	ISO 2613-2:2023
	TD-GC-MS-FID (Siloxanes)	ISO 2620:2024
	AES (total silicon)	ISO 2613-1:2023
Terpenes	µ GC-TCD	ISO 2614:2023
	TD-GC-MS-FID	ISO 2620:2024
Compressor oil	GC-MS (or GC-FID)	ISO 2615:2024
Other VOCs (ketones, hydrocarbons, furans...)	TD-GC-MS-FID	ISO 2620:2024

RI. SE

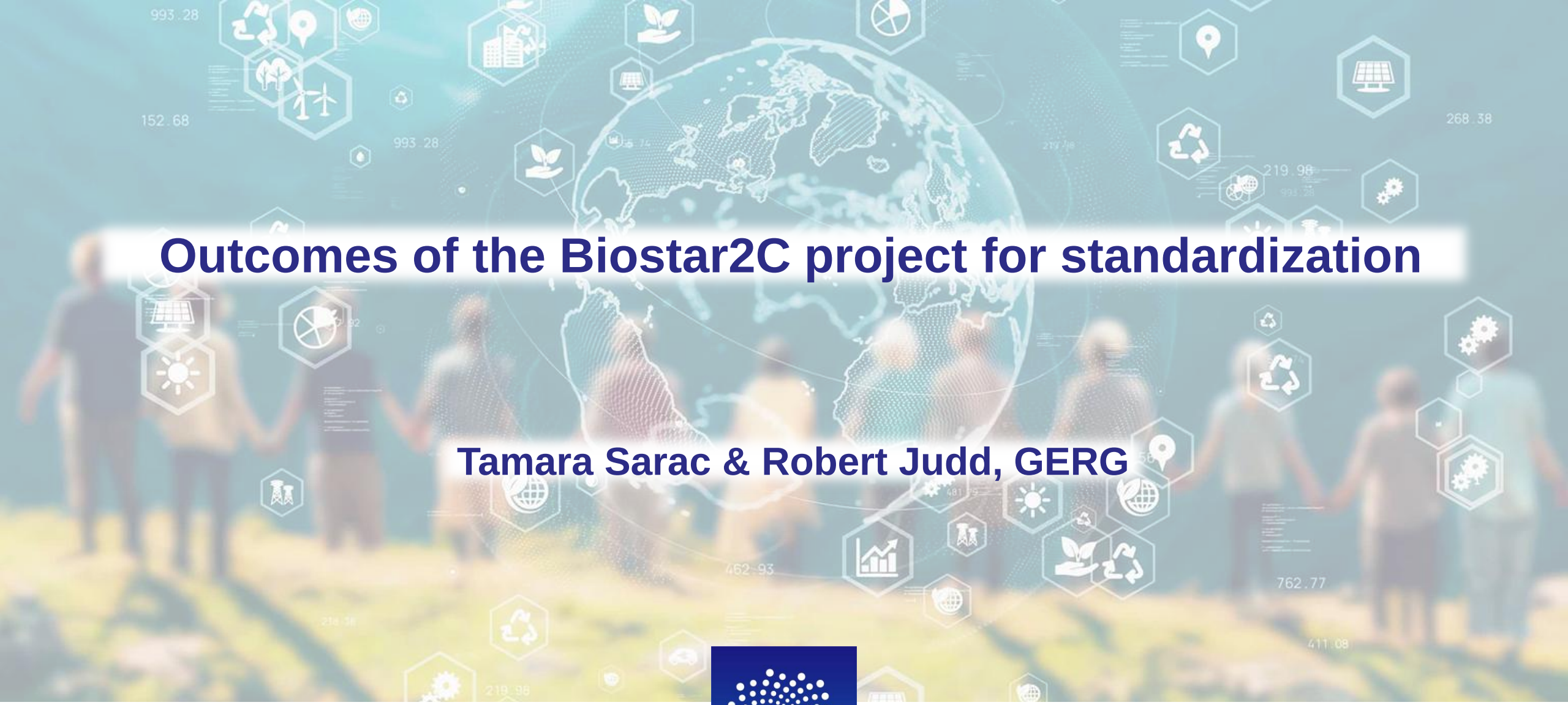
EUROPEAN PARTNERSHIP Co-funded by the European Union METROLOGY PARTNERSHIP EURAMET

Conclusions

- BiometCAP protocol specifies procedures to evaluate the performance of instruments that detect key impurities in biomethane. It addresses various critical parameters including detailed experimental methods to assess these parameters.
- Ensures that the biomethane assessment methods not only adhere to high standards but also contribute to consistent and reliable industry practices.
- The applicability of the protocol was tested across different laboratories using various gas analysers, sampling, validated testing methods and reference standards.
- The protocol will be submitted to ISO/TC193/SC1/WG25 for consideration as a new ISO standard (in the form of a New Work Item Proposal (NWIP) and draft ISO standard text).

Thank you for listening

Questions?



Outcomes of the Biostar2C project for standardization

Tamara Sarac & Robert Judd, GERG

ENERGY GASES

METCCUS

VSL

MET4H2

BiometCAP

EMN Energy Gases Joint Workshop
BiometCAP
26.03.2025, Delft

BioStAR2C – final phase of GERG Biomethane Project

Biomethane trace components and their potential impact on the European gas industry

Robert Judd, GERG
Florent Huet, ENGIE
Gaspard Bouteau, ENGIE
Alexandra Kostereva, GERG
Tamara Sarac, GERG

Funded by the European Union

Objectives of the project

- Supporting the CEN European standardization process through reducing or removing technical barriers to the injection of biomethane in the natural gas network

- Standards (2016):
  - **16723 -1 :** Specifications for biomethane for injection in the natural gas network
  - **16723-2 :** Automotive fuel specification

- These standards specify the biomethane quality expected for injection in gas network and usage as gas fuel regarding the maximum trace compound concentrations

The overall objective of the project is to offer the conditions to a safe development and a competitive positioning of the biomethane chain on the market

BioStAR2c

Objective : Realizing prenormative work assessing the impact of several trace compound on end user appliances

Timeline Towards the removing of technical barriers to biomethane injection into the natural gas grids

GERG biomethane project → Biostar2C project

A multi-phase project aiming to revise the standards limits regarding trace component in biomethane with scientifically based data

Phase 1

GERG gas industry priorities: Status review and gap analysis:

- Siloxanes
- Corrosive components
- Micro-organisms

First standard published in 2016 with trace compound limit not al based on scientific studies

January 2018 – Phase 2a

Combination of GERG priorities & CEN immediate priorities:

- Status review and gap analysis
  - Sulfur
  - Oxygen
  - Health impact assessment
- Experimental program: impact of siloxane on:
  - Industrial boilers
  - Heavy duty vehicles performance

SA/CEN/RESEARCH/475/2017-07

October 2020 – Phase 2b

Follow up from Phases 1 & 2a

WP1: Experimental program on siloxanes impacts

- Engines: test on switching type oxygen sensors

WP2: Experimental program on the impact of sulfur on vehicles After Treatment System (Catalysts)

- Lab test using dedicated burner with given sulfur concentration in natural gas

WP3: preparation for Experimental program on the impact of oxygen and corrosive components on gas facilities:

- Gas grid
- Underground Gas Storage

WP4: Improve knowledge on biomethane

- Biomethane quality database (UK data)
- Literature review on siloxane purification process

CEN/2019/ENER/C2/452-2019

Dec 2022 – Phase 2c

BioStAR2c

Follow up from Phases 1, 2a & 2b

WP2: Experimental program on siloxanes impacts

- Industrial boilers: cycling mode (start and stop)

WP3: Experimental program on the impact of sulfur on vehicles After Treatment System (Catalysts)

- Ageing test
- Vehicle test
- Sulfur ageing modeling

WP4: Experimental program on the impact of oxygen and corrosive components on gas facilities:

- Gas grid
- Underground Gas Storage
- Impact of hydrogen on type 1 CNG steel tanks

WP5: Improve knowledge on biomethane

- Biomethane quality database (Swedish data)
- BioSNG & bioLNG quality data (French data)
- Upgrading process database

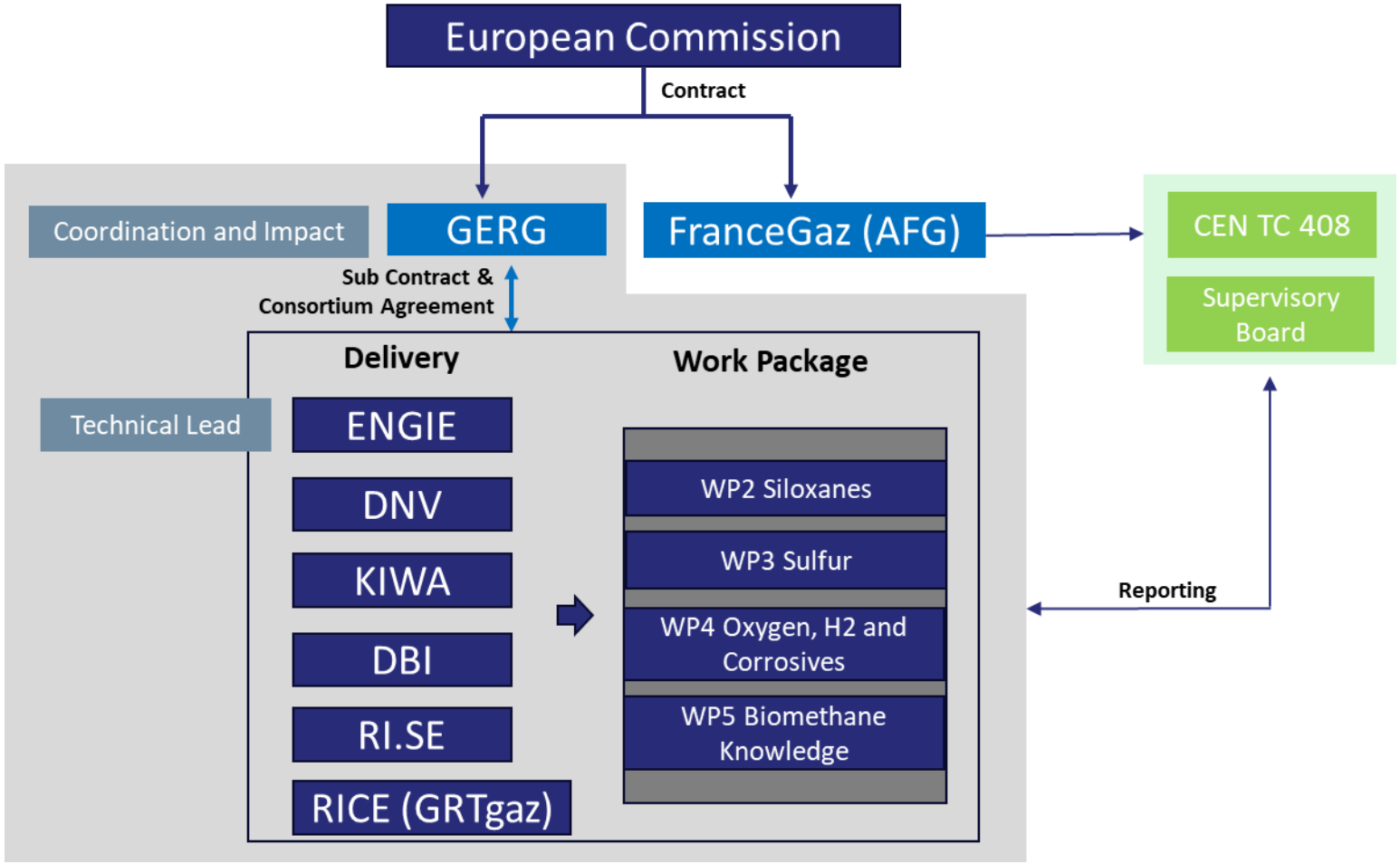
Horizon Europe Grant Agreement No 101112475

Phase 3

Revision of standard EN 16723 part 1&2

End date December 2025

Structure


European Commission
Contract
Coordination and Impact
GERG
FranceGaz (AFG)
Sub Contract &
Consortium Agreement
Delivery
Work Package
Technical Lead
ENGIE
DNV
KIWA
DBI
RI.SE
RICE (GRTgaz)
WP2 Siloxanes
WP3 Sulfur
WP4 Oxygen, H2 and Corrosives
WP5 Biomethane Knowledge
CEN TC 408
Supervisory Board
Reporting

Work Package 2 Status

impact of siloxanes on industrial boilers

Objective and structure of the WP

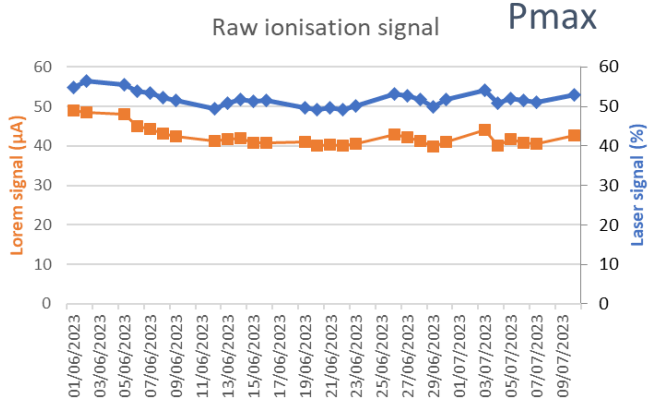
- **OBJECTIVE** : gathering data on the impact of siloxane presence within biomethane on the performance of industrial boilers.
  - the boiler was operated in power modulation mode in order to mimic real usage of such systems in industrial environment.
  - Previous work on continuous mode highlighted a decrease of the ionization signal over test period due to silica deposition on the ionization probe → leading to misfire od the boiler
- **METHODOLOGY** :
  - 4 siloxane concentrations: 5 mgSi/Nm3, 2.5 mgSi/Nm3 , 1.5 mgSi/Nm3 and 1 mgSi/Nm3
  - Power modulation : 450 KW / 90 kW
  - Each concentration tested for a period of 5 cycles (1 cycle/week)
  - Monitored parameters :
    - General performances/heat loss along the 5 cycles for each concentration
    - Pollutant emissions (CO, CO2, NOx, …)
    - Ionization signal degradation
  - At the end of each concentration testing, the boilers will be open in order to gather the silica deposition that will be analyzed

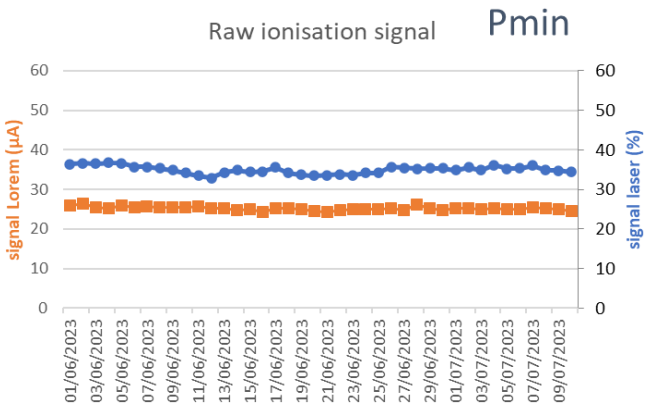
1 MW boiler operated in ENGIE lab CRIGEN (Stains – France)

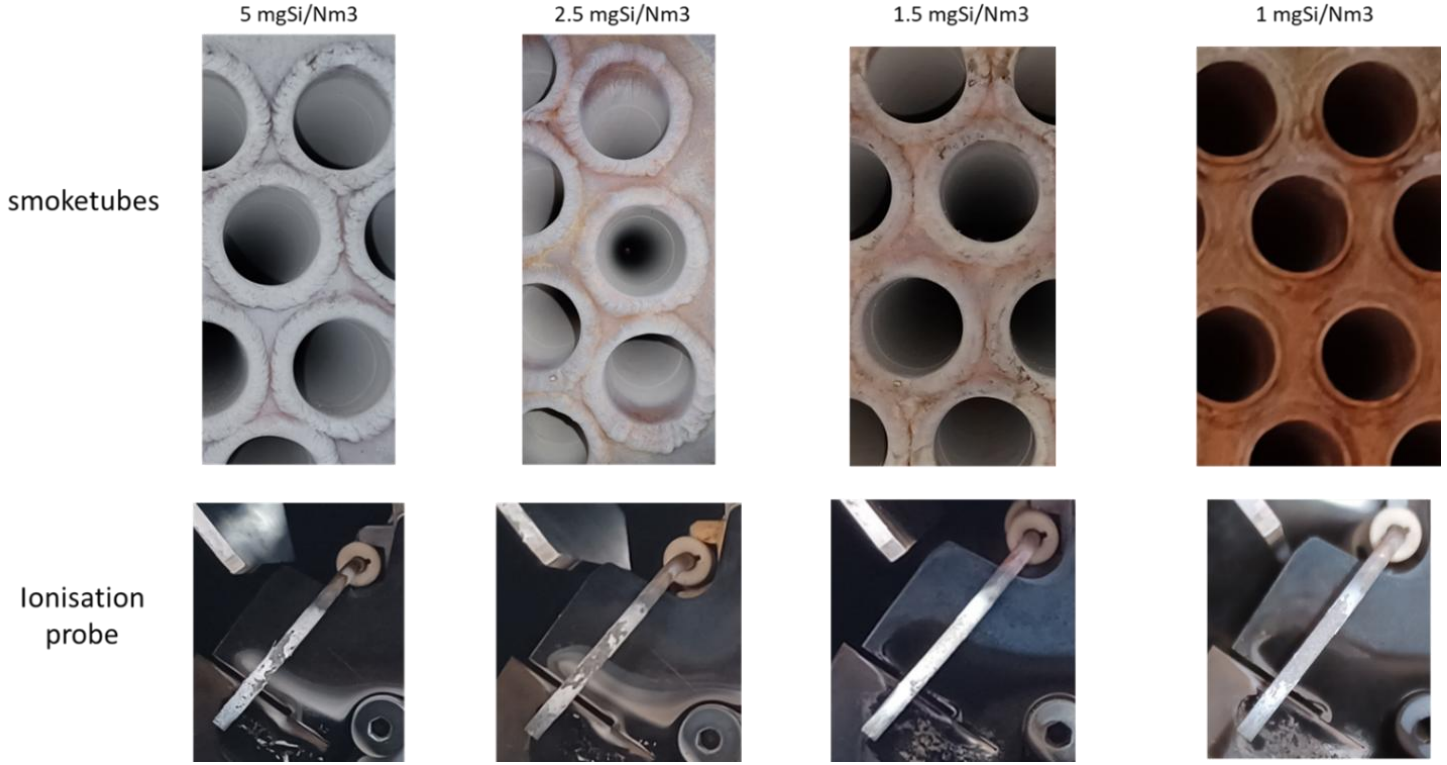
RESULTS EXPLOITATION:
Extrapolation towards realistic biomethane usage for recommendations of adapted siloxane concentration to be implemented in EN 16723 standard revision

WP2 : siloxane impact on industrial boilers

No decrease of the ionisation signal observed → power modulation seems to have beneficial effect



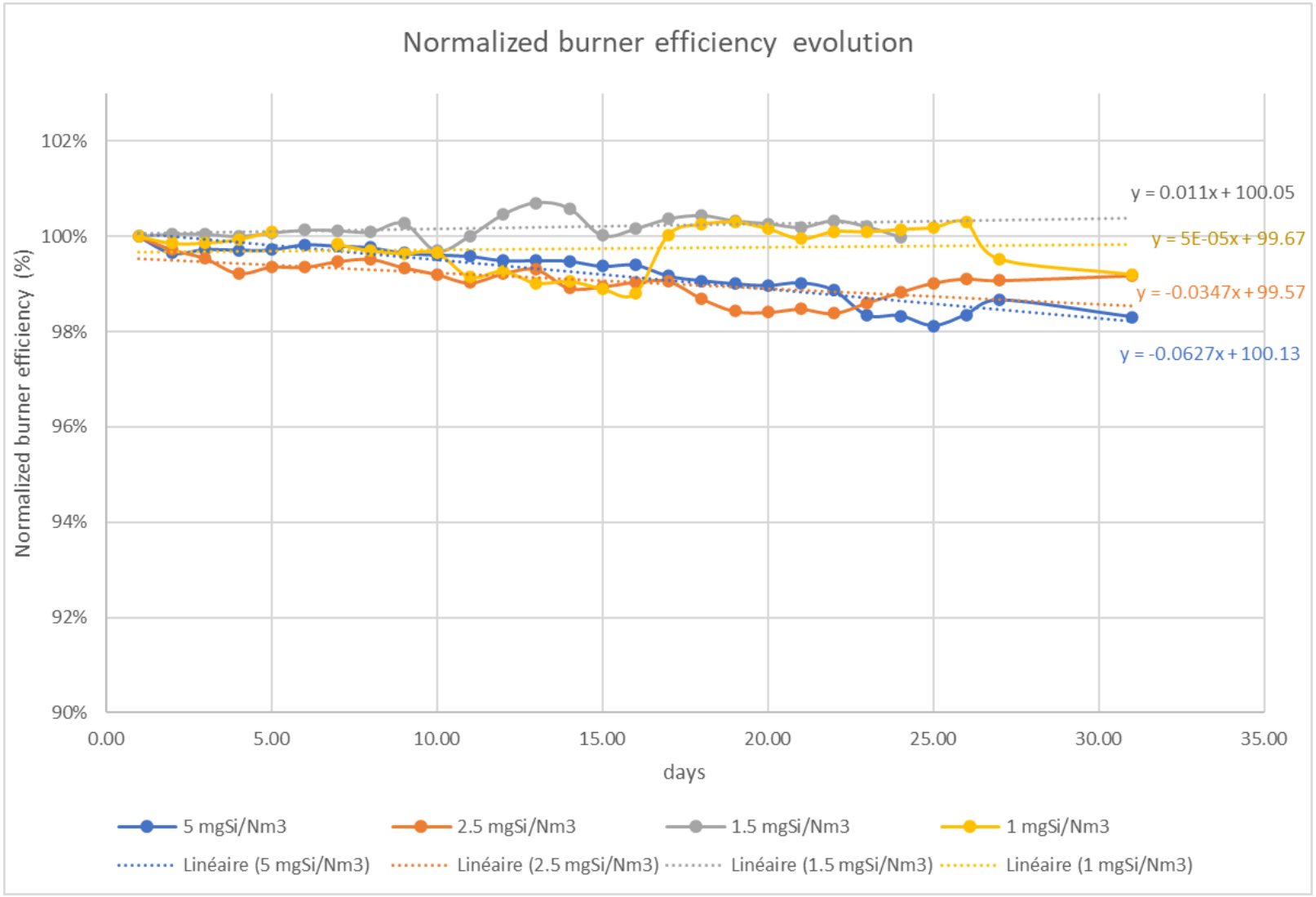




As expected : the lower the siloxane concentration, the lower the silica depositions

→ Cleaning of the boiler along normal maintenance protocol allowed for recovering initial performances

WP2 : siloxane impact on industiral boilers



Based on these different results, the percentage decrease per day used for the different calculation are:

- **For 5 mgSi/Nm³ :** -0.0627 %/day (actual fitting)
- **For 2.5 mgSi/Nm³ :** -0.0347 %/day (actual fitting)
- No burner efficiency decrease observed for 1 and 1.5 mgSi/Nm³

Extrapolation (pessimistic) for calculations

- *For 1.5 mgSi/Nm³ : -0.0188 %/day (extrapolated)*
- *For 1 mgSi/Nm³ : -0.0125 %/day (extrapolated)*

WP2 : siloxane impact on industiral boilers

- **RESULT EXPLOITATION :**
  - **How to consider realisitic usage of biomethane with siloxane on industrial boiler :**

Source : EBA statistical report 2023

- Siloxane are mostly present on biogas from WWTP -> 6% of the overall biogas plant in Europe

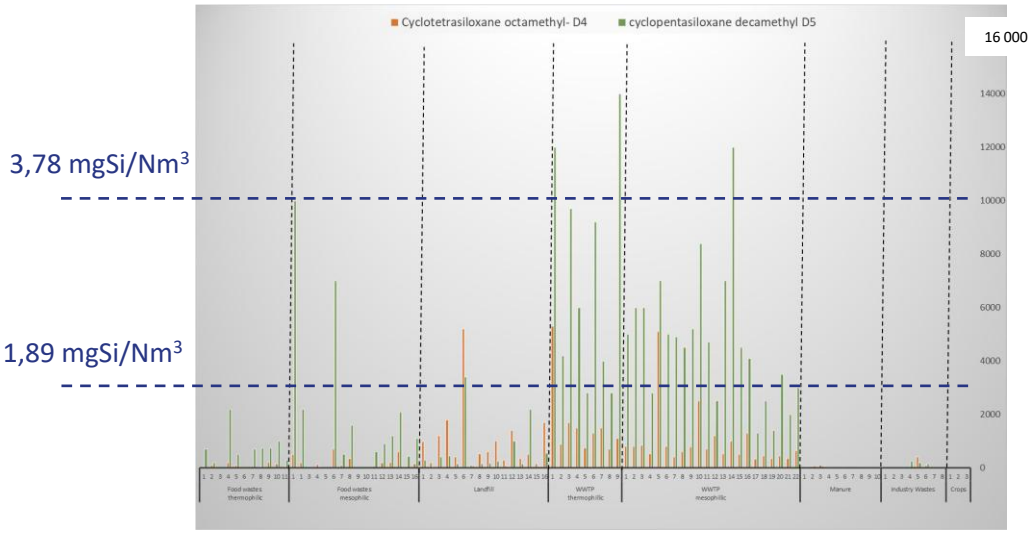
Source : RISE report 2023 – Biostar2C : "Database of biogas and biomethane composition from Swedish data »

- **From WWTP biogas plant** (31 plants): 80% of them show a siloxane concentration (D5) between 0.95 and 3.67 mgSi/Nm3
- **From non WWTP biogas plants** (64 plants):80 % of them shown a siloxane concentration (D5) between 0.02 and 0.83 mgSi/Nm3

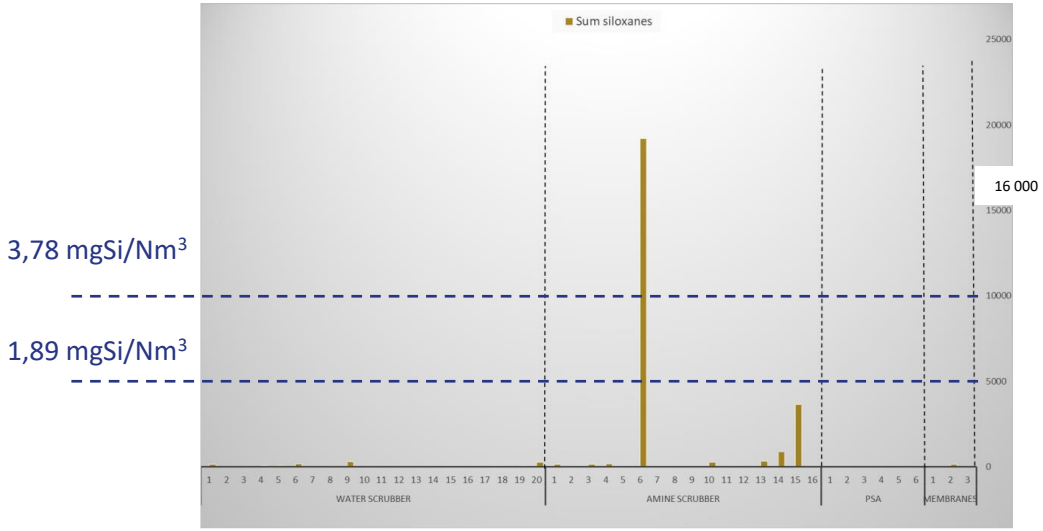
WP 5 Improving biomethane knowledge-Task1 : Biomethane data Sweden → concrete usage

Concentration of siloxane D4 and D5 (90% of all siloxane encountered)

Biogas



Biomethane



- Siloxane are mostly encountered in biogas from WasteWater Treatment (WWTP)Plants
  - (for ref : 10 000 µg siloxane/m^3 = 3,78 mgSi/Nm^3)
- **Biogas upgrading is very efficient to reduce siloxane concentration in biomethane.**
  - Spot measurement (1/ 45 measurements) on amine scrubbing technologies however show strong concentration which can be attributed to the fact that the gas was wet. Those siloxane would probably be removed by dryer.

→ All other measurement show siloxane concentration below 1,5mg Si/Nm^3

WP2 : siloxane impact on industiral boilers

Considering the current scenarios of low WWTP shares and low siloxane concentrations present in biogas, overall impact on industrial boilers of realistic siloxane concentration in biomethane is limited.
Based on results and extrapolation, **2mgSi/Nm3 appears to be a reasonable value to be implemented in EN 16723 standard revision**
Setting up a limit of siloxane at 2mgSi/Nm3 is not too restrictive for biomethane producer while ensuring acceptable performances of industrial boilers between 2 maintenance procedures.

2 mgSi/Nm3	100% bioCH4	50% bioCH4	10% bioCH4
Expected burner performances loss over 12 months period considering siloxane present all over the gas network	9.15%	4.58%	0.92%
Expected burner performances loss over 12 months period considering siloxane only present on WWTP (1/10 of biomethane plants in Europe)	0.91%	0.46%	0.09%

- **Amount of Biomethane to be considered as assumption :**
  - **10 % (French Objective for 2030)**
  - **50 % (European objective for 2050)**
  - **100 % (actual case studied during the tests)**

Work Package 4 Status

Impact of oxygen and corrosives

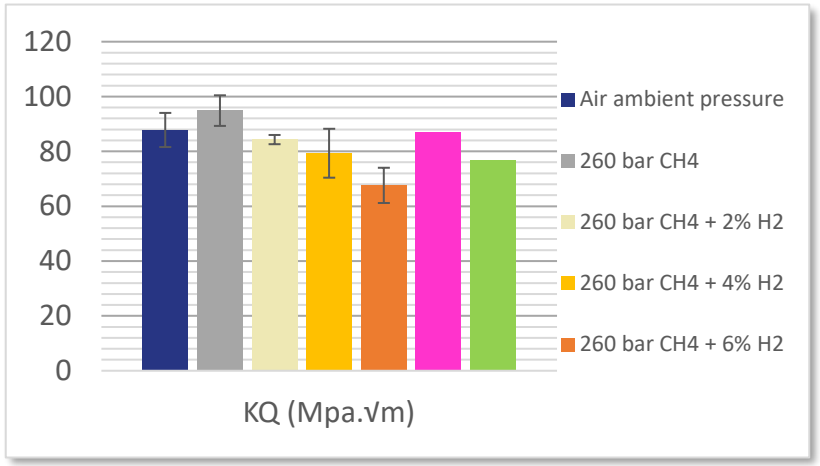
Objective and structure of the WP

- Task 1 : Impact of oxygen on Underground Gas Storage
  - Structure of the task1 : Lead by DNV UK / GLIS
    - Formation Damage Evaluation
    - Microbial Population Identification
    - Elemental Sulfur Generation
    - Surface process equipment impacts
- Task 2 : Corrosion tests
  - Lead by KIWA and GRT Gaz
  - Samples would be placed in each autoclave with at least one sample in the liquid phase, one sample in the gas phase and one sample at the interface
- Task 3 : Impact of H2 on CNG type 1 steel tanks → **focus of today**
  - Objective : Getting better insights on the suitability of CNG type 1 steel tanks with H2
  - Structure of the task 2 :
    - Tests carried out by P' institute (University of Poitiers) as a subcontractor of ENGIE
    - 2 kinds of tests planned : fracture toughness tests and crack growth rate tests - both with 34CrNiMo6 steel

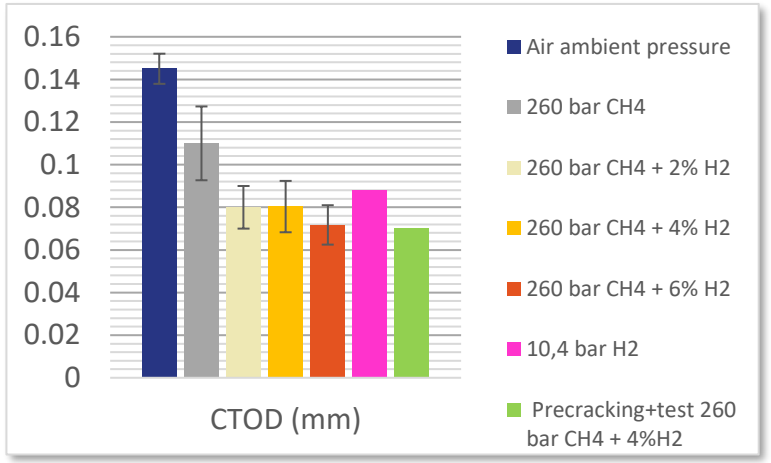
WP4 : Impact of oxygen and corrosives compounds- task 3 H2 impacts

Fracture toughness tests aim to provide information on the stress that a structure with a crack of a certain length can withstand without it propagating.

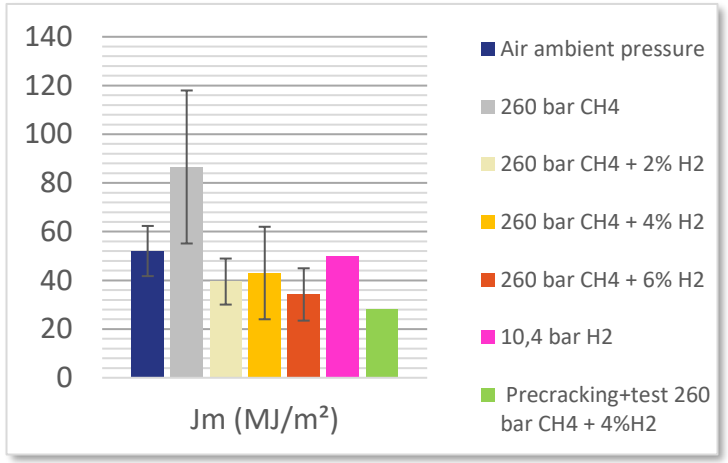
Current limit at 2% H_2



KQ (Mpa.m$^{1/2}$) = stress intensity factor : capacity of a material to resist to crack propagation at a given force



CTOD (mm) : Crack Tip Opening Displacement



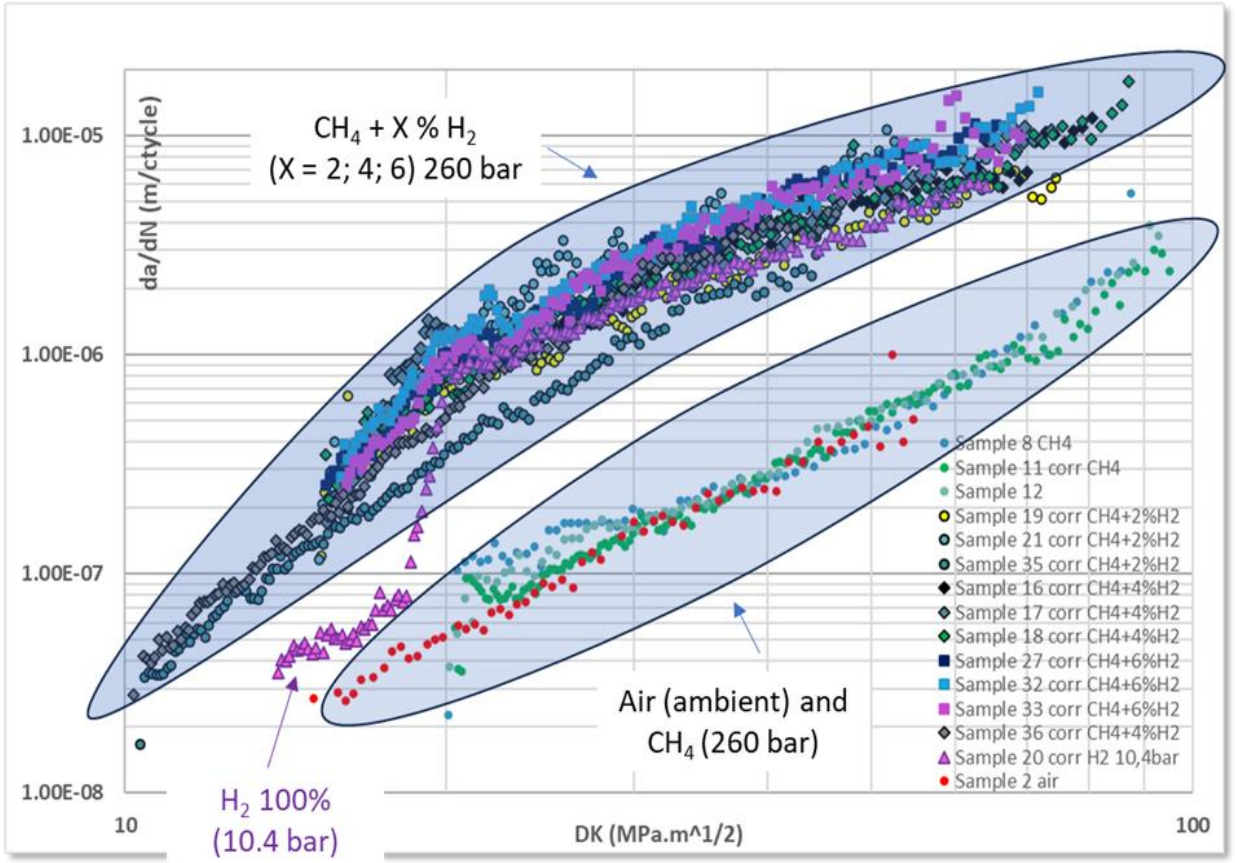
Jm (MJ:m²): plastic strain energy released per unit area of crack surface

- Significant KQ value reduction, with over 17 MPa×√m in difference, is noticed between the 2% H2 mixture and the 6% H2 one.
- Blended samples show a significantly reduced CTOD mean value (~0,08mm).
- The mean Jm values for samples tested under 2%, 4%, and 6% H2 are similar.

WP4 : Impact of oxygen and corrosives compounds- task 3 H2 impacts

Current limit at 2% H_2

Fatigue crack propagation tests aim to assess the lifespan in the presence of a crack-like defect on the inner surface of the tank.



- Adding hydrogen in the gas mixture drastically increase crack propagation rate (approximately an order of magnitude compared to no H2), corroborating findings in existing literature
- Increasing H_2 above 2% (current maximum concentration in both standard EN 16723 and R110 regulation), only show limited effect on the crack propagation over repeated fatigue cycles
- The results seems to indicate that an increase of the allowable maximum H_2% to 4% would be acceptable
- Dedicated analysis on other materials in presence of H2 (engine, pressure regulators, sensors..) would bring a more definitive picture for assesing the impact of an increase of H_2 on gas vehicle lifetime

CONCLUSIONS

CONCLUSIONS

Impact of siloxane on industrial boiler : *current limit at 1 mgSi/Nm³*

- test realization on 4 siloxanes concentrations show that silica deposit can reduce burner yield
  - **A concentration of 2mgSi/Nm³ is recommended for the revision of EN 16723 Standard** for ensuring sufficient performances between 2 maintenance periods (12/15 months)

Impact of H2 on CNG vehicle tanks

- Adding H_2 in biomethane have an impact on Type I reservoir mechanical properties
  - 2% in already accepted in standards and regulation (R110)
- Further adding H_2 (4% and 6%) seem not lead to further reducing mechanical properties of Type I tank material
- Further test on other gas vehicle material are needed to the full picture on H_2 impact (needed for R110 revision) but a **4% H_2 seems to be acceptable for the revision of EN 16723 standard**

Improving Biomethane knowledge

- Biogas and biomethane database was realized on 70 plant in Sweden
- The database help to better understand where does biogas and biomethane stand compared to current standard
  - The database enable to show that Highest concentration of VOC in biogases was produced from food wastes feedstock
  - The database was used to better rationalized the results obtained on siloxane testing

Project updates: Biostar2c - Gerg (www.gerg.eu/biostar2c/)

GERG

THE EUROPEAN GAS RESEARCH GROUP

Thank you for your attention!

robertjudd@gerg.eu

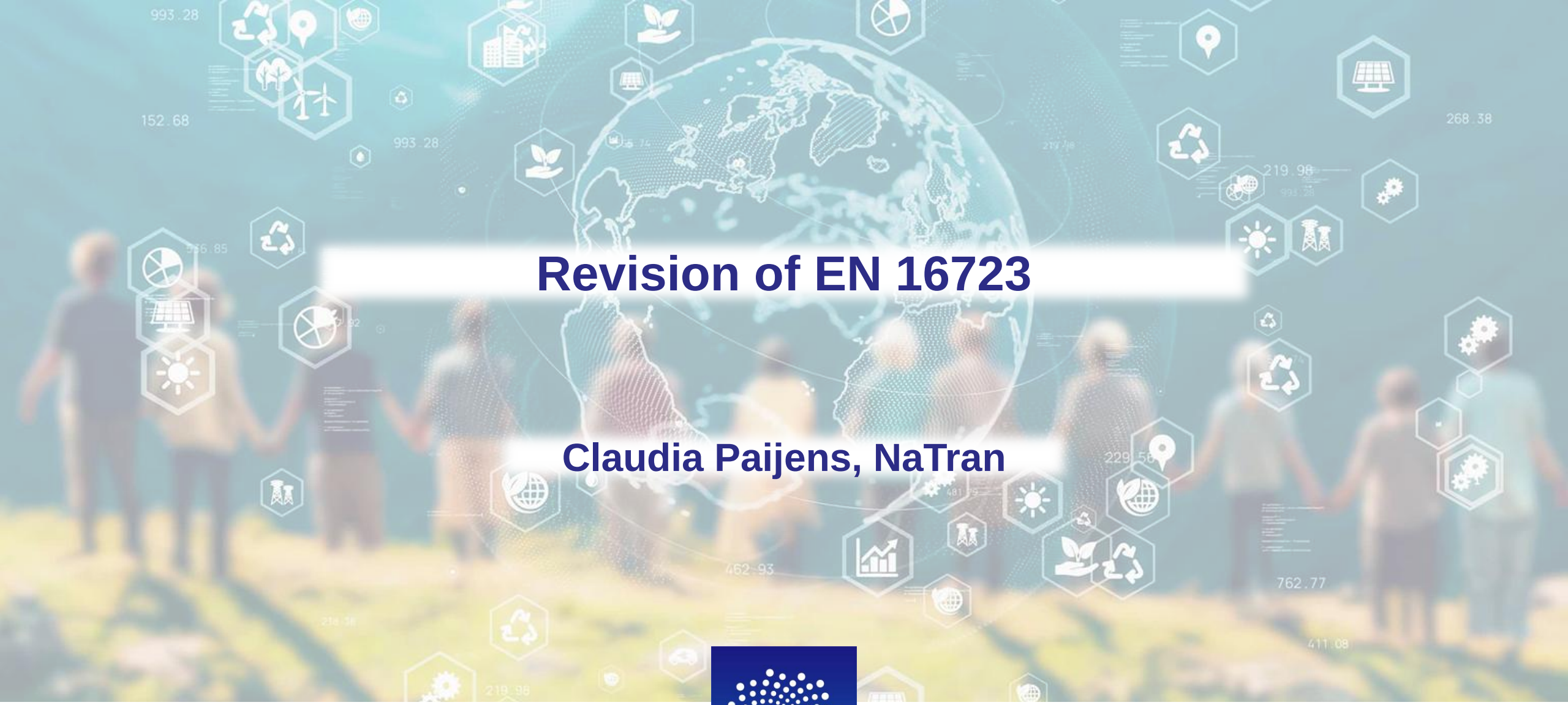
Francegaz

ENSEMBLE, TRANSFORMONS L'ÉNERGIE

BioStAR2c

Funded by the European Union

The Biostar2C project has received funding from the Horizon Europe Programme under Grant Agreement No 101112475.



Revision of EN 16723

Claudia Paijens, NaTran

ENERGY GASES

METCCUS

VSL

MET4H2

BiometCAP

Revision of EN 16723

Biomethane and other renewable and low-carbon methane rich gases – Specifications for injection in the natural gas network and for mixtures with natural gas as automotive fuel

Claudia Paijens
Convenor of CEN/TC 408/WG1
Research Engineer – Gas quality

Background

2011

- **Beginning of biomethane industrialization**, **injection and use**
- Creation of **CEN/TC 408, Biomethane**

2016 - 2017

- Publication of **standards concerning biomethane quality**:
  - EN 16723-1 on biomethane for **injection** in the NG gas grid published in 2016.
  - EN 16723-2 on natural gas and biomethane as **automative fuel** published in 2017

2017 - 2024

- **Lack of information on impact** of sulphur and siloxanes on engines, of oxygen on underground storages, and impact on health
- **GERG Biomethane project**
  Phase 2a (2017-2018)
  Phase 2b (2019-2020)
  Phase 2c (2022-2024)

2022 - 2024

- **Lack of analysis methods on biomethane components** (siloxanes, amines, halogenated compounds, compressor oil, etc.)
- **Publication of various standards** from EURAMET project and ISO/TC 193/SC 1/WG25 Biomethane

2023

- **Creation of CEN/TC 408/WG1** for the revision of EN 16723-1 and EN 16723-2

→ Feb. 2023: **Preliminary work item**

Objectives of the revision of EN 16723 parts 1 & 2

- Change in the title and the scope of CEN/TC 408 to consider the **arrival of new methanes**: **Biomethane and other renewable and low-carbon methane rich gases**
- **Creation of CEN/TC 408/WG 1 Injection & fuel**

  Change in the title and the scope of EN 16723, and merge of the two parts: **Biomethane and other renewable and low-carbon methane rich gases – Specifications for injection in the natural gas network and for mixtures with natural gas as automotive fuel**

GERG
THE EUROPEAN GAS RESEARCH GROUP

BioStAR2c

Review the limit values considering the latest research of the GERG projects

Objectives of the revision of EN 16723 parts 1 & 2

GERG Biomethane project

Phase 1

GERG gas industry priorities: Status review and gap analysis:
- Siloxanes
- Corrosive components
- Micro-organisms

Phase 2a

Jan 2018

Combination of GERG priorities & CEN immediate priorities:
- Status review and gap analysis
  - Sulfur
  - Oxygen
  - Health impact assessment
- Experimental program – Impact of siloxanes on:
  - Industrial boilers
  - Heavy duty vehicles performance

SA/CEN/RESEARCH/475/2017-07

Phase 2b

Oct 2020

Follow up from Phases 1 & 2a

WP1: Experimental program on siloxanes impacts
- Engines: test on switching type oxygen sensors

WP2: Experimental program on the impact of sulfur on vehicles After Treatment System (Catalysts)
- Lab test using dedicated burner with given sulfur concentration in natural gas

WP3: preparation for Experimental program on the impact of oxygen and corrosive components on gas facilities:
- Gas grid
- Underground Gas Storage

WP4: Improve knowledge on biomethane
- Biomethane quality database (UK data)
- Biomethane & bioLNG quality data (French data)
- Literature review on siloxane purification process

CEN/2019/ENER/C2/452-2019

Phase 2c

Dec 2022

BioStAR2c

Follow up from Phases 1, 2a & 2b

WP2: Experimental program on siloxanes impacts
- Industrial boilers: cycling mode (start and stop)

WP3: Experimental program on the impact of sulfur on vehicles After Treatment System (Catalysts)
- Ageing test
- Vehicle test
- Sulfur ageing modeling

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- Gas grid
- Underground Gas Storage
- Impact of hydrogen on type 1 CNG steel tanks

WP5: Improve knowledge on biomethane
- Biomethane quality database (Swedish data)
- Biomethane quality database (French data)
- Upgrading process database

Horizon Europe Grant Agreement
No 101112475

Phase 3

Revision of standard EN 16723 parts 1&2

GERG
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- **Creation of CEN/TC 408/WG 1 Injection & fuel**

  Change in the title and the scope of EN 16723, and merge of the two parts: **Biomethane and other renewable and low-carbon methane rich gases – Specifications for injection in the natural gas network and for mixtures with natural gas as automotive fuel**

GERG THE EUROPEAN GAS RESEARCH GROUP

BioStAR2c

Review the limit values considering the latest research of the GERG projects

Applicability depending on feedstocks?

Include the new normative test methods

Including new types of methane (from pyrogasification, hydrothermal gasification, methanation)

Review the list of compounds if needed

Merge the two parts of the standard

EN 16723 – Applicable common requirements and test methods for biomethane at the point of entry into H gas and L gas networks and as automative fuel

Part 1 - 2016

Natural gas

Parameter	Unit	Limit values[a]		Test method (informative)
		Min	Max	
Total volatile silicon (as Si)	mgSi/m³		0,3 to 1	EN ISO 16017-1:2000 TDS-GC-MS
Compressor oil		a		ISO 8573-2:2007
Dust impurities		a		ISO 8573-4:2001
Chlorinated compounds			See FD CEN/TR 17238	ISO 1911:2010
Fluorinated compounds			See FD CEN/TR 17238	NF X43-304:2007 ISO 15713:2006
CO	% mol		0,1	EN ISO 6974- series
NH3	mg/m³		10	NEN 2826:1999 or VDI 3496 Blatt 1:1982-04 NF X43-303:2011
Amine	mg/m³		10	VDI 2467 Blatt 2:1991-08

[c] Fuelling stations providing LNG should ensure a maximum particle contamination of 10 mg/l of LNG to protect the automotive vehicle system from debris, providing performance equivalent to a filter with maximum pore size of 5 µm nominal and 10 µm absolute with 90 % efficiency.

ISO/TC 193/SC 1/WG25 Biomethane – Update

Number	Title	Publication
ISO/TS 2610	Determination of amines content	**August 2022**
ISO 2611-1	Determination of halogenated compounds — Part 1: HCl and HF content by ion chromatography	**April 2024**
ISO/NWIP 2611-2	Measurement of halogenated VOCs	First draft of a NWIP circulated
ISO 2612	Determination of ammonia content by Tuneable Diode Laser Absorption Spectroscopy	**December 2023**
ISO 2613-1	Silicon content of biomethane — Part 1: Determination of total silicon content by AAS	**May 2023**
ISO 2613-2	Silicon content of biomethane — Part 2: Determination of siloxane content by Gas Chromatography Ion Mobility Spectrometry	**December 2023**
ISO 2614	Determination of terpenes content by micro gas chromatography	**September 2023**
ISO 2615	Determination of the content of compressor oil	**May 2023**
ISO 2620	Determination of VOCs by thermal desorption gas chromatography with flame ionization and/or mass spectrometry detectors (TD-GC-FID/MS)	**June 2024**

EN 16723 – Applicable common requirements and test methods for biomethane at the point of entry into H gas and L gas networks and as automative fuel

Preliminary work item

New normative test methods for biomethane

Parameter	Unit	Limit values[a]		Test method (normative)
		Min	Max	
Total volatile silicon (as Si)	mgSi/m³		0,3 to 1	ISO 2613-1 ISO 2613-2
Compressor oil		a, b		ISO 2615
Dust impurities		b		ISO/NP 24895
Chlorinated compounds			See FD CEN/TR 17238	ISO 2611-1
Fluorinated compounds			See FD CEN/TR 17238	ISO 2611-1
CO	% mol		0,1	EN ISO 6974- series
NH3	mg/m³		10	ISO 2612
Amine	mg/m³		10	ISO/TS 2610

[a] Fuelling stations providing LNG should ensure a maximum particle contamination of 10 mg/l of LNG to protect the automotive vehicle system from debris, providing performance equivalent to a filter with maximum pore size of 5 µm nominal and 10 µm absolute with 90 % efficiency.
[b] The biomethane shall be free from impurities other than “de minimis” levels of compressor oil and dust impurities. In the context of this European Standard, “de minimis” means an amount that does not render the biomethane unacceptable for conveyance and use in end user applications.

EN 16723 – Applicable common requirements and test methods for biomethane at the point of entry into H gas and L gas networks and as automative fuel

Preliminary work item

New normative test methods for biomethane

Under discussion
Call for experts to join the WG

Parameter	Unit	Limit values[a]		Test method (normative)	Applicability (related to feedstock or process)
		Min	Max		
Total volatile silicon (as Si)	mgSi/m³		0,3 to 1	ISO 2613-1 ISO 2613-2	Only for WWTP sludge
Compressor oil		a, b		ISO 2615	
Dust impurities		b		ISO/NP 24895	
Chlorinated compounds			See FD CEN/TR 17238	ISO 2611-1	Not for agricultural waste
Fluorinated compounds			See FD CEN/TR 17238	ISO 2611-1	Not for agricultural waste
CO	% mol		0,1	EN ISO 6974- series	Only for gasification
NH3	mg/m³		10	ISO 2612	
Amine	mg/m³		10	ISO/TS 2610	Only for methanation depending on the origin of CO2
New parameters ? **Terpenes**				ISO 2614	Only with citrus fruits
Butanone				ISO 2620	
Heavy hydrocarbons / PAHs					Only for pyrogasification

What's next?

- **Preliminary work item** from February 2023 → **Until February 2026** to activate the revision
- **Waiting for GERG results**:
  - **April 2025:** Table with recommendations for each parameter, S excluded (waiting for results)
  - **January 2026:** Final report
- Until then: **Ongoing work on the revision** of the standard with the members of the WG

New experts in pyrolysis/pyrogasification, hydrothermal gasification, methanation, Power-to-gas are welcome to join the WG!
Next meeting in June 2025

Thank you!

natran R&I

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Measurement campaign in Denmark and Finland

Alexander Fateev, DTU

ENERGY GASES

METCCUS

VSL

MET4H2

BiometCAP

Measurement campaigns in Denmark and Finland

Alexander Fateev, Sen. Sci.
DTU Chemical Engineering, alfa@kt.dtu.dk
in collaboration with PTB (DE), VTT (FI) and TFS (USA) teams and support from biogas plants staff

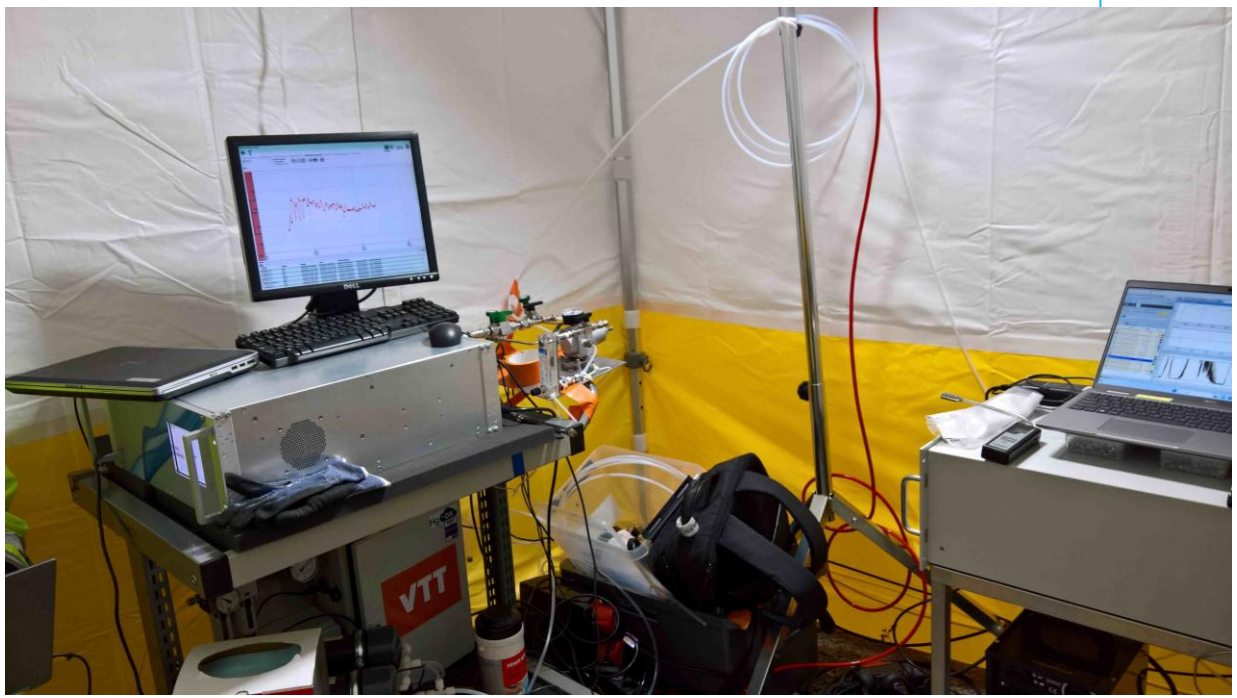
What is in the scope:

- Activities under **WP3**: Performance evaluation of the industrial analysers and reference instrumentation that are used for biomethane conformity assessment
- **Task 3.2**: Laboratory and field trials for the performance evaluation of industrial analysers and reference instrumentation
- Overview of the field measurements in Finland (1x) and Denmark (2x)

VTT+DTU+TFS at Lohja Biogas (FI):

- ❑ new plant
- ❑ commercial biowaste, household biowaste, food industry waste
- ❑ biomethane to gas net (receiver station about 3 km away)
- ❑ CO2 capture/storage ready

BiometCAP workshop at VSL in Delft, March 26th



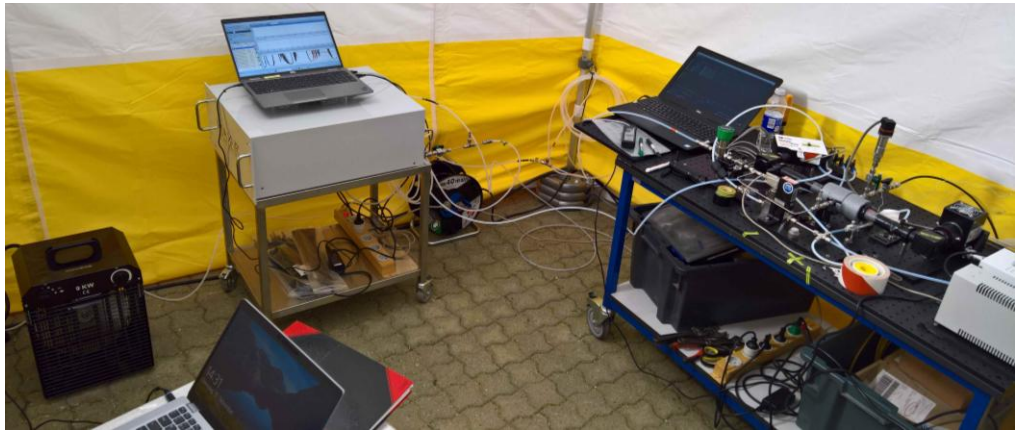
- H2S removal by carbon filters
- CO2 separation by membrane technology (Bright Biomethane)
- Product gas (4.5 bar) and before membrane (after carbon filters) (14 bar) sampling points
- Very clean biomethane with CS2, VOC traces

BiometCAP workshop at VSL in Delft, March 26th

DTU+TFS at Solrød Bioenergy (DK):

- ❑ commercial biowaste
- ❑ food industry waste
- ❑ agriculture products
- ❑ biomethane to gas net

BiometCAP workshop at VSL in Delft, March 26th



- 1st step: H2S removal carbon filters
- 2nd step: VOC removal carbon filters
- CO2 (pressurized) water scrubber (MALMBERG)
- Biomethane contains BTX and terpenes

BiometCAP workshop at VSL in Delft, March 26th

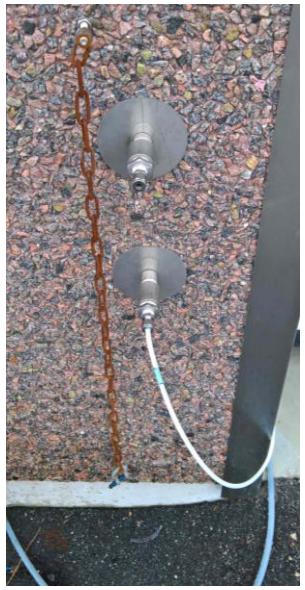
METROLOGY PARTNERSHIP | EURAMET

DTU+PTB+TFS at Ribe Biogas (DK):

- ❑ Oldest biogas production site in DK
- ❑ mainly agriculture origin
- ❑ biomethane to gas net

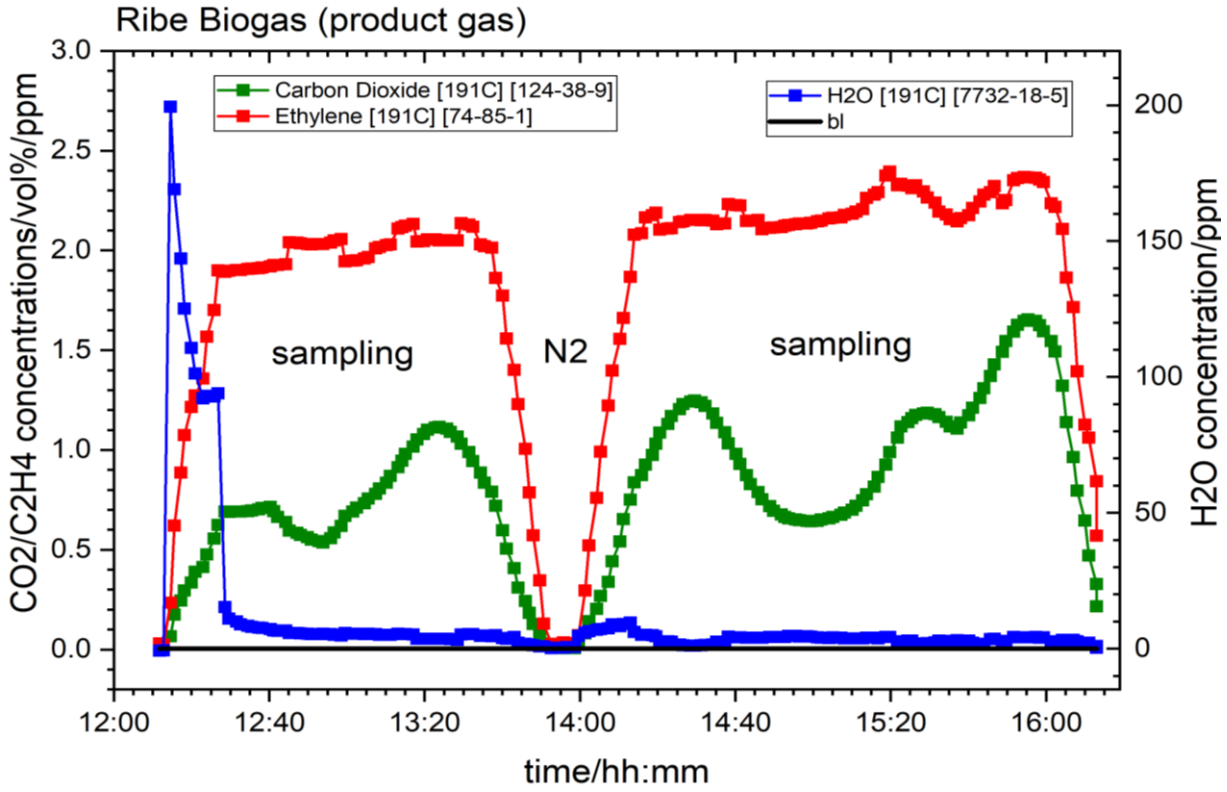
BiometCAP workshop at VSL in Delft, March 26th

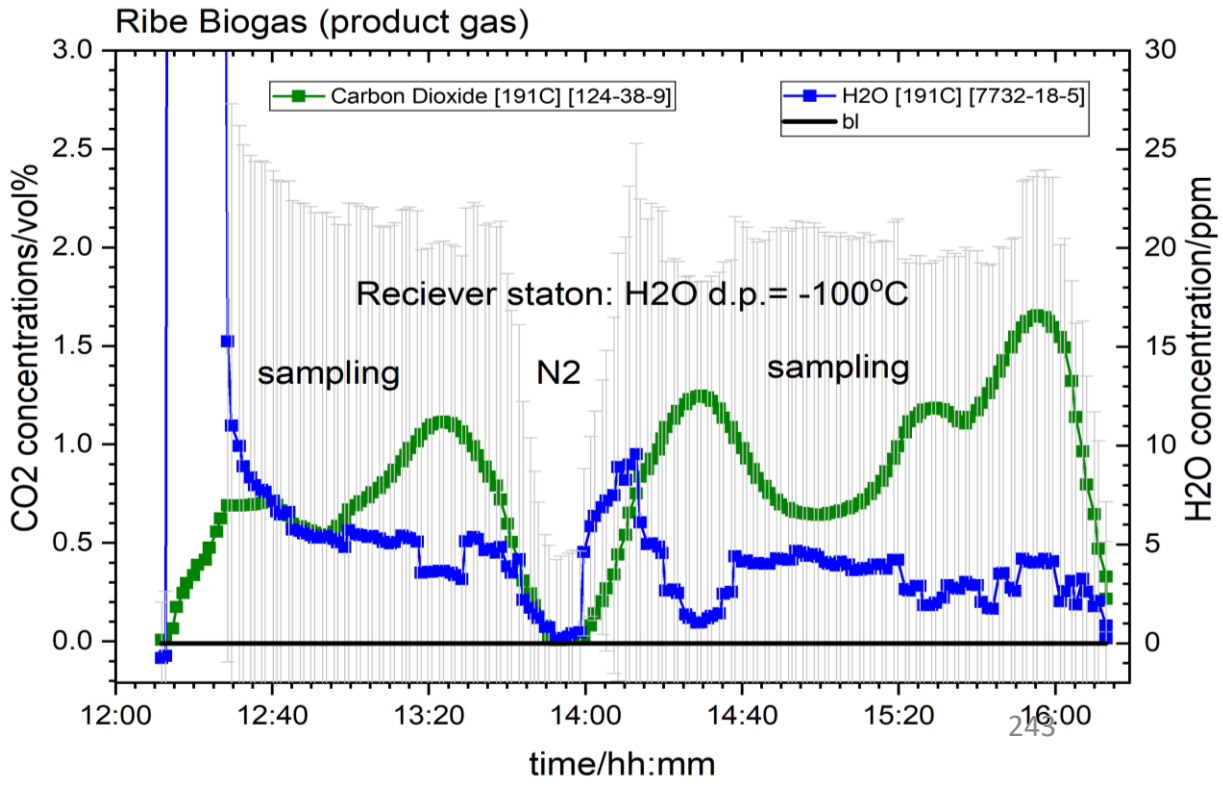
- Amine-based technology
- H2S and CO2 removal in adsorber-stripper system (AMMONGAS)
- Biomethane contains Sx (DMS, CS2), BTX



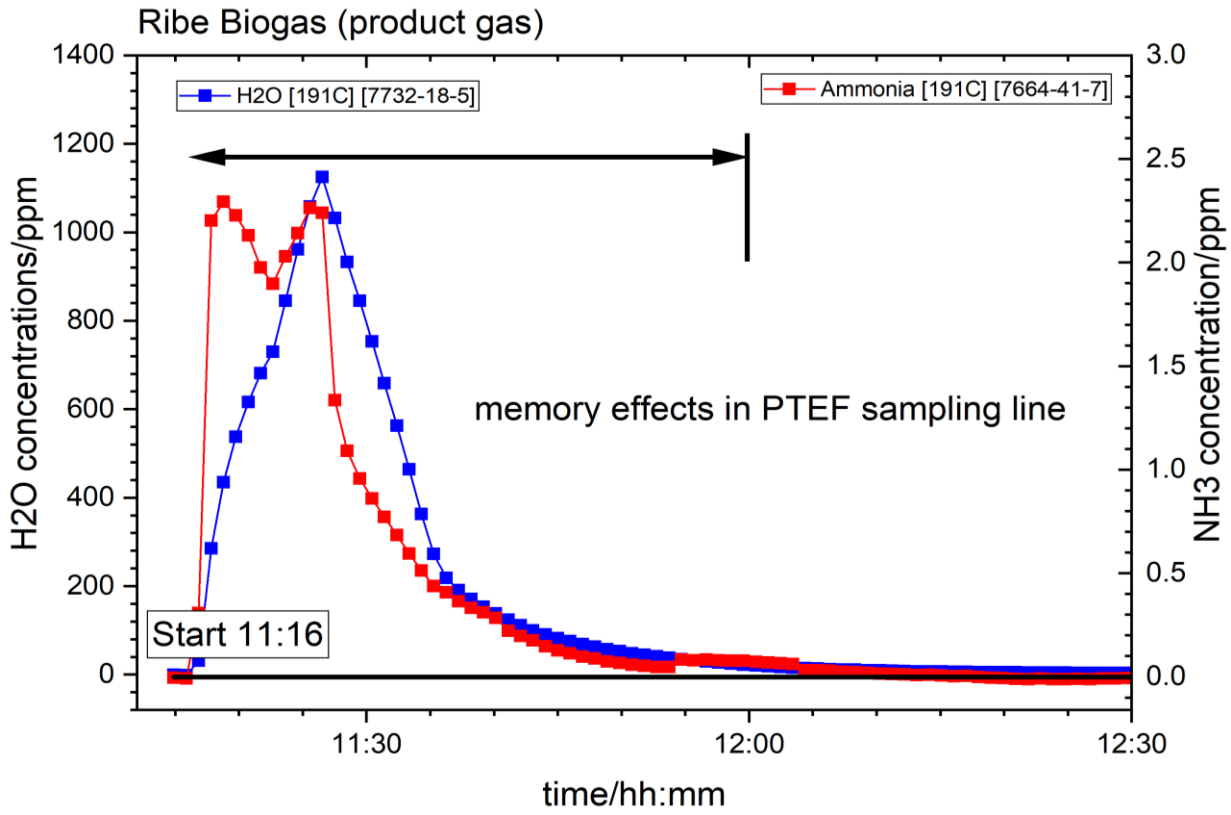
Case study: TFS MAX-iR (FTIR spectrometer) performance evaluation with use of protocol

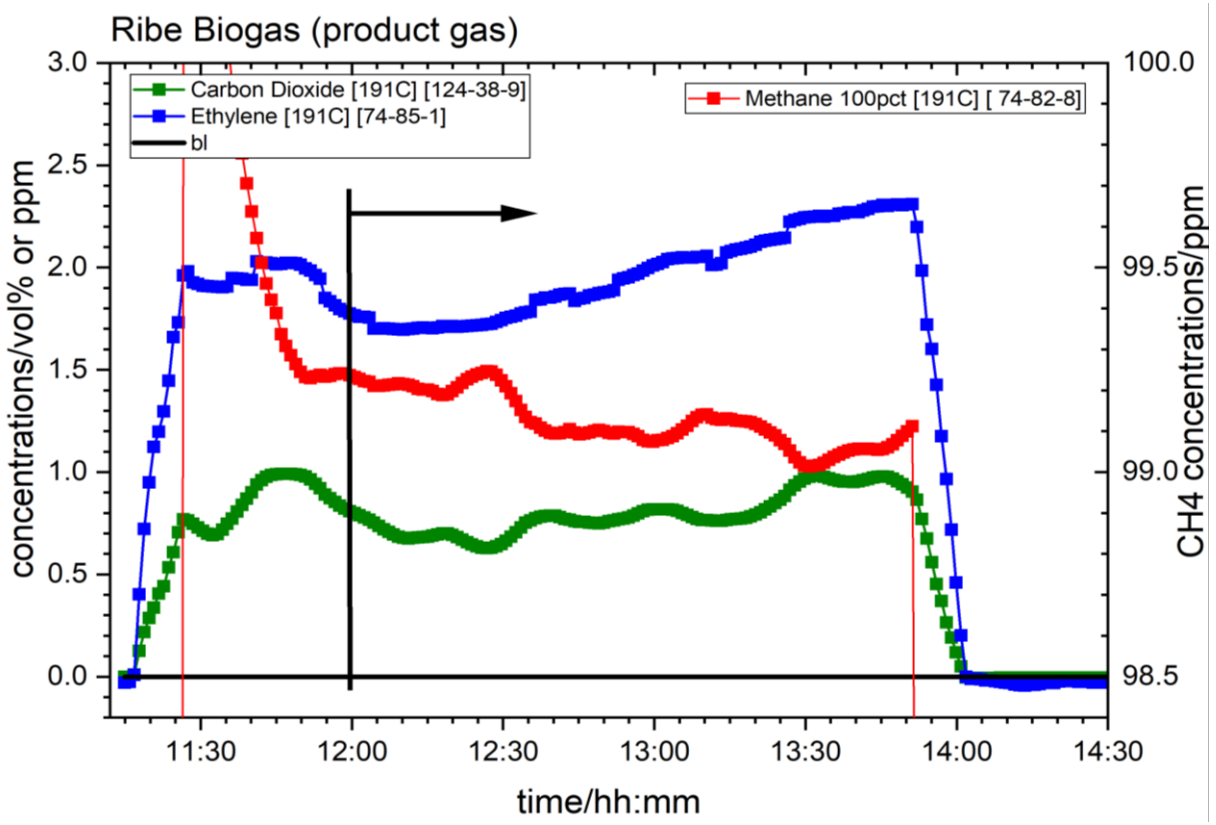
- product gas (= biomethane) varies with time
- base line = measurements with N2 in the FTIR and (optionally) in the sampling line
- ambient temperature variations can potentially affect the base line
- Stop & Go approach: “sampling stop” → “switch to N2”(FTIR only) → “sampling continue”





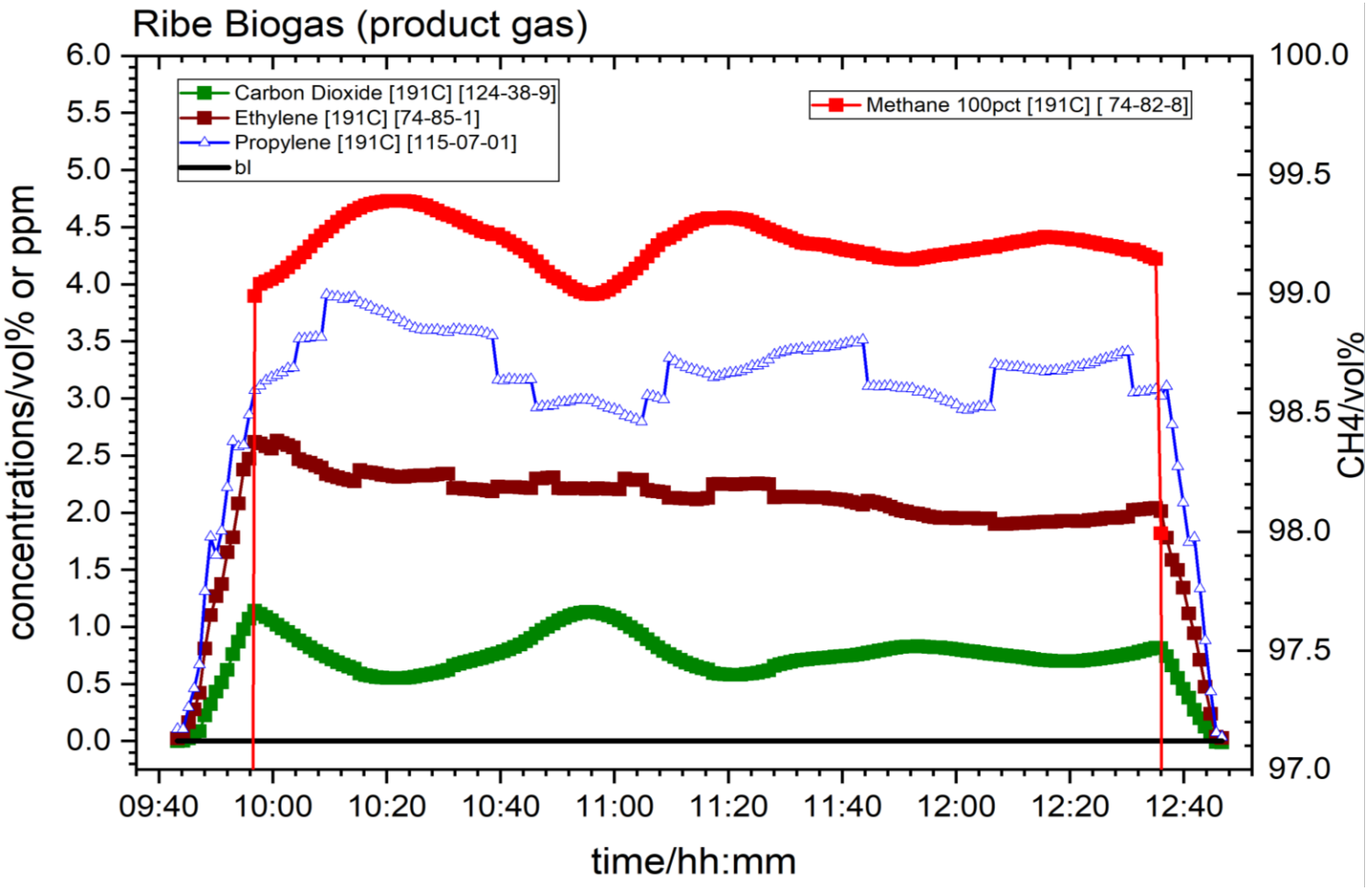
Sampling line (PTEF): memory effects





- Start from “after carbon filter”, then switch to “product gas” (= biomethane)
- FTIR N2 purge and new reference measurements in between
- Takes about 45 min to clean the PTEF sampling line

Case study: product gas analysis with MAX-iR (FTIR spectrometer): correlations

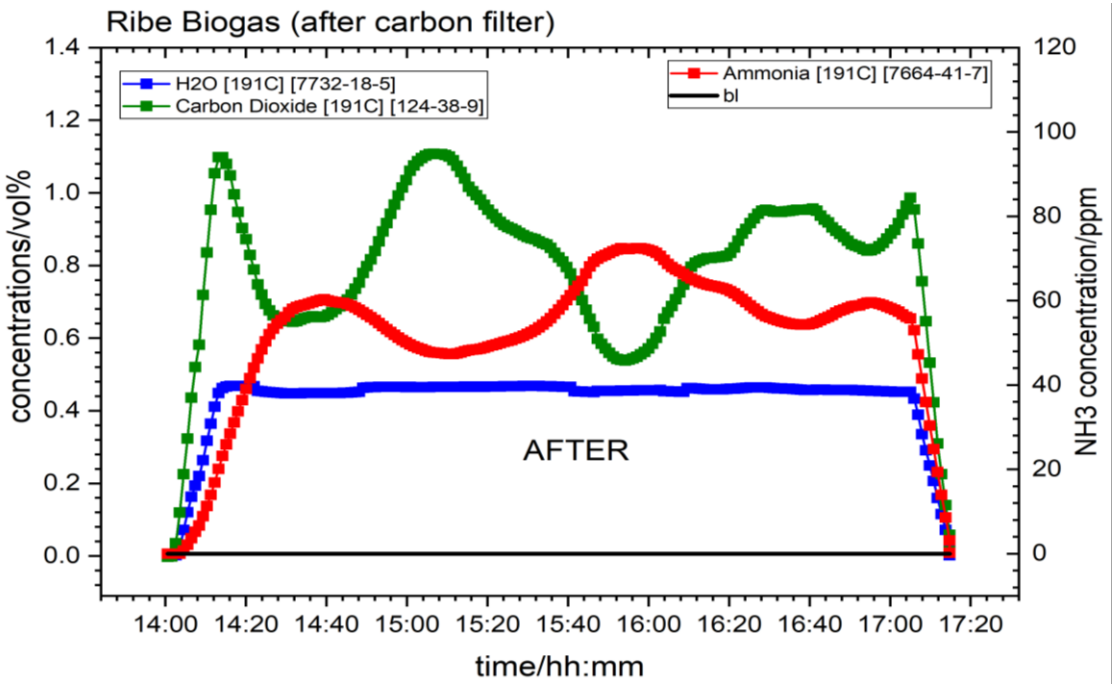


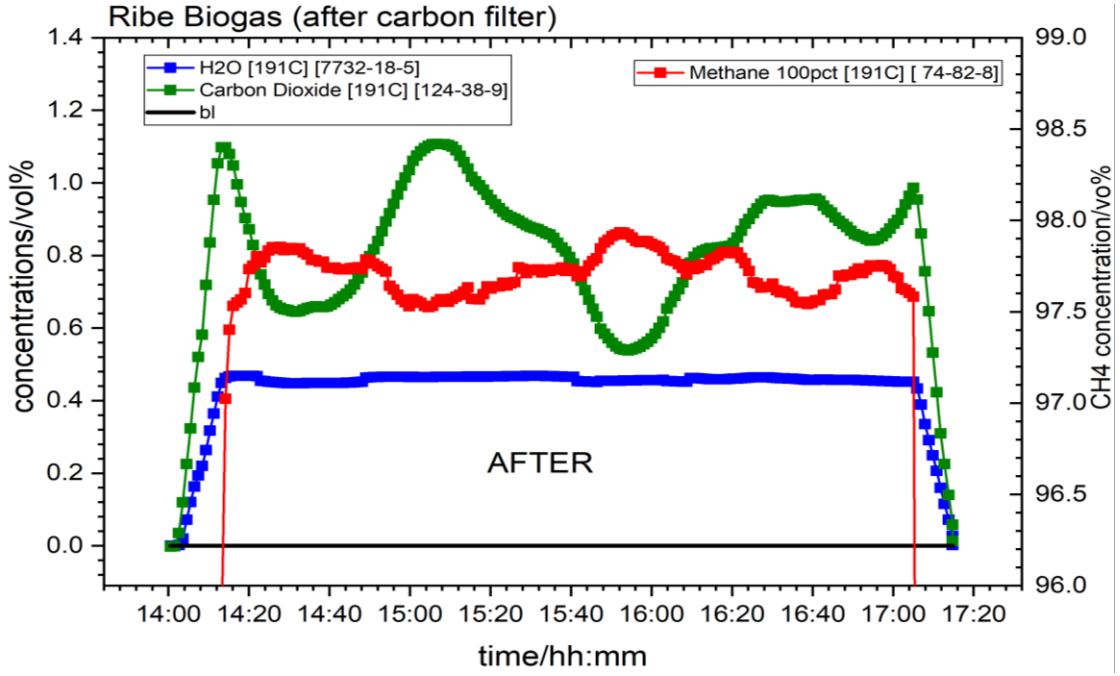
Product gas (= biomethane): real time (process) related observations:

- ❑ NH3 < 2 ppm; no signs for siloxanes and H2S
- ❑ H2O < 5 ppm (H2O d.p. at Receiver Station: - 100 °C)
- ❑ VOC (propylene) and CH4 vs. CO2: opposite phase time-correlations
- ❑ about 1 hr. period
- ❑ Compliant with EN16723

Case study: process gas analysis with MAX-iR (FTIR spectrometer): correlations

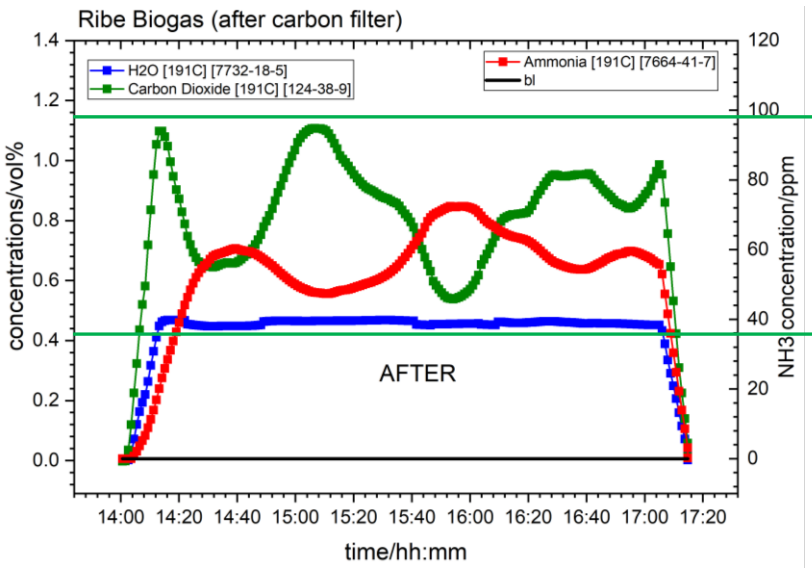
[after carbon filter → compression → fine filter (dryer) → receiver station]

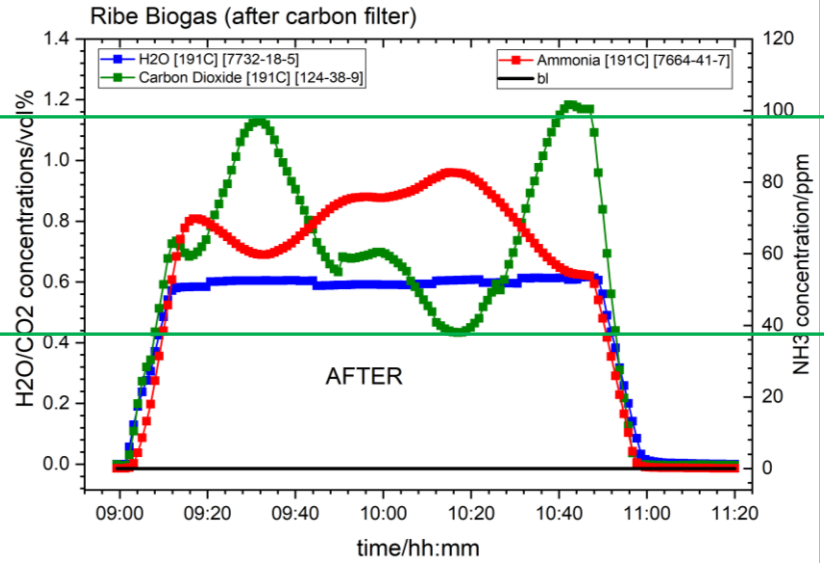


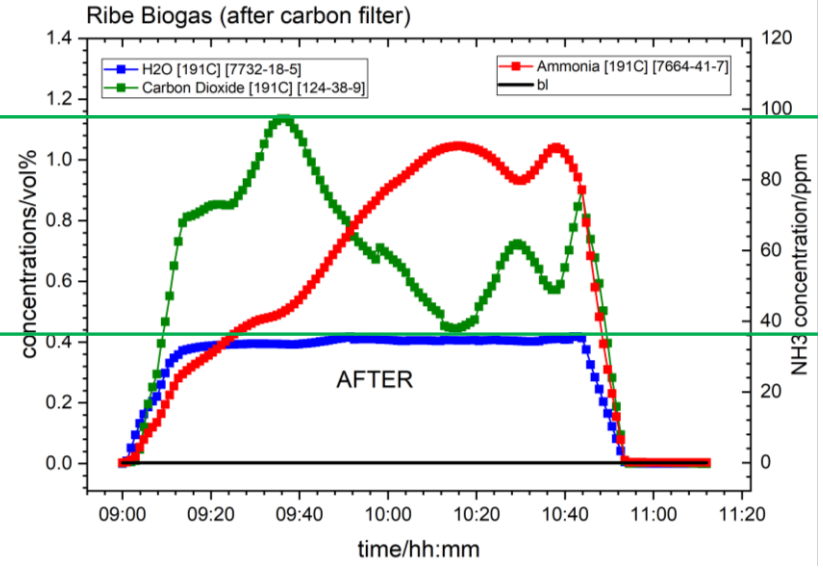


- ❑ NH3 and CH4 vs. CO2: opposite phase time-correlations
- ❑ Non-homogeneous CO2 scrubbing (flow patterns in CO2 adsorption column)
- ❑ NH3 comes after H2O from sampling start
- ❑ H2O is defined by ambient temperature (sampling line)

Case study: process gas analysis with MAX-iR (FTIR spectrometer): NH3

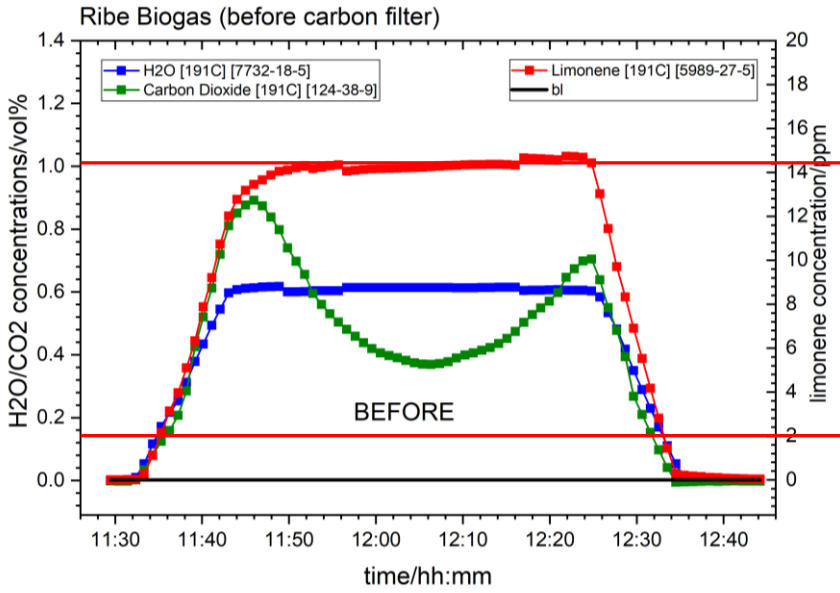


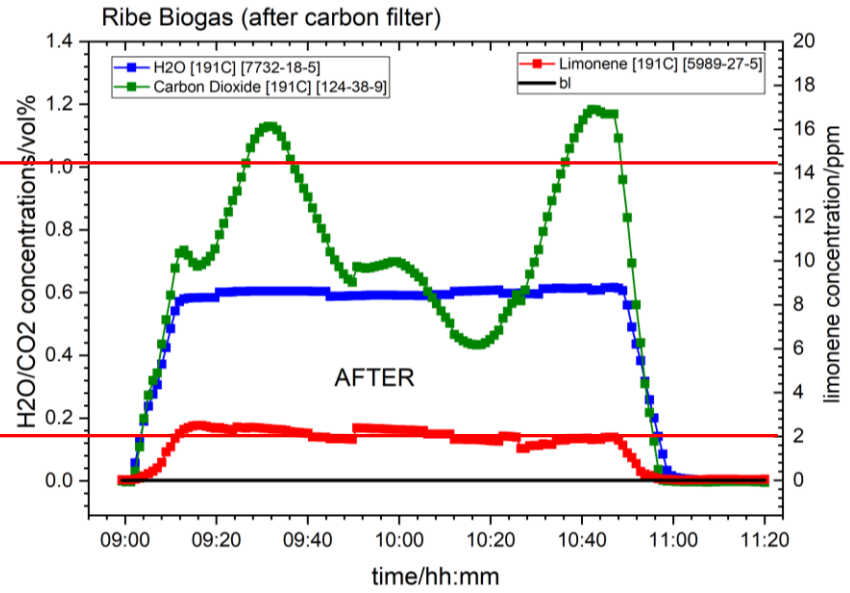


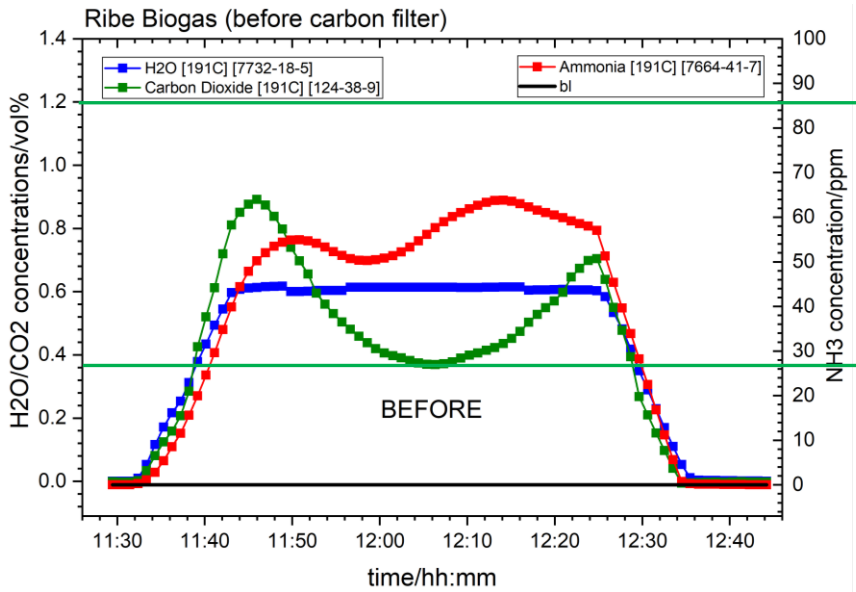


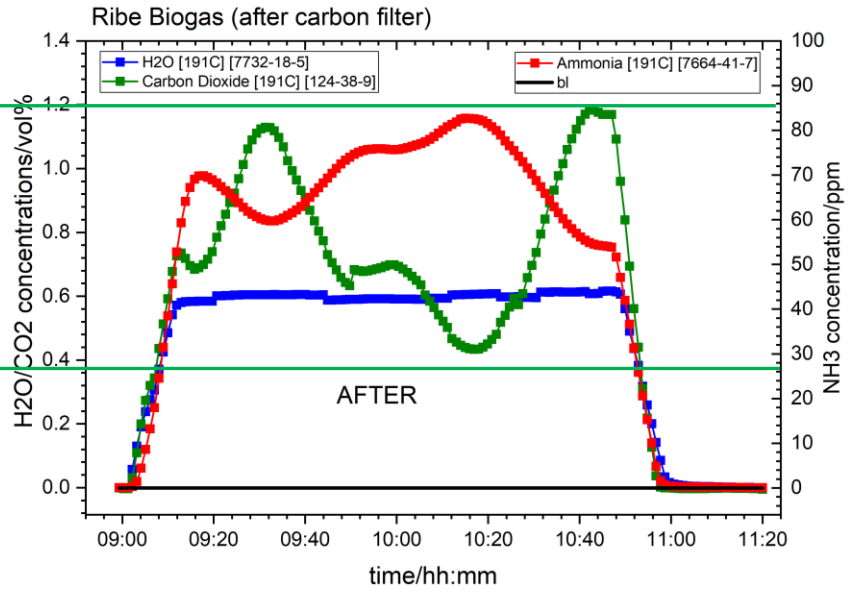
- ❑ Non-uniform scrubbing causes large CO2 and NH3 variations
- ❑ Better CO2 capture causes higher NH3 emissions (and CH4 yield)
- ❑ NH3 can be released from gas or liquid phases (in adsorber and/or stripper)
- ❑ NH3 is a decomposition product from scrubber (amine oxidation product)

Case study: process gas analysis with MAX-iR (FTIR spectrometer): VOC and NH3









VOC carbon filter performance:

- ❑ Same day measurements
- ❑ Terpenes (limonene) time dependence does not depend on other variations
- ❑ Carbon filter reduces VOC's (terpenes) but does not influence onto NH3
- ❑ Lower CO2 variations (= more stable CO2 capture process) lead to lower variations in NH3 emission

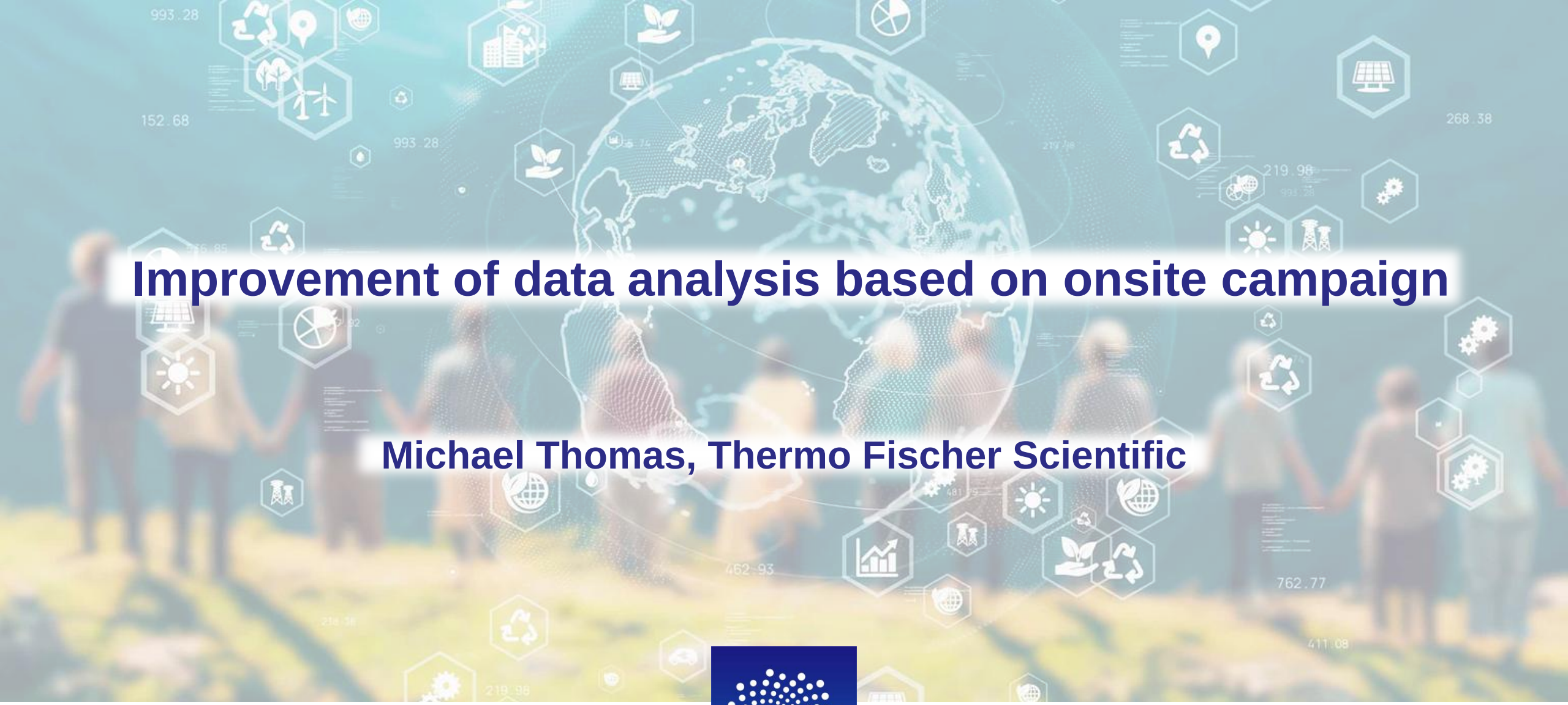
Lessons learned:

- Broad variations in minor gas components
- Compliance with biomethane-to-gas-grid specifications (GC-based at Receiver Stations based on EN16723): H2S, CO2, O2, H2O(d.p.), CH4
- Process data analysis can be relevant to amine-based CO2 capture (e.g. in MetCCUS project, morning session)
- On-line analysis is a must when there are in process variations
- Off-line gas analysis can only be used for a representative gas analysis

Acknowledgements

- **Lohja (FI), Ribe (DK) and Solrød (DK) biogas plants personnel and management**: for the support, help and fruitful discussions

- The project **BiometCAP 21NRM04** has received funding from the European Partnership on Metrology, co-financed from the European Union's Horizon Europe Research and Innovation Programme and by the Participating States



Improvement of data analysis based on onsite campaign

Michael Thomas, Thermo Fischer Scientific

ENERGY GASES

METCCUS

VSL

MET4H2

BiometCAP

Introducing

Trevor Tilmann

Applications Engineer, Environmental & Process Monitoring

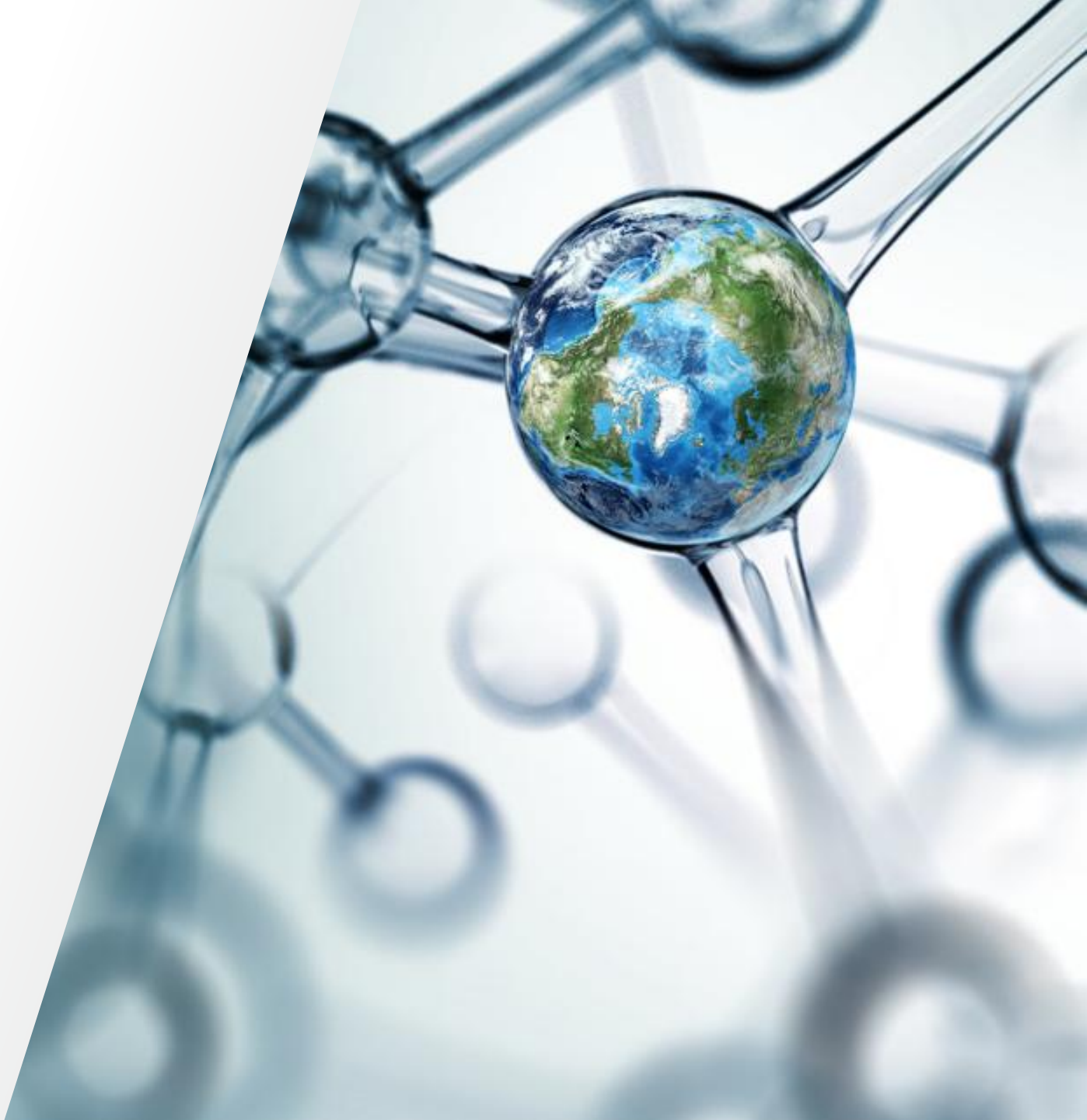
- BSc in Chemistry from Central Michigan University
- Joined Thermo Fisher Scientific in 2023
- Expert in FTIR gas analysis, continuous emissions monitoring, and method development
- Currently focused on developing clean energy applications for the FTIR product line

Improvement of data analysis based on onsite campaign

Trevor Tilmann

Applications Engineer

26th March, 2025



The world leader in serving science

Key Method Improvements Performed

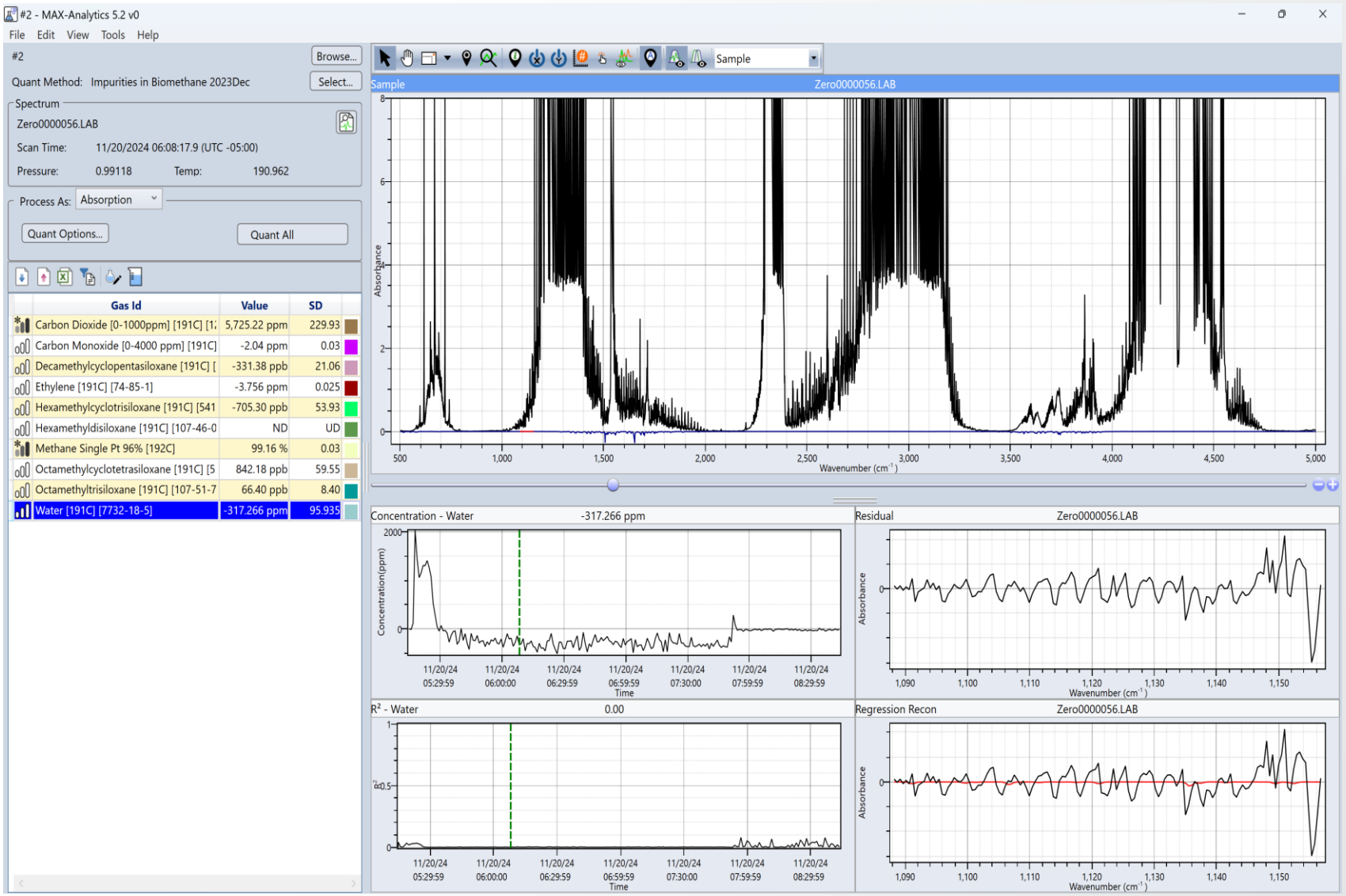
1. Improved 99.99%+ Methane to improve residuals in FTIR fingerprint region
2. Improved CO_2 calibration to "fill in" concentration gap
3. Improved primary quant region of moisture to improve residuals across mid-IR
4. Including other VOC's which are/were not considered in original method

Original Method Results

Indicates high R^2 value

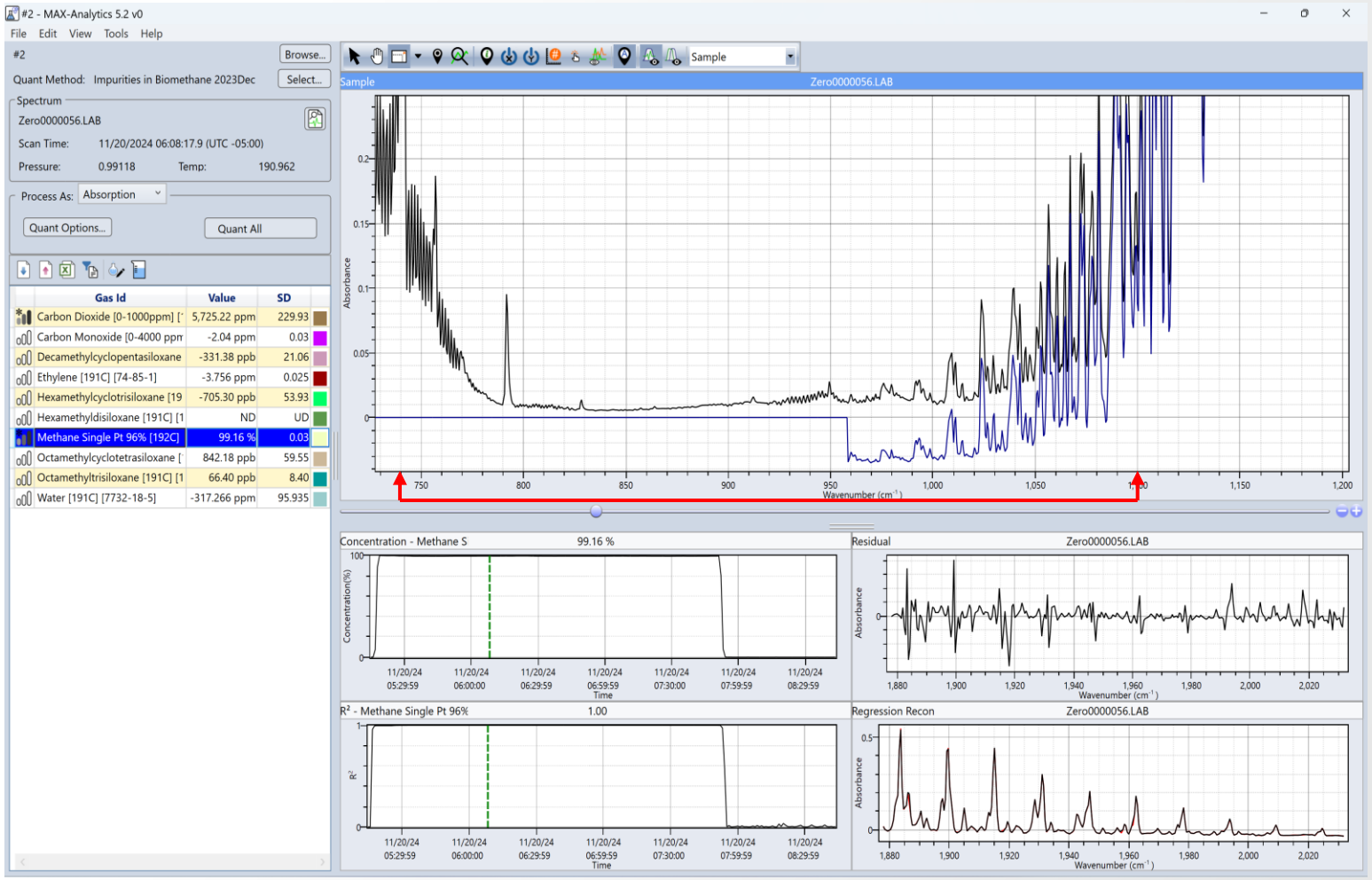
Indicates low R^2 value

* Indicates potential issues with reference



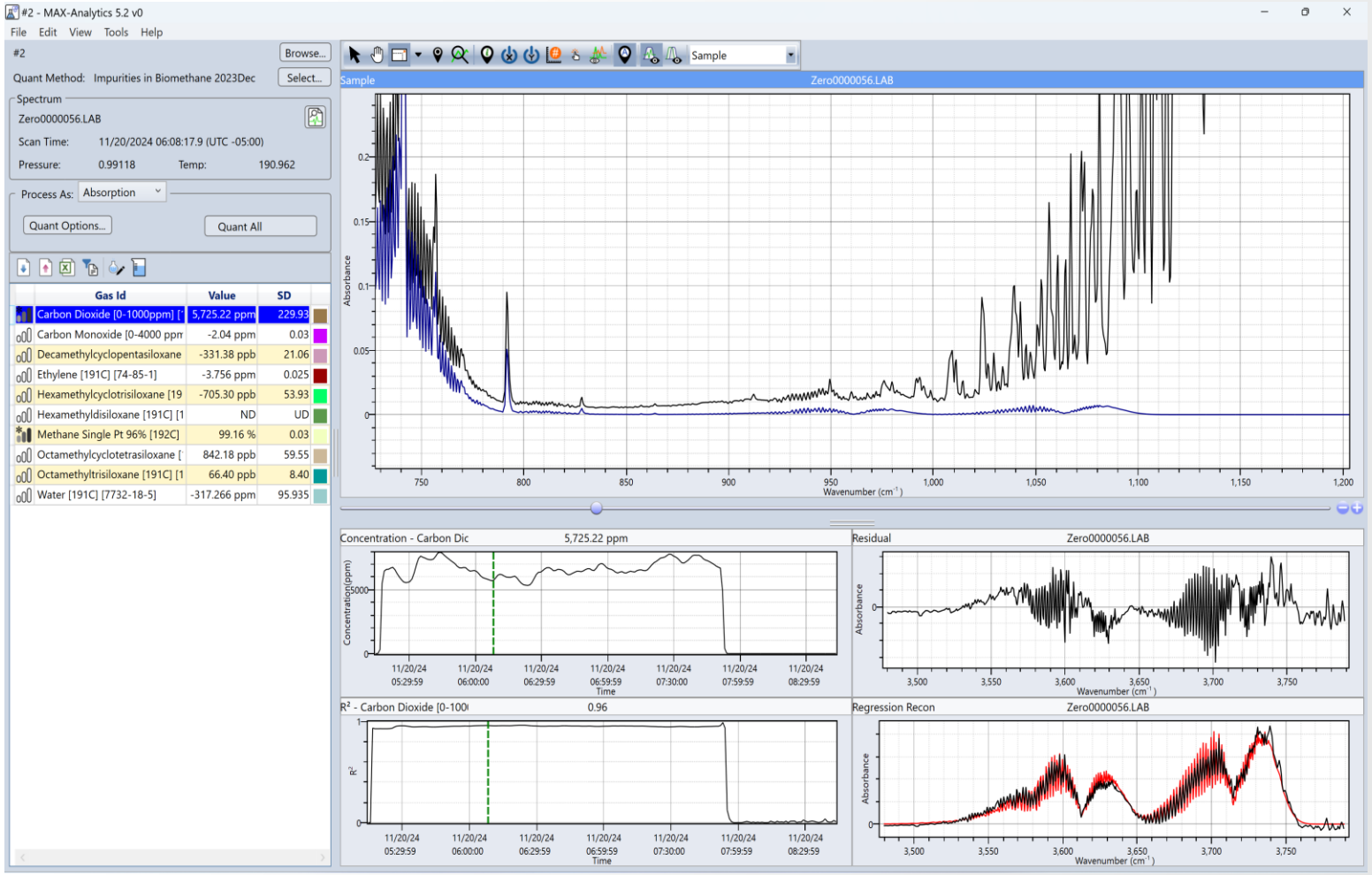
Original Method Results – Fingerprint Region

- Incomplete spectrum of CH_4 in fingerprint region creates biased results for:
  - Siloxanes
  - Ethylene



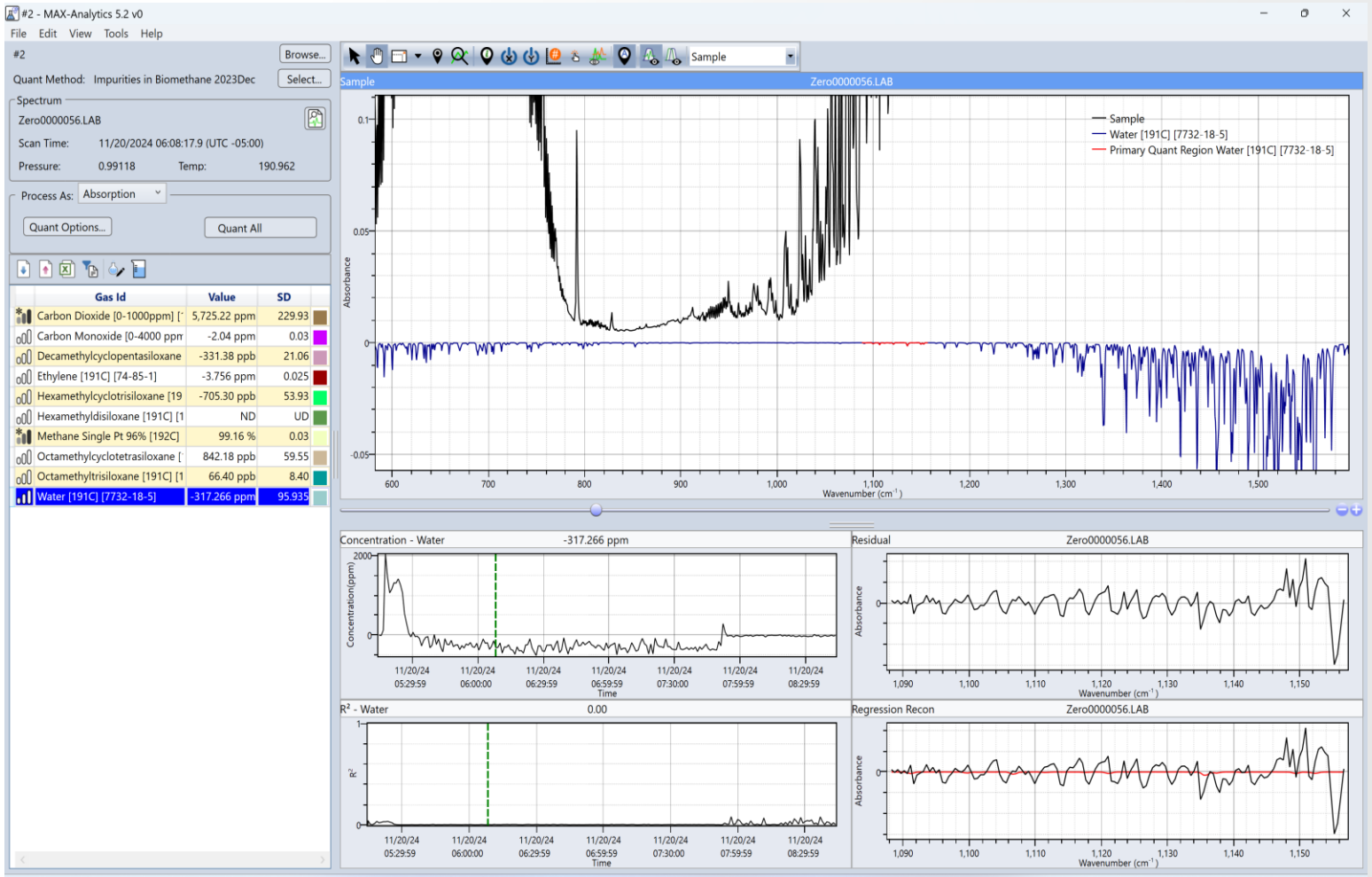
Original Method Results – CO2 Inaccuracy

- Poor Regression Reconstruction for CO_2
  - Provided CO_2 reference was from ND-1000ppm
  - Sample concentrations were higher
- Created poor peak matching of CO_2 spectrum in fingerprint region
  - Attributes to poor quantification of siloxanes, carbon monoxide, and ethylene.

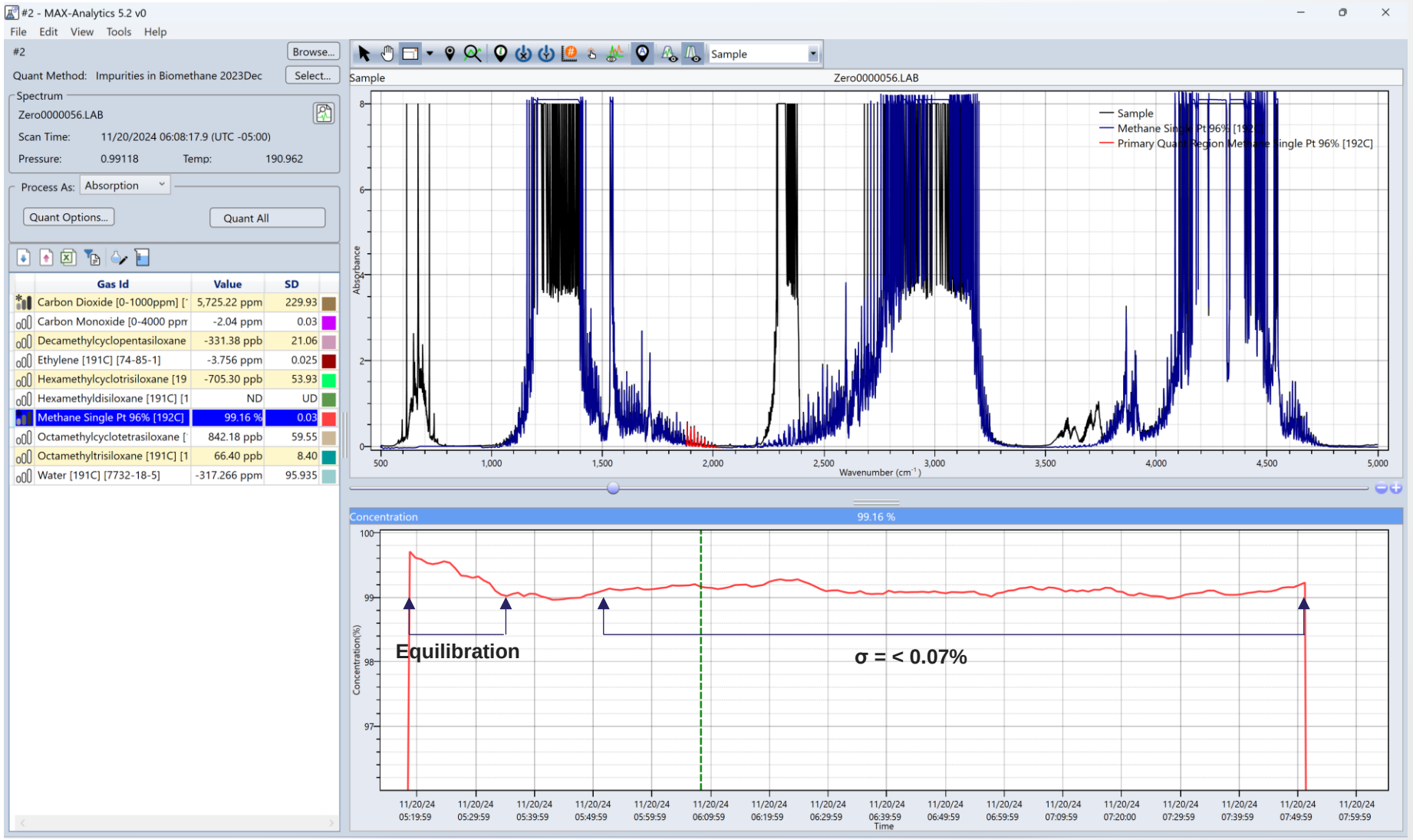


Original Method Results – Moisture Inaccuracy

- Poor Regression Reconstruction for H_2O
  - Primary quant region conflicting with high concentrations of biomethane
- Created poor peak matching of H_2O spectrum across mid-IR
  - Attributes to poor quantification of impurities

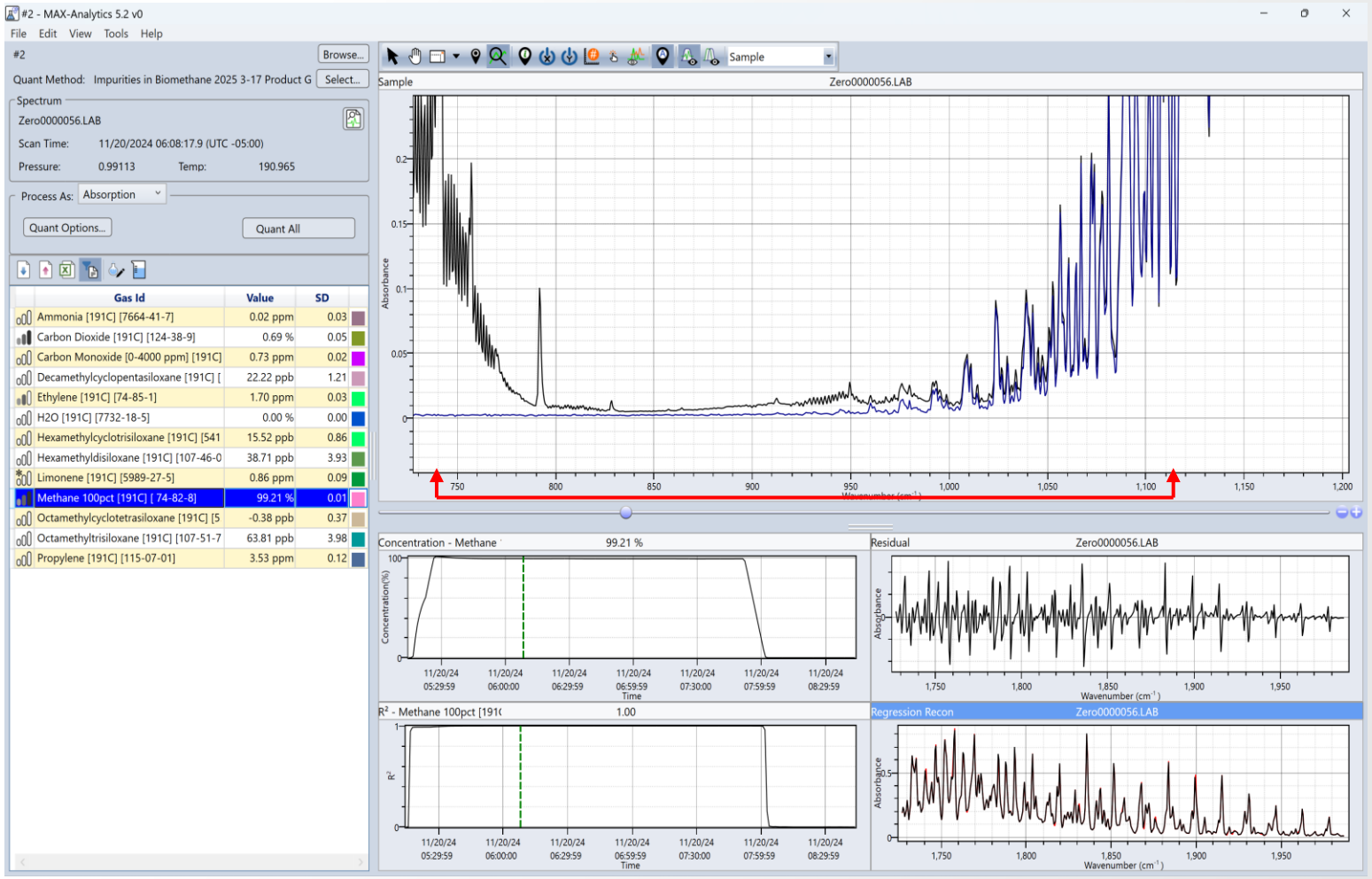


Original Method - Biomethane Absolute Purity



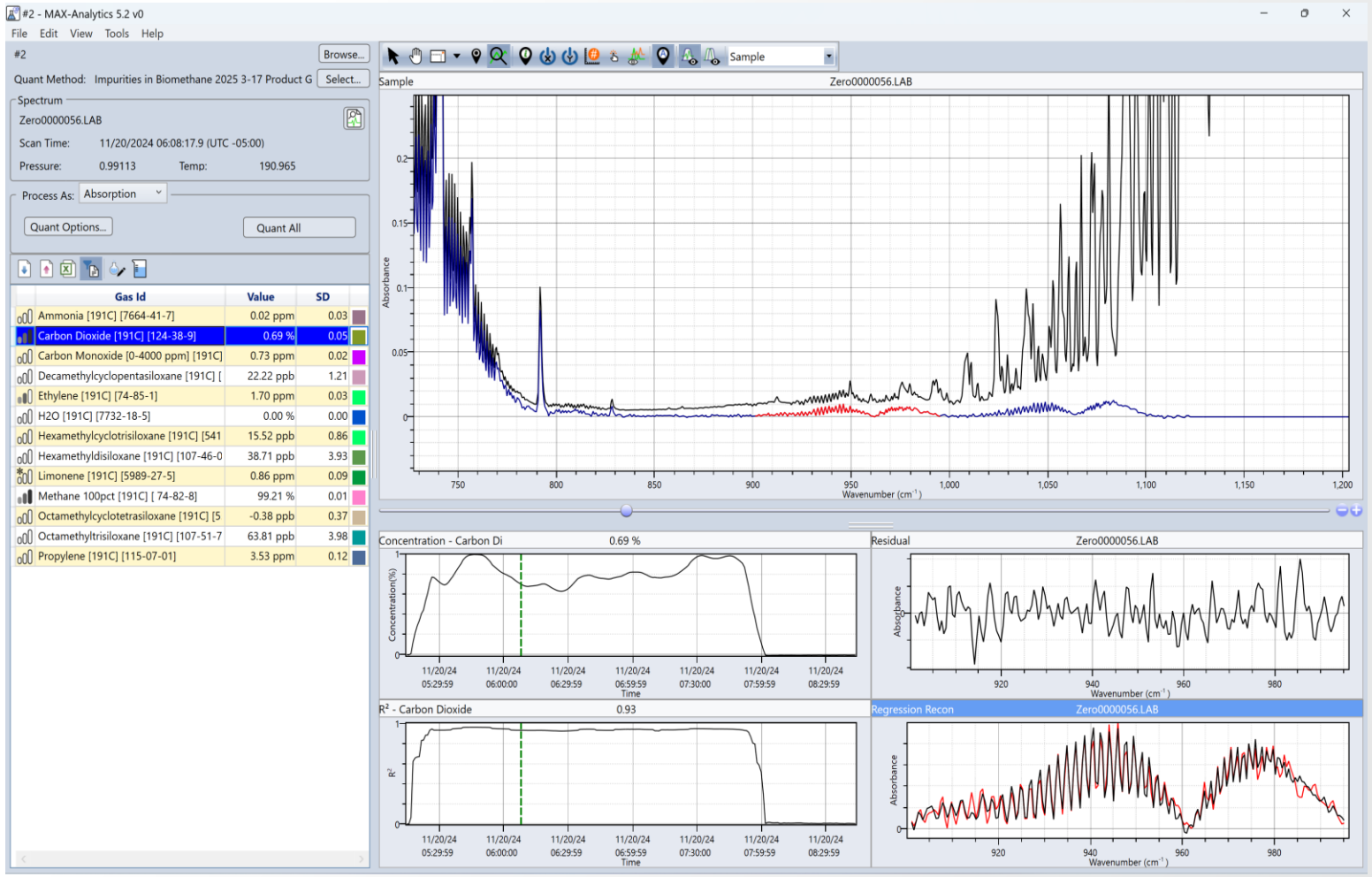
Optimized Method Results – Fingerprint Region

- Acquired 99.99% CH_4 spectrum on MAX-iR
  - Ensures matching resolution and apodization
  - Important for light MW gases which have very narrow rotational absorption bands
- Optimized regions for ethylene and siloxanes based on spectral residuals
- Determined other VOCs in fingerprint not accounted for in model:
  - Propylene
  - Limonene



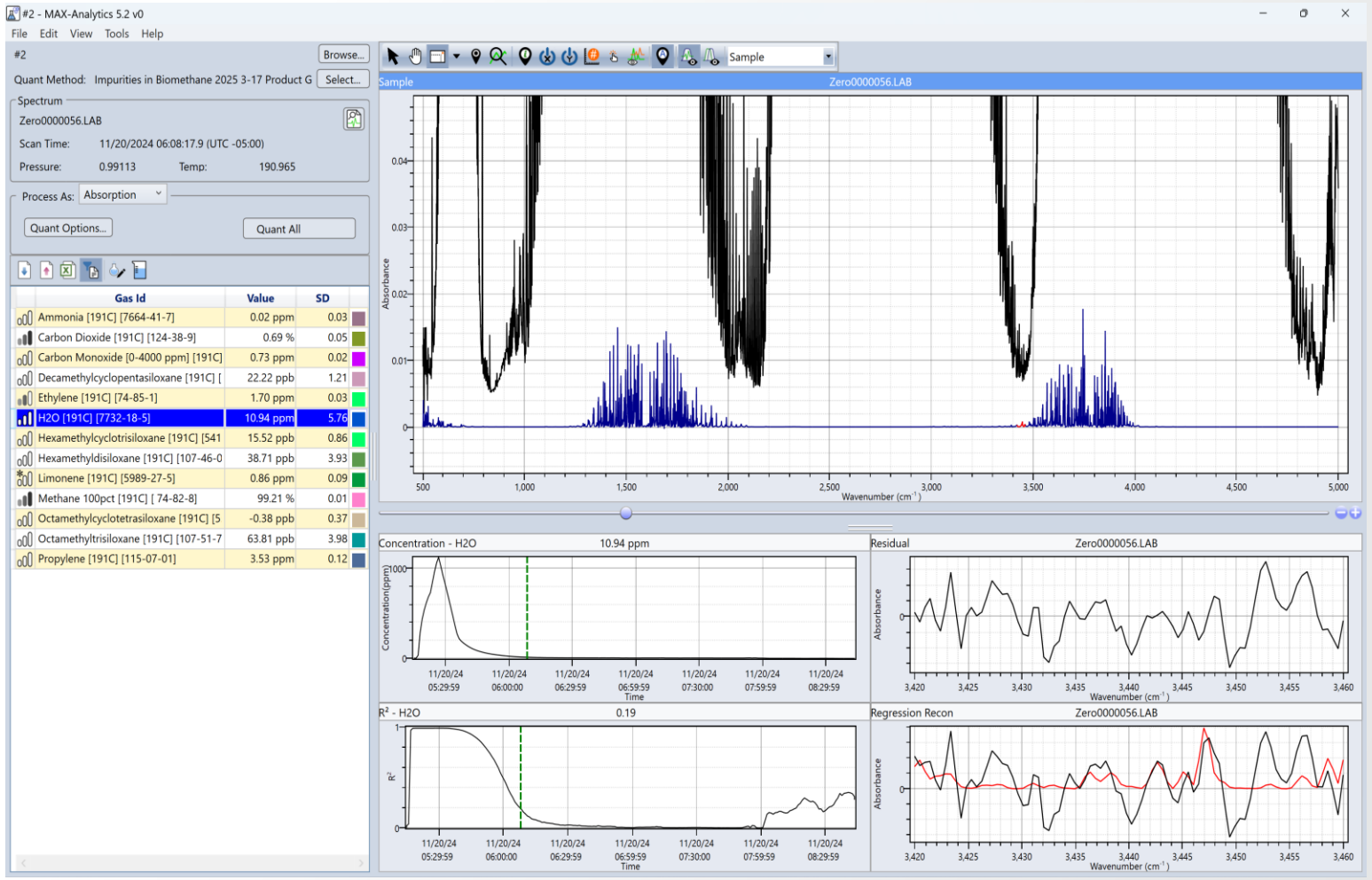
Optimized Method Results – CO_2

- Acquired 0.1% to 1.0% concentration CO_2 calibration spectra to "fill in" calibration gap
- Adjusted primary quant region from 3650cm^{-1} to 960cm^{-1}
- Created excellent peak matching of CO_2 spectrum across mid-IR
  - Eliminated bias in CO measurements.
  - Decreased residuals in fingerprint region.

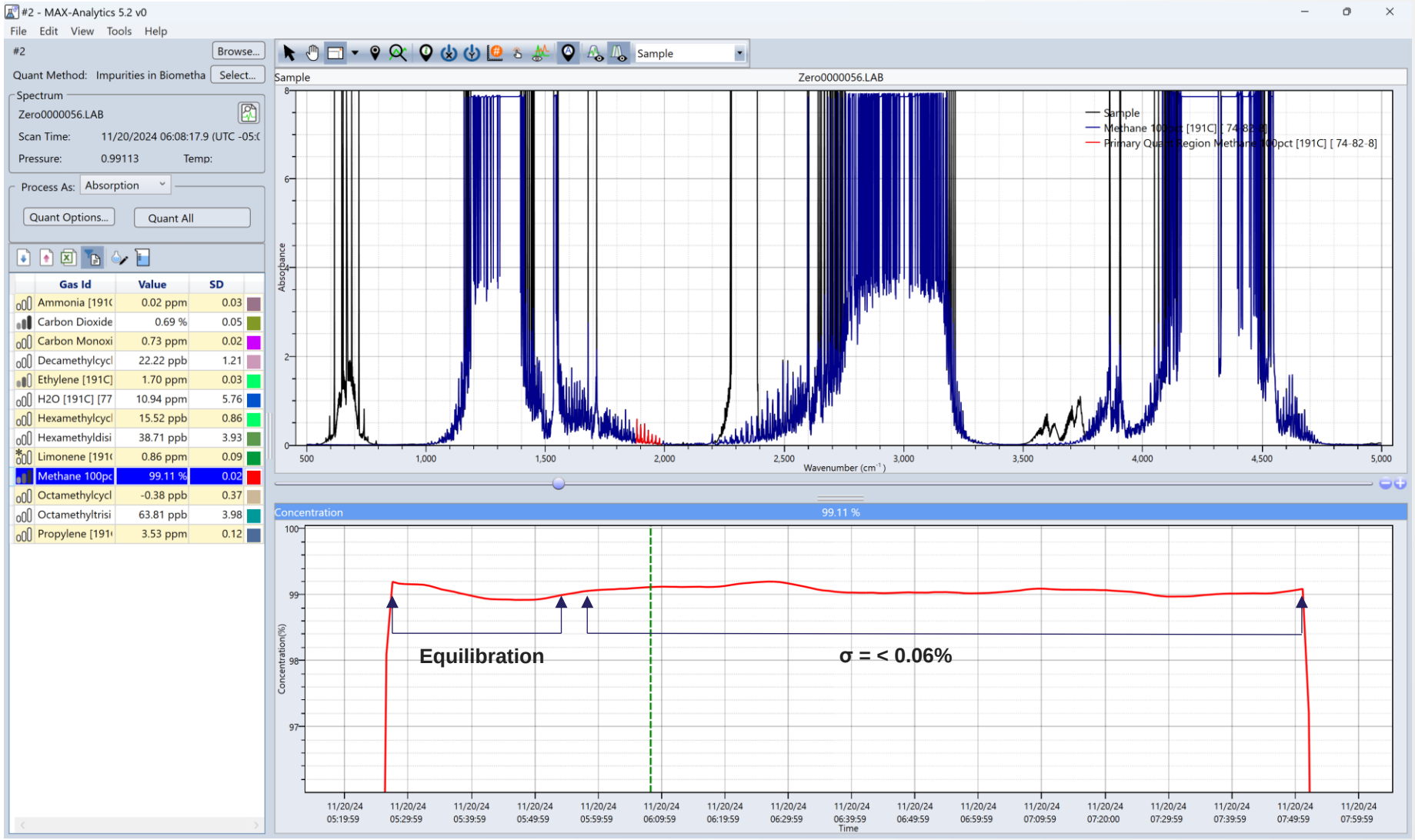


Optimized Method Results – Moisture

- Adjusted H_2O spectral quant region in a "quiet" CH_4 spectral region (3400 to 3500 cm-1)
  - Allowed for accurate quantification without bias from CH_4
- Created excellent peak matching of H_2O spectrum across mid-IR
  - Improved quantification of all components.



Optimized Method - Biomethane Absolute Purity



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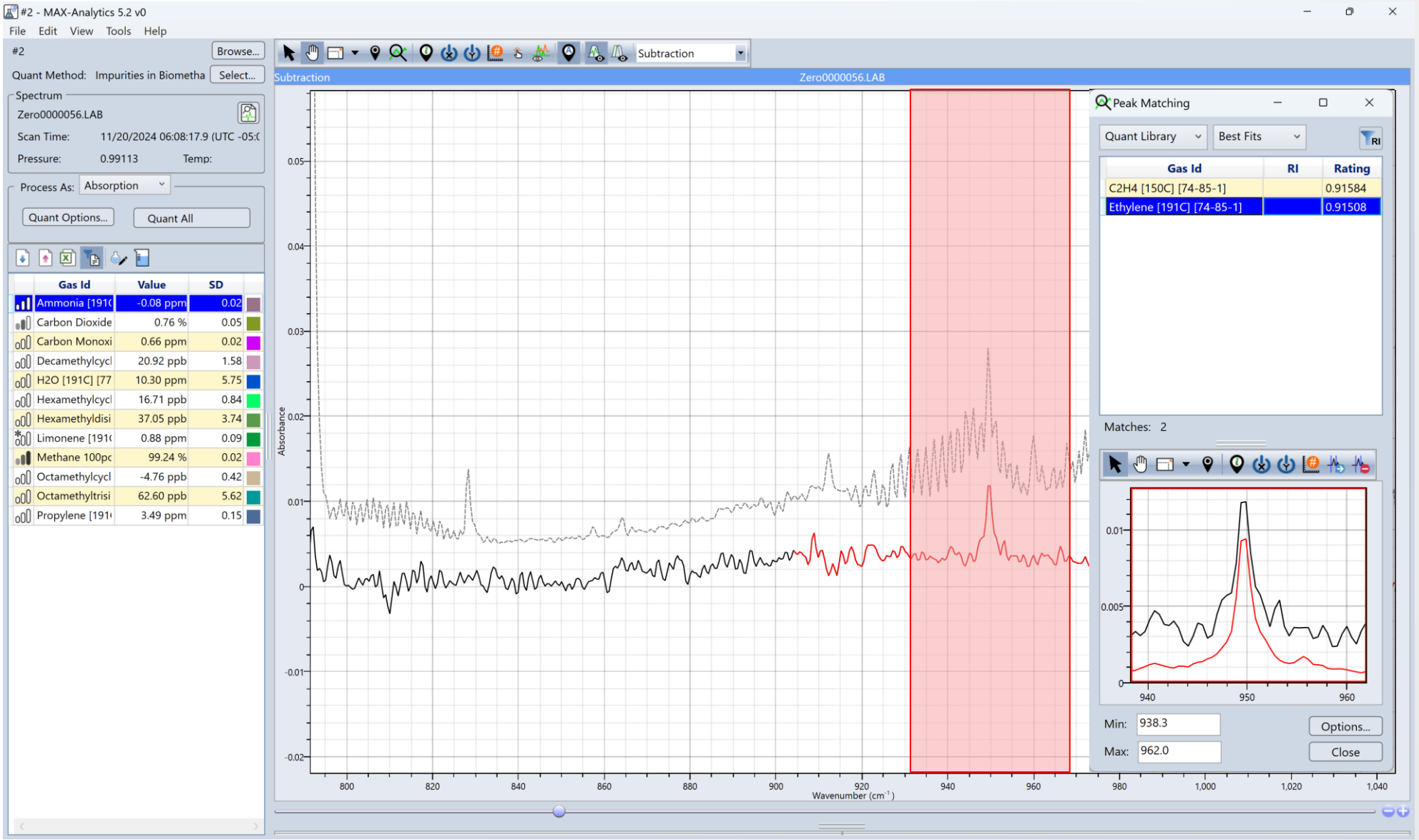

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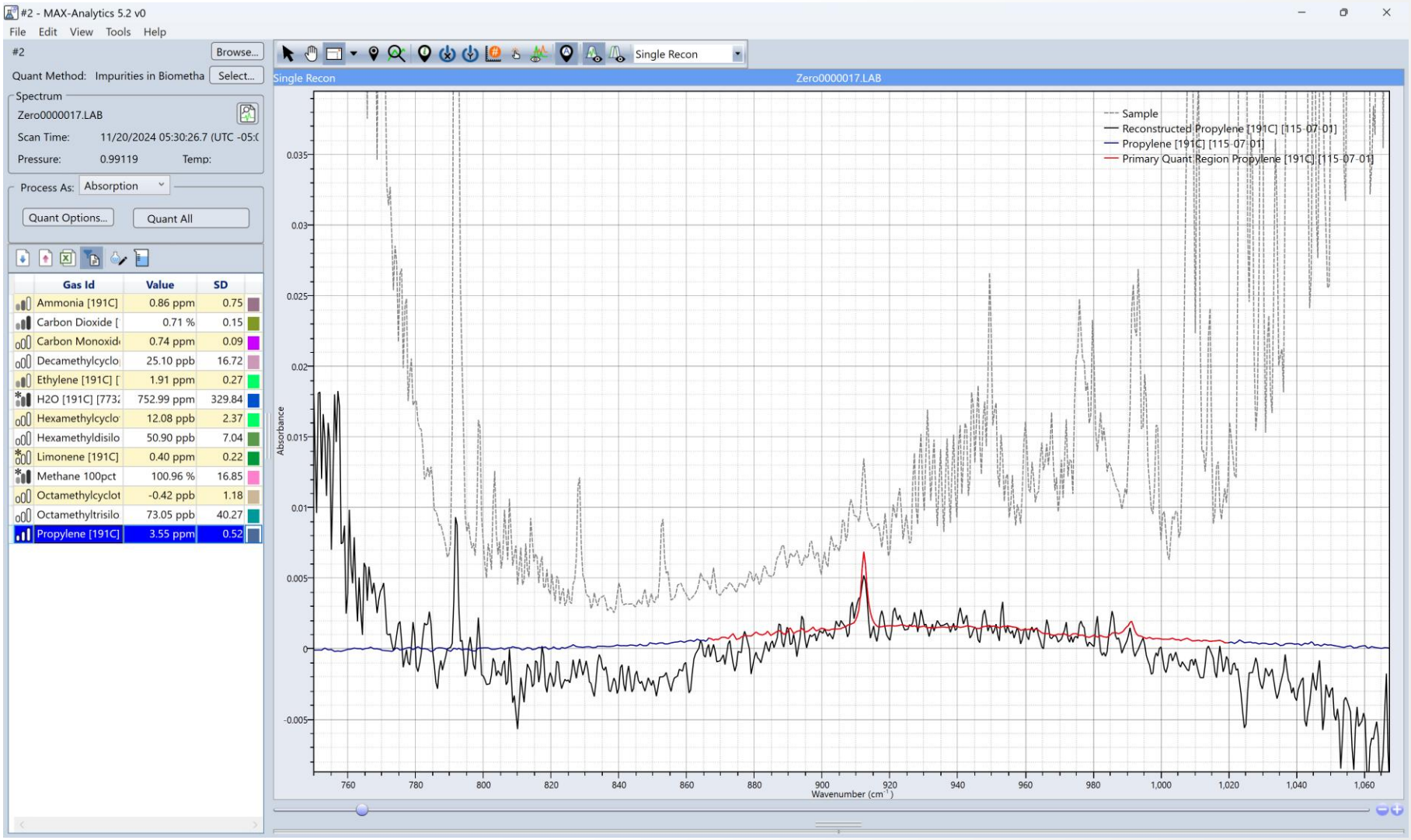


Optimized Method Results

Ribe Biogas – Product Gas – 20/11/2024

Quant Method	Original				Optimized			
Calculation	Min	Max	Average	σ	Min	Max	Average	σ
Ammonia (ppmv)	-	-	-	-	-0.01	0.07	0.02	0.02
Carbon Dioxide (%v)	0.53	0.78	0.66	0.06	0.63	0.98	0.80	0.10
Carbon Monoxide (ppmv)	-2.21	-1.99	-2.14	0.05	0.52	0.76	0.64	0.07
Decamethylcyclopentasiloxane (ppmv)	-0.63	-0.33	-0.48	0.09	0.00	0.02	0.01	0.01
Ethylene (ppmv)	-3.78	-3.19	-3.49	0.18	1.69	2.31	1.97	0.21
Moisture (ppmv)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hexamethylcyclotrisiloxane (ppmv)	-1.41	-0.67	-1.03	0.21	0.01	0.04	0.03	0.01
Hexamethyldisiloxane (ppmv)	ND	ND	ND	ND	0.00	0.04	0.01	0.01
Limonene (ppmv)	-	-	-	-	0.73	1.64	1.29	0.25
Methane (%v)	98.98	99.28	99.11	0.06	98.99	99.22	99.08	0.05
Octamethylcyclotetrasiloxane (ppmv)	0.82	1.55	1.20	0.21	-0.01	0.00	-0.01	0.00
Octamethyltrisiloxane (ppmv)	0.06	0.12	0.08	0.01	-0.01	0.07	0.03	0.02
Propylene (ppmv)	-	-	-	-	3.29	4.12	3.75	0.19

Recommendations for Optimal Detection

1. Periodically monitor the MAX-iR "laser frequency" by running a water spectrum in the diagnostics menu.

2. Periodically span the 99.99% CH4 spectrum using a reference CH4 cylinder.

3. Use stainless steel heated lines for sampling to maintain sample integrity.

National Metrology Institute

VSL Welcome
Met4H2 workshop

Elvira Huizeling – Director Operations

March 27th, 2025

VSL: National Metrology Institute of the Netherlands

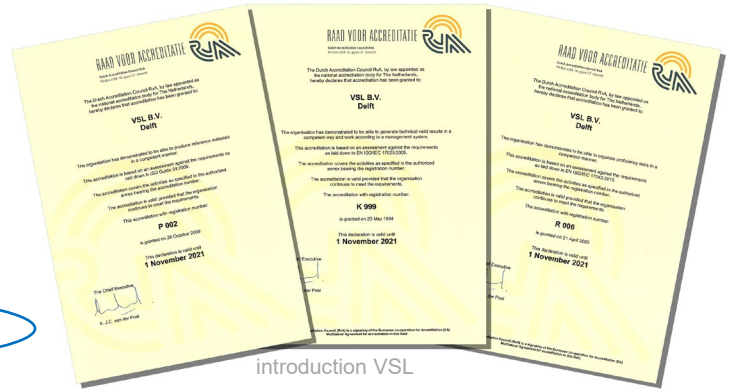
- Metrology is the science of measurement.

Mol – hoeveelheid stof
Candela – lichtsterkte
Kilogram – gewicht
Meter – lengte
Seconde – tijd
Ampere – electrische stroomsterkte
Kelvin – absolute temperatuur

National Metrology Institute

VSL: National Metrology Institute of the Netherlands

- National (primary) measurement standards
- Private organisation with public task
- ~100 colleagues, 50% MSc - PhD
- Independent and reliable
- Internationally active
- Service package:
  - Standards
  - Innovation (research & development)
  - Data science
  - Calibrations
  - Reference materialen
  - Consultancy
  - Metering reviews
  - VSL CMC Certificates
  - Metrology College

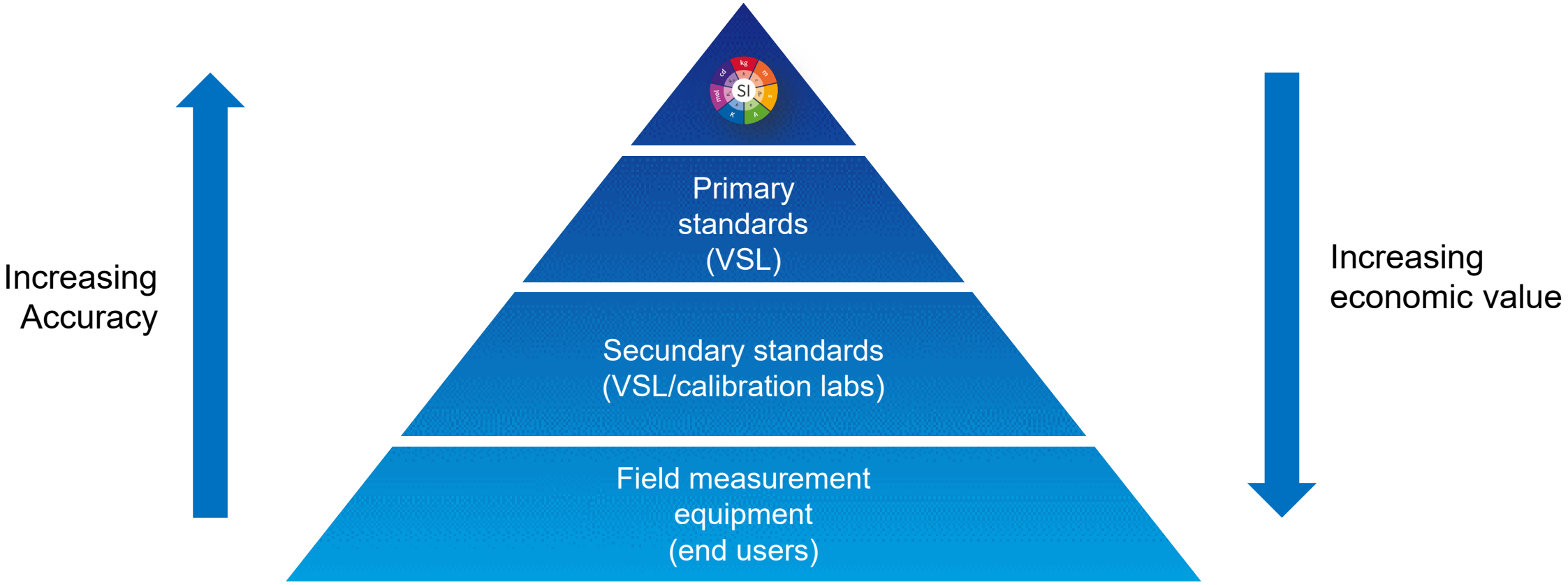


National Metrology Institute

Measurements Beyond all doubt

CIPM MRA

Traceability Chain



National
Metrology
Institute

Technologies

- Chemistry
- Mass, Pressure, Vacuum
- Electricity
- Geometry
- Ionizing radiation
- Optics
- Flow (LD, HD, VL, LNG)
- Temperature and Humidity
- Time and Frequency
- Data Science and Modelling

National Metrology Institute

Interest metrology


Trade

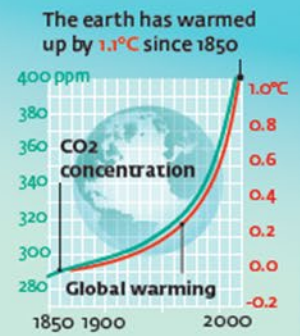

Industry

Science

Health


Society

Moving towards 2030 and 2050 with hydrogen



If we do nothing the global temperature will rise by another 4°C by 2100

22 April 2016
Paris Agreement
Global warming set at a max. 2°C. This requires
CO2-reductions
in the Netherlands of:
- **40-50%** by 2030
- **85-100%** by 2050

Hydrogen as a fuel and as a raw material can help to achieve CO2-reduction targets

Hydrogen pipeline
Linking hydrogen industries in Zeeland and the Delta region

Pilot project HyStock
Converting solar energy into hydrogen in Zuidwending

Hamburg

Port of Amsterdam

Port of Rotterdam

North Sea Port

Antwerpen

Chemelot

Ruhrgebied

18

The energy transition requires new forms of infrastructure and intelligent use of existing networks. Gasunie wants to invest in new infrastructure for renewable gases such as hydrogen.

Hydrogen is a clean energy carrier. H_2 combustion yields only water vapour.

- Conversion
- Transport
- Storage

2015 | 2016 | 2017 | 2018 | 2019 | 2020 | 2021 | 2022 | 2023 | 2024 | 2025 | 2026 | 2027 | 2028 | 2029 | 2030 | 2031 | 2032 | 2033 | 2034 | 2035

1 **Hydrogen pipeline** Linking hydrogen industries in Zeeland and the Delta region

2 **Pilot project HyStock** Converting solar energy into hydrogen in Zuidwending

3 **Wind turbine** generating hydrogen

4 **ISPT Hydrohub** 1 MW test centre

5 **Hydrogen refuelling station network** North of the Netherlands

6 **20 H2 buses** Province of Groningen

7 **GZI Next** Hydrogen plant including a hydrogen fuel station

8 **20-40 MW Electrolyser** Green power into H2. 100 MW in 2024

9 **Element 1** Gasunie / TenneT / Thyssengas power-to-gas pilot

10 **Green hydrogen value chain** with Engie: towards a 100 MW electrolyser

11 **Hydrogen storage** in salt caverns

12 **Magnum power station** First turbine on hydrogen (±700,000 households)

13 **100 MW Electrolyser**

14 **IJmuiden Ver** Wind farm, possible onshore electrolysis

15 **h-vision** Large-scale switch to hydrogen for power stations and chemical processes. Capture and storage of CO2

16 **Magnum power station** All three turbines on hydrogen: > 2 million homes supplied with power

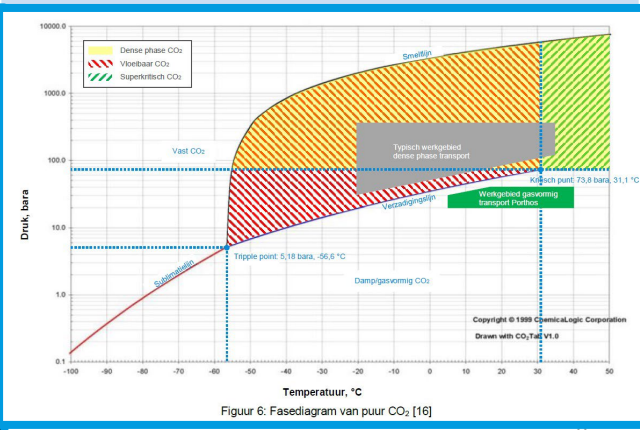
17 Further deployment H2 - and CO2 network Zeeland

18 **National hydrogen transport network** H2-pipeline network links major industrial areas Eemshaven, IJmuiden, Rotterdam, Chemelot, Zeeland and the Ruhr area

19 **North Sea Wind Power Hub** An island where power from offshore wind farms is partially converted into hydrogen that is piped onshore

Research: H_2, CO_2

Gas transport	Domestic/distribution grids	Mobility	CCUS
• HyTROS (2024-2029) • H2 primary standard, Fase I, Fase II, Fase III (2024 – 2027) • H2FlowTrace (2024 - 2027) • DNV – H2Met JIP 100 % H2 (2024 - 2025) • CryoMet (2025 - 2028) • SmartGasNet (2025 - 2028) • MetNH3Energy (2025 - 2028)	• Met4H2 (2022-2025) • HyTROS (2024-2029) • H2FlowTrace (2024 - 2027) • SmartGasNet (2025 - 2028)	• Green Transport Delta (NL project) • CryoMet (2025 - 2028) • MetroHyVe3 (2025 - 2028) • Cool-pipe/LiT (2025 – 2029)	• MetCCUS (2022 – 2025)



Figuur 6: Fasediagram van puur CO_2 [16]

Overview of the project

Adriaan van der Veen, VSL

ENERGY GASES

METCCUS

VSL

MET4H2

BiometCAP

VSL

National Metrology Institute

MET4H$_2$

Measurement infrastructure for the hydrogen supply chain

Adriaan van der Veen

Project coordinator

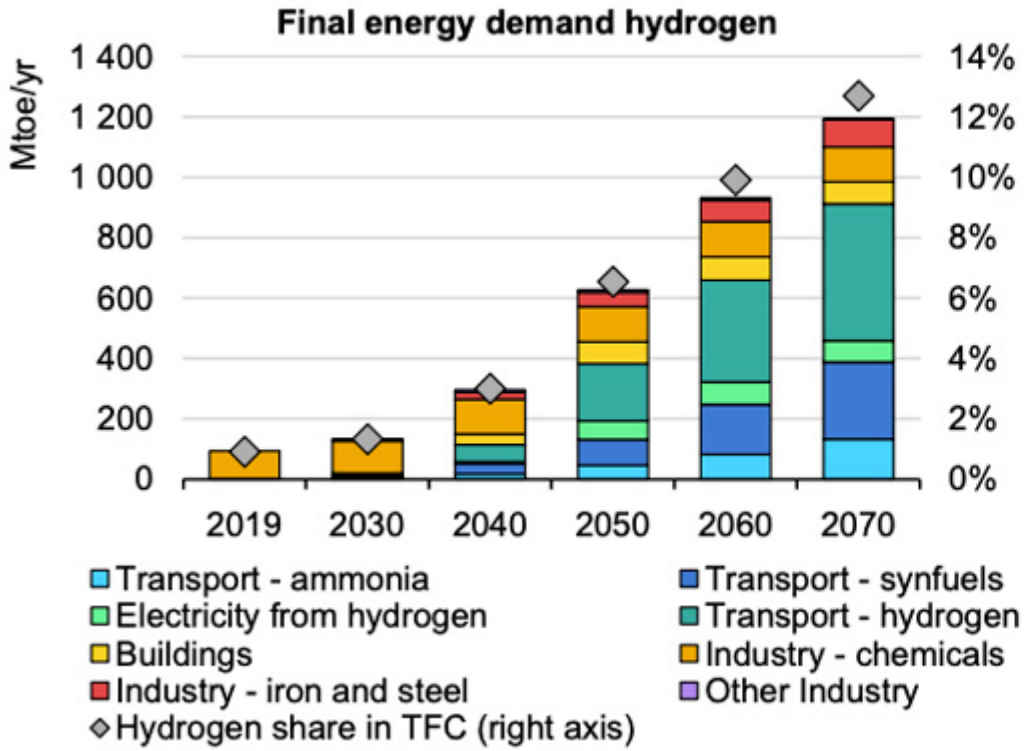
M30 Workshop Met4H$_2$

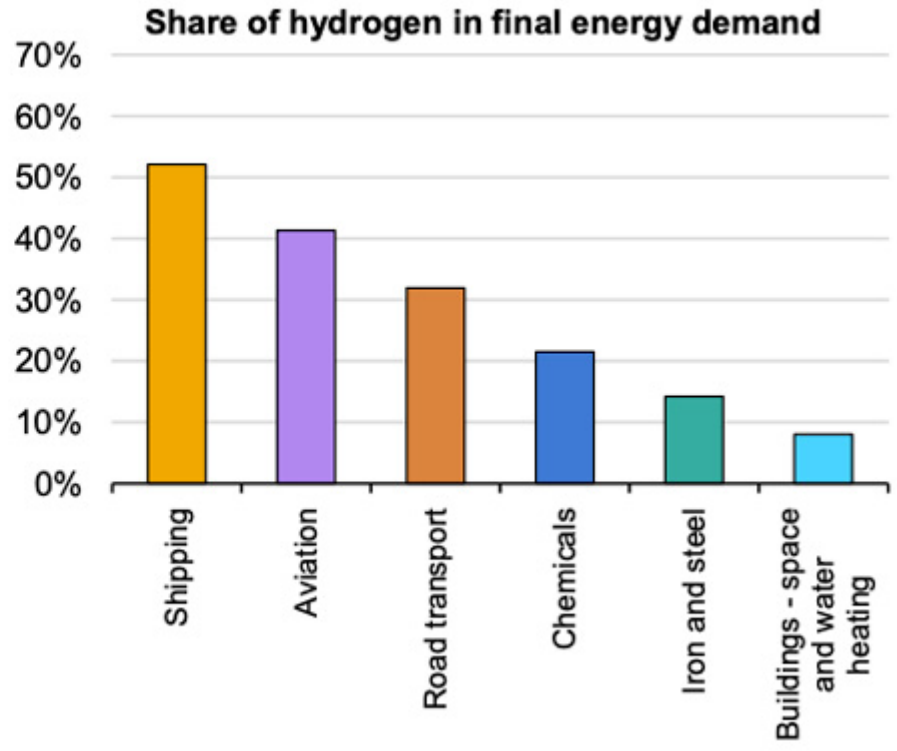
Delft, The Netherlands, 27 March 2025

Need and drivers

- “Unless there are rapid and large-scale reductions in greenhouse gas emissions, limiting warming […] to 1.5 °C will be beyond reach” [IPCC, 2021]
- European Green Deal (EGD) is Europe’s response to decarbonise energy use and to shift to renewable energy sources
- Hydrogen, produced from electricity from renewable sources, is at the centre of this energy transition
- To make the transition, hydrogen supply chains need support by good measurements for health, safety, environment and fiscal purposes
- Proposal addresses the stakeholder needs as documented by the EMN Energy Gases, supports actions needed in the short-term as well as in the longer-term

We need to get started NOW!





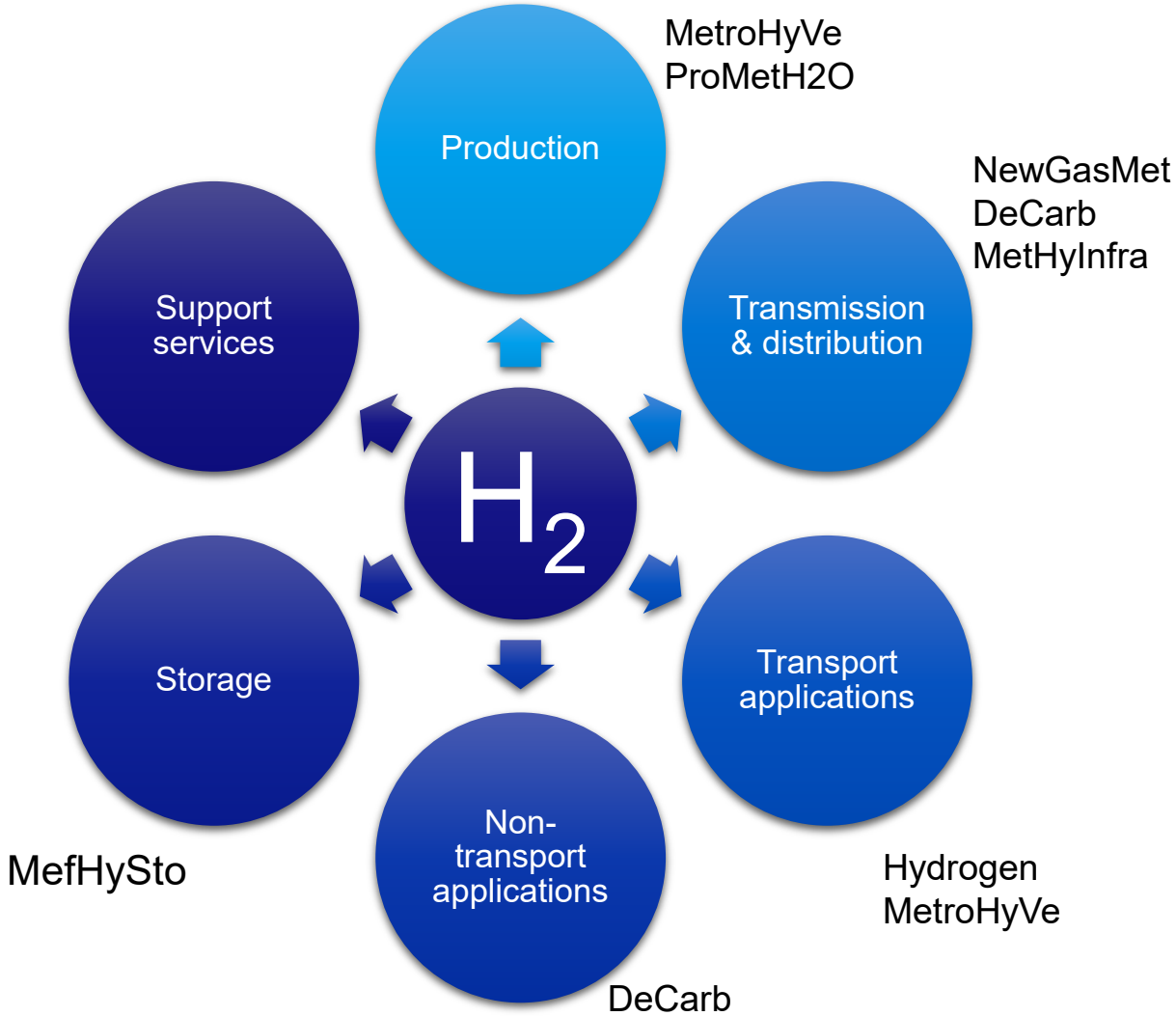
Source: IEA, Energy Technology Perspectives, 2020

Partners

VSL National Metrology Institute
VTT
BAM Bundesanstalt für Materialforschung und -prüfung
le cnam Conservatoire national des arts et métiers
SICK Sensor Intelligence.
ZAE BAYERN Bayerisches Zentrum für Angewandte Energieforschung
Politecnico di Torino
Univerza v Ljubljani
PTB Physikalisch-Technische Bundesanstalt Nationales Metrologieinstitut
NIPPON GASES
RI.SE Research Institutes of Sweden
DFM Danish National Metrology Institute
NPL
LABORATOIRE NATIONAL DE MÉTROLOGIE ET D'ESSAIS LNE
DTU Danmarks Tekniske Universitet
CESAME exadébit SA
ČESKÝ METROLOGICKÝ INSTITUT
NORCE
TÜV SÜD
CEM CENTRO ESPAÑOL DE METROLOGÍA
Bundesamt für Eich- und Vermessungswesen
Justervesenet
INRiM ISTITUTO NAZIONALE DI RICERCA METROLOGICA
FORCE TECHNOLOGY
ENVIRONMENT PARK Parco Scientifico Tecnologico per l'Ambiente
Eidgenössisches Institut für Metrologie
GERG THE EUROPEAN GAS RESEARCH GROUP

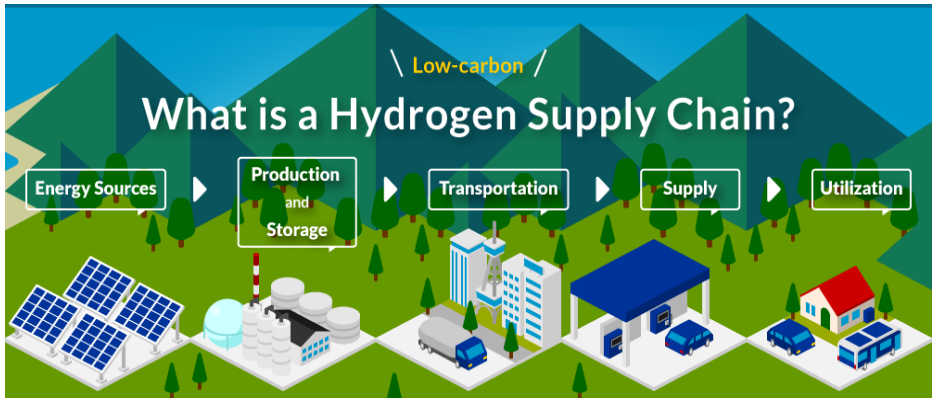
Hydrogen supply chains: measurement support services

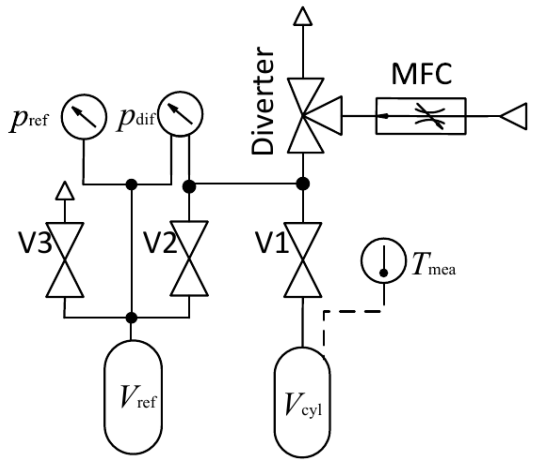
- Health Safety and Environment
- Flow meter calibration for hydrogen-enriched natural gas and hydrogen
- Quality assurance for hydrogen, now also for non-transport applications
- Sensor testing and qualification
- Billing and fiscal regimes
- … supplementing services coming from previous projects for transport applications, storage, and quality monitoring

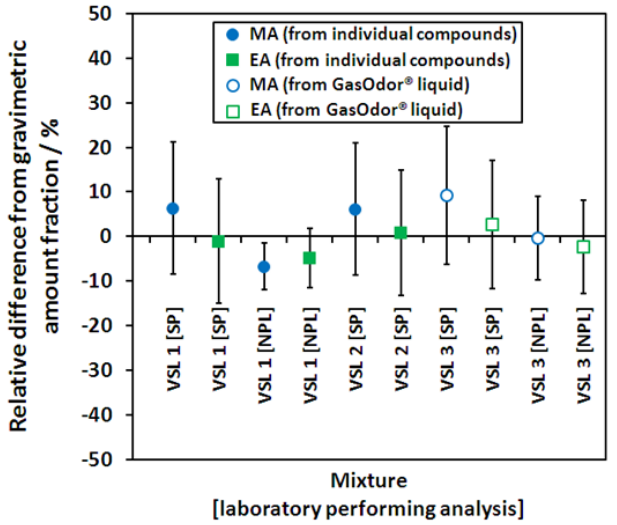


Health, safety and environment (WP1)

- Primary standards for leak flow rate measurements (10^{-6} to 10^{-9}) mol s^{-1}
- Characterisation methods for permeation analysis of sealings, liners etc. (-40 to 120) °C, (0.1 to 10) MPa, (10 to 90) % RH
- Validation protocols and test rigs for hydrogen sensors (hydrogen and impurity content)
- Measurement standards for measuring odorant levels in hydrogen-enriched natural gas and hydrogen (sulfurous and sulfur-free odorants)

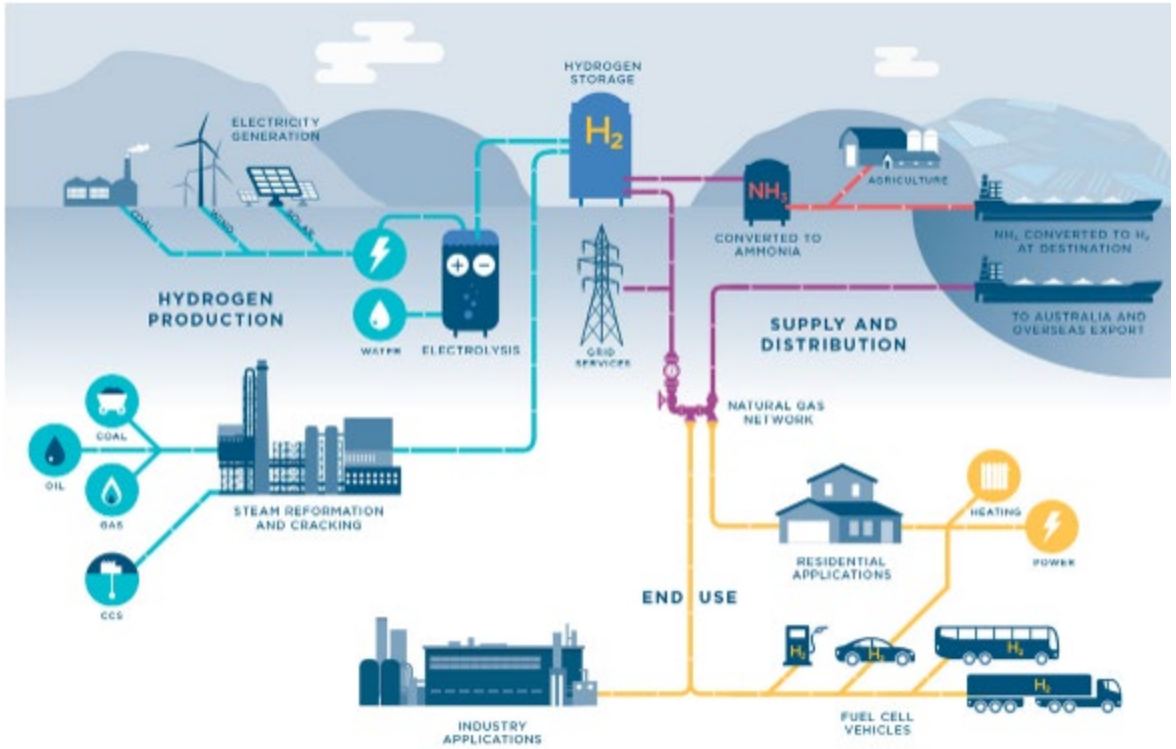






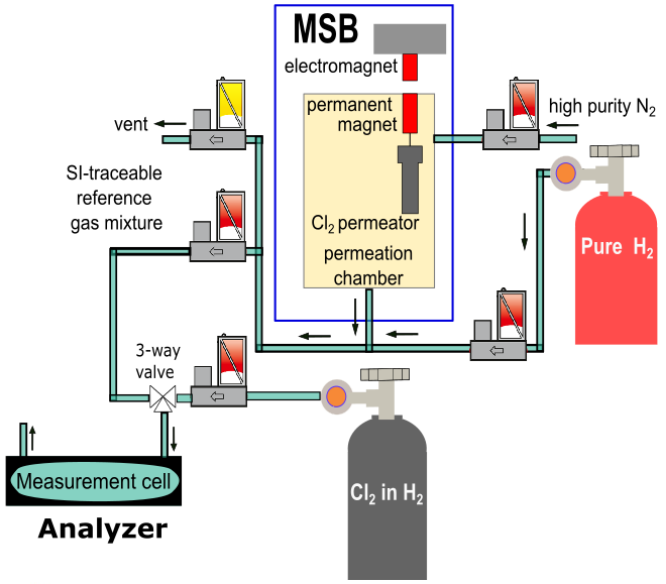
Flow measurement (WP2)

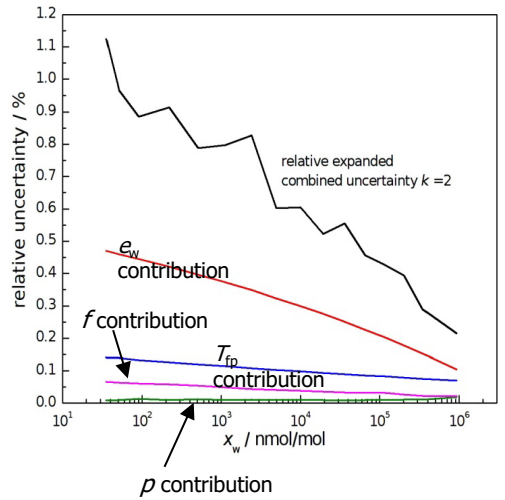
- Overview of the state-of-the-art in flow metering of hydrogen and hydrogen blends
- Intercomparison of flow measurement standards for hydrogen-enriched natural gas
- Flow standards for domestic gas meters for hydrogen, including assessment of impurity impact (up to 2 %)
- Development of metrological traceability chains for large-scale hydrogen transportation



Hydrogen quality (WP3)

- Development of gas sampling methods for online and offline use
- Humidity standards for the amount fraction water in hydrogen (up to 6 MPa)
- Measurement standards for impurities typical for alkaline electrolysers (e.g., chlorine, hydrogen chloride, and water)
- Measurement standards for hydrogen quality during transportation (e.g., odorisation compounds, ammonia)

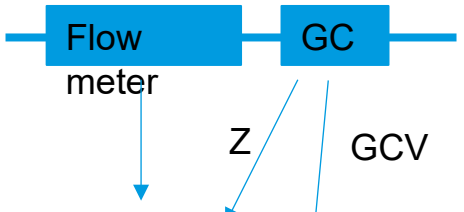




Uncertainty in fiscal metering (WP4)

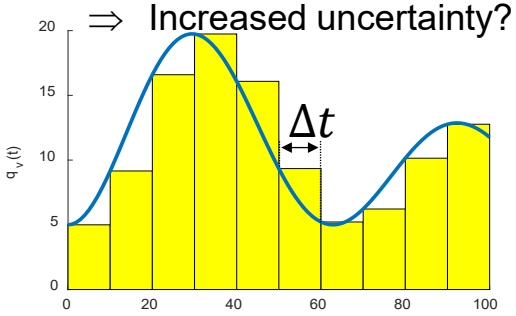
- Development of a framework for the uncertainty evaluation of the total quantity and energy provided
- Improvement of the uncertainty evaluation by taking into account the dependencies between measurement results
- Practical evaluation of natural gas and hydrogen-enriched natural gas data
- Practical evaluation of hydrogen and liquid hydrogen data

1. Correlations
=> Increased uncertainty?



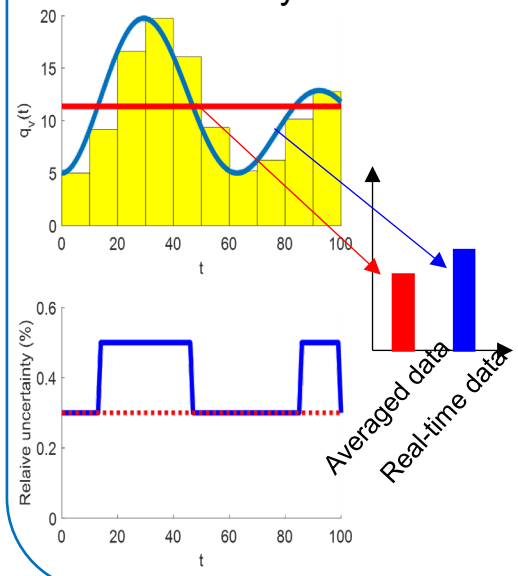
$$E = V \frac{P T_b Z_b}{P_b T Z} \times H_b$$

2. Integration over time
⇒ Increased uncertainty?



$$\int_{t_0}^{t_1} q_v(t)dt \neq \Delta t \sum_{i=1}^{N} q_{v,i}$$

3. Fluctuation in flow rates etc, but average values applied => Increased uncertainty?



Project outputs

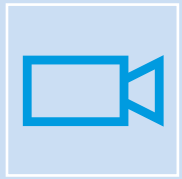
- Measurement infrastructure supporting the safe application of hydrogen
- Understanding of impact of impurities on hydrogen flow metering
- CMCs for flow metering of hydrogen mixed with natural gas
- Pathways for dissemination of metrological traceability of (high-volume) hydrogen flow metering
- Good practice guide on hydrogen quality along the supply chain
- Novel spectroscopic methods for, e.g., Cl_2, NH_3, and a validated infrastructure for total sulfur in hydrogen
- Humidity standard for water dewpoint measurement in hydrogen gas grids
- Good practice guide for fiscal metering of hydrogen-enriched natural gas and hydrogen

Save the date!

Topics:

1. Standards for hydrogen leak measurement
2. Performance assessment of hydrogen sensors
3. Calibration of flow meters for grade A hydrogen
4. Traceability chains for hydrogen flow metering
5. Comparison of humidity standards for hydrogen
6. Traceable quality monitoring of hydrogen
7. Evaluation of measurement uncertainty in fiscal metering
8. Hydrogen metering for custody transfer

Final workshop:
18 September 2025



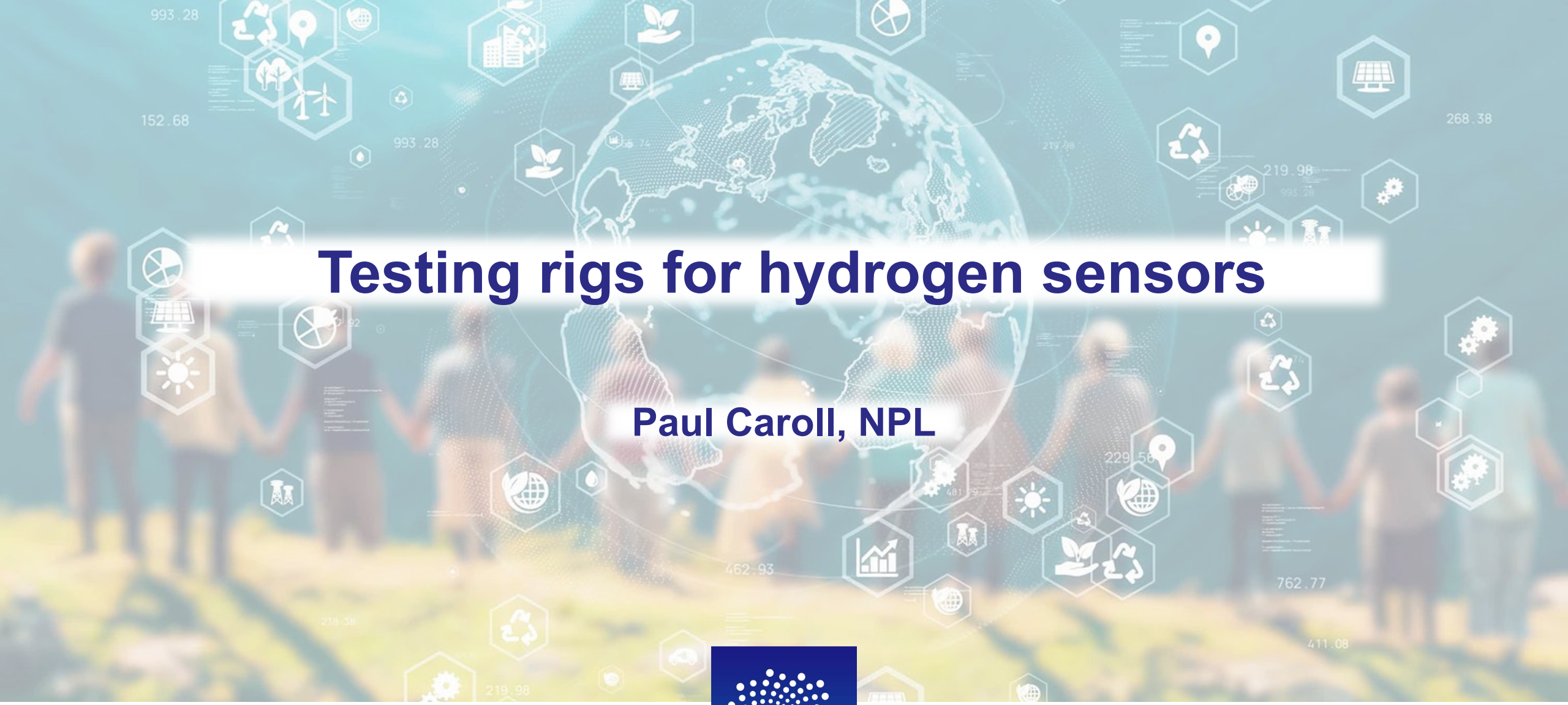
Form: **virtual**

Acknowledgment

Interested? Want to be involved?

Contact us at avdveen@vsl.nl or visit our website at https://met4h2.eu

“The project 21GRD05 (Met4H2) has received funding from the European Partnership on Metrology, co-financed from the European Union’s Horizon Europe Research and Innovation Programme and by the Participating States.”



Testing rigs for hydrogen sensors

Paul Caroll, NPL

ENERGY GASES

METCCUS

VSL

MET4H2

BiometCAP

Testing rigs for hydrogen sensors

Workshop Met4H2

Delft, The Netherlands, 2025-03-27

Karine Arrhenius, Sandra Hultmark, Oliver Büker, RISE

Shirin Khaki, NPL

EUROPEAN PARTNERSHIP Co-funded by the European Union METROLOGY PARTNERSHIP EURAMET

Testing rigs for hydrogen sensors

Introduction

- The competitiveness of the hydrogen supply chain depends directly on its safety and the safety of the facility where hydrogen is used, stored or transported
- Hydrogen has a very broad flammability range (4 to 74% in air) and is prone to leaks due to its small molecular size, less dense than air
- Chemical sensors respond to a particular analyte in a selective and reversible way, and are crucial technology for the safe use of hydrogen

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Testing rigs for hydrogen sensors

Safety hydrogen sensors

- Monitor the level of hydrogen to detect and/or quantify hydrogen leak: can be used to trigger alarms and activate ventilation or shut down systems to prevent hydrogen to reach flammable levels. Their working range usually covers at least up to the LEL. Current applications: Room/area monitoring for safety where hydrogen leakage may occur e.g. battery, detection of leaked hydrogen, process monitoring and control, stationary and mobile fuel cell applications

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Testing rigs for hydrogen sensors

Hydrogen purity sensors

- Are used to monitor the quality of hydrogen. Example of application: quality control process to check the compliance with the requirements in the international standards (ISO 14687: 2019 or EN17124:2022) and ISO 19880-8:2024) for hydrogen fuel.
- Sensors need to be able to detect low level of components such as O2, CO, H2S, H2O in pure hydrogen.
- Limited availability: manufacturers mainly propose existing solutions for other matrices (air, N2).
- Must be checked for hydrogen by ensuring that the hydrogen itself will not give rise to a signal before further testing.
- These sensors must be intrinsically safe

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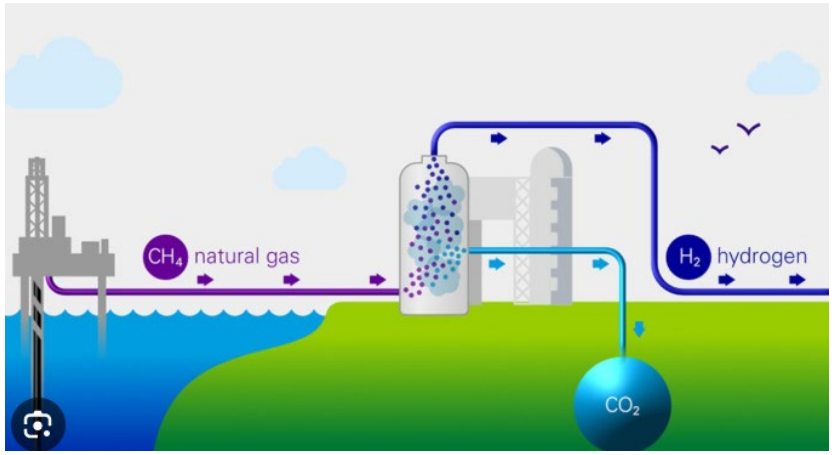
Testing rigs for hydrogen sensors

Hydrogen in gas mixtures sensors

- Hydrogen can be injected into the existing natural gas network where it can be transported to the consumers.
- Amount of hydrogen must be controlled so the H2/CH4 mixture satisfies the gas quality requirements of the pipeline set by legislations and standards.

- H2 produced by steam methane reforming reaction: Gas produced contains 2 to 10 vol-% CH4 as residual



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Testing rigs for hydrogen sensors

What do we do in Met4H2?

- Review of the state-of-the-art including techniques, existing protocols, test rigs, applications
- Development of a protocol to metrologically test sensors
- Development of two rigs to test sensors
  1. NPL: rig able to test 1 to 5 sensors for at least one contaminants in H2
  2. RISE: rig able to test different types of sensors
- Test of the protocol using both rigs
- Write guideline on validation, calibration and verification of sensors

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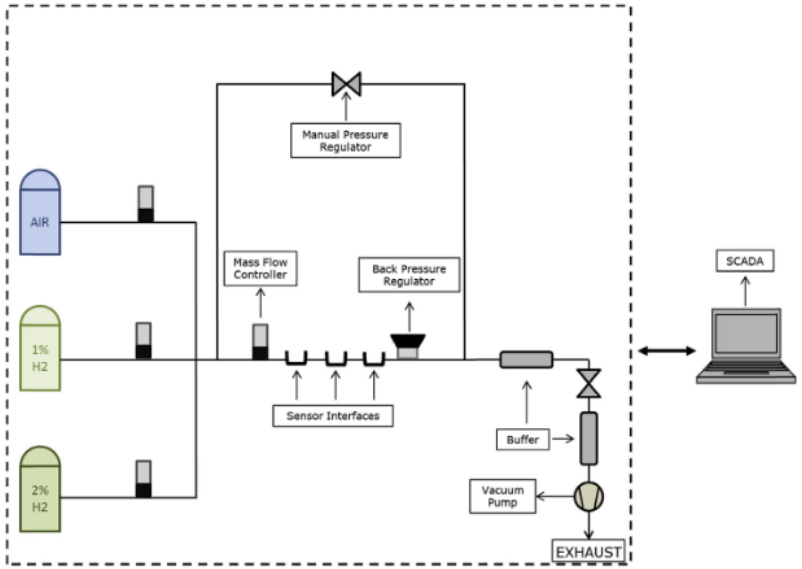
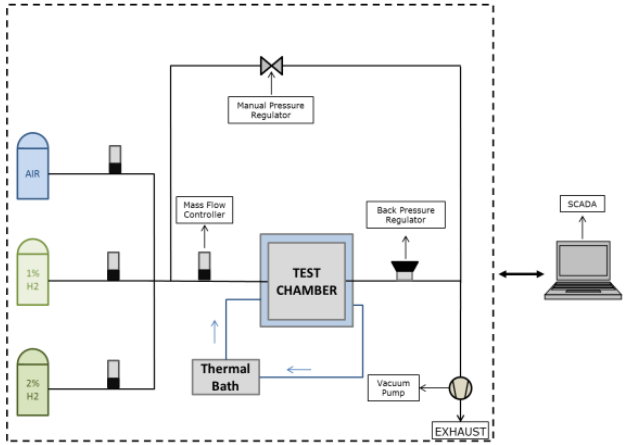
Testing rigs for hydrogen sensors

Protocol

Two common methods to test sensors



Flow-through test



Chamber test

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Testing rigs for hydrogen sensors

Protocol

Testing of each metric clearly defined in a table

	What to do	Evaluation of results	Pressure conditions	Comments
Precision	6-15 replicates for at least 10 min during a short timescale using a single test gas having a volume fraction at the midpoint of the measuring range using a flow at the midpoint of the flow interval. Calculate the standard deviation	Calculate the standard deviation of the replicates	0.8 to 1.2 bar, kept constant within ±0.1 bar throughout the duration of the test 15°C and 25°C kept constant within ±2 °C throughout the duration of the test 20 % and 80 % within ±10 % throughout the duration of the test.	For sticky" impurities*, the duration of the test should be extended (to the time needed to obtain a stable signal). A reference analytical instrument can be used to confirm that the sensor is exposed to the amount of analyte present in the test gas

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Testing rigs for hydrogen sensors

Protocol

Covers:

Precision

Trueness/accuracy

Response time

Stability and drift

Selectivity or cross-interference

Limit of quantification

Nominal range, saturation

Resolution

Hysteresis

Reversibility

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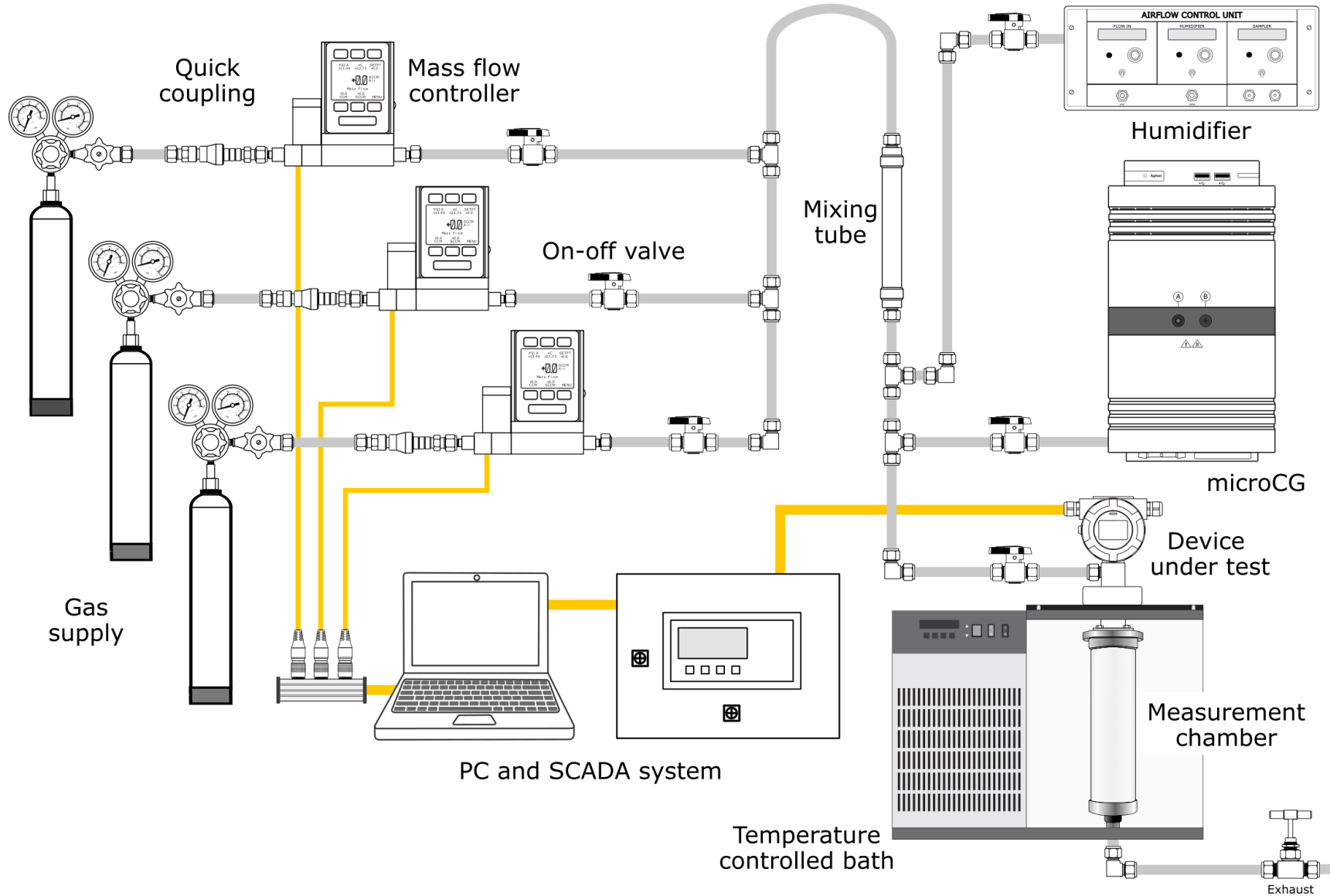

MET4H2

RI. SE

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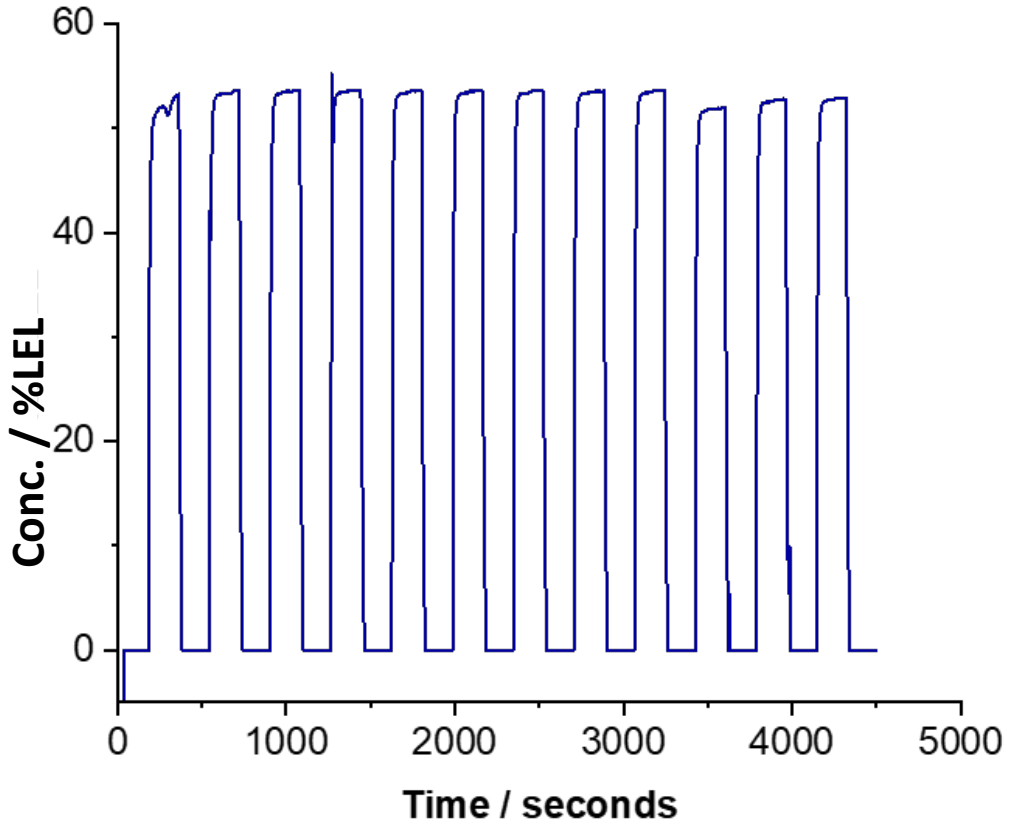
Sensor performance evaluation: precision

The consistency of repeated measurements and is a measure of the standard deviation of results obtained by carrying replicate measurements. The precision can be expressed as repeatability.



Replicates at 2.153 vol-% (around 54%LEL)
LEL= Lower explosive limit Lowest concentration of a gas that can ignite and cause explosion if an ignition source is present.

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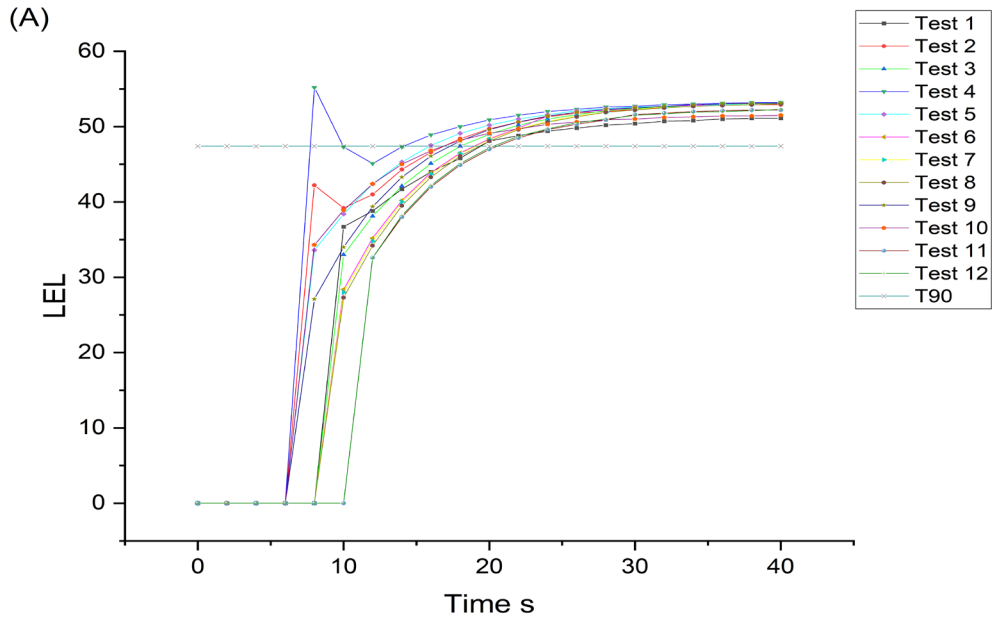
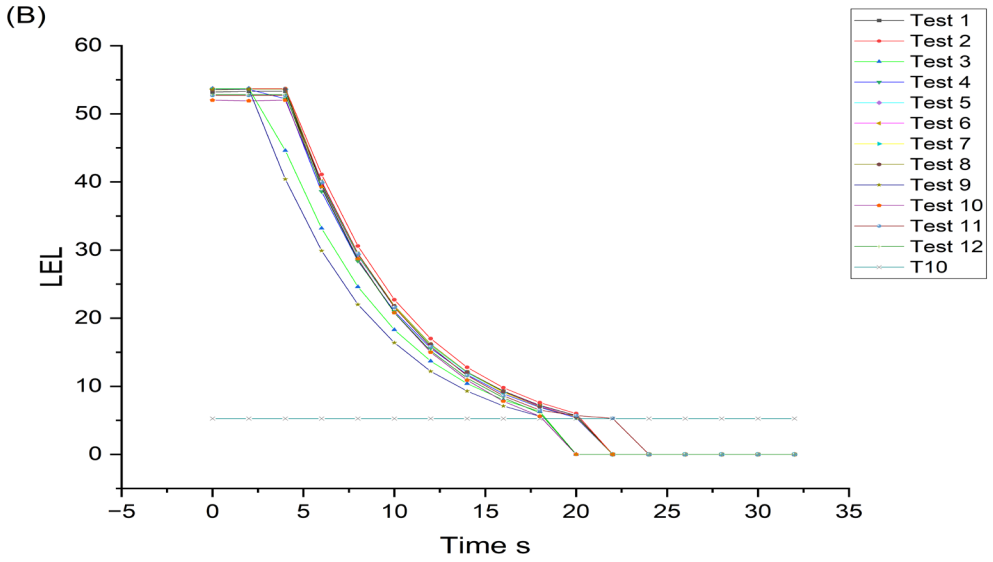
Sensor performance evaluation: Response time

T90 corresponds to the time to reach 90% of the applied target gas concentration or its stable reading. The recovery time **T10** is defined as the time to fall to 10% of final value after step removal of measured variable.

- .





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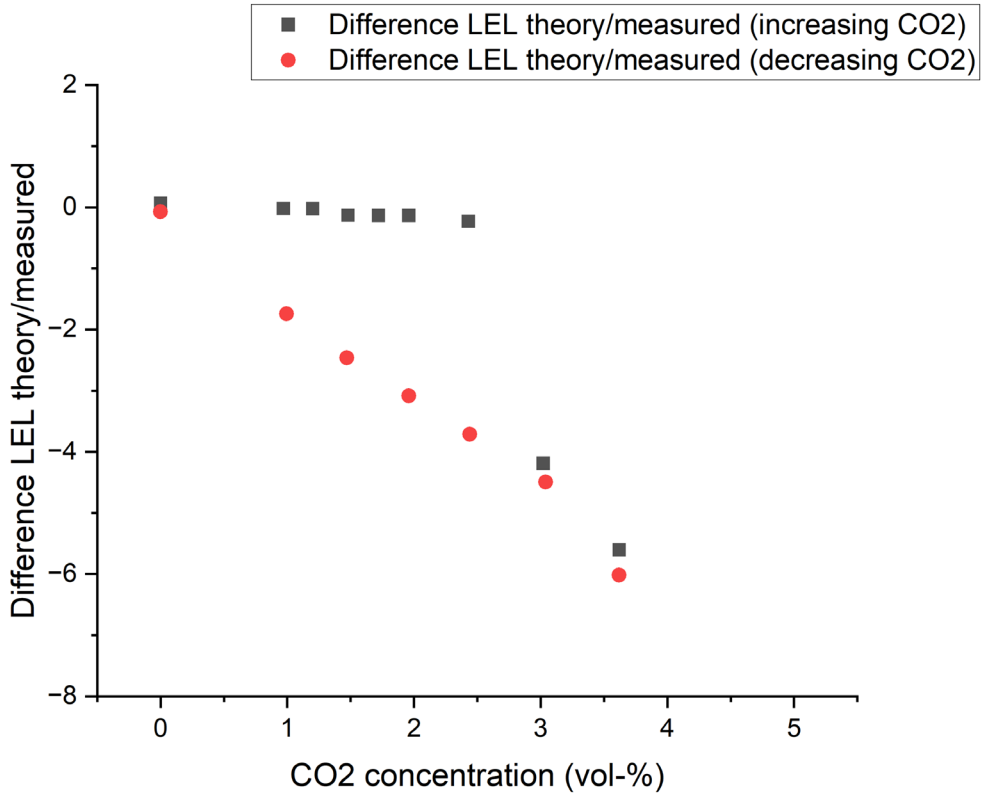
Sensor performance evaluation: Cross-sensitivity

Sensors are designed to be selective to a specific compound or to a certain type of compounds.

In the presence of some non-targeted compounds, a signal may be produced leading to errors in the measurement of the target compound (either higher or lower than predicted).



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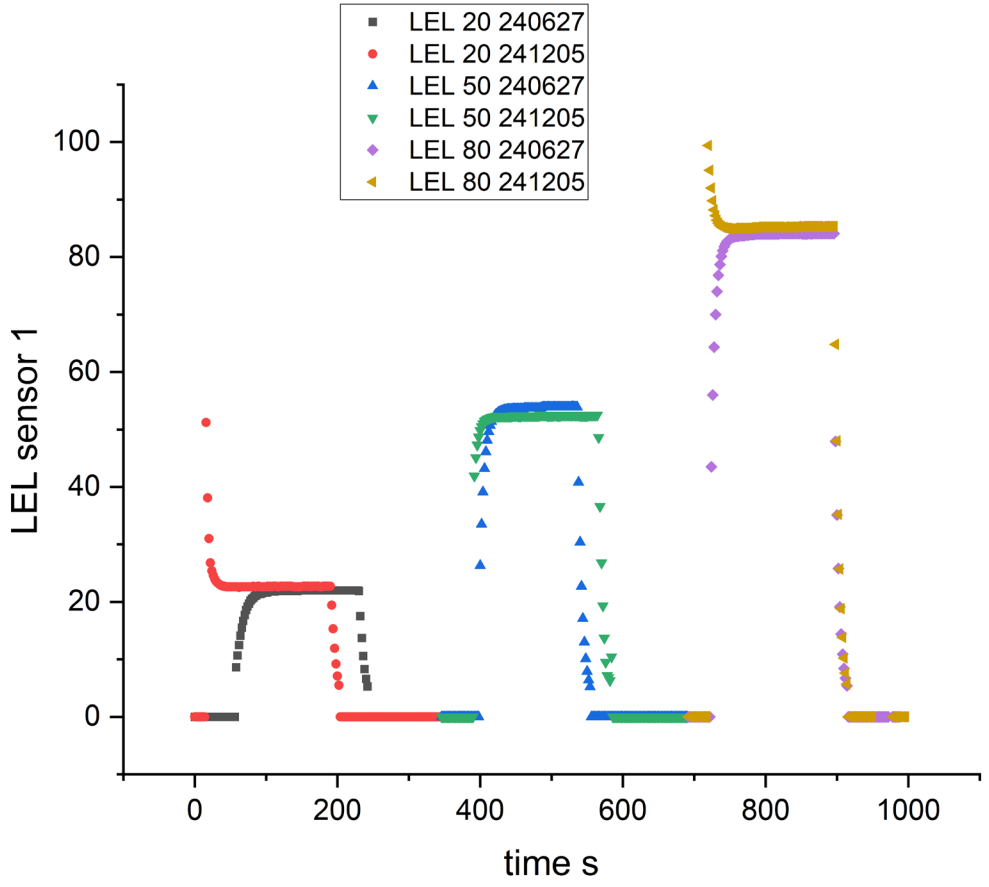
Stability

Drift is a temporal change in the response of an instrument to a constant concentration. Drift implies that the performance of a measuring instrument changes, and re-calibration must be performed.



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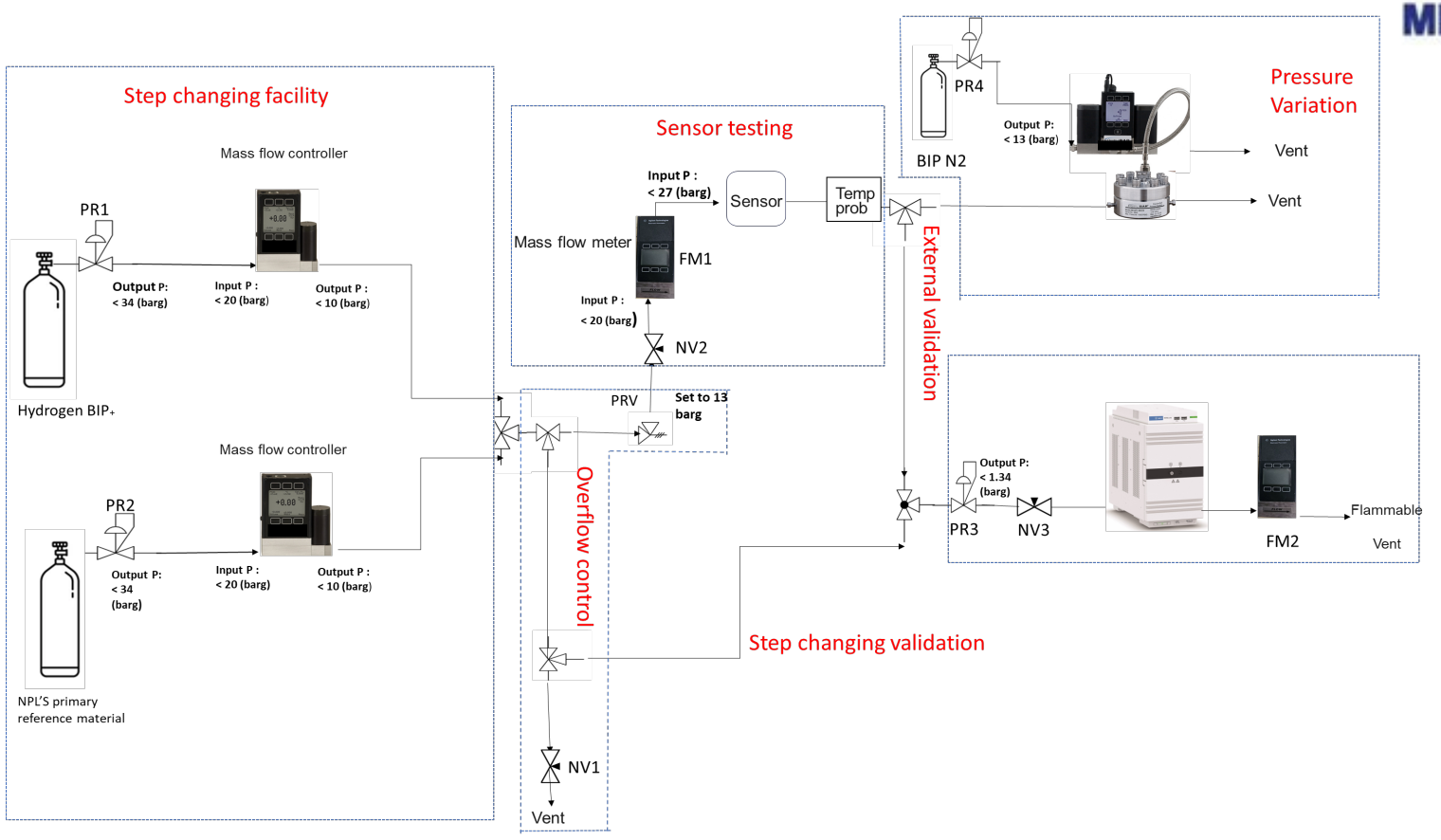
Rig for sensor testing impurities

- Rapid change of amount fraction;
- **Rapid change of pressure up to 10 barg (140 psig);**
- **Constant monitoring of temperature of the gas;**
- External validation of amount fraction delivered to sensor via a parallel line to NPL calibrated gas analyser.
- **Validation of amount fraction generated by the step changing facility via a parallel line to NPL calibrated gas analyser.**

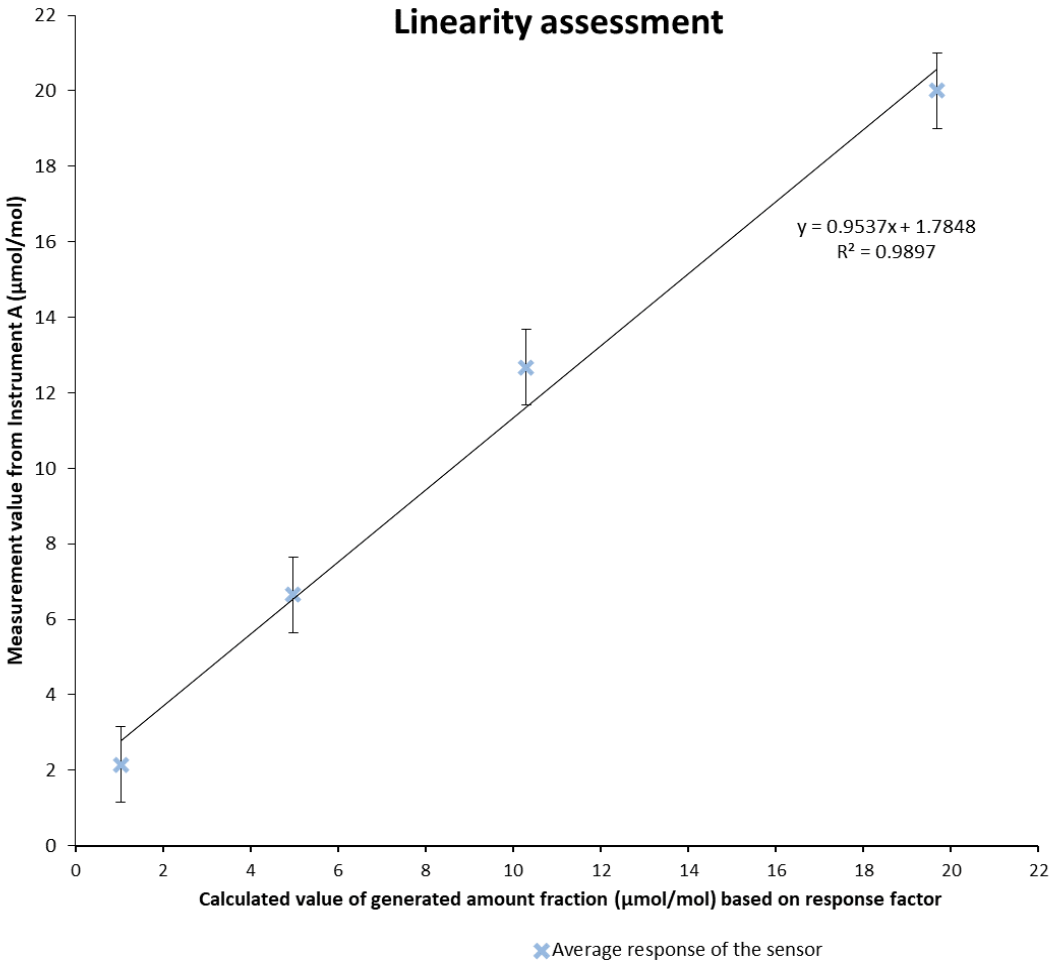


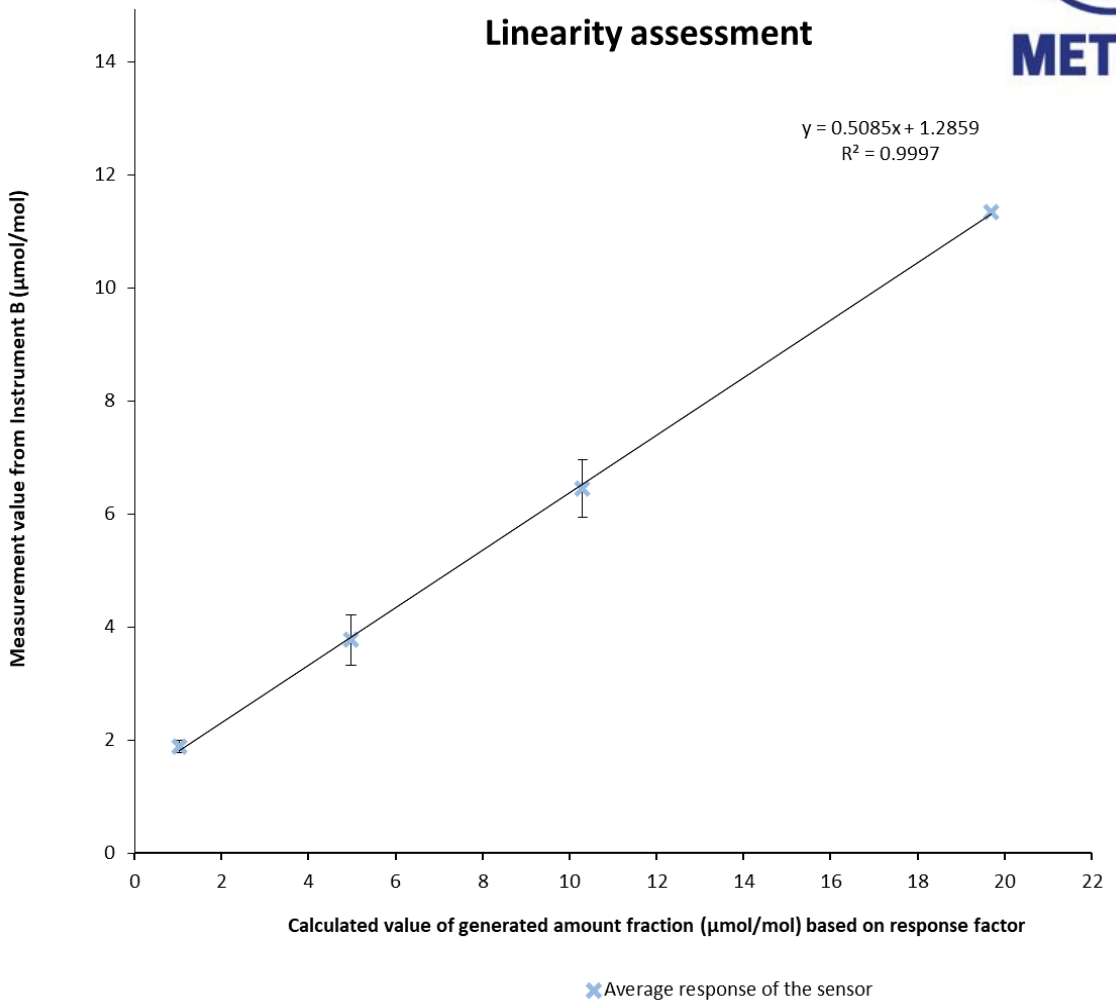
Achievements: compatible with most contaminants in H2 (i.e., O_2 from 0.5 to 20 µmol/mol); fast response (< 20 seconds)

National Physical Laboratory

EUROPEAN PARTNERSHIP Co-funded by the European Union METROLOGY PARTNERSHIP EURAMET

Linearity

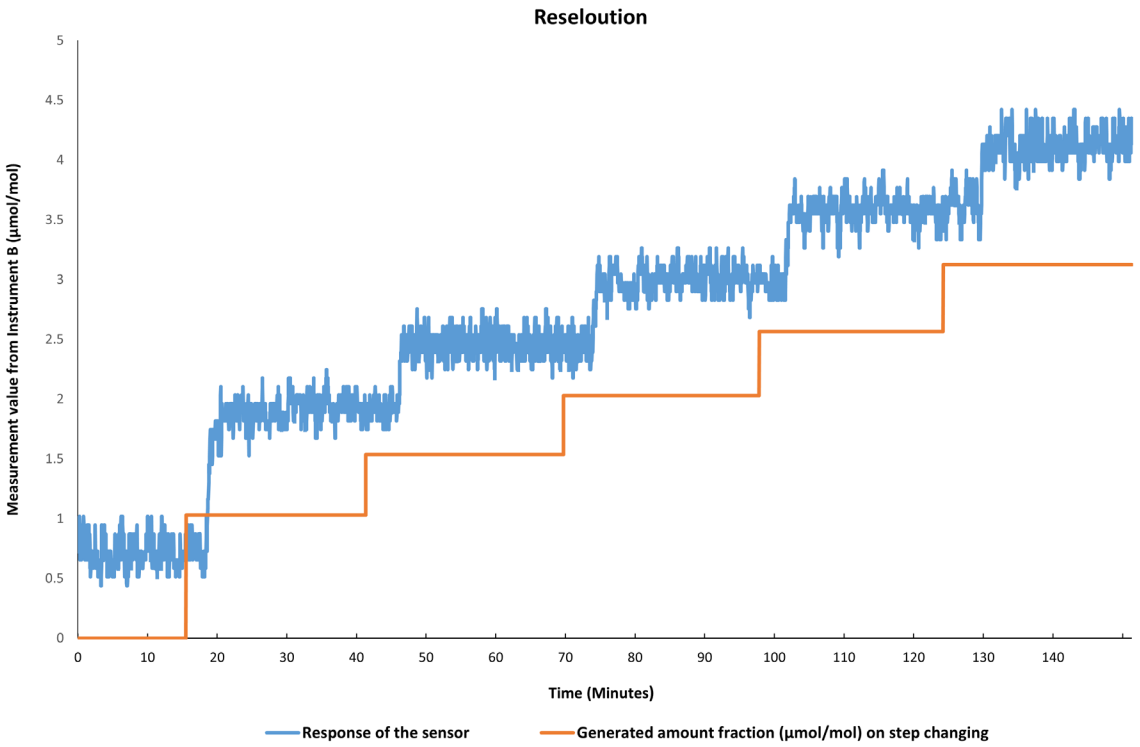


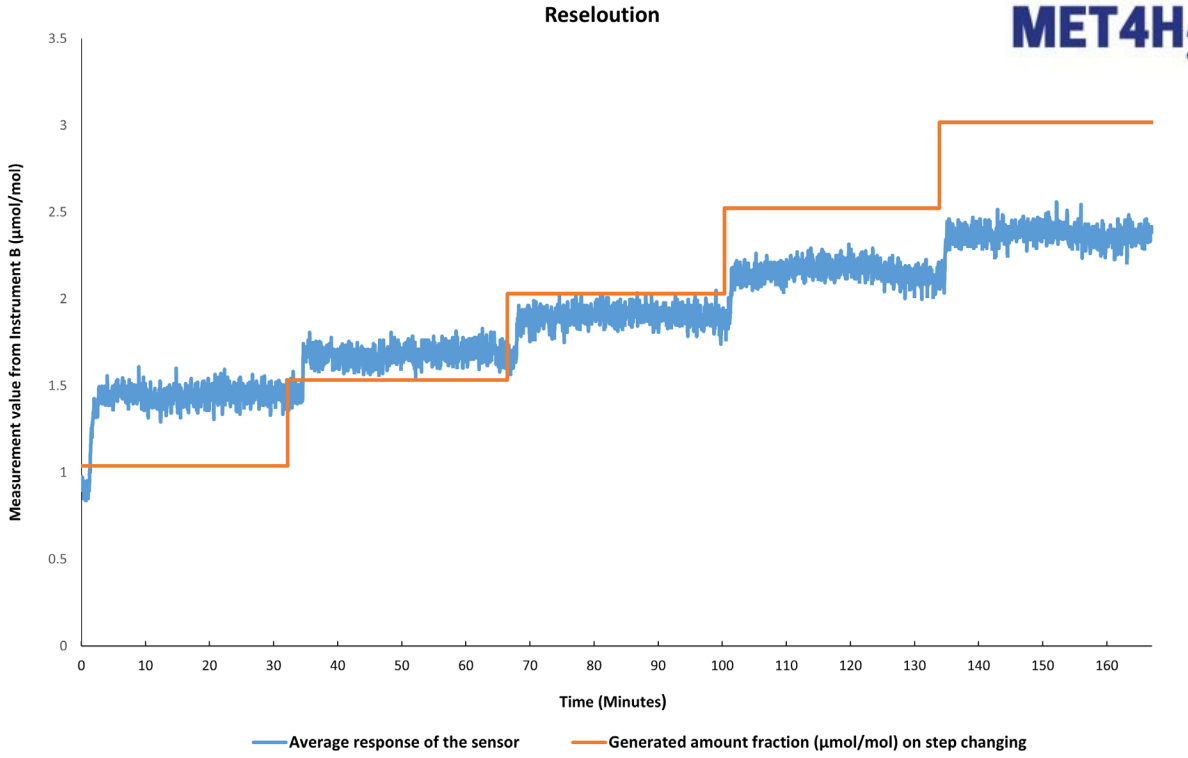


NPL National Physical Laboratory

EUROPEAN PARTNERSHIP Co-funded by the European Union METROLOGY PARTNERSHIP EURAMET

Resolution





Initial generated amount fraction (µmol/mol) on step changing	Generated amount fraction (µmol/mol) on step changing	Generated step incerment	Change incerment recorded by Sensor A	Change incerment recorded by Sensor B
1.038	1.534	0.496	0.498	0.248
1.534	2.029	0.495	0.610	0.228
2.029	2.524	0.494	0.567	0.257
2.524	3.017	0.493	0.547	0.215

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EURAMET

Testing rigs for hydrogen sensors

Guidelines

Validation of sensors
Implies demonstrating that a given sensor is able to perform the measurements it is intended to do. Evaluation of the metrics and comparison of the results with end-user´s needs

Verification of sensor
Can be defined as the process of ensuring that the data provided by the sensors remains accurate and consistent over time.
Other definitions: checking the performances against specifications provided by the sensor´s developer or site verification: check some metrics online

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Testing rigs for hydrogen sensors

Guidelines

Adjustment of sensor
Process entails adjusting the response of a sensor to align its output accurately with its input by a recognized reference. This operation can be needed if the sensor´s output show a bias or a drift of response with time

Calibration of sensor
Operation performed on a sensor that, under specified conditions

1) Established a relation between the values with associated uncertainties provided by measurement standards and corresponding indications with associated uncertainties of the sensor
2) Uses this information to establish a relation for obtaining a measurement result from an indication given by the sensor

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Testing rigs for hydrogen sensors

EUROPEAN PARTNERSHIP
Co-funded by the European Union
METROLOGY PARTNERSHIP
EURAMET

Novel facilities for hydrogen flow meters

Edvardas Venslovas, JV

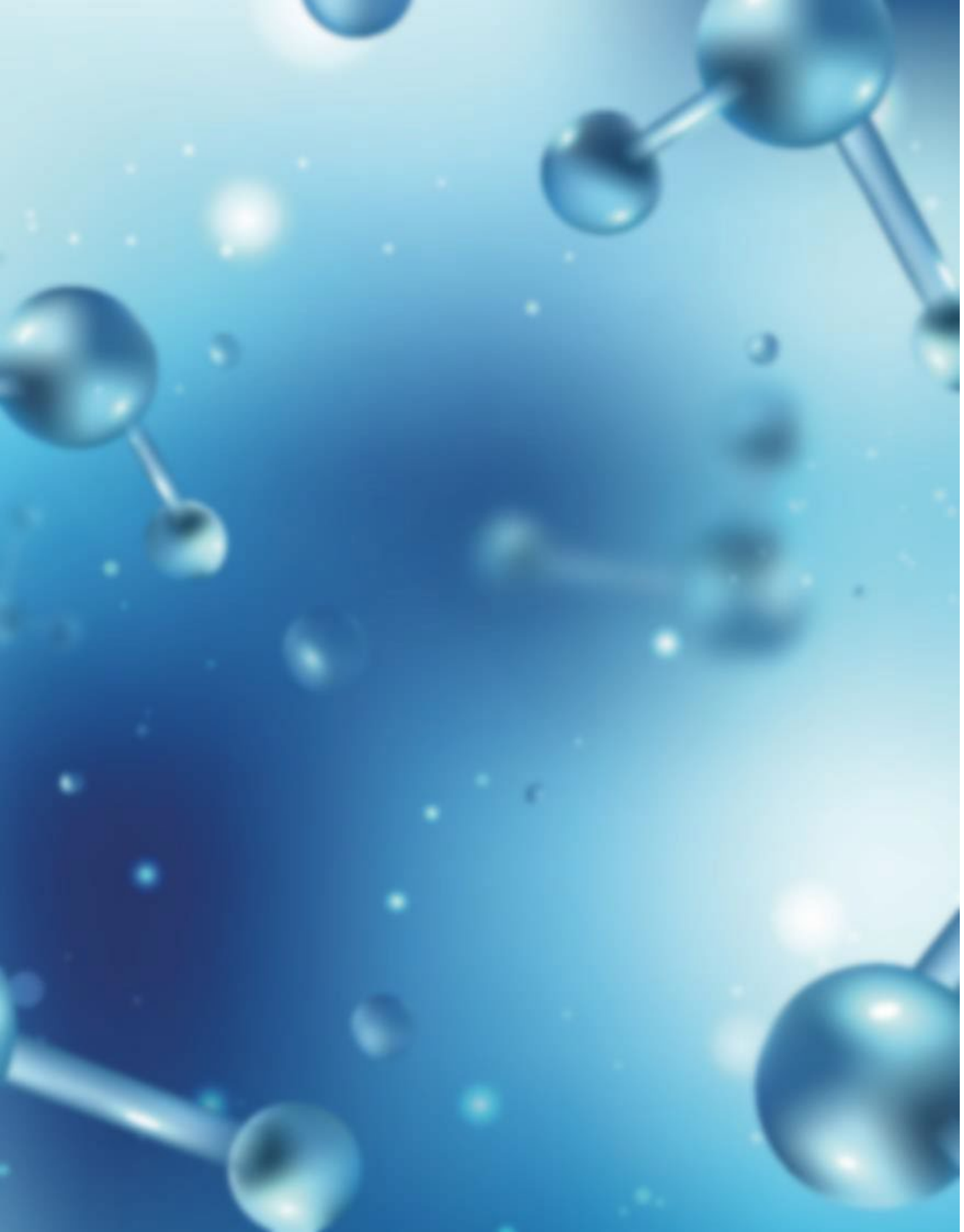
ENERGY GASES

METCCUS

VSL

MET4H2

BiometCAP



NOVEL FACILITIES FOR HYDROGEN FLOW METERS

Stakeholder Workshop
27th of March 2025, Delft
Edvardas Venslovas, Justervesenet, on behalf of WP2 partners

PARTNERS IN WP2

MET4H2

VSL National Metrology Institute

Bundesamt für Eich- und Vermessungswesen

CESAME exadébit SA

ČESKÝ METROLOGICKÝ INSTITUT

Justervesenet

CEM CENTRO ESPAÑOL DE METROLOGÍA

le cnam Conservatoire national des arts et métiers

DTU Danmarks Tekniske Universitet

DFM

METAS

Endress+Hauser

FORCE TECHNOLOGY

TÜV SÜD

INRiM ISTITUTO NAZIONALE DI RICERCA METROLOGICA

Politecnico di Torino

LNE

NIPPON GASES

NORCE

BAM Bundesanstalt für Materialforschung und -prüfung

GERG THE EUROPEAN GAS RESEARCH GROUP

PTB Physikalisch-Technische Bundesanstalt Nationales Metrologieinstitut

RI.SE Research Institutes of Sweden

ENVIRONMENT PARK Parco Scientifico Tecnologico per l'Ambiente

NPL

Univerza v Ljubljani

VTT

ZAE BAYERN Bayerisches Zentrum für Angewandte Energieforschung

OVERVIEW OF WP2 OBJECTIVES

MET4H$_2$

- Develop **measurement standards** to calibrate and validate flow meters under actual conditions of pressure and temperature, e.g., at fiscal metering points,
- such that they can be used to accurately quantify flow rates of hydrogen (+HENG) through the hydrogen supply chain,
- and to facilitate compliance wrt. OIML R137 (Gas meters), OIML R140 (Measuring systems for gaseous fuels), and the MID.

TASKS

MET4H2

1

Collection of hydrogen flow metering results

2

Intercomparison with blends of hydrogen and natural gas

3

Domestic meter accuracy hydrogen with impurities

4

Traceability chain for large-scale hydrogen transportation

TASKS – OUTPUT

MET4H2

1

Collection of hydrogen flow metering results

- **Technical report**
  - Status of European gas distribution grid (available: https://met4h2.eu/news-and-publications/publications/)
  - LH2 supply chains
  - Evaluation of existing gas models for gas flow suitable for hydrogen (available, same link as above)

2

Intercomparison with blends of hydrogen and natural gas

- **Report** on inter-comparison of flow metering for blends of H2 up to 20 % and NG

3

Domestic meter accuracy hydrogen with impurities

- D3: **Paper** on H2 flow metering on blends of NG and up to 20 % H2 blends, and gas mixtures with 98 % H2

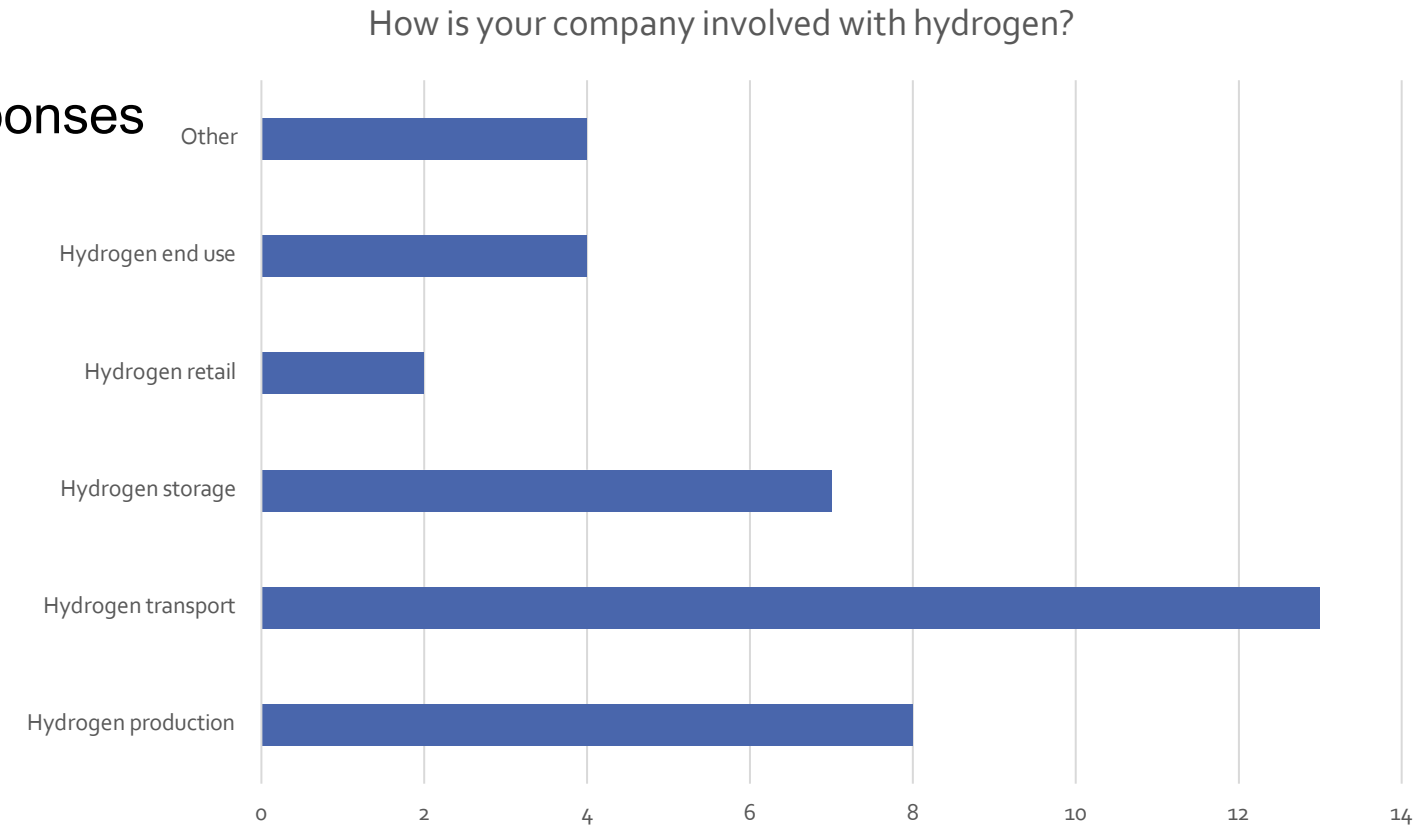
4

Traceability chain for large-scale hydrogen transportation

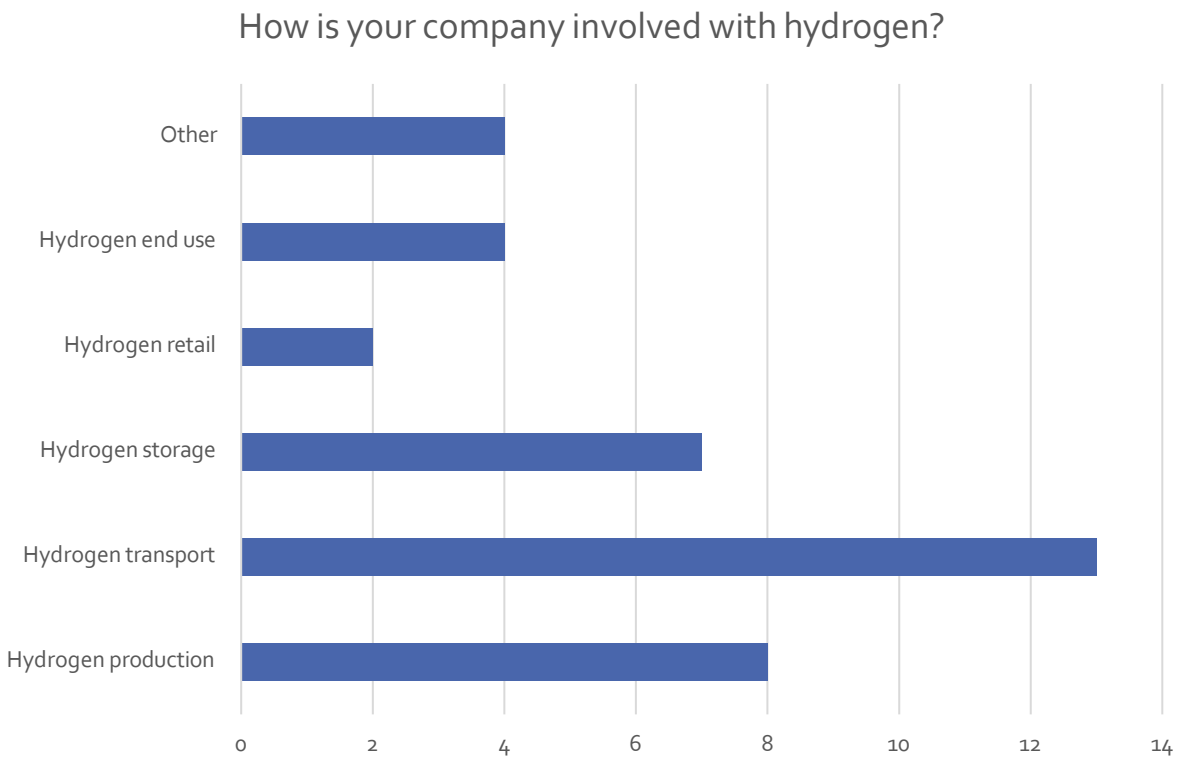
- D4: **Technical report**
  - Flow rates >0.2 kg/min
  - 3 options for ensuring traceability

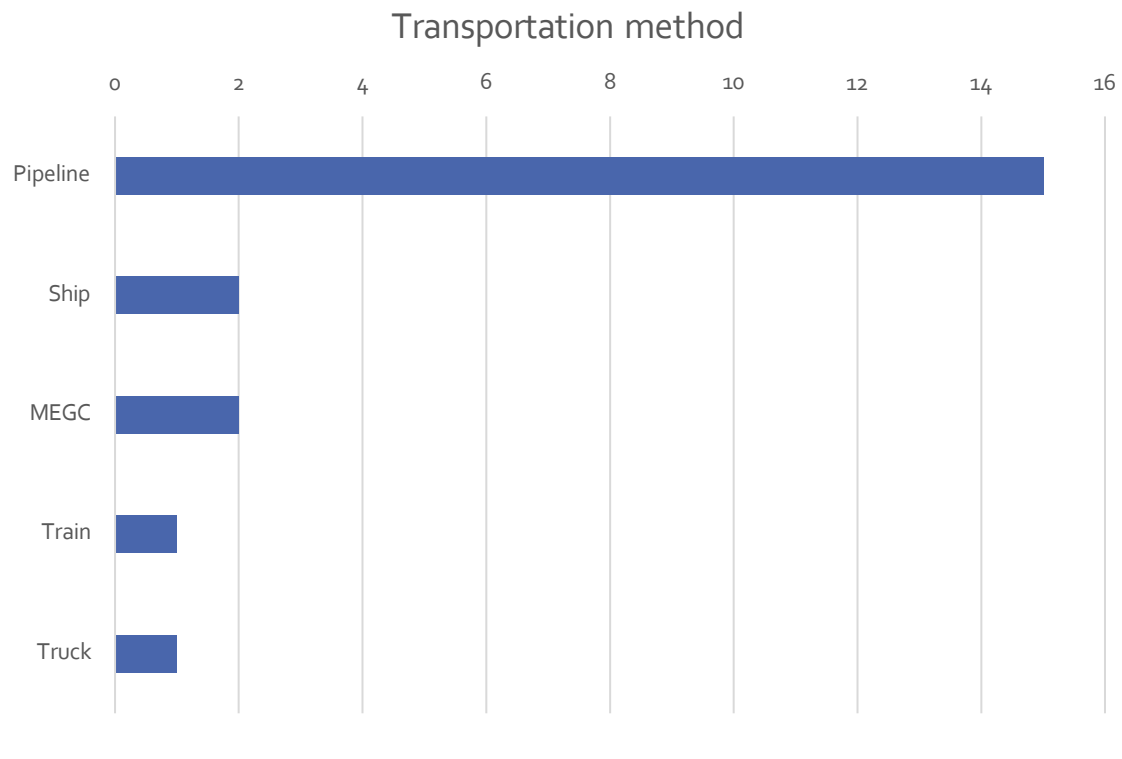
MOTIVATION

- Survey of stakeholders on their traceability and flow measurement needs
- Contacted 75 people, 18 responses
- Targeted mainly:
  - Shipping
  - Storage
  - Production

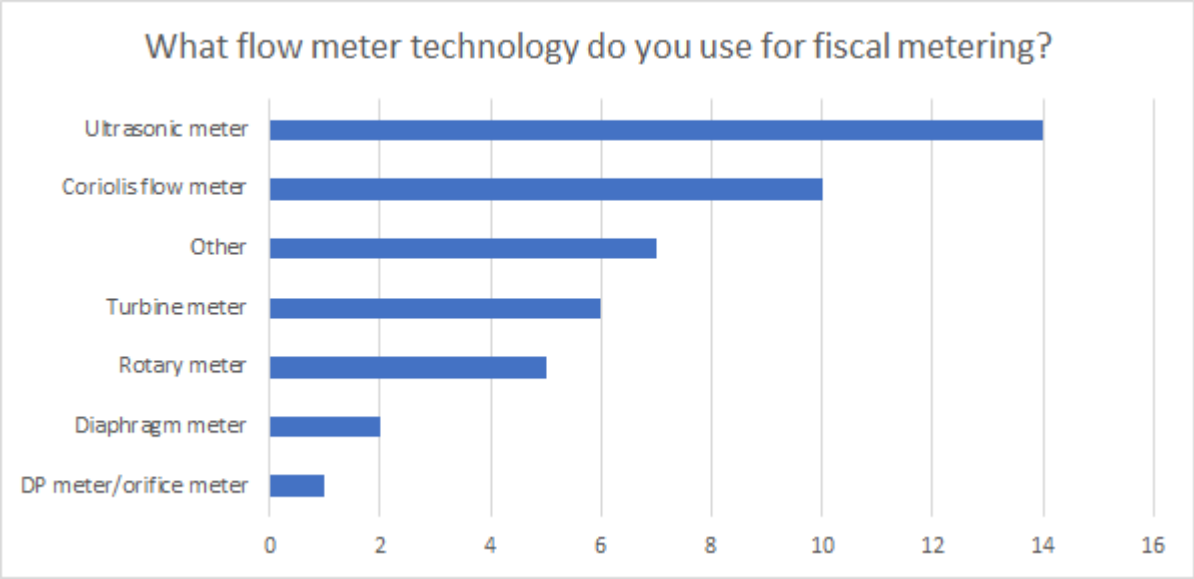


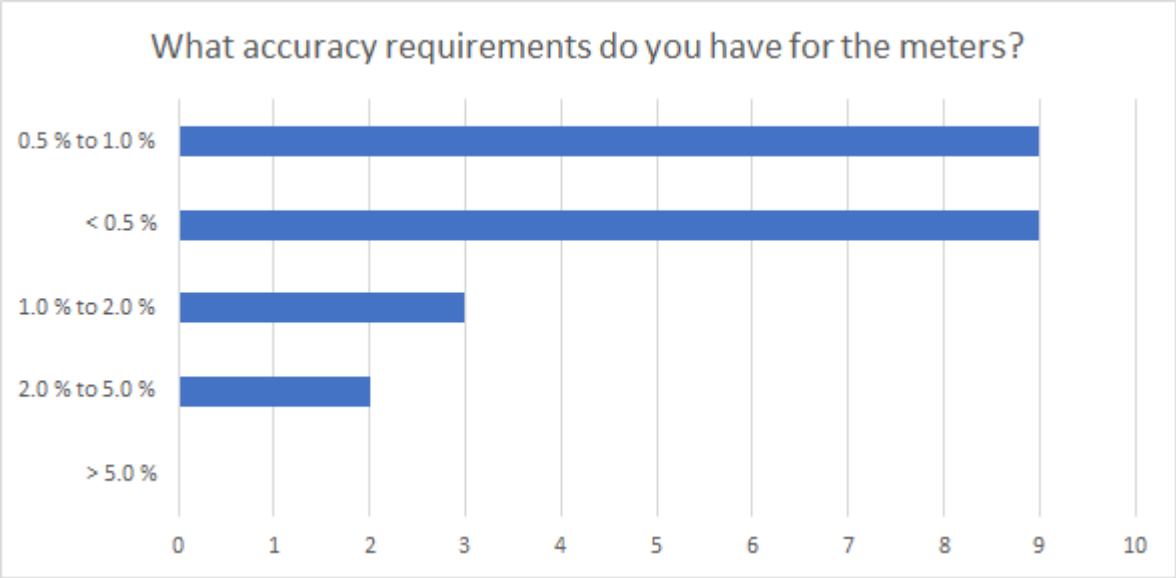
MOTIVATION


How is your company involved with hydrogen?
Other
Hydrogen end use
Hydrogen retail
Hydrogen storage
Hydrogen transport
Hydrogen production
0
2
4
6
8
10
12
14


Transportation method
0
2
4
6
8
10
12
14
16
Pipeline
Ship
MEGC
Train
Truck

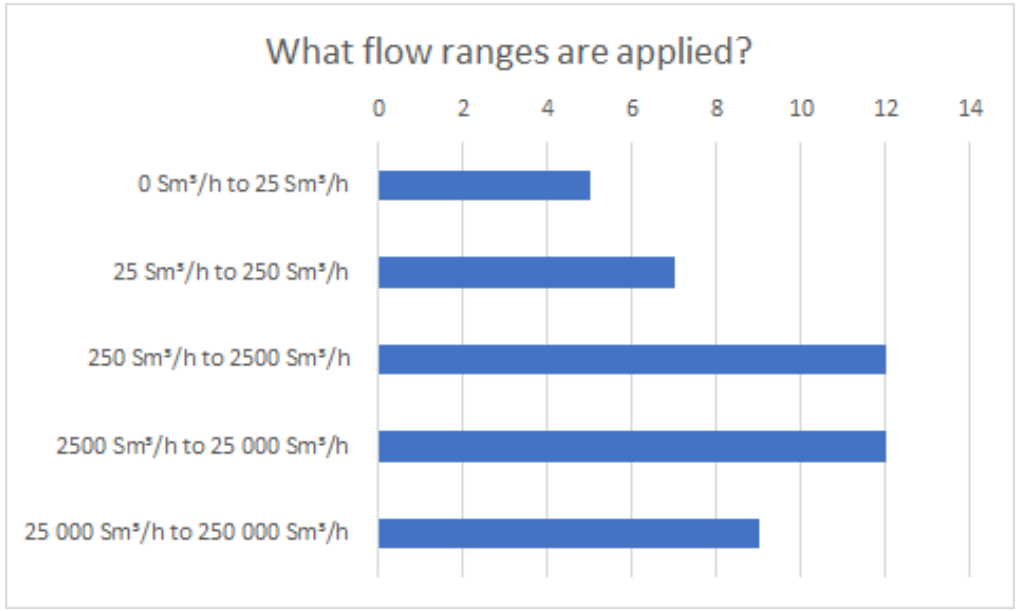
MOTIVATION

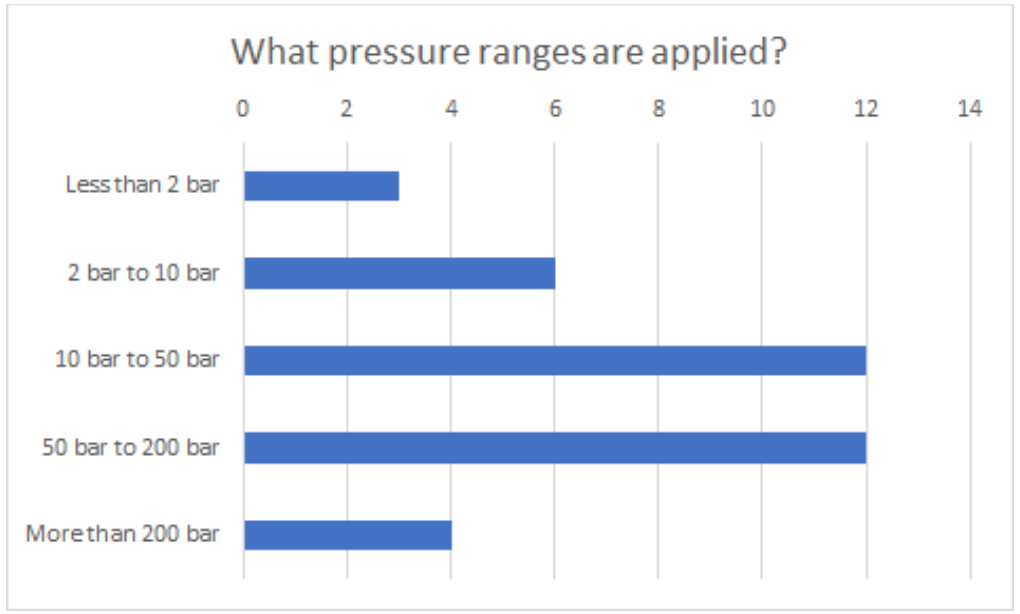


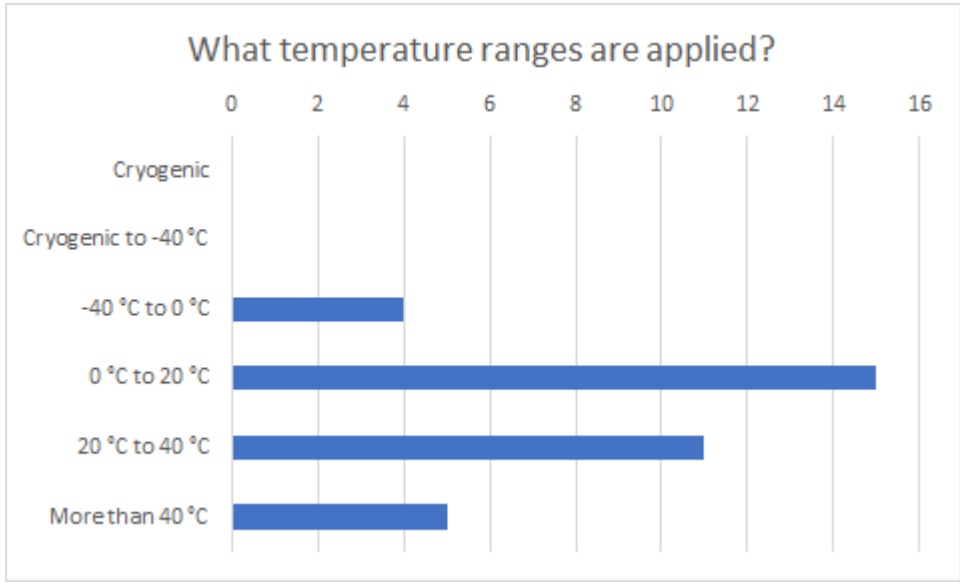


Other category: used mainly to indicate that «no fiscal meter is installet yet» (4 answers), or different technology (2 answers)

MOTIVATION


What flow ranges are applied?
0
2
4
6
8
10
12
14
0 Sm³/h to 25 Sm³/h
25 Sm³/h to 250 Sm³/h
250 Sm³/h to 2500 Sm³/h
2500 Sm³/h to 25 000 Sm³/h
25 000 Sm³/h to 250 000 Sm³/h


What pressure ranges are applied?
0
2
4
6
8
10
12
14
Less than 2 bar
2 bar to 10 bar
10 bar to 50 bar
50 bar to 200 bar
More than 200 bar


What temperature ranges are applied?
0
2
4
6
8
10
12
14
16
Cryogenic
Cryogenic to -40 °C
-40 °C to 0 °C
0 °C to 20 °C
20 °C to 40 °C
More than 40 °C

SURVEY RESULTS

	ṁ [kg/h]	p [bar(a)] 1	2	3	4	5	6	7	8	9	10	20	30	40	50	60	70	80	90	100	200	>200
Small Nozzle	0.0075																					
	0.75																					
	0.40																					
	8																					
	13																					
	20																					
Large Nozzle	50																					
	120																					
Master Meter	400																					
	500																					
	5 000																					
	28 000																					
	225 000																					

Indicates the survey demands for flow.

Indicates the demands with most response for calibration according to the survey.

Indicates the existing calibration facilities for hydrogen.

Clearly, there is a gap. This project will make plans and strategies to cover the gap.

FACILITIES

- New facilities
- Facility under construction
- Planned facility
- Existing facilities

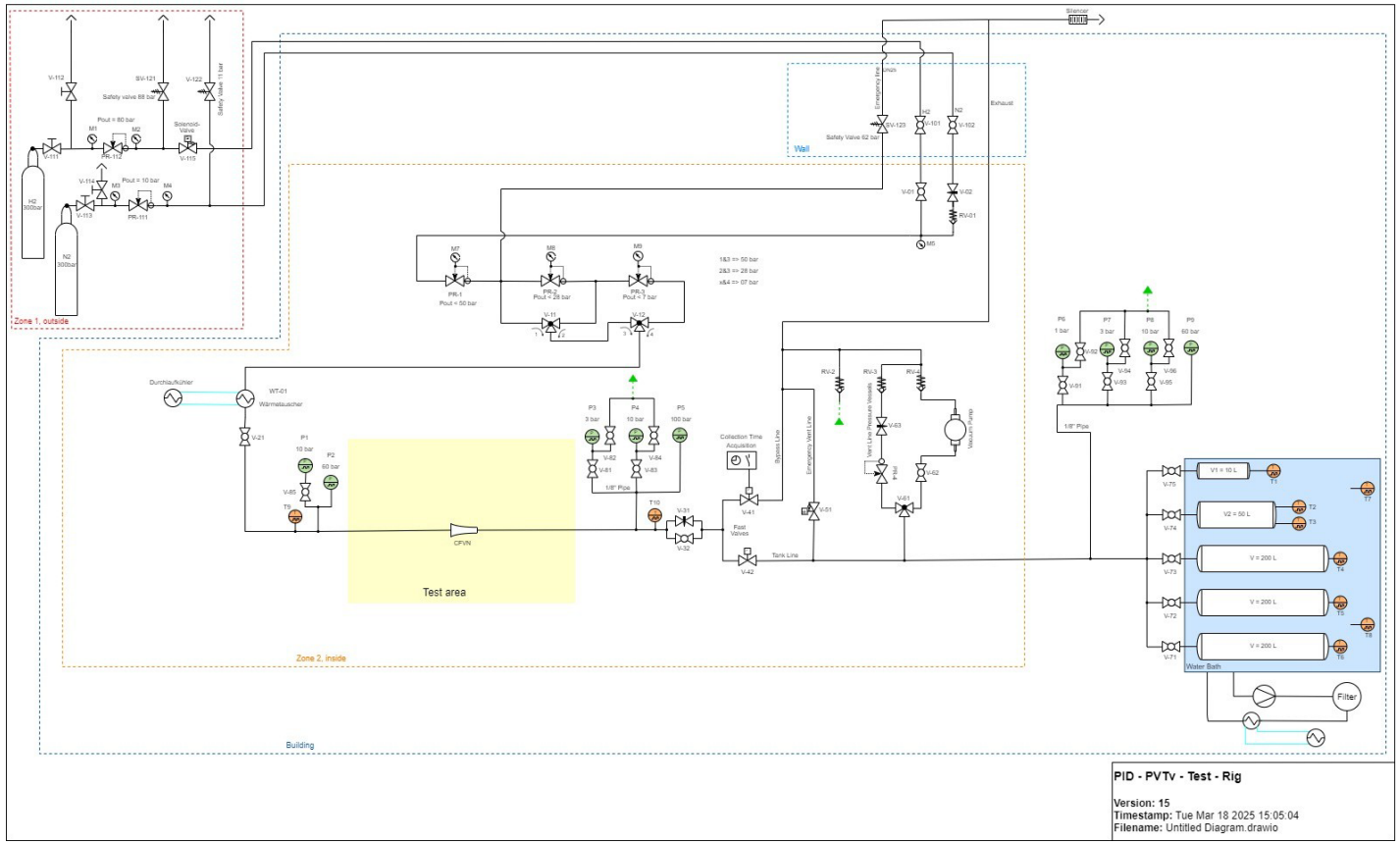
FACILITIES (BACKGROUND)

- New facilities
- Facility under construction
- Planned facility
- Existing facilities

Background: partners outlined in red started design and construction work on primary H2 flow standards, as part of the work in the EMPIR project MetHyInfra. All of them pVTt type systems.
https://www.methyinfra.ptb.de/the-project/

METAS FACILITY

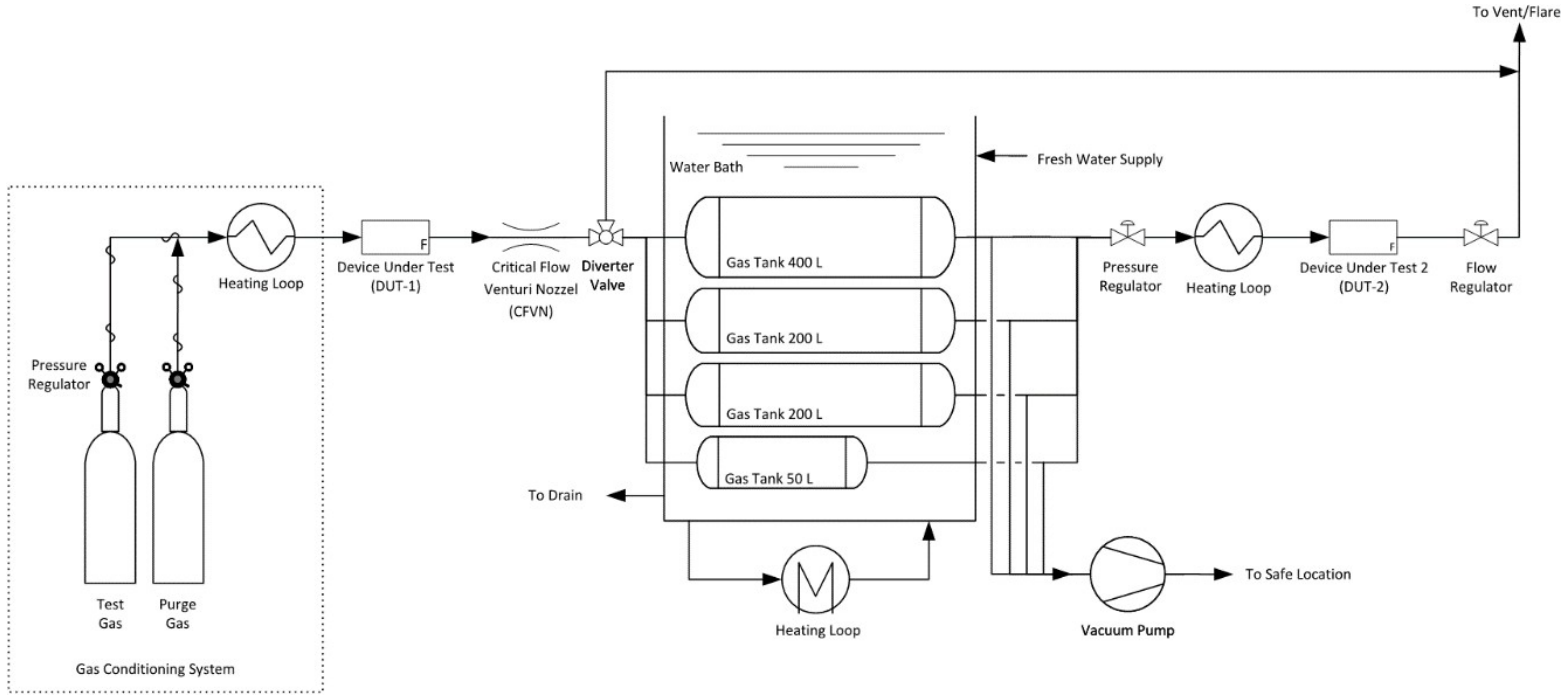
- **Under construction, ready for H_2 in September 2025**
- Primary standard (pVTt)
- Flow rate range: (0 – 180) Nm^3/h
- Uncertainty < 0.3 % (k=2)
- Gases: H_2, HENG, N_2



Contact person: Marc de Huu, METAS.

JV FACILITY

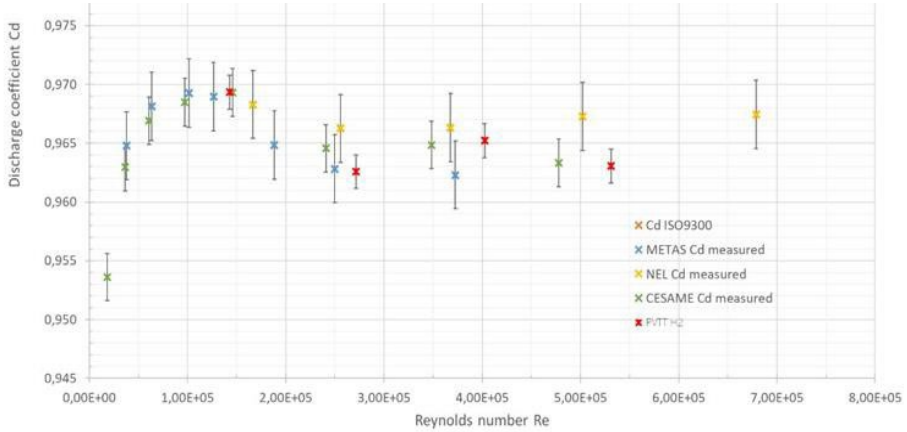
- **Planned** — tender published
  - Not available in time
- Primary or secondary level
- Flow rate range: 0 – 100 Sm^3/h
- Uncertainty < 0.3 % (k=2)
- New: adapted with a new line for domestic gas meter testing
- Gases: H2, NG, blends, N2

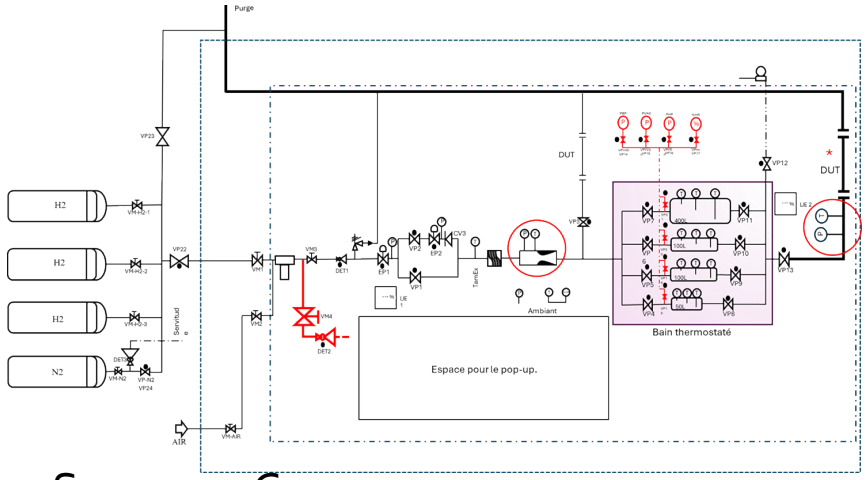


Contact person: Edvardas Venslovas, Justervesenet.

CESAME FACILITY

- **Adaptation of hydrogen flow standards for NG blends**
  - CESAME: validation tests ongoing
  - First results with MetHyInfra WP2 nozzles obtained.
  - Results compared to CESAME, METAS, NEL results.
  - These results seem to be in line. (See figure)
  - Characteristics of the bench:
    - 1-80 bar for nozzles calibration
    - 1 bar for meters calibration
    - 0.4 kg/h - 30 kg/h
    - Targeted uncertainty 0.3 %
    - Air, H_2, N_2, CH_4, blends





Contact person: Hamidou Soumare, Cesame.

CESAME FACILITY

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  - First results with MetHyInfra WP2 nozzles obtained.
  - Results compared to CESAME, METAS, NEL results.
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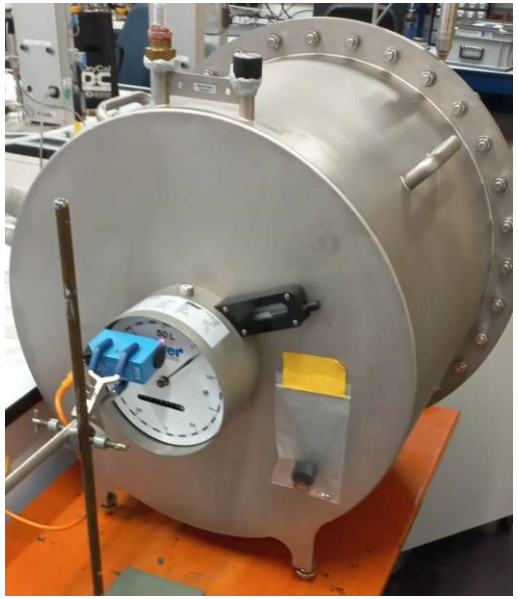
    - 1 bar for meters calibration
    - 0.4 kg/h - 30 kg/h
    - Targeted uncertainty 0.3 %
    - Air, H_2, N_2, CH_4, blends

VSL FACILITY

- **Calibration facility for household gas meters using 98 % hydrogen blends (VSL)**
- Flow rate range: 0 – 18 m^3/h
- Pressure: atmospheric
- Tested with various gases, and with helium
  - Calibration curve constructed based on testing. Behaviour for hydrogen assumed on the universal working of drum-type gas meters



Front and rear parts of the drum-type gas meter (the reference)

Contact person: Marcel Workamp, VSL.

EXISTING FACILITIES — FORCE AND VSL

FORCE Piston Prover
Flow rate range: 2 – 400 m^3/h
Pressure: 1 – 66 bar
Upgraded to work with HENG
for this project.

VSL Gas Oil Piston Prover
Flow rate range: 3 – 230 m^3/h
Pressure: 1 – 62 bar

- EuReGa participants

Contact person: Kurt Rasmussen, FORCE.

Contact person: Marcel Workamp, VSL.

TESTING — TWO SETS OF TESTS

MET4H2

Domestic meter testing
(98 % H2 + impurities)

TÜV SÜD (1)

VSL National Metrology Institute

CESAME-exadébit SA

Analysis + reporting

Justervesenet

ČESKÝ METROLOGICKÝ INSTITUT

Intercomparison
(HENG, 20% H2)

FORCE TECHNOLOGY

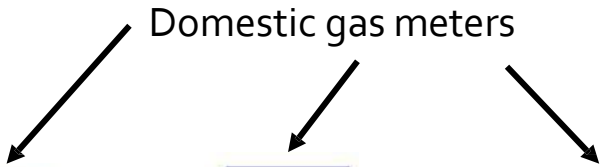
VSL National Metrology Institute

CESAME-exadébit SA

METAS

(1): Participating with domestic gas meter facility for H2, not primary standard

TESTING — DOMESTIC GAS METERS



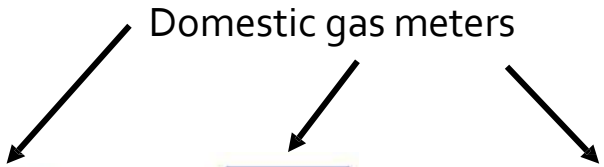
Domestic meter testing
(98 % H2 + impurities)

Intercomparison
(HENG, 20% H2)

Test different technologies:
- Thermal mass
- Rotary meter
- USM

Not an intercomparison.
Meters not necessarily circulated.

TESTING — DOMESTIC GAS METERS



Domestic meter testing
(98 % H2 + impurities)

Test different technologies:
- Thermal mass
- Rotary meter
- USM

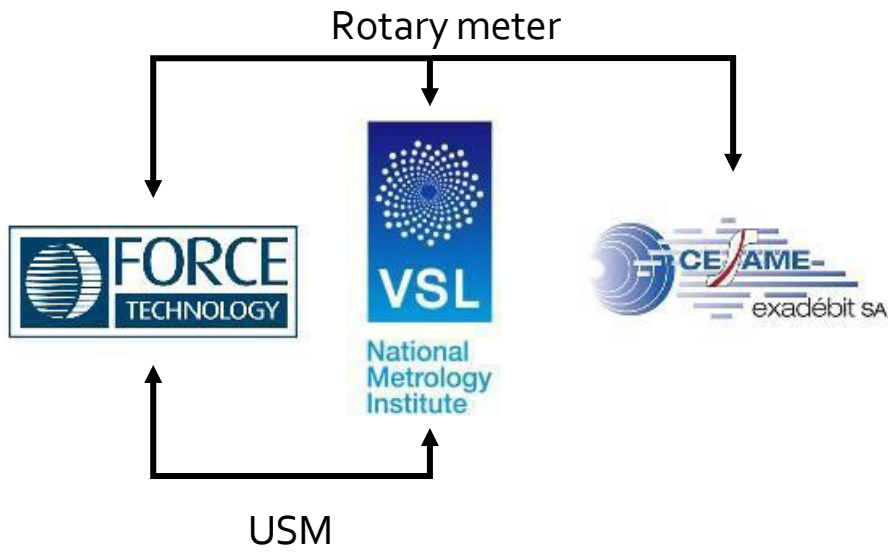
Central question: Are the domestic gas meters within MPE of class 1.0 or 1.5 in MID? Does the presence of impurities up to 2 % by vol. alter behavior?

Intercomparison
(HENG, 20% H2)

INTERCOMPARISON

Domestic meter testing
(98 % H2 + impurities)

Intercomparison
(HENG, 20% H2)



(ITRON Delta S-Flow G100 2" meter)

- Q_{max} = 160 m³/h, P_{max} = 101.2 bar

- Q_{max} = 200 m³/h, P_{max} = 98 bar(g)

FLOWSIC550

SUMMARY

- 2 new facilities finished
- 1 facility under construction, 1 facility planned
- 1 facility introduced hydrogen measurement
- 2 sets of tests planned
  - Domestic meters
  - Rotary + USM

MET4H$_2$

Thank you!

Edvardas Venslovas, on behalf of WP2 partners

Contact: eve@justervesenet.no

Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or EURAMET. Neither the European Union nor the granting authority can be held responsible for them.

The project has received funding from the European Partnership on Metrology, co-financed from the European Union's Horizon Europe Research and Innovation Programme and by the Participating States.

EUROPEAN PARTNERSHIP

Co-funded by the European Union

METROLOGY PARTNERSHIP

EURAMET

Improving water vapour measurement in industrial hydrogen applications

Rugiada Cuccaro & Rezvaneh Nobakht (INRiM)

ENERGY GASES

METCCUS

VSL

MET4H2

BiometCAP

21GRD05 - Metrology for the hydrogen supply chain
M30 Stakeholder Workshop
27th of March 2025, Delft

IMPROVING WATER VAPOUR MEASUREMENT IN INDUSTRIAL HYDROGEN APPLICATIONS

R. Cuccaro*, R. Nobakht, V. Fernicola

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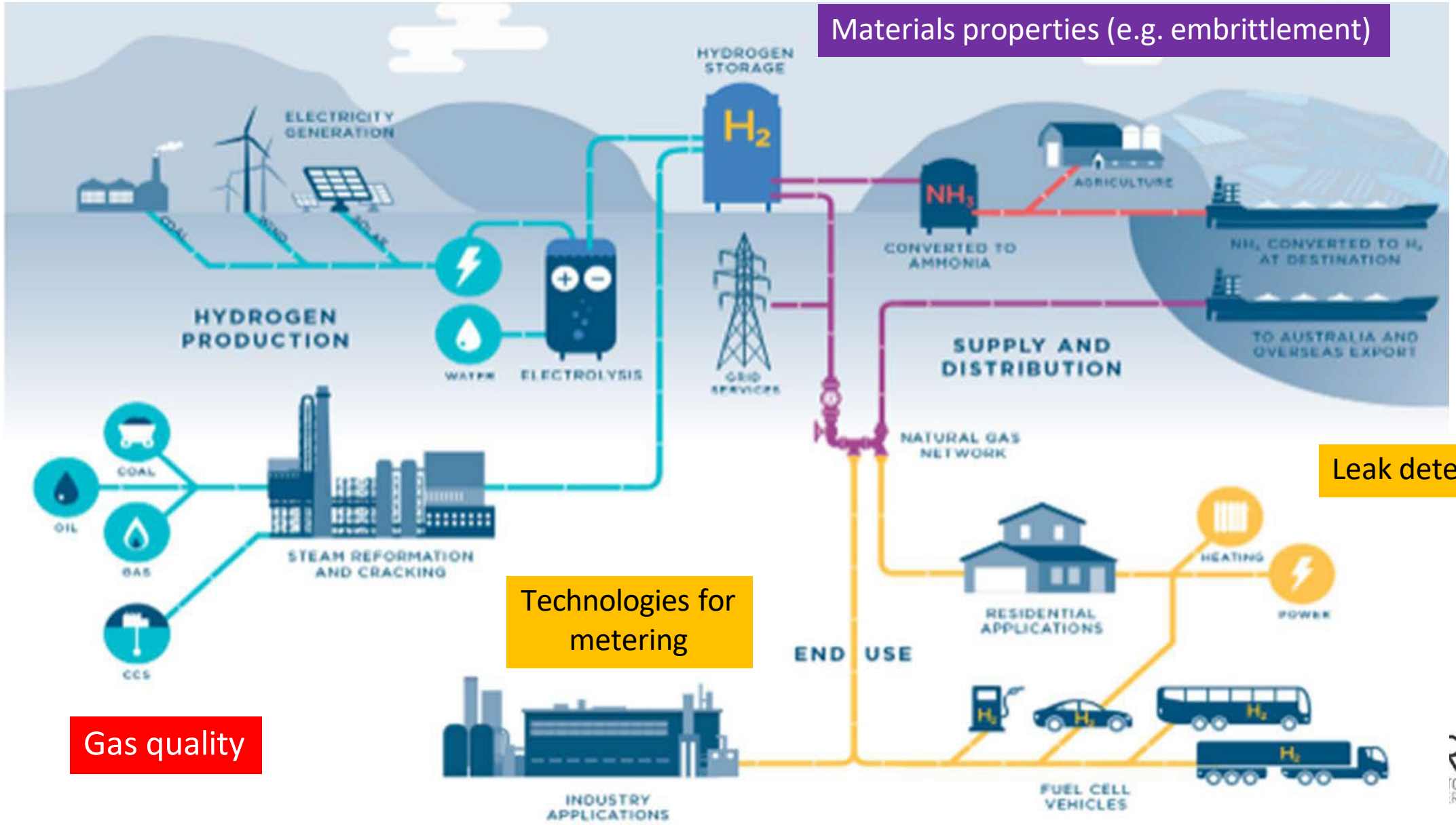
Energy Transition Challenges



Materials properties (e.g. embrittlement)

Leak detection

Technologies for metering

Gas quality

Hydrogen sources impact on gas quality

GREEN

Renewable hydrogen: refers to hydrogen produced through the electrolysis of water and with the electricity stemming from renewable sources. The full life-cycle greenhouse gas emissions of the production of renewable hydrogen are close to zero.

BLUE

Fossil-based hydrogen with carbon capture: A subpart of fossil-based hydrogen, but where greenhouse gases emitted as part of the hydrogen production process are captured.

GREY

Fossil-based hydrogen: refers to hydrogen produced through a variety of processes using fossil fuels as feedstock, mainly the reforming of natural gas or the gasification of coal. This represents the bulk of hydrogen produced today.

Hydrogen quality requirements

Quality control of H_2 leads to an increase in the performance and lifetime of fuel cells and improves the fair trade market.

H_2 INJECTED IN THE NG GRID

Parameter	Unit	Min	Max
Hydrogen	mol - %	98.0	-
Carbon monoxide	ppm	-	20
Total sulphur content	mg S/m³ (n)	-	21
Carbon dioxide	ppm	-	20
Hydrocarbons (including Methane)	mol-%	-	1.5
Inerts (Nitrogen, Argon, Helium)	mol-%	-	2.0
Oxygen	ppm (mol)	-	10
Total halogenated compounds	ppm (mol)		0.05
drocarbon lewpoint	°C at 1-70 bar(a)		-2
Water dewpoint	**°C at 70 bar(a)**	**-**	**-8**

Amount fraction limit
58 ppm

EASEE-gas, CBP 2022-001/01 Hydrogen Quality Specification

H_2 FOR PEM FUEL CELL ROAD VEHICLE APPLICATION

Contaminant	Amount fraction limit / ppm
Total hydrocarbons	2
Methane	100
Oxygen	5
Helium	300
Nitrogen	300
Argon	300
Carbon dioxide	2
Carbon monoxide	0.2
Total sulphur compounds	0.004
Formaldehyde	0.2
Formic acid	0.2
Ammonia	0.1
Halogenated compounds	0.05
Water	**5 ppm**

ISO 14687:2019, Hydrogen fuel quality product specification

Hydrogen quality: the case of water vapour

One of the most challenging impurities for hydrogen quality control is **water vapour**.

Water vapour carried over into the hydrogen gas creates significant problems within distribution, storage, HRS, on-board vehicle systems.

- Water condensation on HRS nozzle
- Acid formation

Improving measurement in the range
5 ppm < x_w < 50 ppm in the field

- **Common practice: sensor calibration in Air/N_2**
- **Need: sensor calibration in H_2 for traceable and robust quality control**

State of the art of industrial process measuring devices

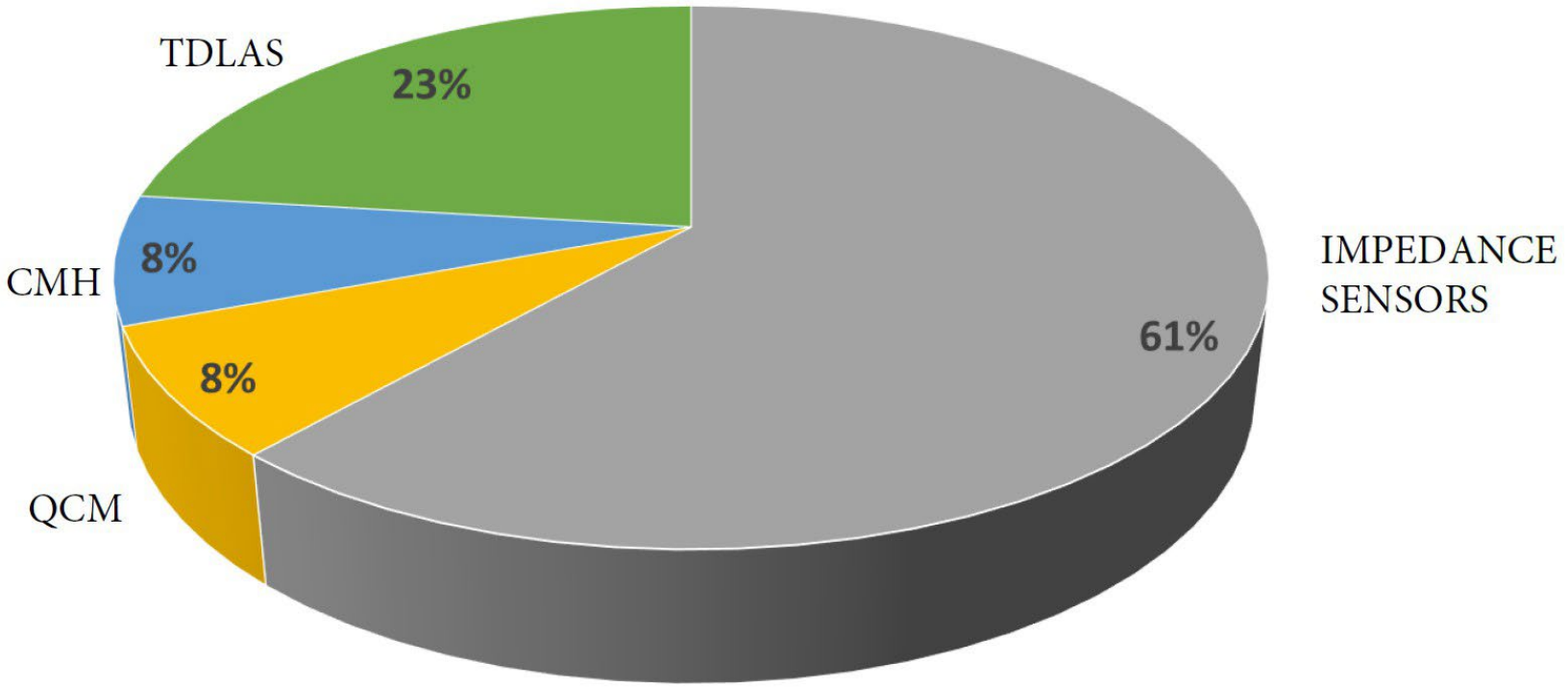
Example of process measuring devices for traceable measurements of water in H_2NG **mixtures** and **pure** H_2.

Aluminum oxide technology sensors

Quartz Crystal Microbalance

Infrared laser spectroscopy (e.g., CEAS, CRDS, TDLAS)

Industrial measuring technology currently implemented in NG transmission grids



CMH: Chilled mirror hygrometer
QCM: Quartz microbalance hygrometers
TDLAS: Tunable diode laser absorption spectrometers

Metrology for the hydrogen supply chain

MET4H$_2$

THE PROJECT

The aim is to develop **calibration** and **measurement methods**, as well as improve standards, to facilitate reliable, traceable, and accurate onsite measurement for the safe use of pure hydrogen in leak testing, flow measurement, material compatibility assessment, and **quality assessment**.

WP3 – HYDROGEN GAS QUALITY

The aim of this work package is to develop the metrological tools to ensure reliable and traceable measurements necessary to apply appropriate quality control on hydrogen throughout the supply chain to support the transition into green hydrogen. Hydrogen gas quality is a critical parameter in an emerging supply chain with a large scope of applications (i.e. home boiler, industry heat, power to electricity, or transport).

- ❑ **TASK 3.1 – DEVELOPMENT OF GAS SAMPLING METHODS SUITABLE FOR ON-LINE AND OFF-LINE USE**
- ❑ **TASK 3.2 – IMPROVING MEASUREMENT QUALITY AND CALIBRATION FOR WATER VAPOUR AMOUNT FRACTION**
- ❑ **TASK 3.3 – GAS QUALITY FOR ALKALINE ELECTROLYSER AND INDUSTRIAL DEMONSTRATION**
- ❑ **TASK 3.4 – GAS QUALITY FOR HYDROGEN DISTRIBUTION**

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Improving measurement quality and calibration for water vapour amount fraction

The objective is to provide the hydrogen community with a reliable and proven system to generate reference water vapour values.

DEVELOPMENT OR UPGRADE OF HUMIDITY GENERATOR IN H_2

- INRIM will design, develop and validate a transportable precision humidity generator (TPHG).
  - Water vapour amount fraction between 0.5 µmol/mol and 50 µmol/mol at pressures up to 5.5 MPa (or equivalent between -55 °C and -10 °C pressure dew point).
  - Target uncertainty of water amount fraction between 3 % and 5 %.
- VSL will upgrade its current high-pressure frost-point generator to be used with hydrogen in the range of 0.5 µmol/mol up to 100 µmol/mol up to 6 MPa.

PREPARATION OF PRIMARY GAS REFERENCE MATERIAL OF WATER VAPOUR IN GAS CYLINDERS

NPL will trial the preparation of primary gas reference material of 0.5 µmol/mol water vapour in 3 types of hydrogen gas cylinders. NPL will evaluate the accuracy and stability of the cylinders.

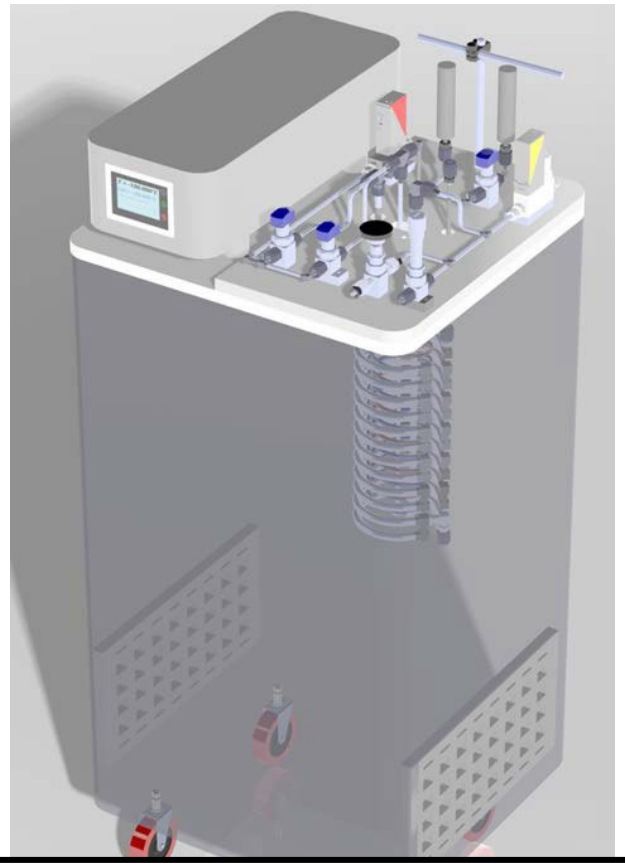
ORGANISATION OF THE FIRST EVER COMPARISON INVOLVING DYNAMIC HUMIDITY GENERATORS IN HYDROGEN.

D5: "*Report on the results of the intercomparison on trace water in hydrogen standards over the nominal range from 0.5 µmol/mol to 50 µmol/mol with conclusions on the recommendations for future improvements*".
(NPL, INRiM, VSL, DTU, POLITO)

INRiM - Precision Humidity Generator (PHG) for H_2

MET4H$_2$

Design



System in operation

Heat exchanger and saturator

TECHNICAL CHARACTERISTICS:

- **Frost point temperature: -55 °C < T_{fp} < -10 °C at pressure**
- **Water vapor amount fraction: 0.5 µmol/mol < x_w < 50 µmol/mol**
- Pressure: 0.1 MPa < P < 5.5 MPa; tested up to 3 MPa
- Target Uncertainty: 3 % < $u_r(x_w)$ < 5 %

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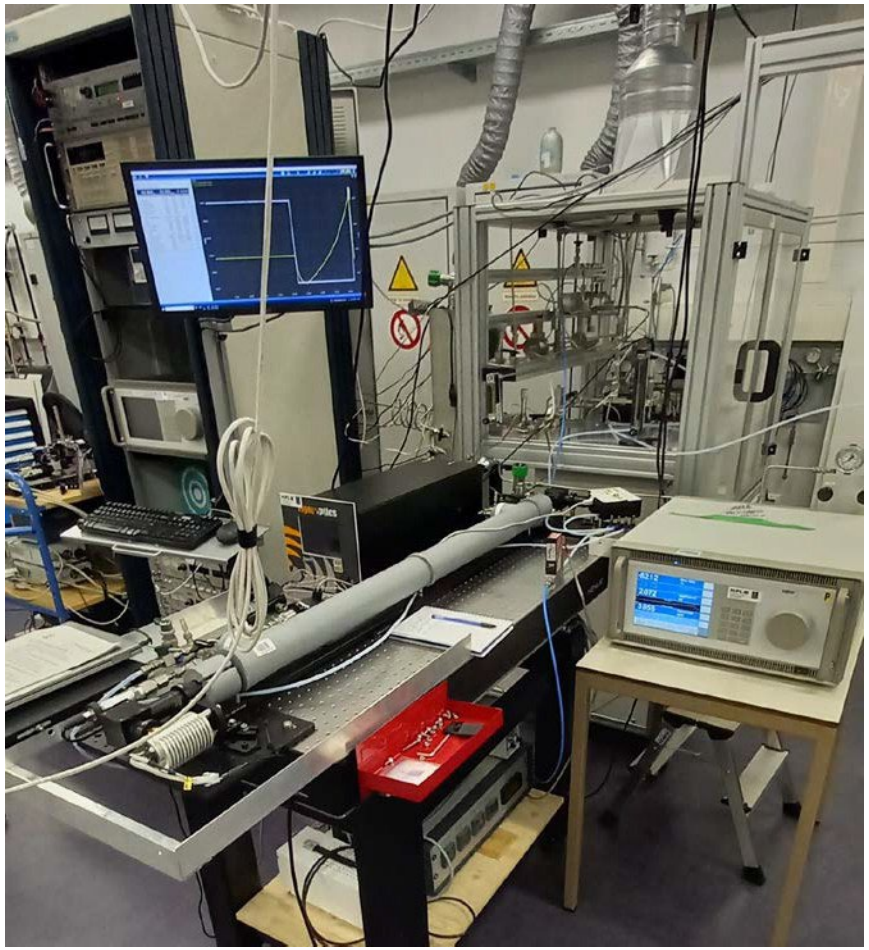
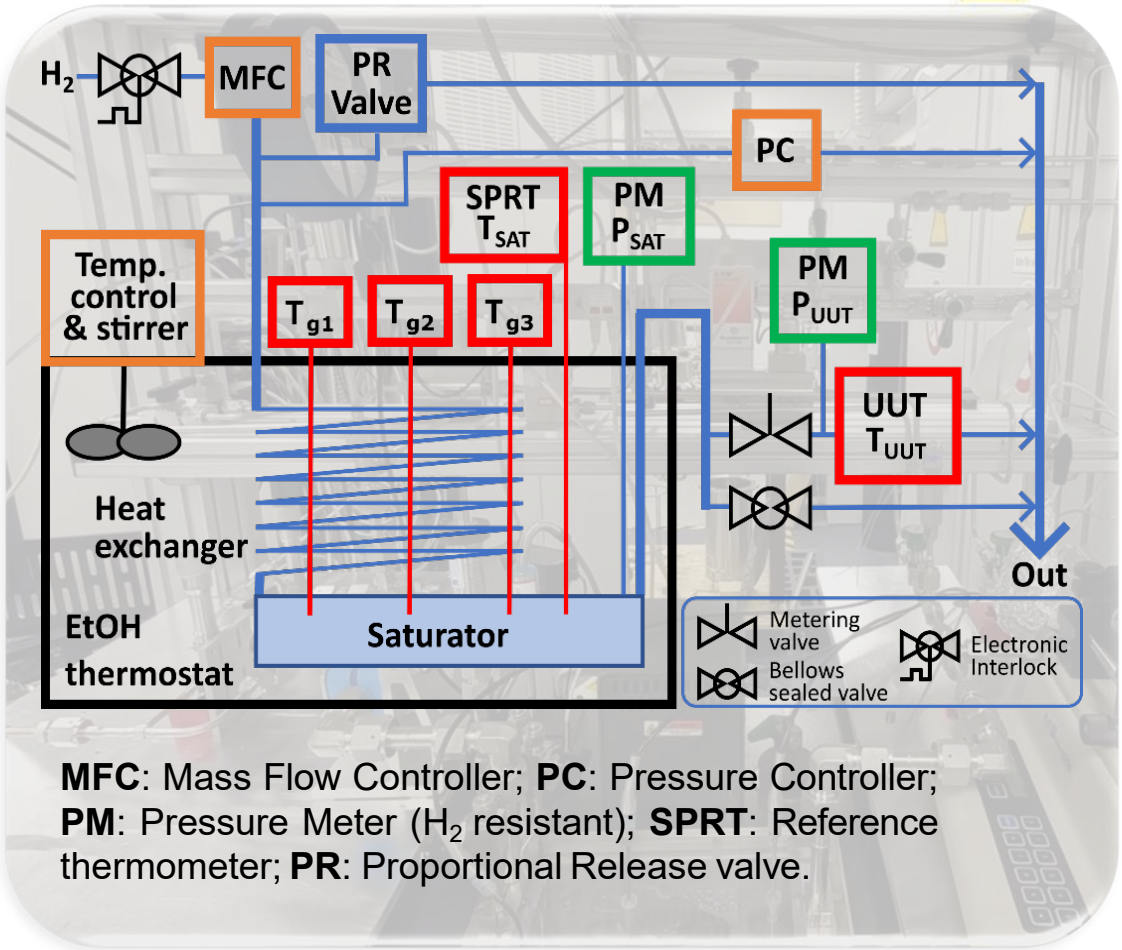
VSL - High-Pressure Dewpoint Generator





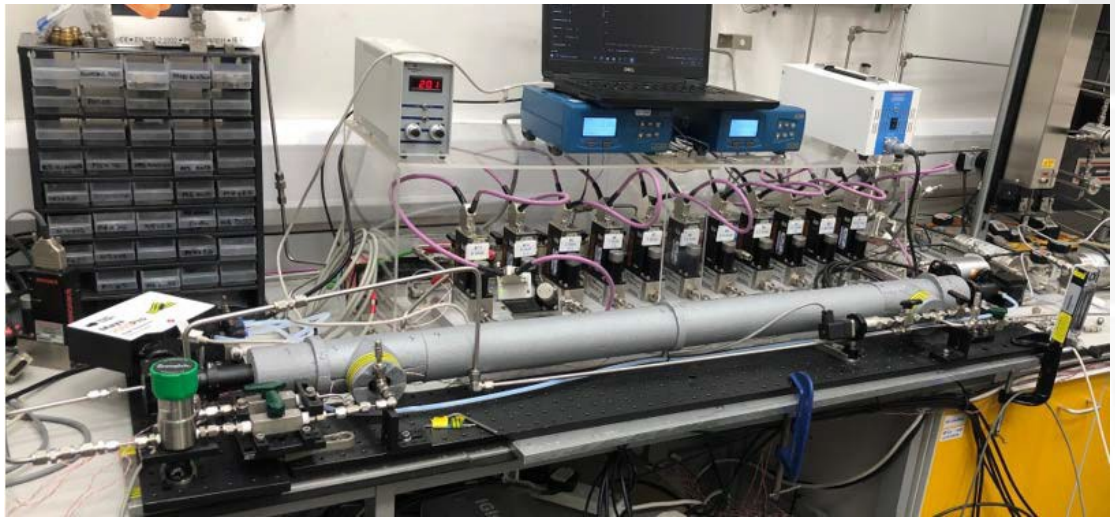
MFC: Mass Flow Controller; **PC**: Pressure Controller; **PM**: Pressure Meter (H_2 resistant); **SPRT**: Reference thermometer; **PR**: Proportional Release valve.

TECHNICAL CHARACTERISTICS:

- **Frost point temperature: -80 °C < T_{fp} < +20 °C at pressure**
- **Water vapor amount fraction: 0.5 µmol/mol < x_w < 100 µmol/mol**
- Pressure: 0.1 MPa < P < 6 MPa; tested up to 6 MPa
- Target Uncertainty: 3 % < $u_r(x_w)$ < 5 %

Contact:
Matthijs Panman
mpanman@vsl.n

NPL - Multi-gas, multi-pressure primary standard humidity generator



TECHNICAL CHARACTERISTICS:

- **Frost point temperature: -60 °C < T_{fp} < +15 °C at pressure**
- **Water vapor amount fraction: 0.5 µmol/mol < x_w < 0.5 %**
- Pressure: 0.1 MPa < P < 3 MPa; tested up to 3 MPa

Contact:
Paul Carroll
paul.carroll@npl.co.uk

National Physical Laboratory

Ongoing inter-laboratory comparison of water vapour realisations

NPL, INRIM, VSL, DTU, POLITO: Inter-laboratory comparison of water vapour realisations and measurements in hydrogen in the range of amount fractions between nominally 0.5 µmol mol^{-1} and 50 µmol mol^{-1}

Inter-laboratory comparison of standards for trace water in hydrogen over the nominal range -60 °C to -15 °C frost-point temperature (0.5 µmol mol^{-1} to 50 µmol mol^{-1})

Inter-laboratory comparison protocol

Table 2 Measurement values at 0.2 MPa test pressure:

Nominal Frost-point temperature / °C	Nominal equivalent water vapour amount fraction / µmol mol^{-1}
-60.7	5
-52.3	15
-42.3	50

Table 3 Measurement values at 3 MPa test pressure:

Nominal Frost-point temperature / °C	Nominal equivalent water vapour amount fraction / µmol mol^{-1}
-59.0	0.5
-40.0	5
-17.3	50

Figure 1 Overview of the comparison schedule

Table 1 List of the transfer standard hygrometers.

Manufacturer	Model	Serial number	Measurement principle	Operating range	Inlet pressure range / MPa	Compatible gas species
MBW	373 LX-HP	14-0610	Chilled-mirror condensation	-60 °C to +20 °C	0.1 to 3	Air, N_2, H_2
Tiger Optics	F7700 -ATM	6159-145-0	CRDS water vapour spectrometer	0 – 1750 µmol mol^{-1}	0.2 to 0.96	Air, N_2, H_2
DTU	Proto-type	n/a	Far-UV spectroscopy	1 - 300 µmol mol^{-1}	0.1 to 4 (H_2) 0.1 to 10 (N_2)	N_2, H_2

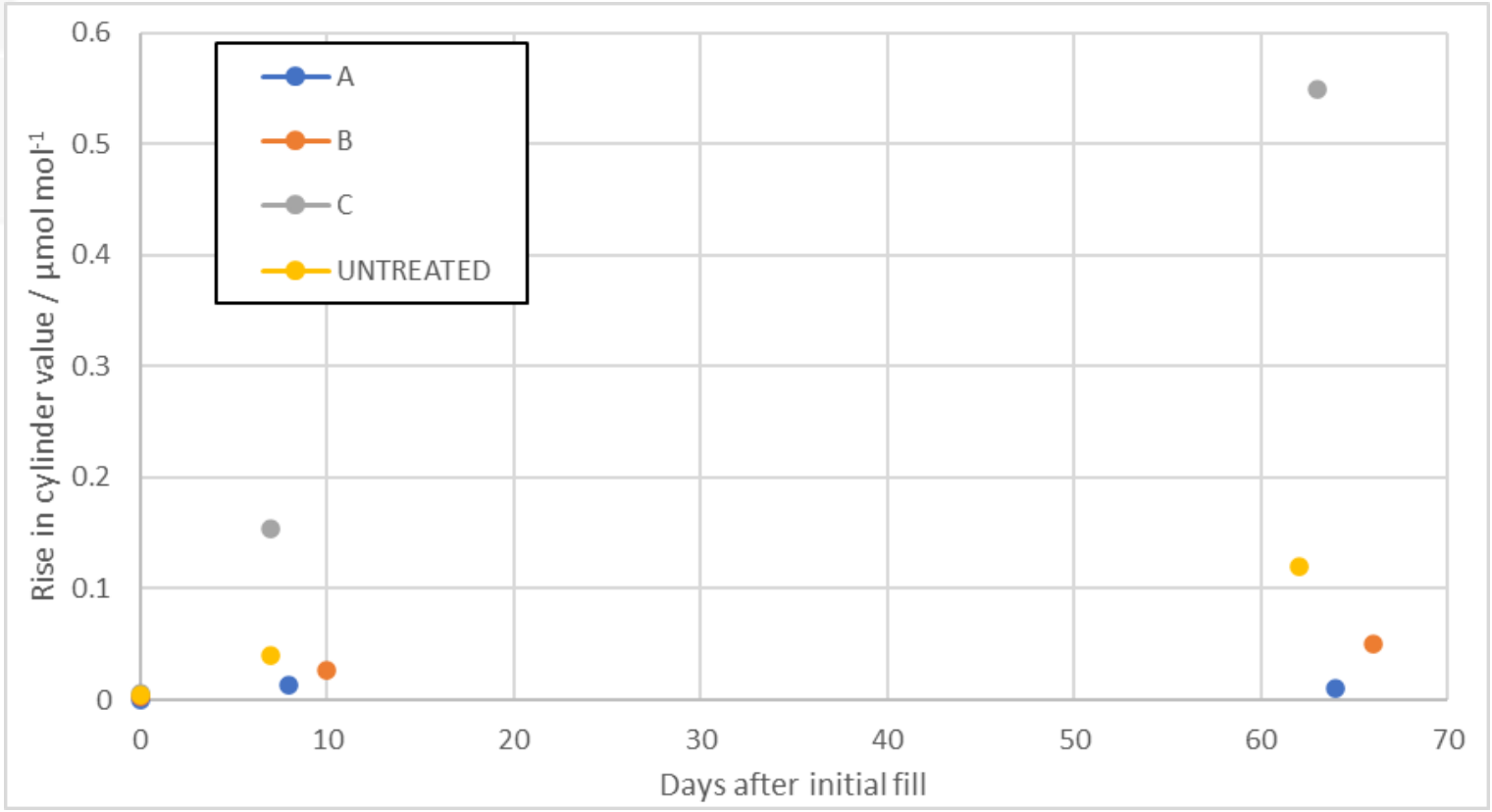
NPL - H_2O reference cylinder production with primary humidity traceability

MET4H_2

Preparation of primary gas reference material of 0.5 µmol mol^{-1} water vapour in cylinders.

Novel method transfers NPL multi-gas, multi-pressure primary standard humidity generator traceability to binary H_2O gas mixtures in cylinders.

NPL is evaluating the accuracy and stability of three surface coating types of cylinders + UNTREATED.



10 litre cylinders (Coating types A,B,C and UNTREATED) filled to 3 MPa with 0.5 µmol mol^{-1} water vapour in hydrogen.

Initial measurements of instrument measuring gas from static cylinder all in agreement to within ±0.02 µmol mol^{-1} when compared with measurements of dynamic source of reference gas from NPL generator.

After 2 months measurements from cylinders of two coating types show promising stability.

NPL National Physical Laboratory

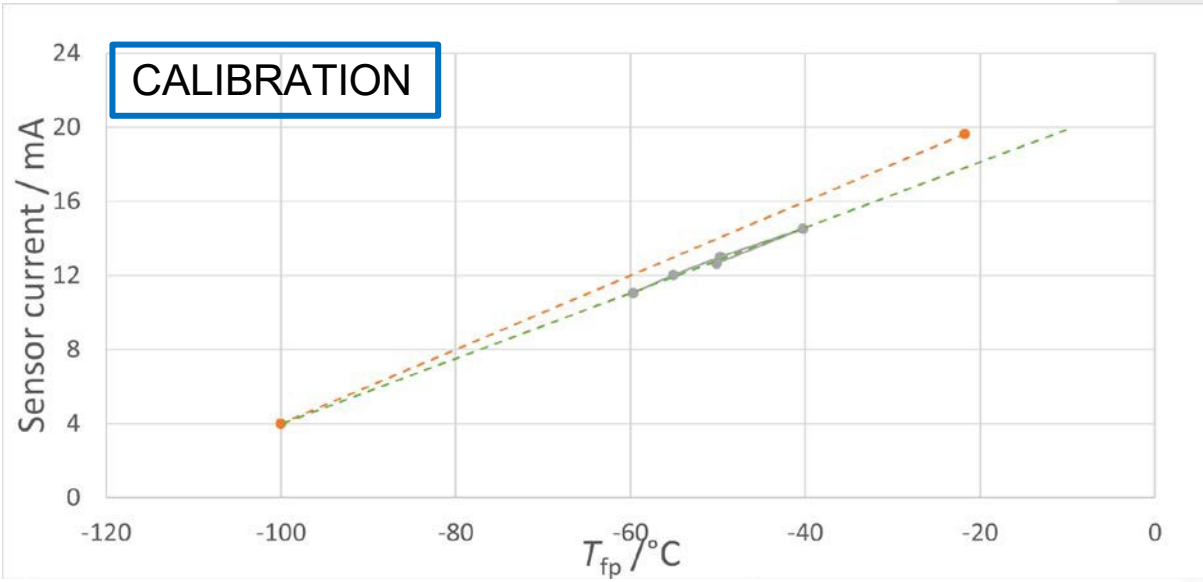
Calibration of industrial dew-point transmitter in N_2 and H_2

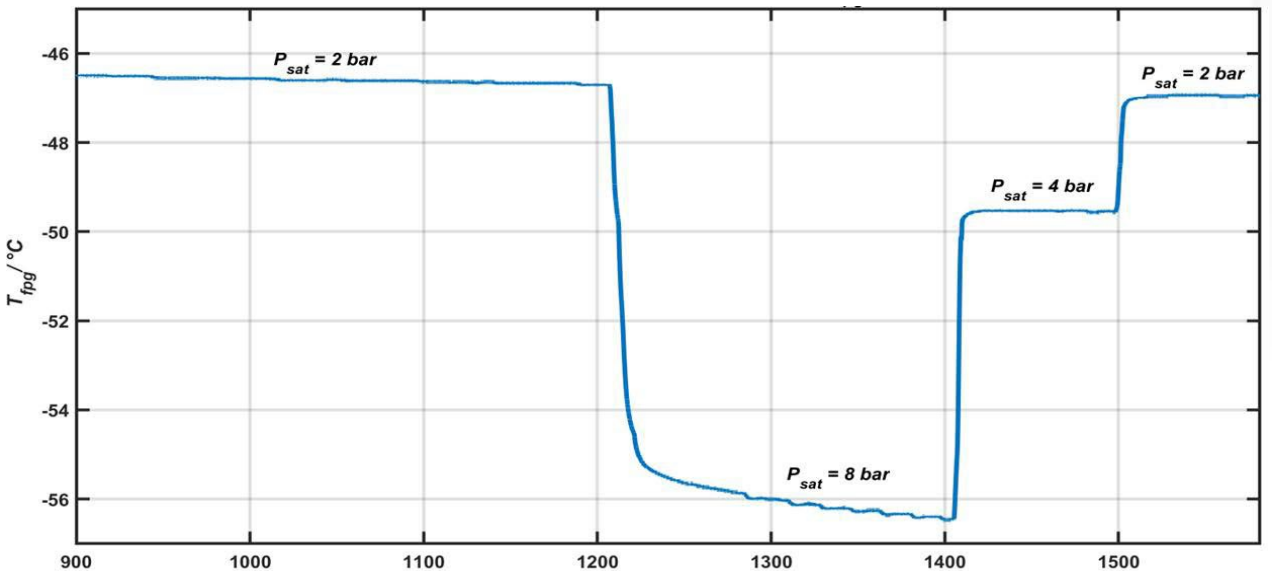
MET4H_2

Impedance sensors: Capacitance Aluminium Oxide Sensors

Measurement range:
-100 °Cdp up to -20 °Cdp
Pressure rating: 0.01 bar up to 350 bar

Measurement range:
-100 °Cdp up to +20 °Cdp
Pressure rating: up to 450 bar





Online and onsite monitoring at an alkaline electrolyser at the Torino Airport

The demonstration was carried out on the 3 kW AEM electrolyser installed at Torino Airport.

Online and onsite monitoring at an alkaline electrolyser at the Torino Airport

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Online and onsite monitoring at a hydrogen production plant

The demonstration was carried out at the Nippon Gases production plant in San Salvo - Italy

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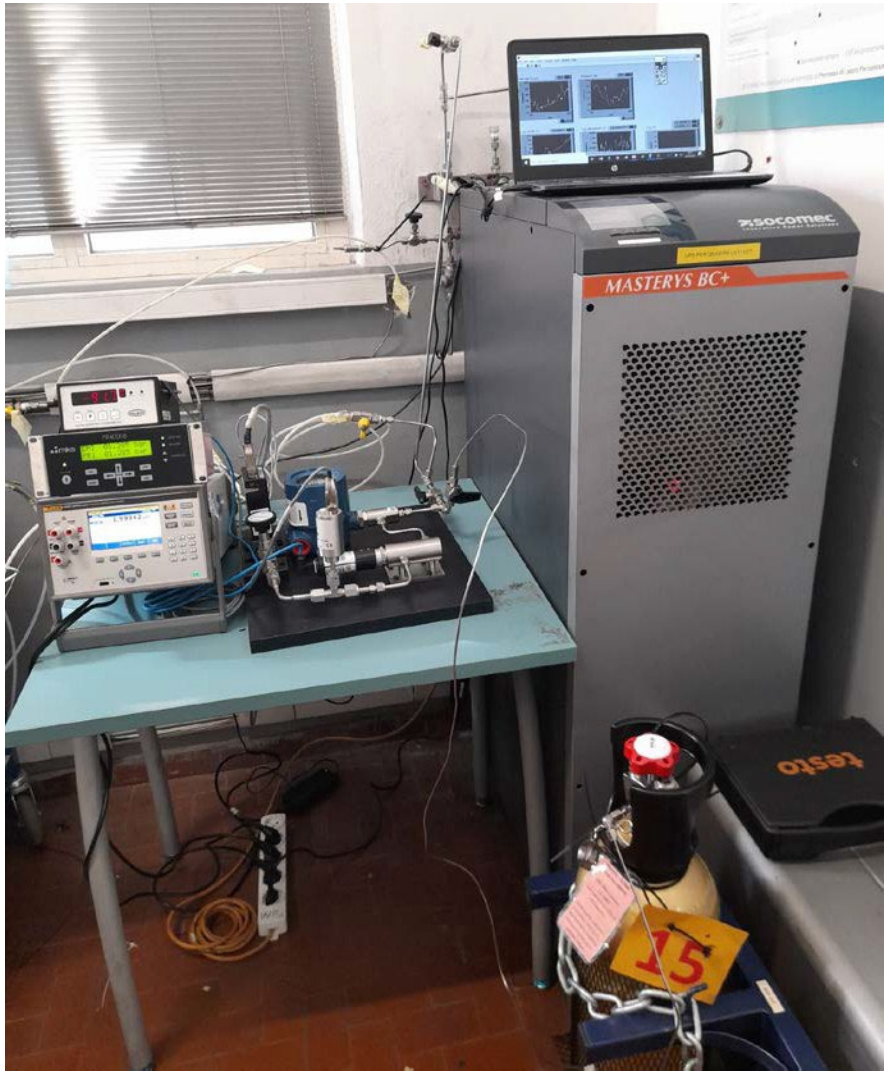

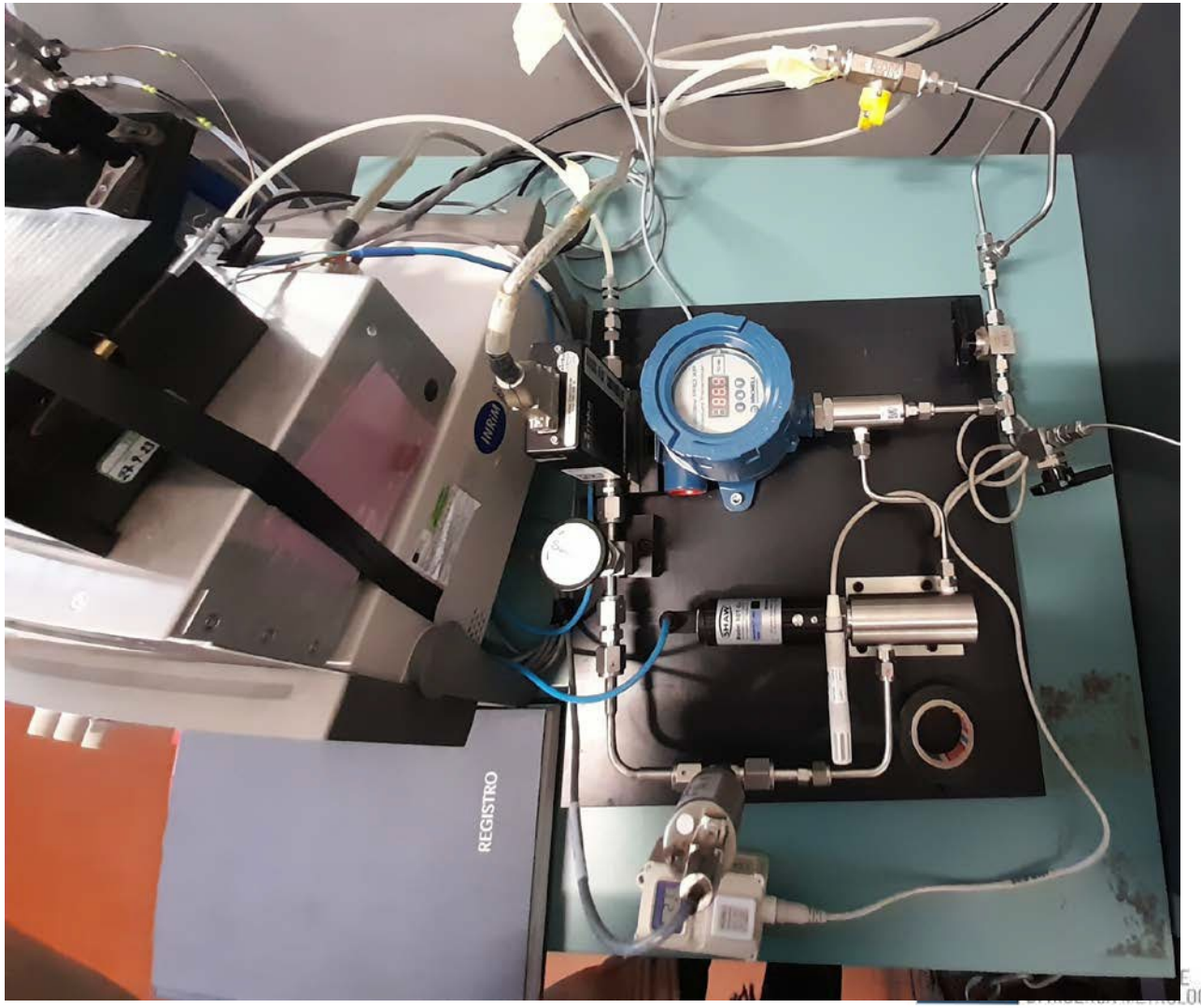

Expected outcomes

D6: *Good practice guide on metrologically traceable quality monitoring in the hydrogen supply chain, including offline measurements and onsite calibration, and recommendations for future improvements of ISO 19880-8 and ISO 21087*

A3.3.8 M36	INRIM, BAM, CEM, DFM, NPL, PTB, VSL, VTT, DTU, ENVIPARK, Nippon Gases, and POLITO will review the good practice guide from A3.3.7. Once agreed by the consortium, the coordinator on behalf of INRIM, BAM, CEM, DFM, NPL, PTB, VSL, VTT, DTU, ENVIPARK, Nippon Gases, and POLITO will submit the guide to EURAMET as deliverable **D6:** *"Good practice guide on metrologically traceable quality monitoring in the hydrogen supply chain, including offline measurements and onsite calibration, and recommendations for future improvements of ISO 19880-8 and ISO 21087".*	**INRIM**, BAM, CEM, DFM, NPL, PTB, VSL, VTT, DTU, ENVIPARK, Nippon Gases, POLITO

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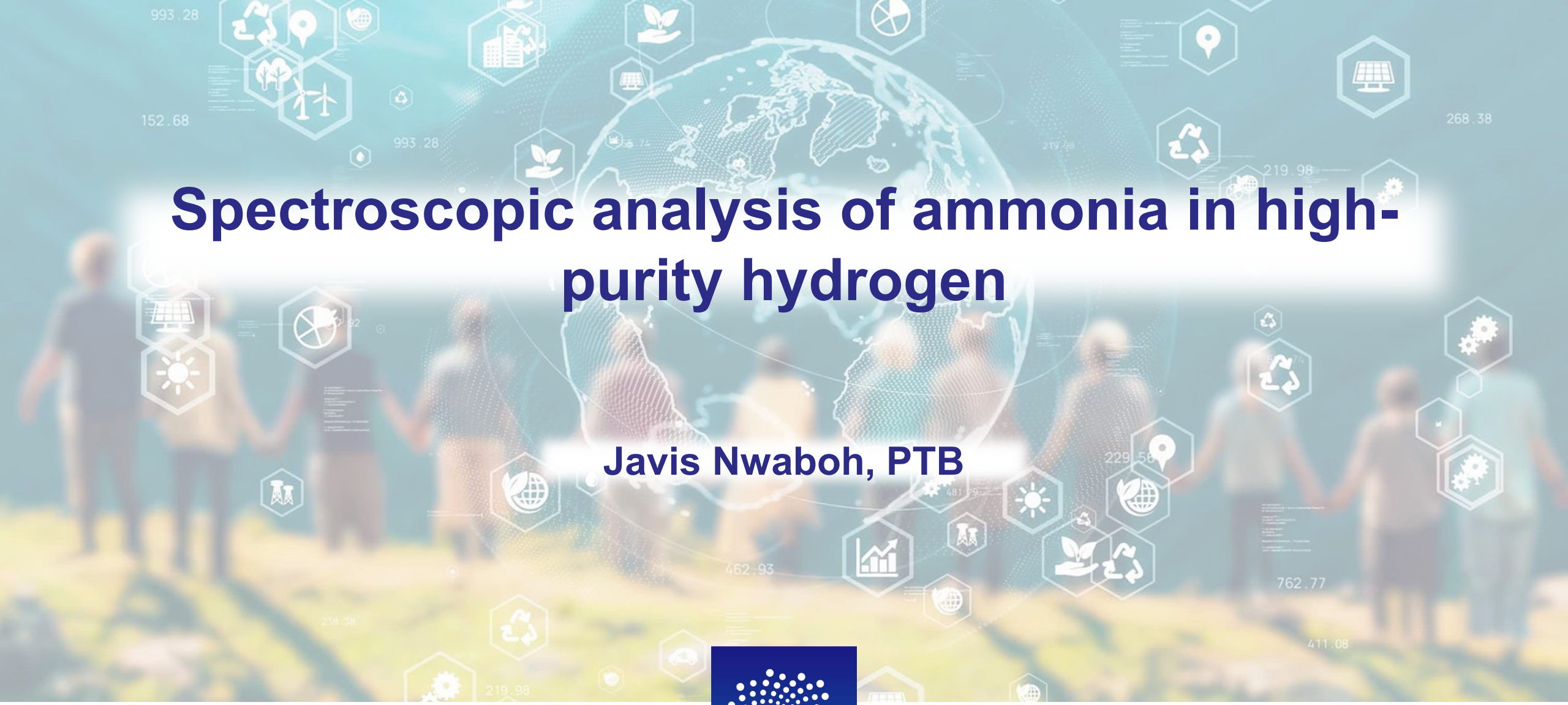
Acknowledgments

This work has been carried out within the project "**Metrology for the hydrogen supply chain**". The project has received funding from the European Partnership on Metrology, co-financed by European Union's Horizon 2020 research and innovation programme and by the Participating States (Grant number: EPM 21GRD05 MET4H2).

THANK YOU FOR YOUR ATTENTION!

This work has been carried out within the project "**Novel methods of testing for measurement of natural gas and hydrogen mixtures**". The project has received funding from the European Union's Horizon programme (Grant number:101101540 — THOTH2 — HORIZON-JTI-CLEANH2-2022-1)



Spectroscopic analysis of ammonia in high-purity hydrogen

Javis Nwaboh, PTB

ENERGY GASES

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VSL

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BiometCAP

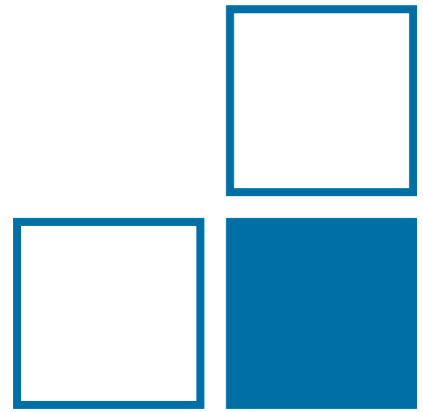
Physikalisch-Technische Bundesanstalt
Braunschweig and Berlin
National Metrology Institute

MET4H2

Spectroscopic analysis of ammonia in high-purity hydrogen

Javis Nwaboh,
Gourab Dutta-Banik, Victor Gorschelev, Volker Ebert, Andrea Pogany

Working group 3.42: Spectroscopic Gas Analysis and Reference data



Joint workshop EMN for Energy Gases (27.03.2025)

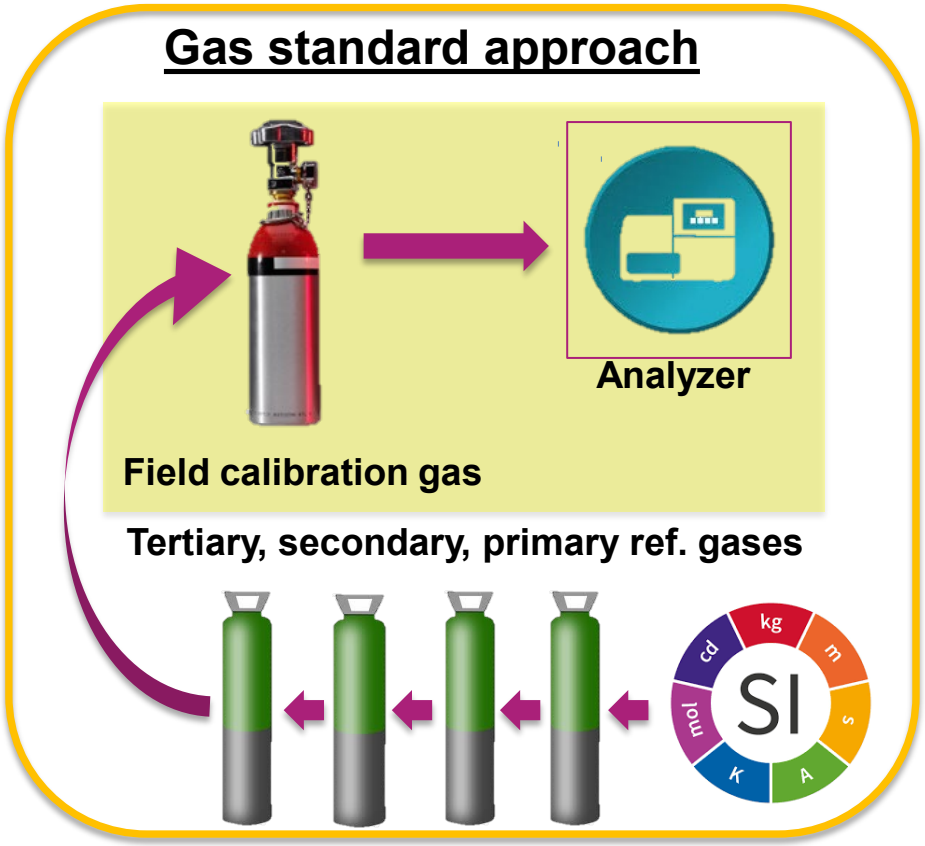
Introduction

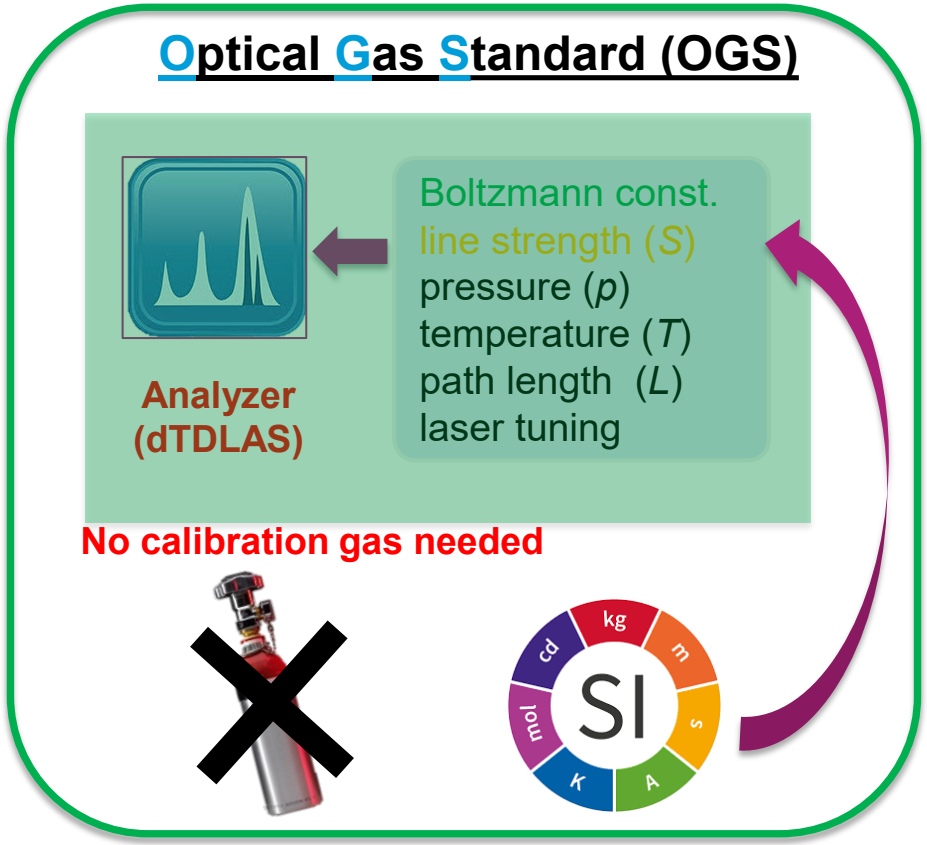
- Hydrogen is an energy gas that is use in a variety of applications e.g. in fuel cells
- NH_3 is a contaminant in high purity Hydrogen
- **Accurate an reliable methods** are needed to quantify NH_3 in H_2 for quality control
- Laser absorption spectroscopy provide an option to develop traceable test methods based e.g. on an **Optical Gas Standard (OGS)**

H_2- Purity analysis

Analyte	Limit (ISO14687), µmol/mol
CO	0.2
H_2O	5.0
NH_3	0.1
O_2	5.0
CH_4	100
HCl	0.05
H_2	NA

Optical Gas Standard (OGS)

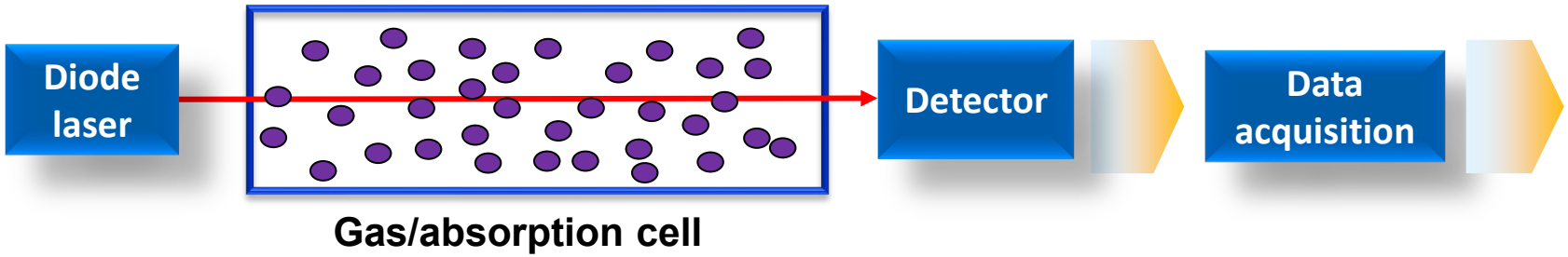


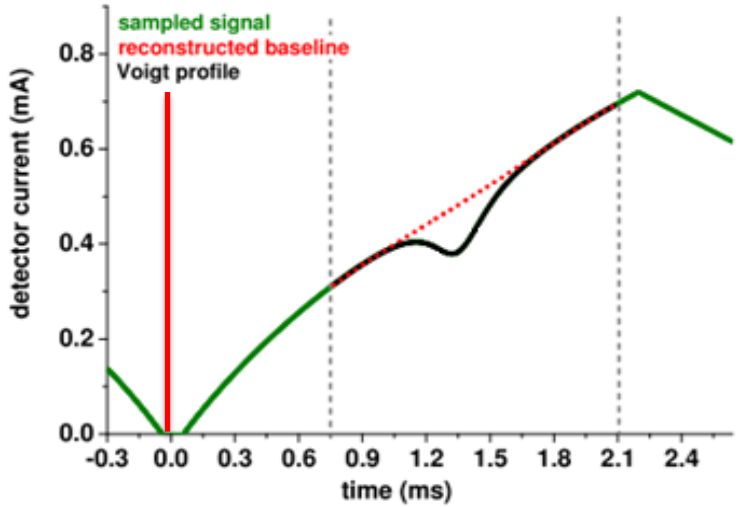


An **Optical Gas Standard** is a laser spectrometer that can provide amount of substance fractions **(concentration)** that are **directly traceable to the SI.**

Example technique for OGS development

direct Tunable Diode Laser Absorption Spectroscopy (dTDLAS)

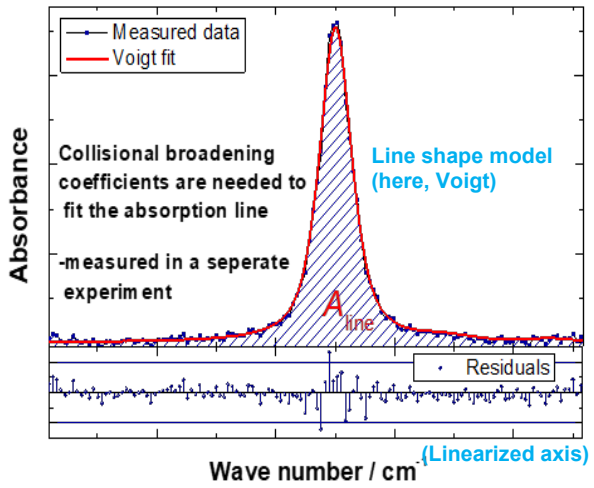




Amount fraction

$$x_{CO} = \frac{k_B \cdot A \cdot T}{S \cdot p \cdot L}$$

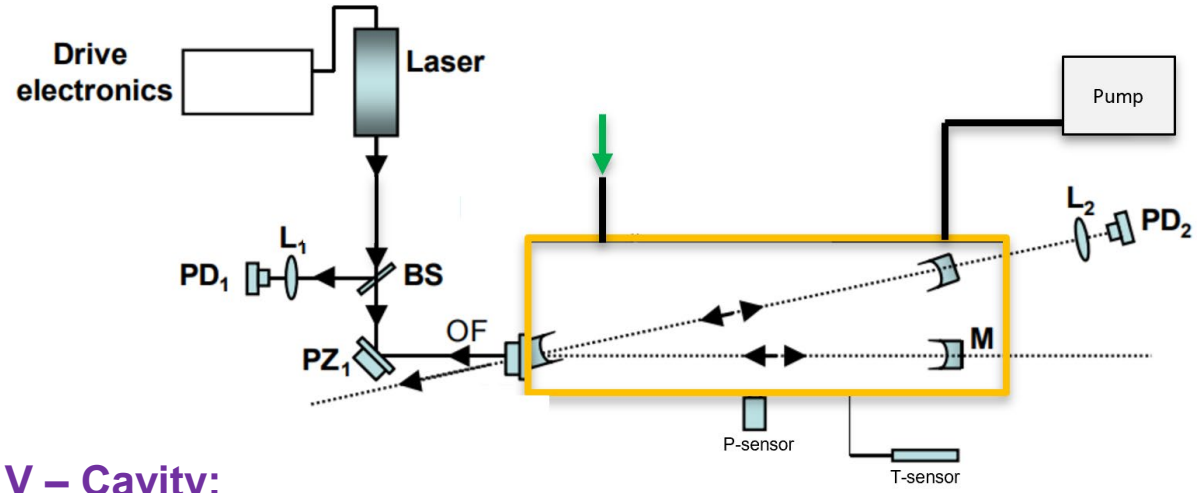
measured, constants, molecular data



Time to frequency conversion via Etalon measurement

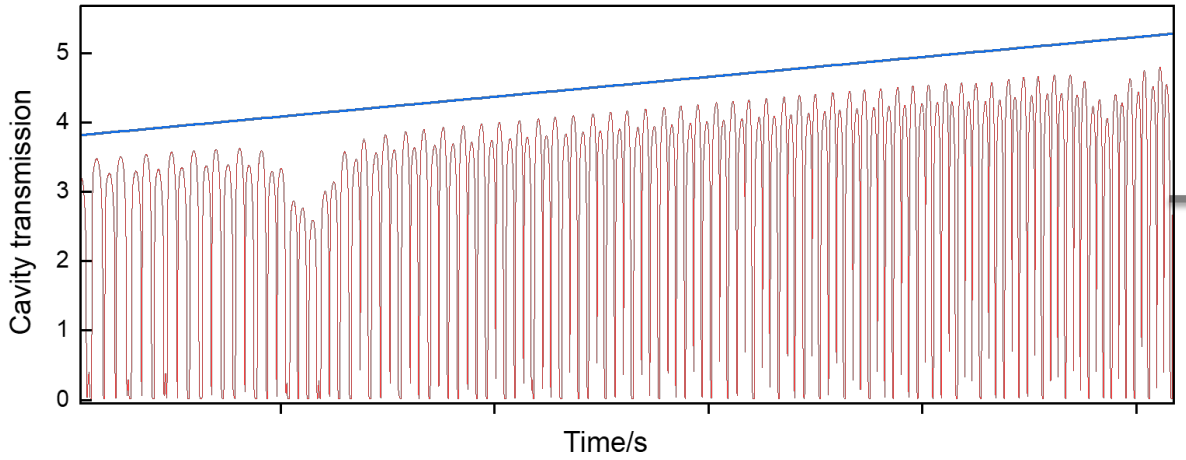
Measurement technique: NH_3 measurements in H_2

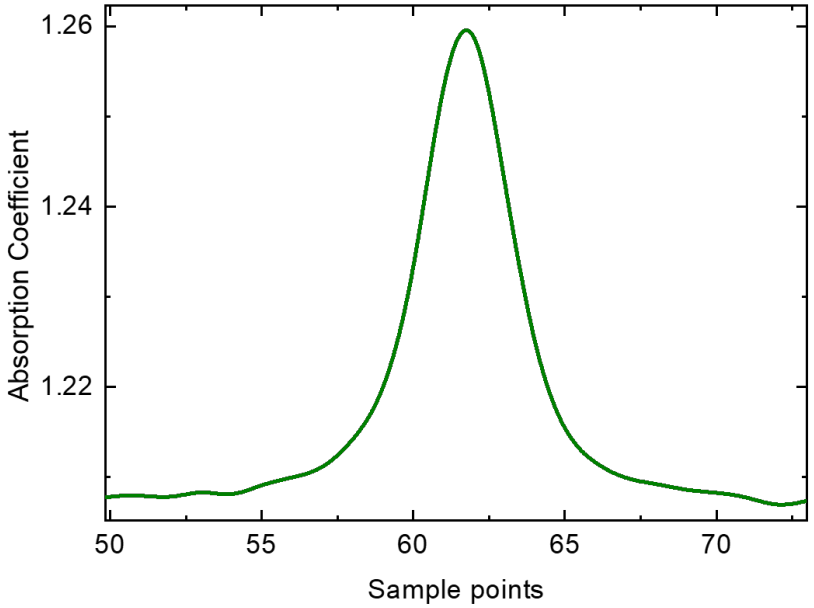
Optical Feedback Cavity Enhanced Absorption Spectroscopy (OF-CEAS)



V – Cavity:

50 ml volume, fast response, safety consideration





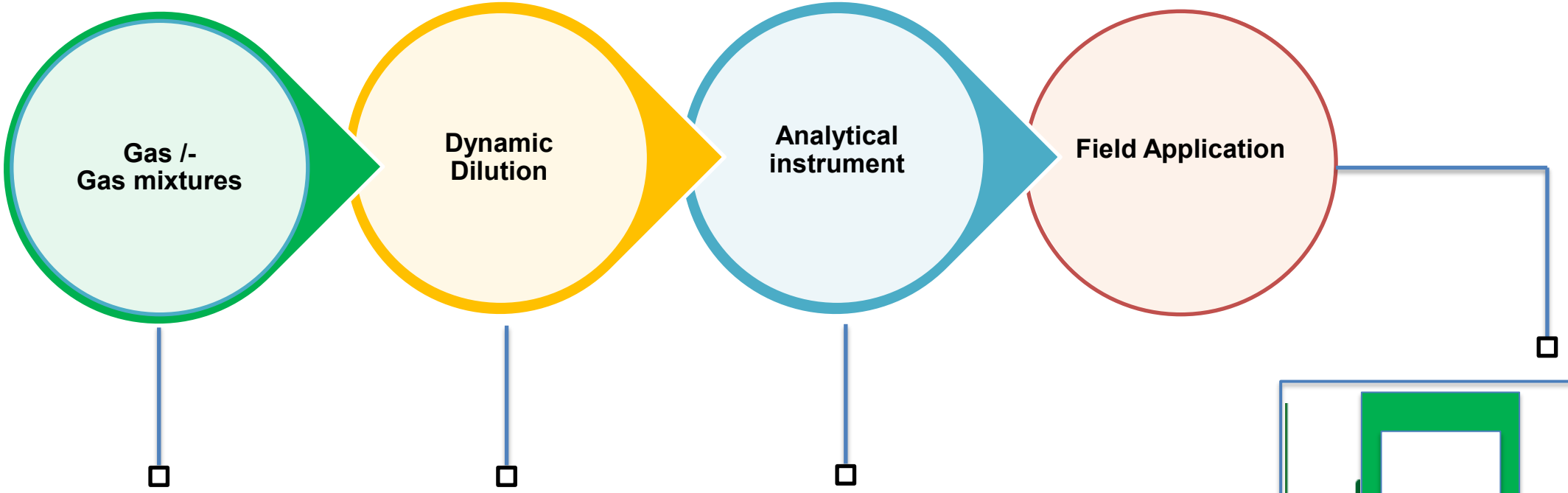
$$x_{NH_3} = \frac{\alpha_{int} \cdot k_B \cdot T}{S_T \cdot p}$$

Concept of an OGS can be applied

Infrastructure NH_3 measurements in H_2

Preparative

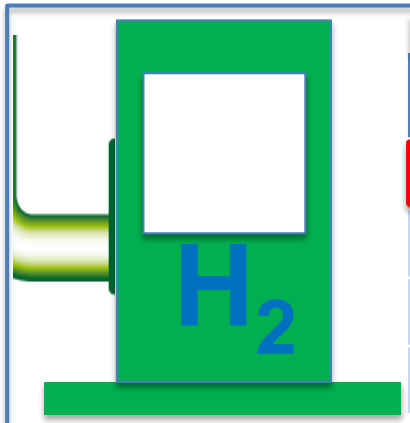
Analytical



- Test gas mixtures NH_3 (> 10 µmol/mol) in N_2 or hydrogen

- Dilution using N_2 or H_2 and employing critical orifices or mass flow controllers

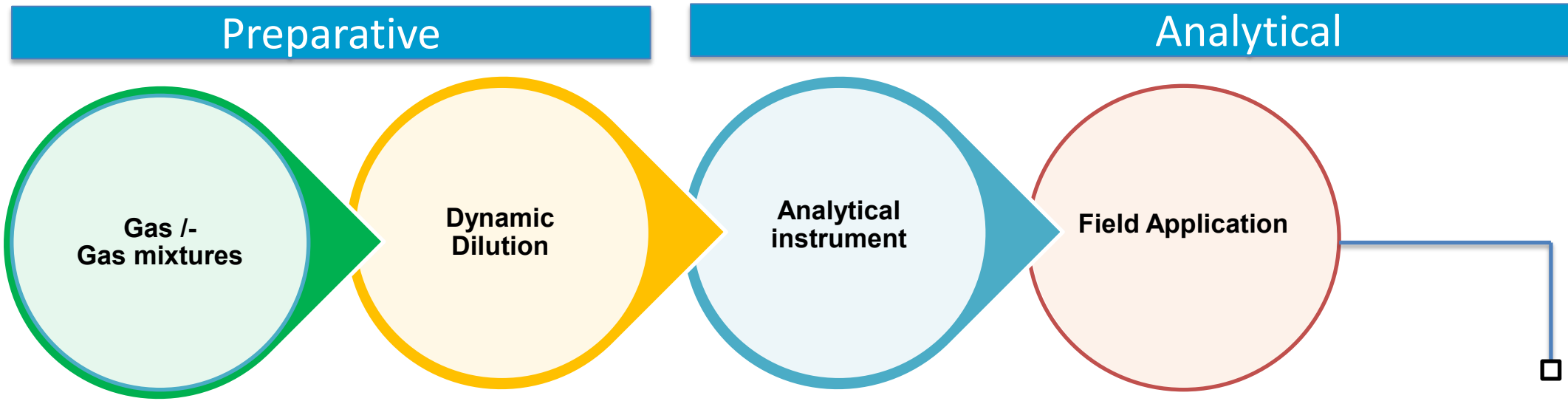
- OF-CEAS spectrometer providing traceable amount fraction results

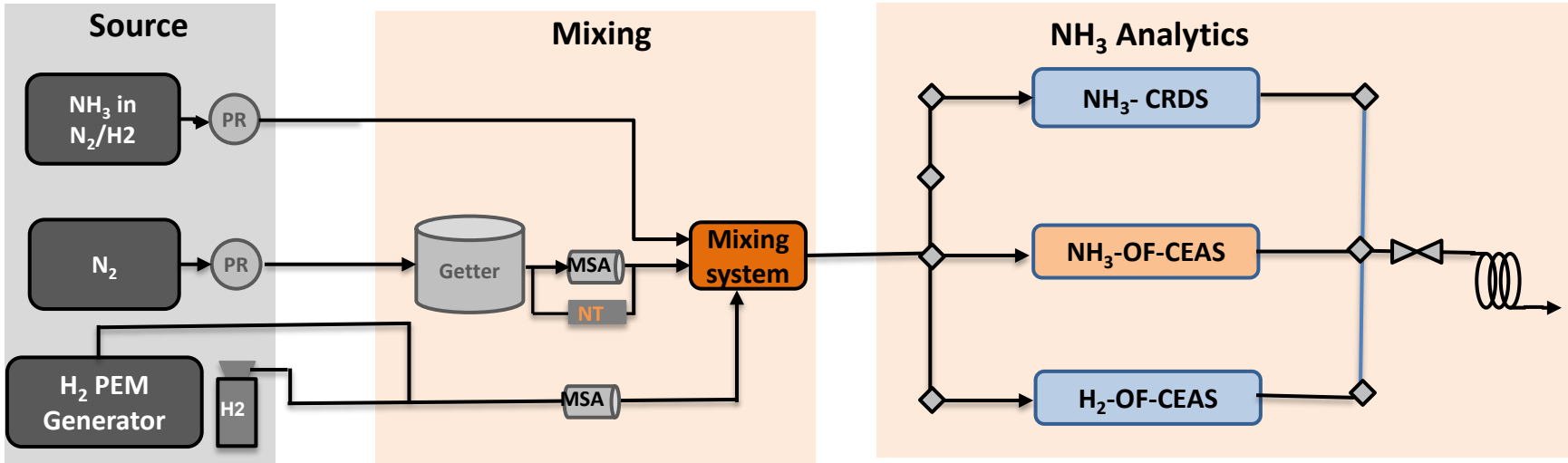


H2 purity

Analyte	Limit (ISO14687), µmol/mol
NH_3	0.1
O_2	5.0
CO	0.2
H_2O	5.0

Infrastructure NH_3 measurements in H_2

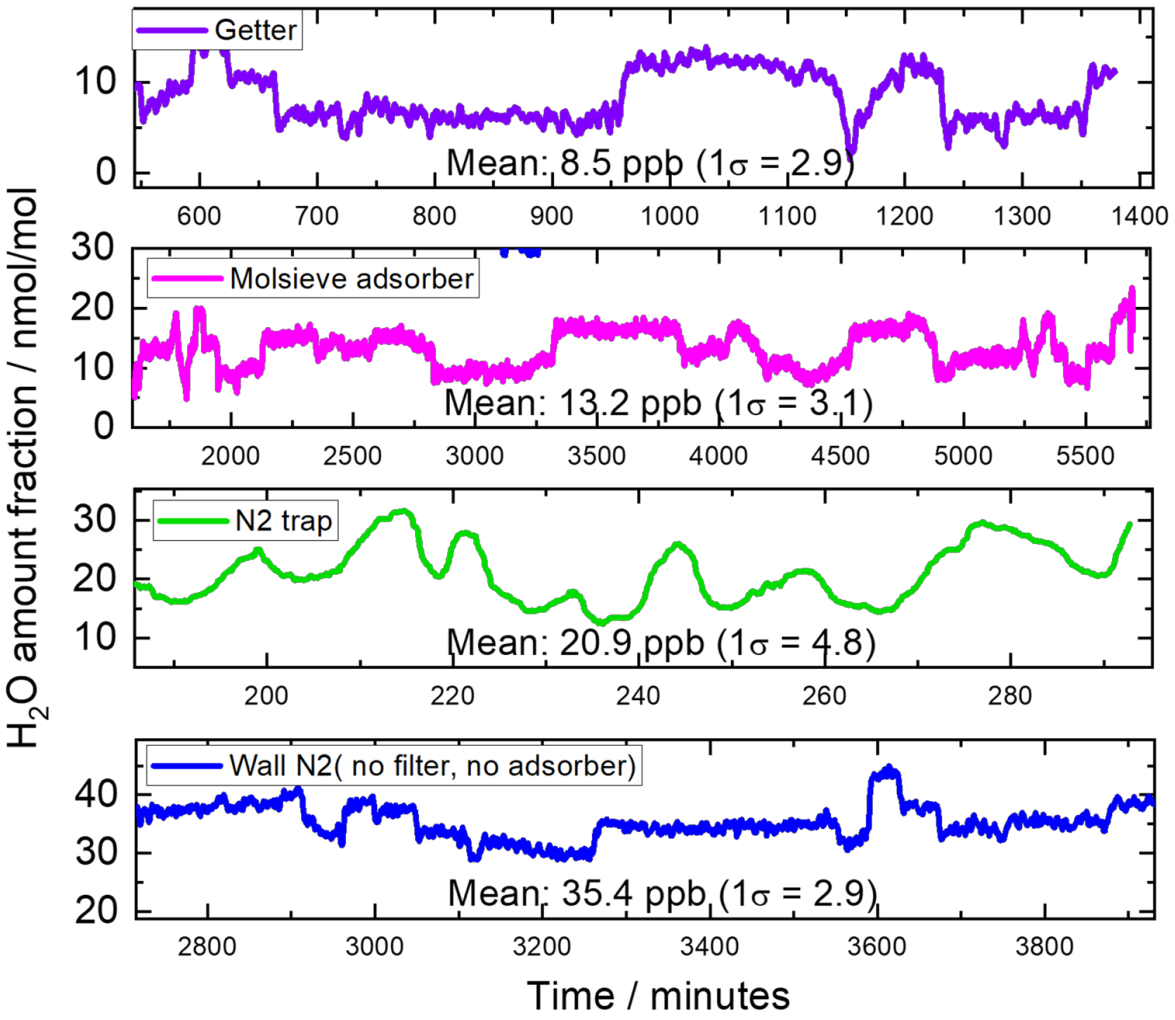


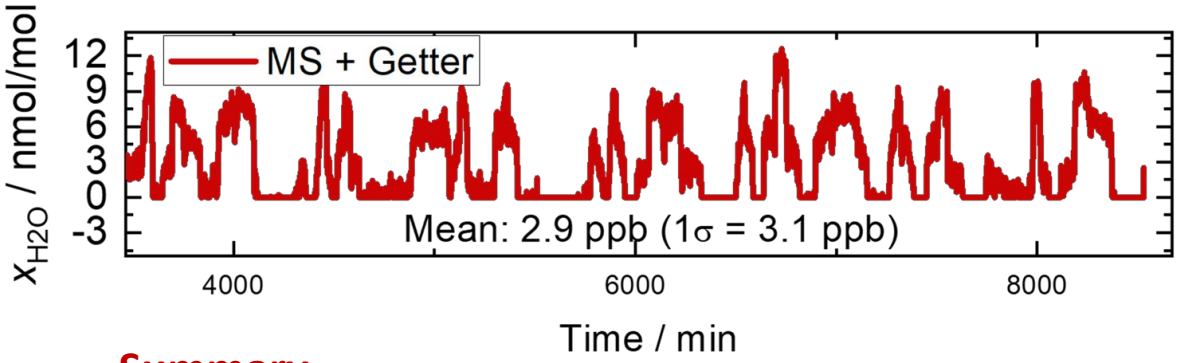


- NT: Liquid Nitrogen trap
- MSA: Molecular sieve adsorber
- PEM: Proton Exchange Membrane
- PR: pressure regulator
- CRDS: Cavity ringdown spectroscopy
- OF-CEAS: Optical feedback cavity enhanced absoption spectroscopy

H_2O background in N_2 matrix

Some tests and challenges

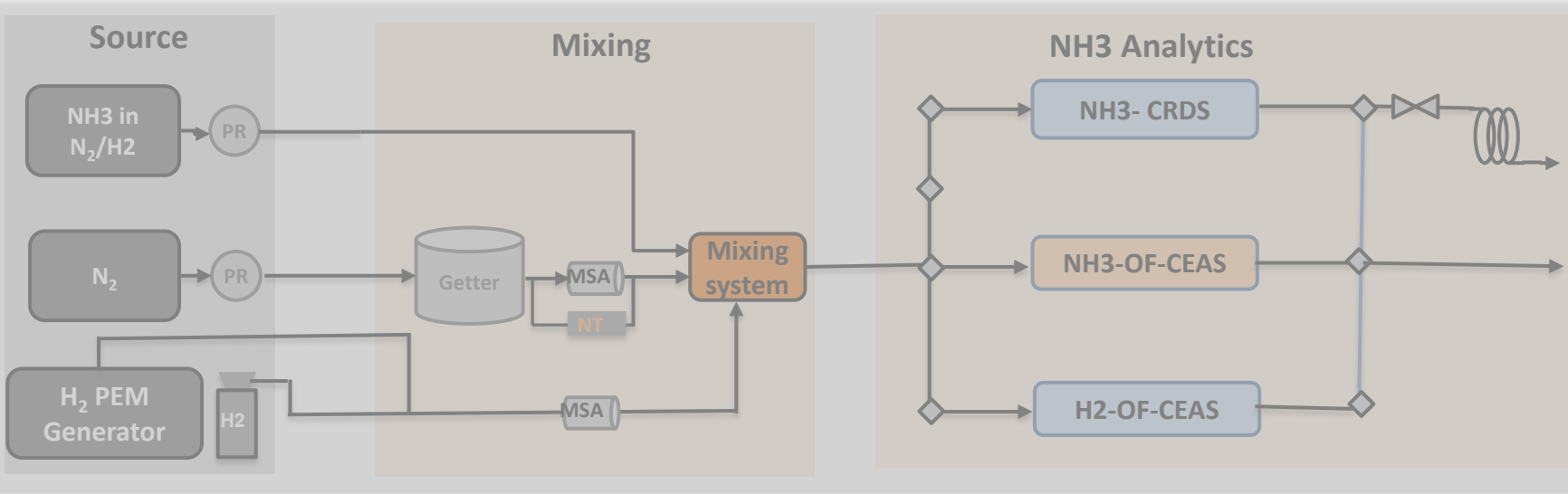




Summary

Adsorber, trap	H_2O level	1σ H_2O
None	35.4 ppb	2.9 ppb
Liquid N_2 trap (LN2-T)	20.9 ppb	4.8 ppb
Mölsieve (MS)	13.2 ppb	3.1 ppb
Getter (GT)	8.5 ppb	2.9 ppb
GT+MS	2.9 ppb	3.1 ppb

Method development approach



- OGS: optical gas standard
- NT: Liquid Nitrogen trap
- MSA: Molecular sieve adsorber
- PEM: Proton Exchange Membrane
- PR: pressure regulator
- CRDS: Cavity ringdown spectroscopy
- OF-CEAS: Optical feedback cavity enhanced absoption spectroscopy

1. Test the instrument for NH_3 in N_2 - **method development**

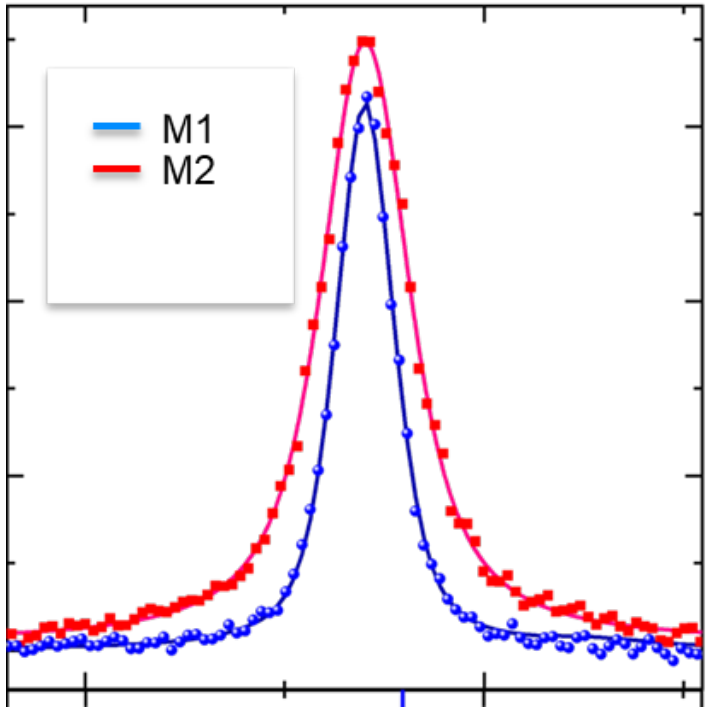
2. Perform NH_3 impurity measurements in H_2 – **application of method**

$N_2 \rightarrow H_2$

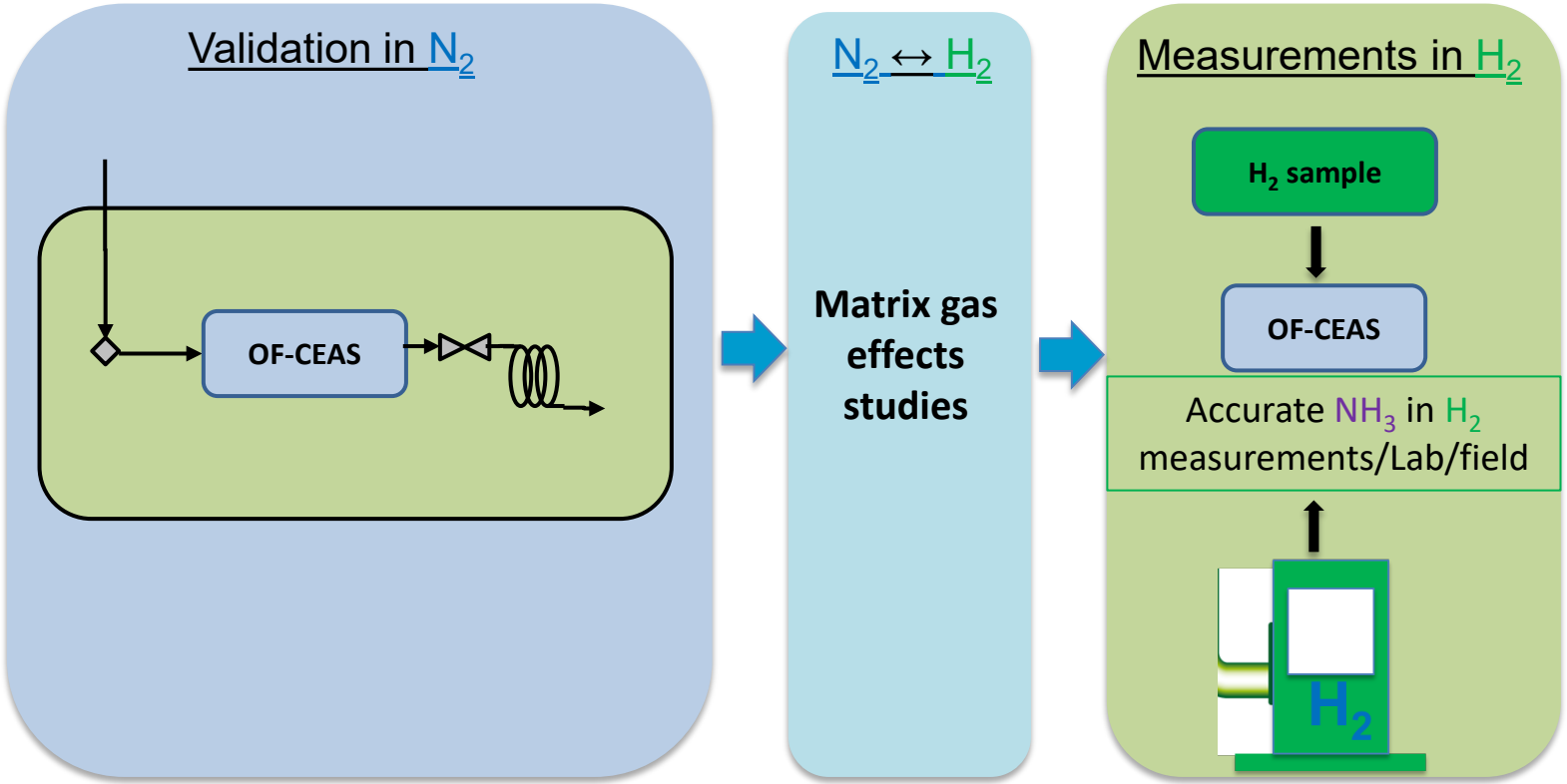
Method development approach

Gas matrix

1. For the same NH_3 amount fraction in different gas matrices, e.g.
   a) **Nitrogen (N_2)**
   b) **Hydrogen (H_2)**



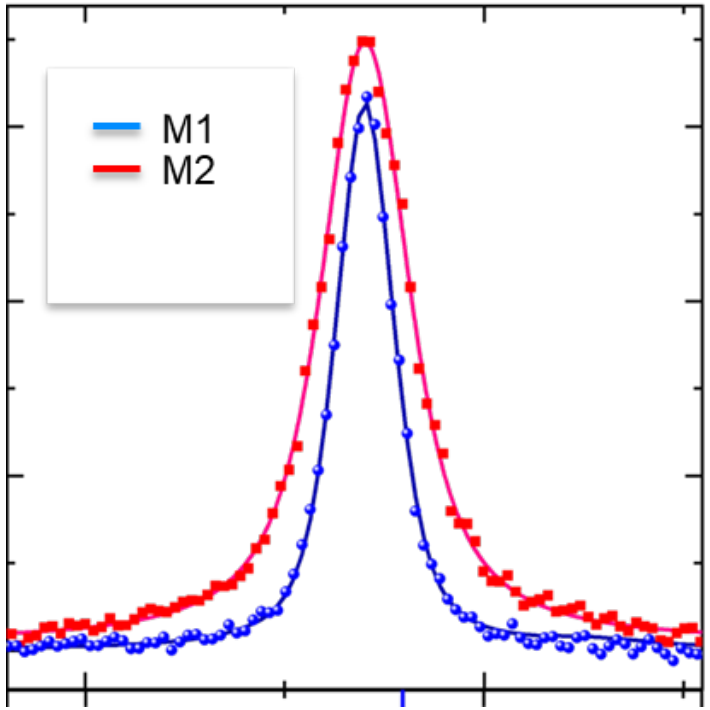
Matrix gas effect illustration



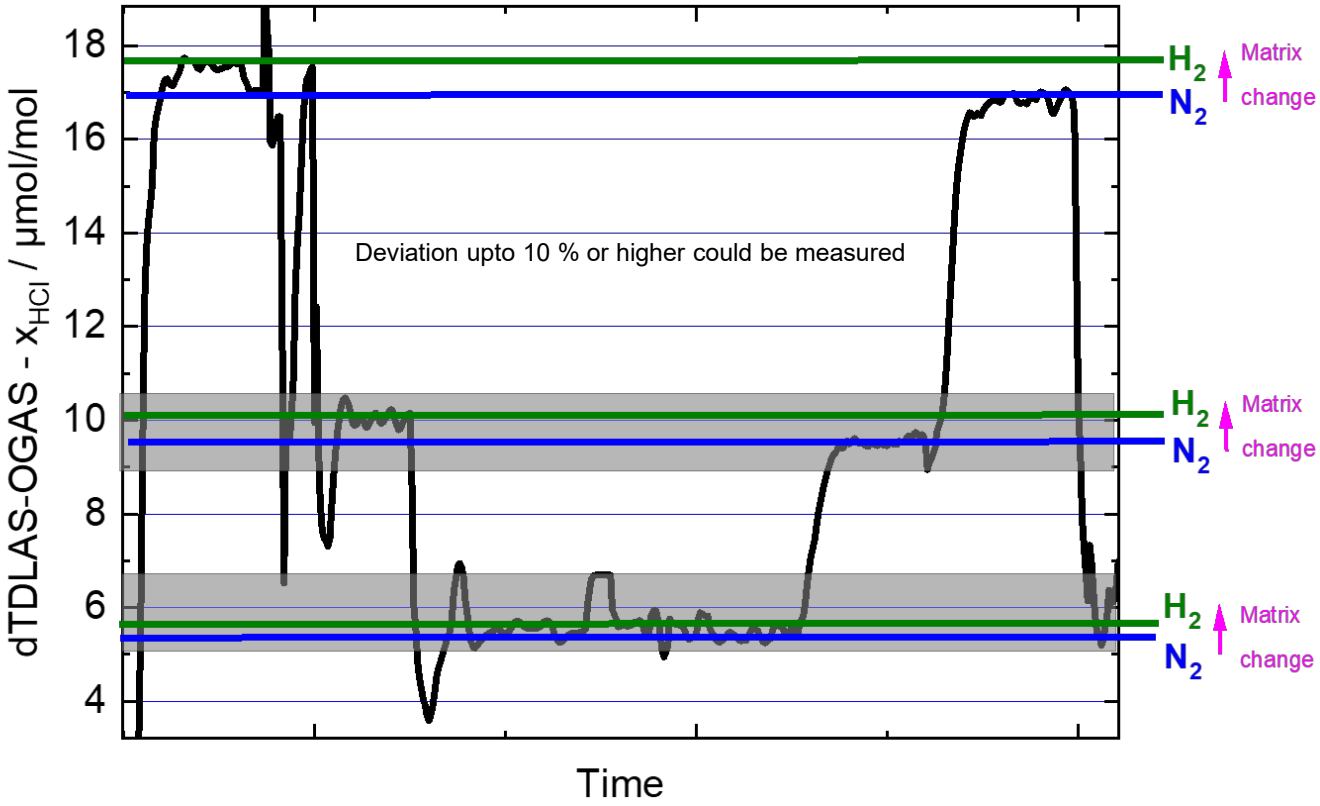
Calibrated analyzer‘s issues: matrix effects

Matrix effects

1. For the same NH_3 amount fraction in different gas matrices, e.g.
   a) Nitrogen (N_2)
   b) Hydrogen (H_2)



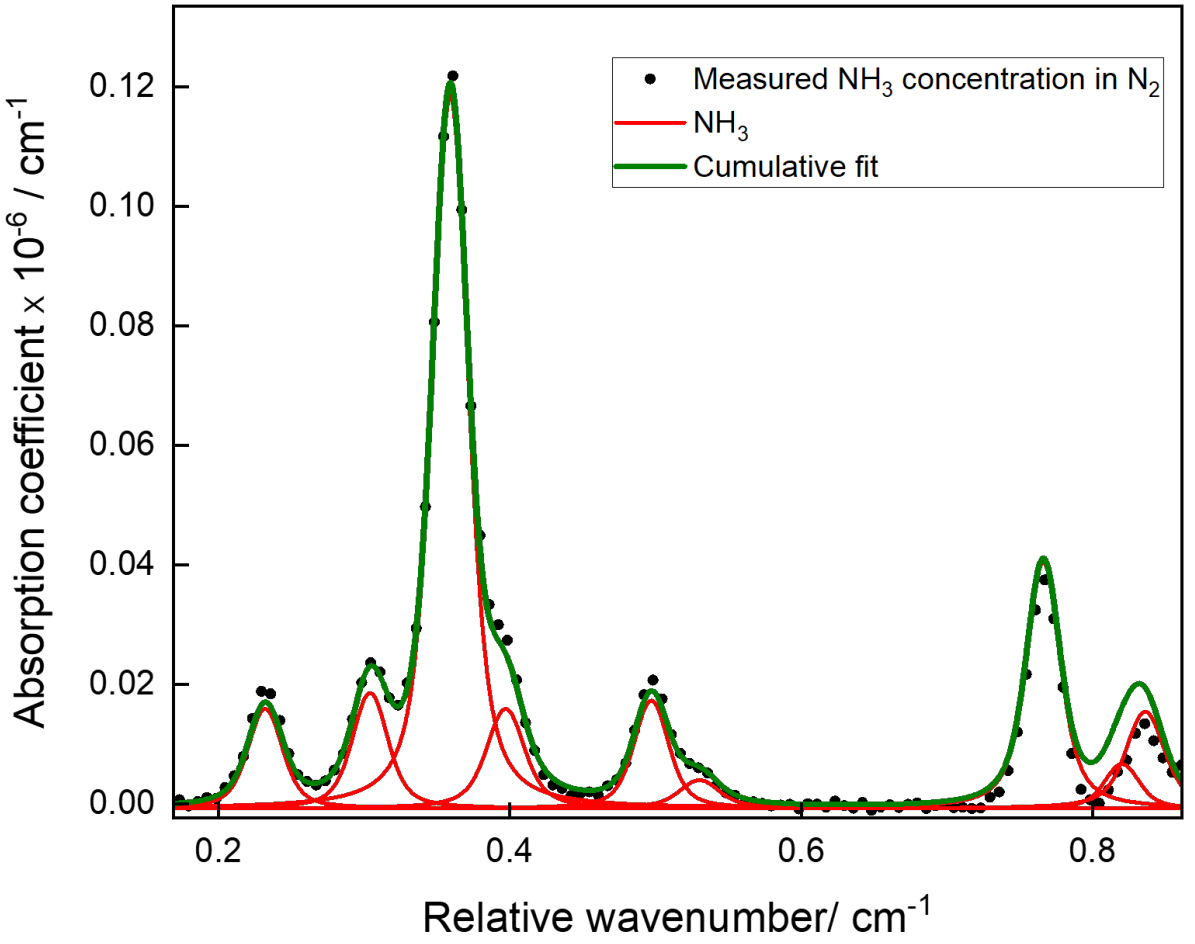
Matrix gas effect illustration



Typical spectra NH_3 in N_2

- Example spectra of NH_3 in N_2
- 7 NH_3 ines are fitted
- α_{int} (thus line Area) is used for NH_3 amount fraction valuation
- NH_3 amount fractions are evaluated using the equation

$$x_{NH_3} = \frac{\alpha_{int} \cdot k_B \cdot T}{S_T \cdot p}$$



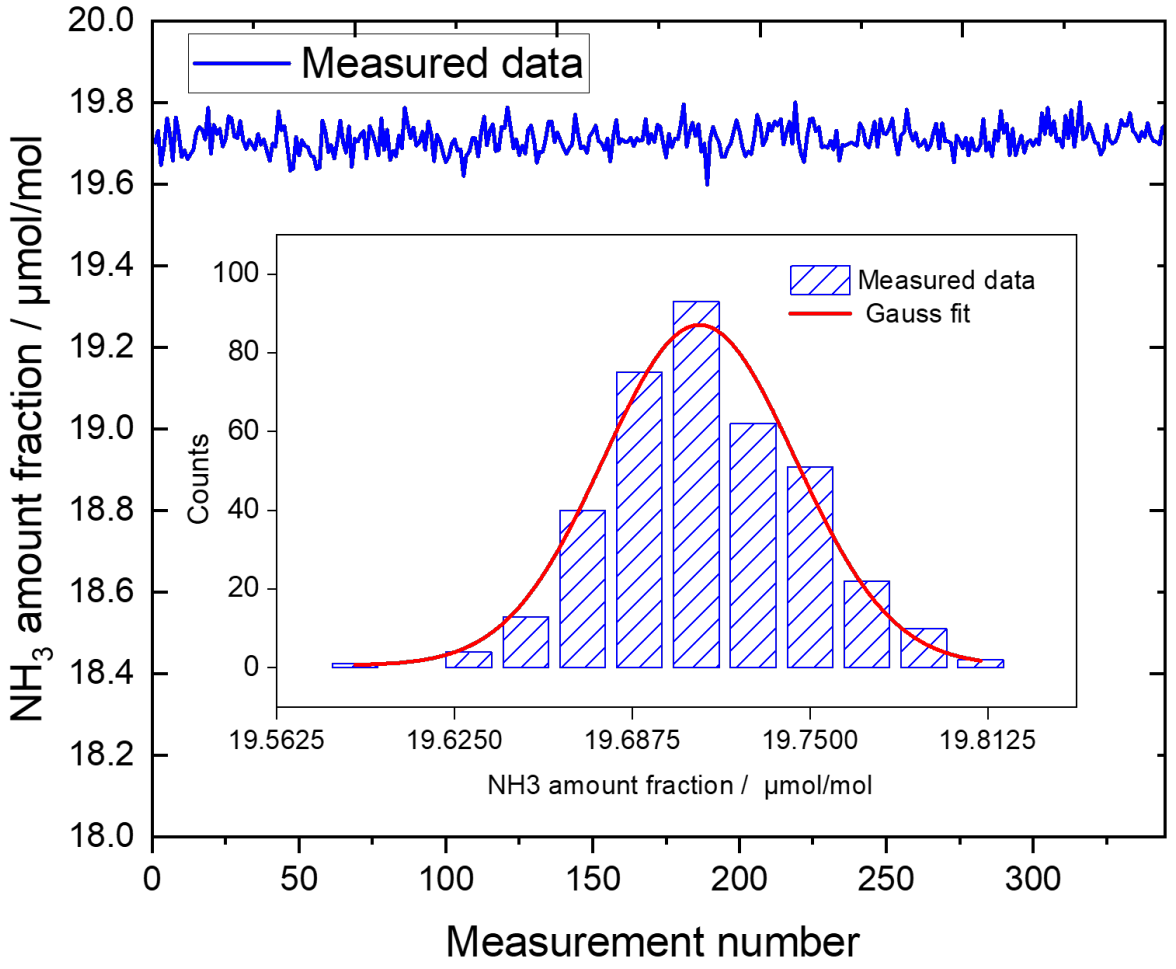
Measurement results of NH_3 in N_2

Method validation

- Measurements @ 19.3 µmol/mol
  - 1 σ = 33 nmol/mol

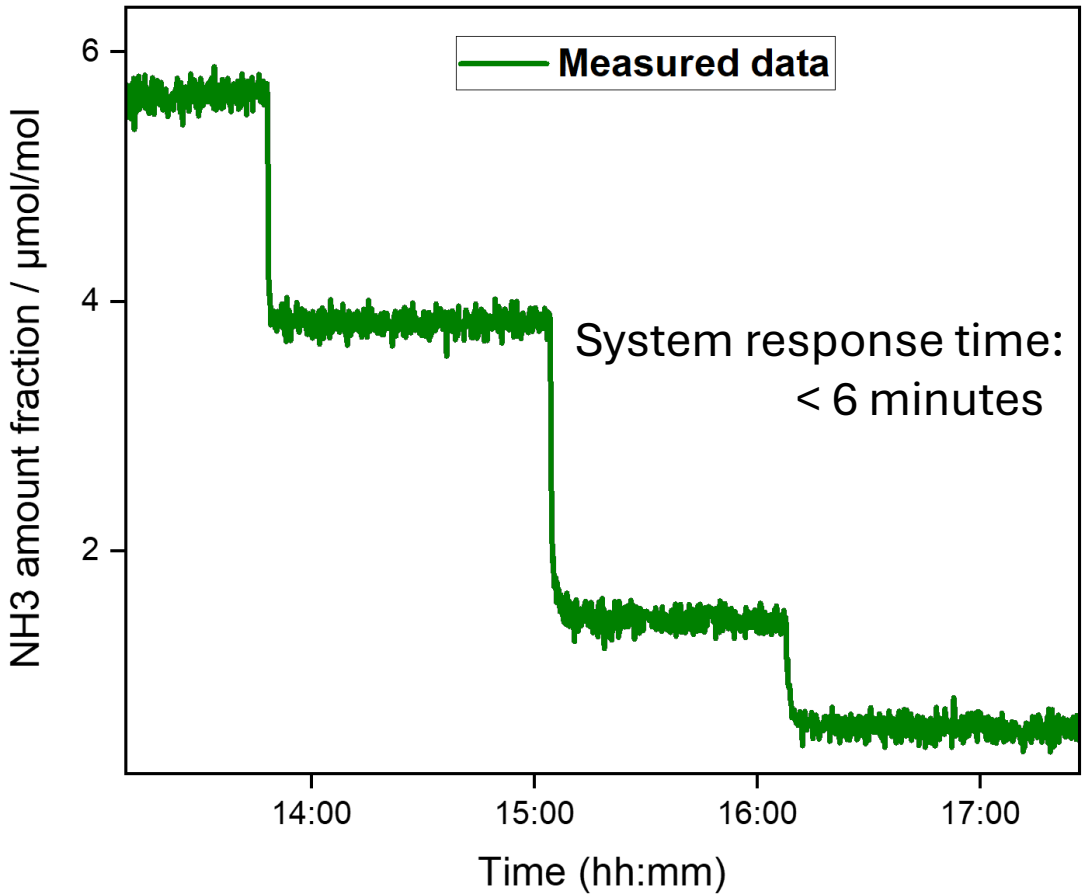
- NH_3 in N_2 results
  - Gas mixture value: (19.30±0.97) µmol/mol
  - Measured value: (19.70±0.99) µmol/mol
    - Measured value is **in agreement** with the cylinder-based gas mixture value

- A histogram of the results with a Gaus fit shows a normal distribution of the results around the mean value

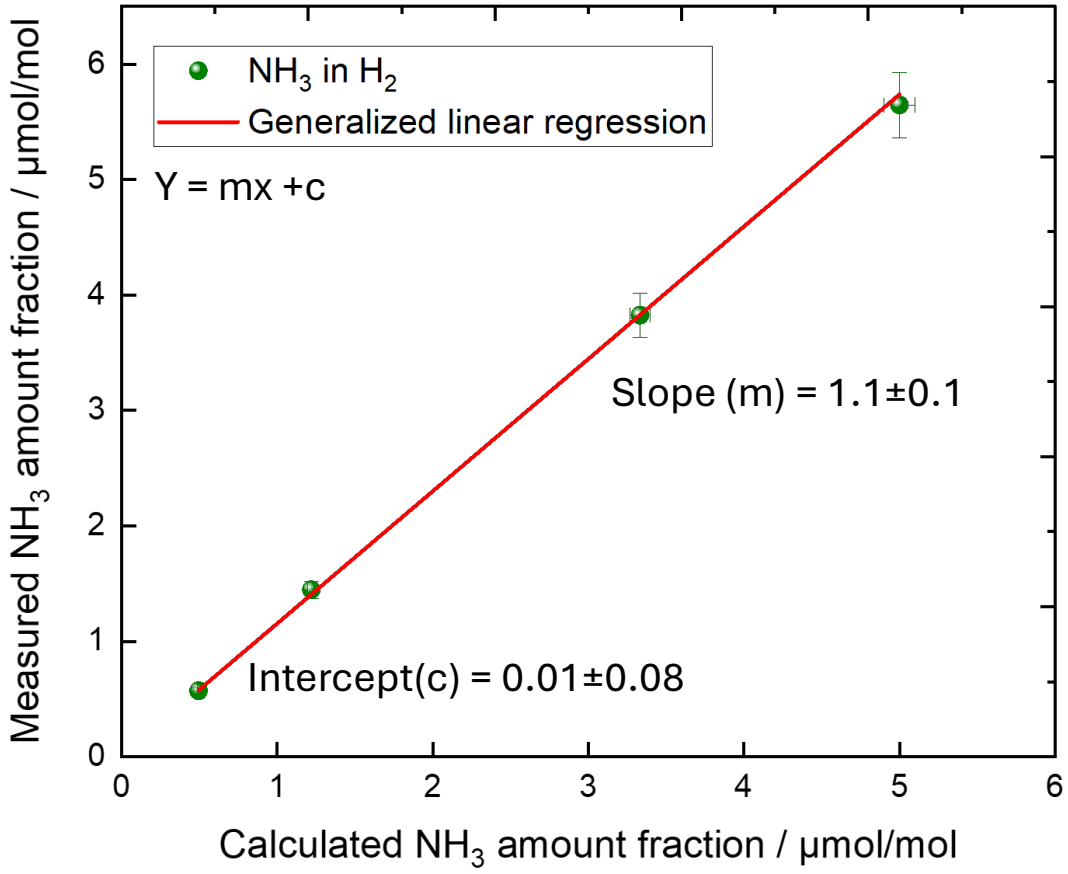


Measurement results of NH_3 in H_2

Response time

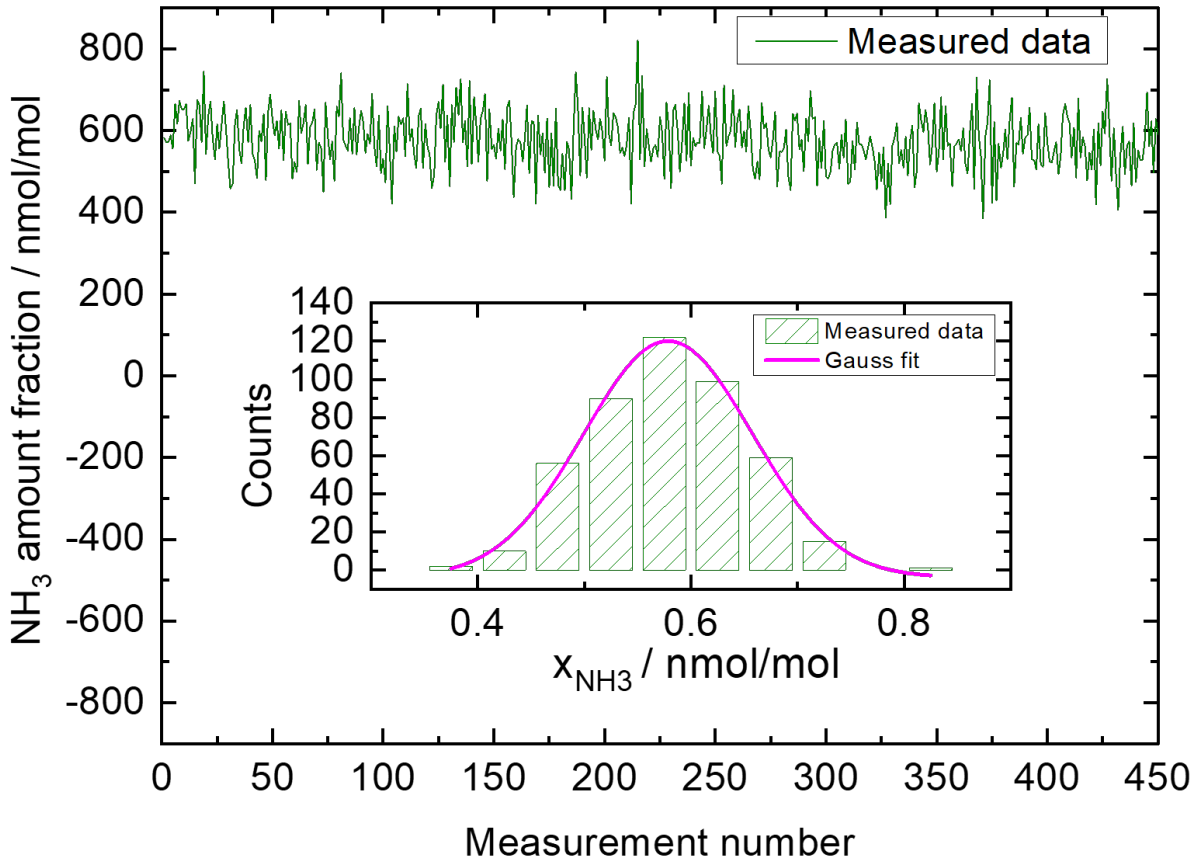


Linearity

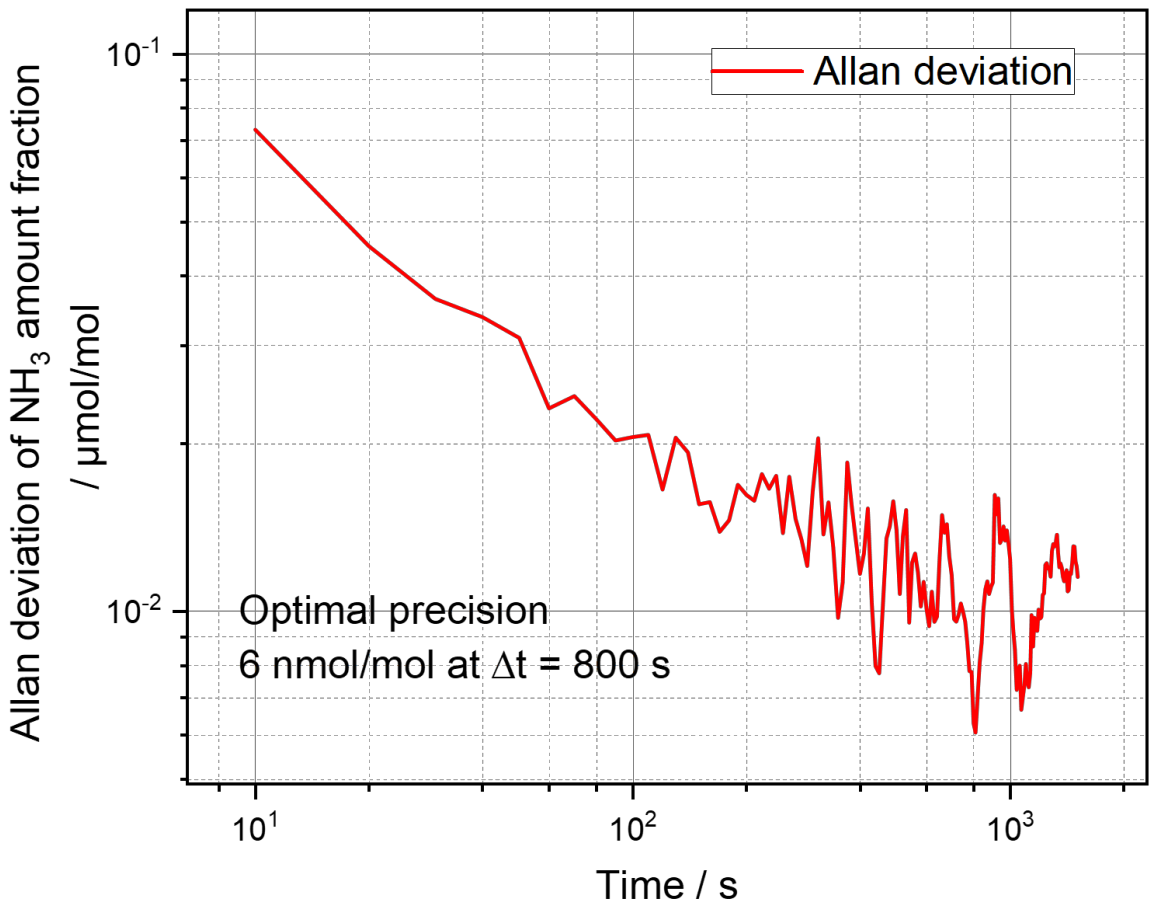


Measurement results of NH_3 in H_2

System stability



Precision



Summary

- A spectrometric method for NH_3 measurement in high purity H_2 has been developed at PTB
- The capability of the OF-CEAS instrument has been tested for NH_3 amount fraction between 0.05 and 6 µmol/mol
- The instrument is being developed to be operated as an Optical Gas Standard for NH_3 measurement in H_2

Thanks for your attention!

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Serial correlation and autoregression in gas metering data

Federica Gugole, VSL

ENERGY GASES

METCCUS

VSL

MET4H2

BiometCAP

VSL

National Metrology Institute

TU/e EINDHOVEN UNIVERSITY OF TECHNOLOGY

MET4H2

On the autocorrelation of measurement results for gas volume and calorific value in fiscal metering in gas grids

Federica Gugole

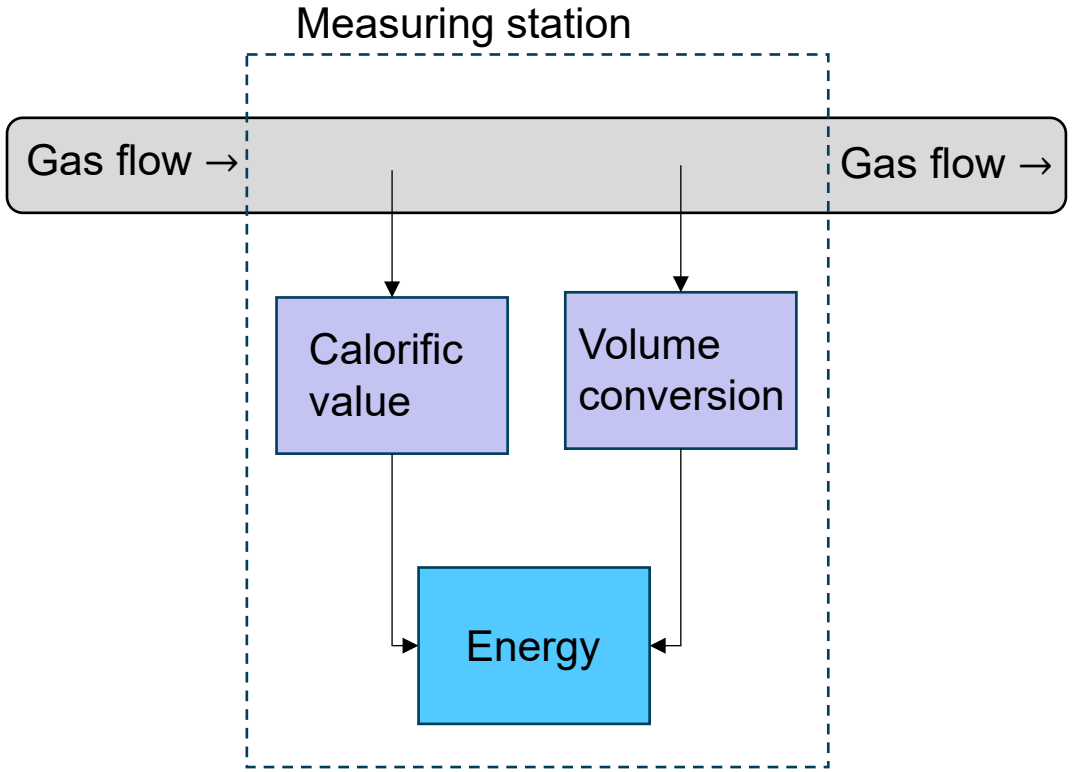
Meng Li

Adriaan van der Veen

Can we keep using the current gas infrastructure once H2 joins the game?

A measuring station for fiscal metering often consists of

- Flow meter measuring the volume flow rate of the gas
- Gas chromatograph (GC) measuring the gas composition



The energy is then computed as

$$E = V \cdot H$$

V is the normal volume

H is the calorific value

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How to calculate the uncertainty is also part of the infrastructure!

Standards for the energy determination (ISO 15112, OIML R140) assume independence of measurement results

$$E_{tot} = \sum E_t = \sum V_t H_t$$

$$u^2\,(E_{tot}) = \sum u^2\,(E_t) = \sum E_i^2 (u_{rel}^2(V_t) + u_{rel}^2(H_t))$$

This assumption might lead to costly errors once hydrogen is introduced in the gas grid

Improvements investigated in Met4H2:

- **Temporal correlations in subsequent measurements due to the continuous underlying process**
- Correlations due to the instrumentation
- Error introduced by approximating the total with a finite sum

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Available data

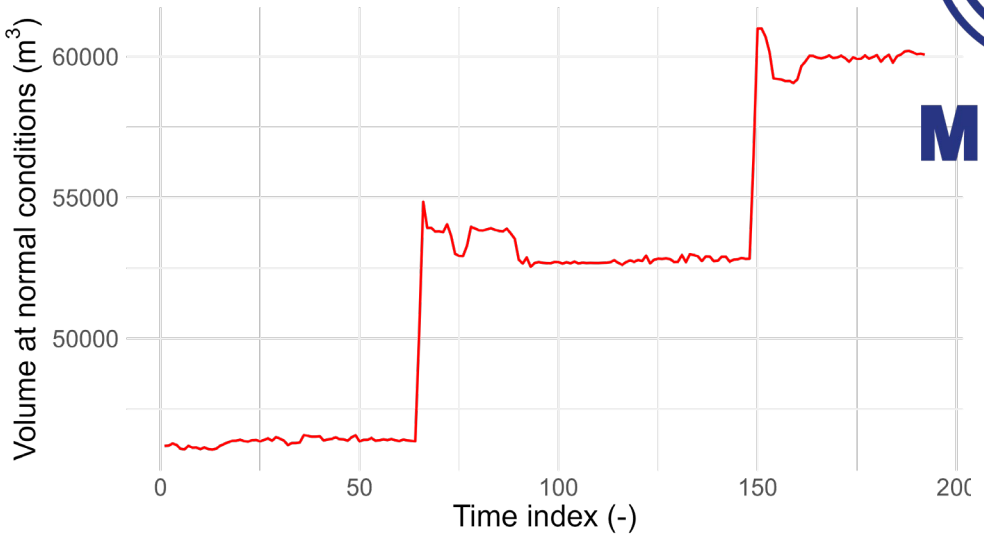
Two days of measurements with data points recorded every 15 mins

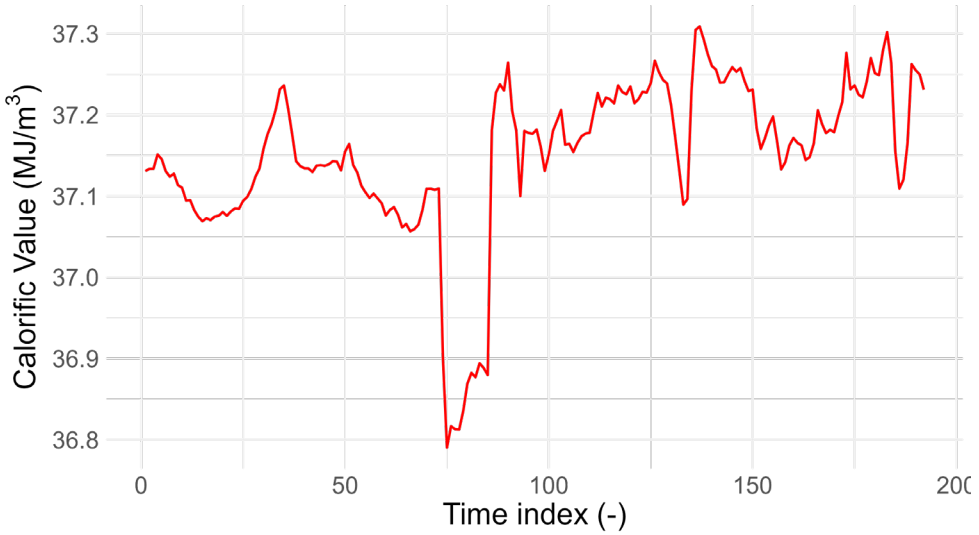
→ 192 data points

Volume flow rate measured by an ultrasonic flow meter

Gas composition measured by a gas chromatograph

Calorific value determined by an equation of state





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We consider the data **after** correcting for known errors

Corrections due to, e.g., drift or calibration errors should be applied to the data prior to the autocorrelation analysis

Data are transformed to their equivalent in normal conditions to avoid detecting correlations due to, e.g., changes in temperature or pressure

Remaining correlation is actual correlation in the measurand, and it is due to the inertia of the physical process

Plan

1. Segment the series in stationary blocks

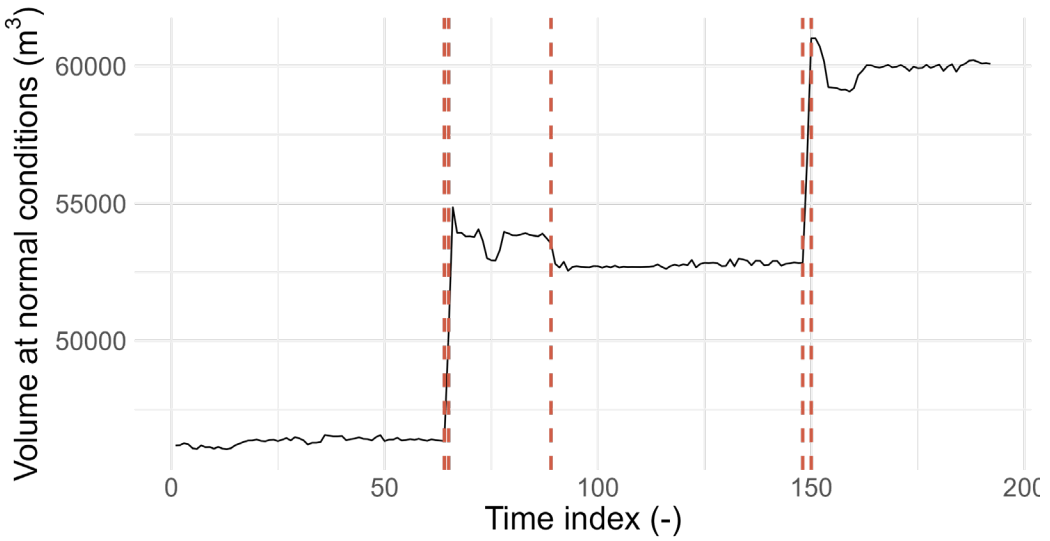
2. Fit a time series model

3. Calculate uncertainties with and without correlations

1. Automatic data segmentation using change detection methods

Two methods:

- BinSeg (binary segmentation)
  - Approximate method
  - Indicated to detect significant jumps
- PELT (Pruned Exact Linear Time)
  - Exact method
  - Detects also more subtle changes



Example of segmentation results using BinSeg.

Selected subseries are checked for stationarity via the Augmented Dickey-Fuller test

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2. Time series analysis: some useful statistical tools

AR: autoregressive; expresses the current value as a linear combination of a finite number of past values of the same variable

MA: moving average; describes the dependence of the current value on the current and past values of another variable

ARMA: autoregressive moving average

ACF: autocorrelation function; measures the correlation between observations at different distances apart

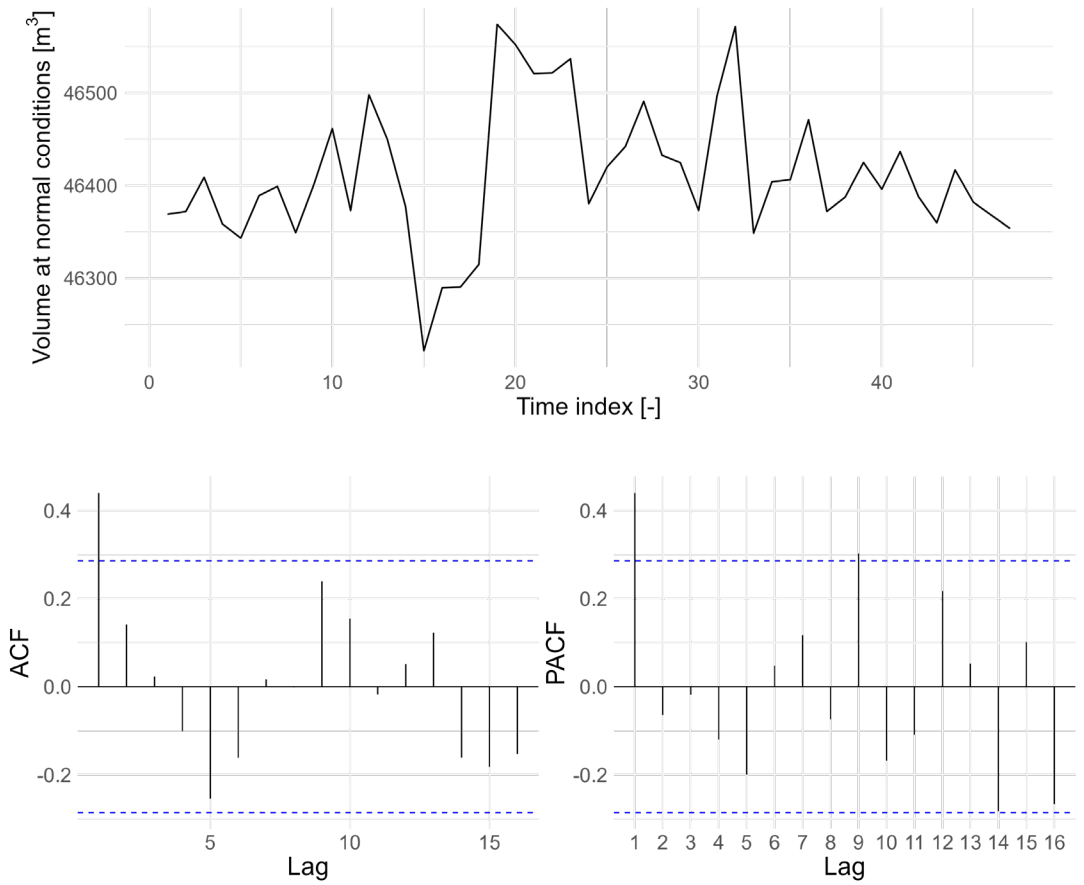
PACF: partial ACF; computes the correlation between two variables with the linear effect on a third variable removed

2. The volume can be described by an AR(1) model

Three stationary subseries from the given data

(Partial) autocorrelation function shows correlation between V_t and V_{t-1}

We fit an autoregressive (AR) model of order 1 to the volume time series



Example of stationary subseries of the volume data, its ACF and PACF.

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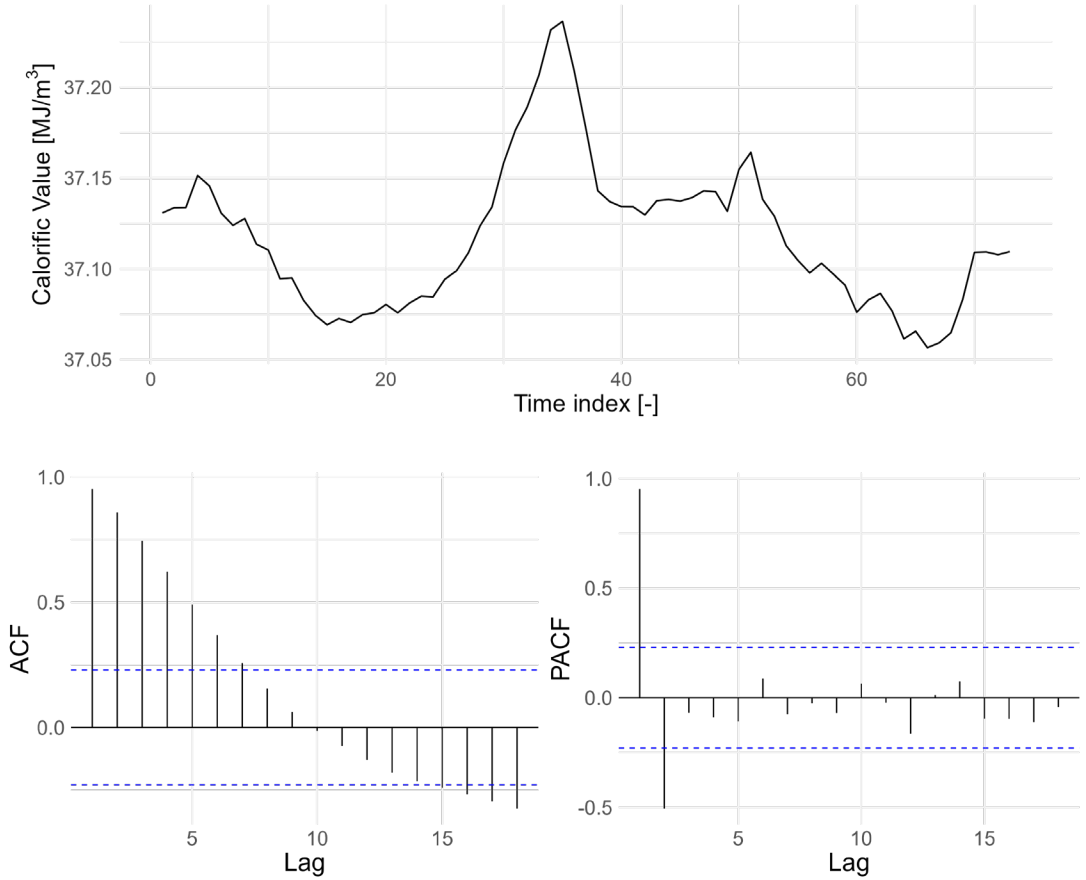
2. The calorific value can be described by an AR(2) model

Two stationary subseries from the given data

Partial autocorrelation function shows correlation between H_t, H_{t-1} and H_{t-2}

We fit an AR model of order 2 to the calorific value time series



Example of stationary subseries of the calorific value data, its ACF and PACF.

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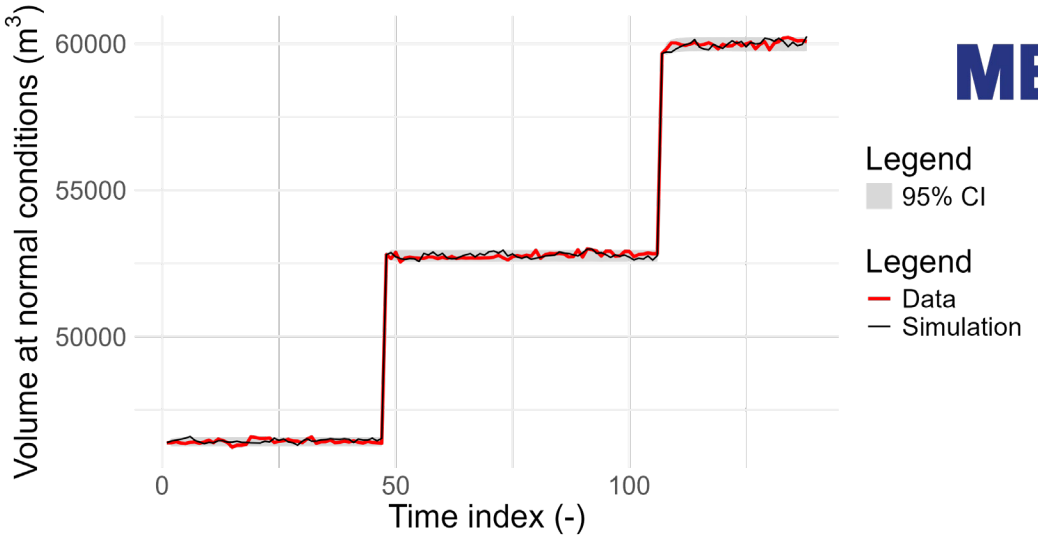
2. AR(1) and AR(2) describe well the volume and the calorific value data, respectively

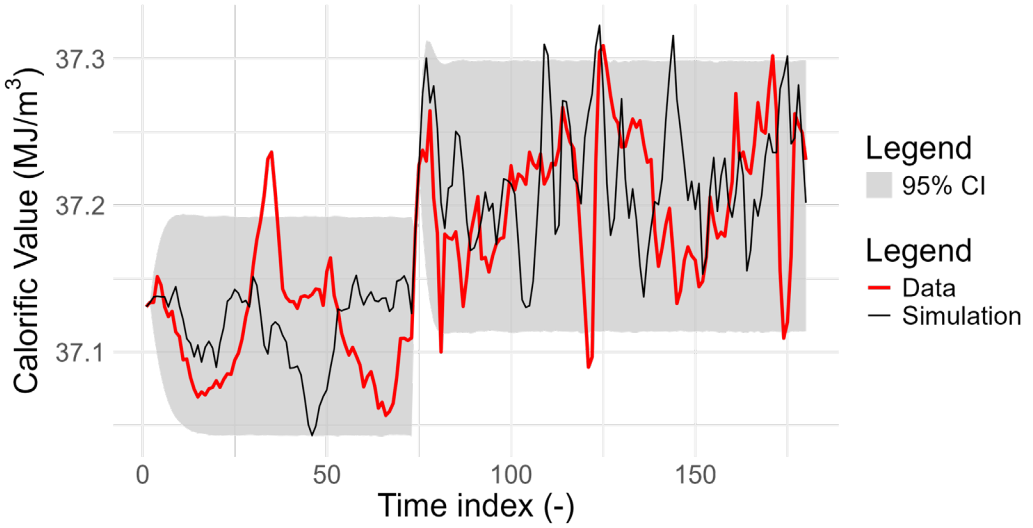
Using the models fitted to the data, we generate 100 000 synthetic time series

The experimental data are within the 95% CI identified by the simulations

The individual simulations display similar behaviour as the experimental data

→ The fitted models are a good representation of the experimental data





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3. The evaluation of uncertainty does **not** include the instrumental measurement uncertainty

The law of propagation of uncertainty with correlated input quantity

$$u_c^2(y) = \sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i}\right)^2 u^2(x_i) + 2 \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{\partial f}{\partial x_i} \frac{\partial f}{\partial x_j} u(x_i, x_j)$$

$$E_{tot} = \sum_{t=1}^{N} E_t = \sum_{t=1}^{N} V_t H_t$$

Serial correlations influence only the uncertainty obtained by the statistical data analysis

Correlations due to, e.g., instrumentation are treated separately

3. In case of independent measurement results, the uncertainty is given by the sample standard deviation

The law of propagation of uncertainty without correlated input quantity

$$u_c^2(y) = \sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i}\right)^2 u^2(x_i)$$

$$E_{tot} = \sum_{t=1}^{N} E_t = \sum_{t=1}^{N} V_t H_t$$

The uncertainty of the volume and of the calorific data is calculated from the data as

$$\sigma_{V_t} = \mathrm{std}(\{V_t\}_{t=1,\ldots,N})$$

$$\sigma_{H_t} = \mathrm{std}(\{H_t\}_{t=1,\ldots,N})$$

3. When including the correlations, the (co)variance is given by the AR processes

AR(1) $V_t = \mu_{V_t} + \alpha V_{t-1} + Z_t$

$$\sigma^2_{V_t} = \gamma_{V_t}(0) = \frac{\sigma^2_{Z_t}}{(1-\alpha^2)}$$

$$\gamma_{V_t}(1) = \alpha\gamma_{V_t}(0)$$

AR(2) $H_t = \mu_{H_t} + \beta_1 H_{t-1} + \beta_2 H_{t-2} + W_t$

$$\sigma^2_{H_t} = \gamma_{H_t}(0) = \frac{(1-\beta_2)\sigma^2_{W_t}}{(1+\beta_2)(1-\beta_1-\beta_2)(1+\beta_1-\beta_2)}$$

$$\gamma_{H_t}(1) = \beta_1\gamma_{H_t}(0)/(1-\beta_2)$$

$$\gamma_{H_t}(2) = (\beta_1^2 + \beta_2 - \beta_2^2)\gamma_{H_t}(0)/(1-\beta_2)$$

3. Extra care required to calculate the covariance of the product of two random variables

The energy is given by the product of two random variables

Covariance of products of random variables

(Bohrnsted and Goldberger, 1969)

$$\begin{aligned}&\mathrm{Cov}(XY, UV)\\&= E[X]E[U]\mathrm{Cov}(Y,V) + E[X]E[V]\mathrm{Cov}(Y,U) + E[Y]E[U]\mathrm{Cov}(X,V)\\&+ E[Y]E[V]\mathrm{Cov}(X,U) + \mathrm{Cov}(X,U)\mathrm{Cov}(Y,V) + \mathrm{Cov}(X,V)\mathrm{Cov}(Y,U)\end{aligned}$$

This formula considers all the effects arising from the presence of covariances

3. The serial correlation increases the estimated uncertainty by circa 50 %

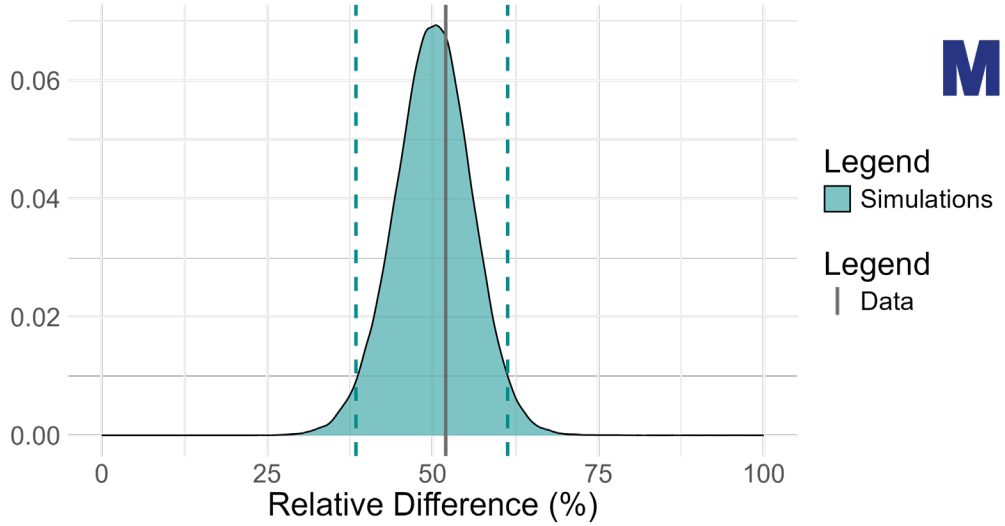
Relative difference calculated on simulated data

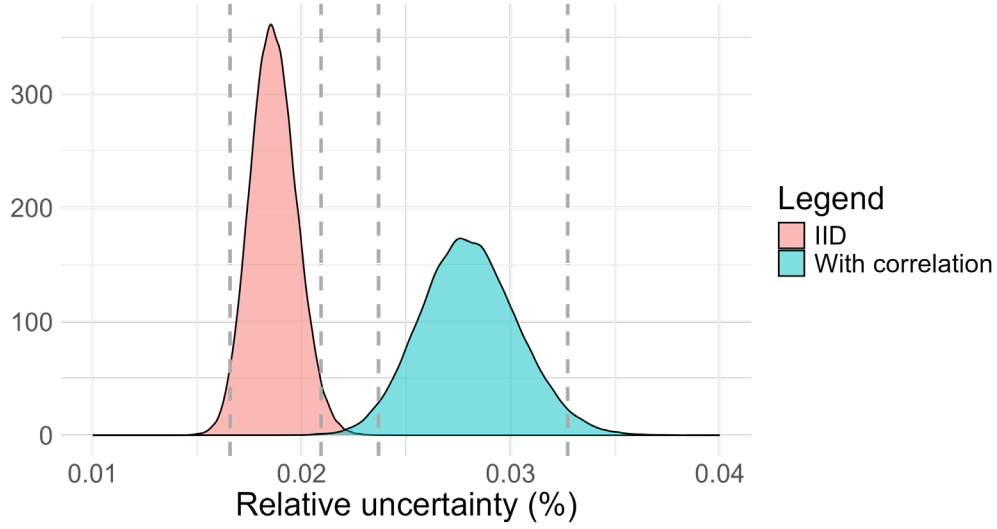
$$\frac{u_{cor}(E_{tot}) - u_{iid}(E_{tot})}{u_{iid}(E_{tot})} \cdot 100\%$$

Relative uncertainty $x \in \{cor, iid\}$

$$u_{x,rel}(E_{tot}) = \frac{u_x(E_{tot})}{E_{tot}} \cdot 100\%$$

Including the serial correlation increases the uncertainty by circa 50 % on average





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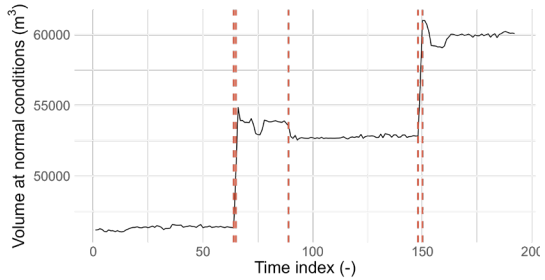
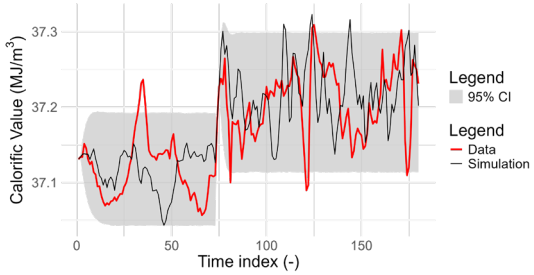
Conclusions

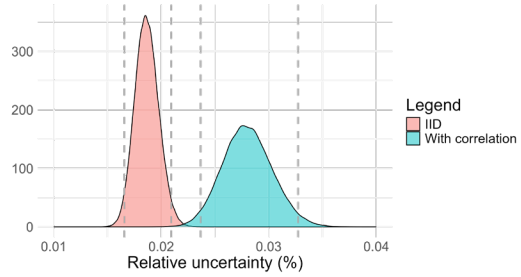
1. Segment the series in stationary blocks
   - BinSeg
   - PELT



2. Fit a time series model
   - AR(1) for the volume
   - AR(2) for the calorific value



3. Calculate uncertainties with and without correlations
   - Including the serial correlation leads to an increase in the uncertainty of circa 50 %



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Further work

1. Correlation due to instrumentation

2. How to combine the serial correlation with the correlation due to instrumentation

3. Error introduced by approximating the total with a finite sum

Check Met4H2 website for updates!

https://met4h2.eu/

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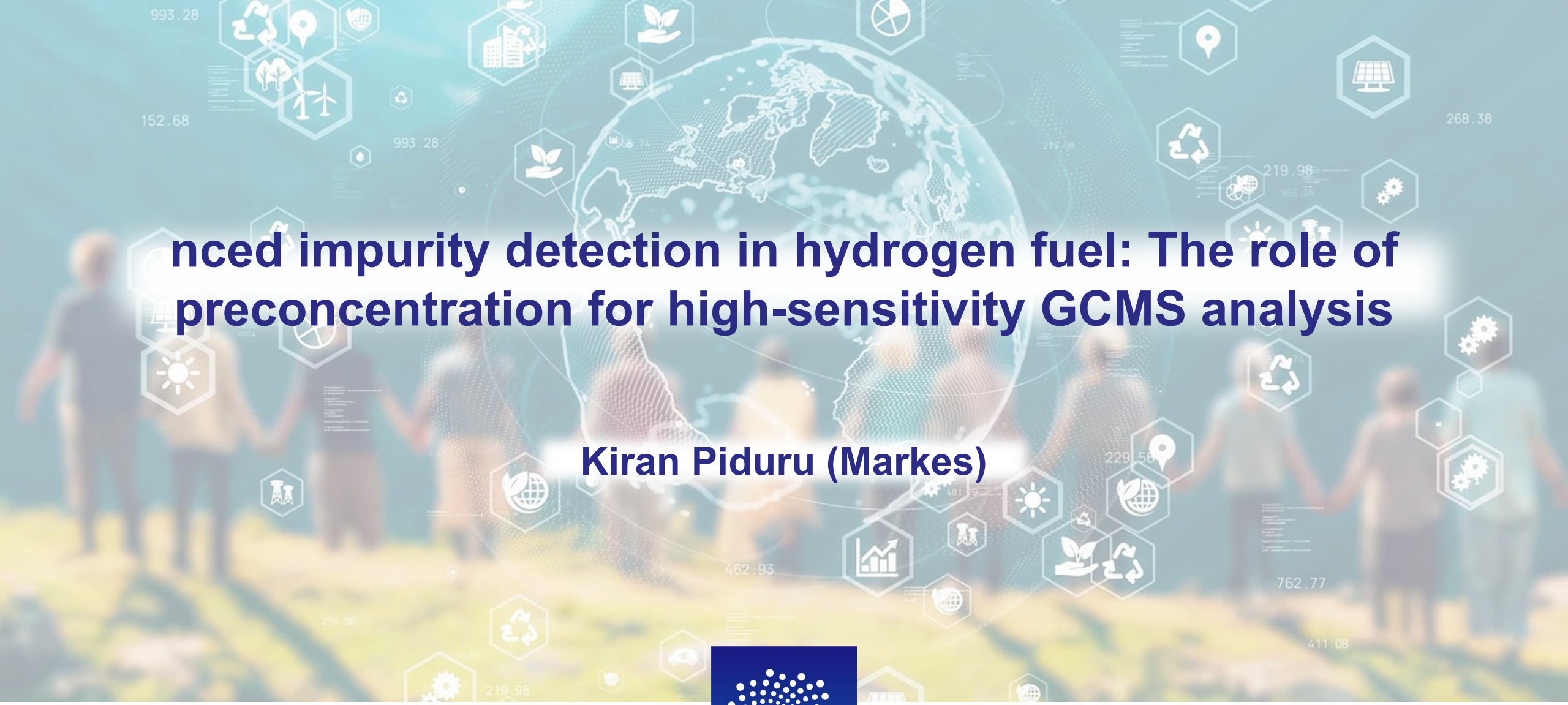
Funded by the European Union. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union or EURAMET. Neither the European Union nor the granting authority can be held responsible for them.

The project has received funding from the European Partnership on Metrology, co-financed from the European Union's Horizon Europe Research and Innovation Programme and by the Participating States.



nced impurity detection in hydrogen fuel: The role of preconcentration for high-sensitivity GCMS analysis

Kiran Piduru (Markes)

ENERGY GASES

METCCUS

VSL

MET4H2

BiometCAP

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Advanced Impurity Detection in Hydrogen Fuel:

The Role of Preconcentration for High-Sensitivity GCMS Analysis

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Met4H2 Workshop

Agenda for this Discussion

- Quick Intro- Markes
- Hydrogen Standard methods
- ASTM 7892 Amendments – Method update
- Thermal Desorption Intro
- Hydrogen Sampling approaches for TD-GC-MS/SCD/FID
- TD-GCMS and TD-GCSCD data
- Instrumental Configuration for Energy Gases analysis

Markes International – Global leader in analytical thermal desorption systems

Over 25 years of trace volatile organic analysis

Wide range of products for sampling and analysis of trace volatile and semi-volatile organic compounds

- Expertise in VOCs and SVOCs analysis
- Global presence and collaborations with leading OEMs
- Future-proof instruments – hydrogen compatible

SepSolve Analytical

SCHAUENBURG Analytics

Helping laboratories *"Discover more – Deliver more"* from every sample

Hydrogen Quality standards- Compliance

Maximum concentration of individual contaminants

Maximum concentration of individual contaminants (µmol/mol)	GB/T 37244 & SAE J2719	ISO 14687 EN 17124
Water	5	5
Total hydrocarbons	2	2
Methane	- /100	100
Oxygen	5	5
Helium	300	300
Nitrogen	100 / 300	300
Argon	100 / 300	300
Carbon dioxide	2	2
Carbon monoxide	0.2	0.2
Total sulfur compounds	0.004	0.004
Formaldehyde	0.01 / 0.2	0.2
Formic acid	0.2	0.2
Ammonia	0.1	0.1
Halogenated compounds	0.05	0.05
Particle concentration	1 mg/kg	1 mg/kg

ISO 14687:Hydrogen fuel quality-Product specification
This Standard specifies the minimum quality characteristics of hydrogen fuel as distributed for utilization in vehicular and stationary applications.

CEN/EN 17124: Hydrogen fuel - Product specification and quality assurance for hydrogen refueling points dispensing gaseous hydrogen - Proton exchange membrane (PEM) fuel cell applications for vehicles.

GB/T 37244: Fuel specification for proton exchange membrane fuel cell vehicles-Hydrogen

SAE J2719 is US standard that establishes hydrogen fuel quality levels for fuel cell vehicles

Hydrogen quality standards

Maximum concentration of individual contaminants

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Water	5	5
Total hydrocarbons	2	2
Methane	- /100	100
Oxygen	5	5
Helium	300	300
Nitrogen	100 / 300	300
Argon	100 / 300	300
Carbon dioxide	2	2
Carbon monoxide	0.2	0.2
Total sulphur compounds	0.004	0.004
Formaldehyde	0.01 / 0.2	0.2
Formic acid	0.2	0.2
Ammonia	0.1	0.1
Halogenated compounds	0.05	0.05
Particle concentration	1 mg/kg	1 mg/kg

Acetylene, Acetone, Benzene, Butane, Decane, Decene,Cyclo-hexane, Ethylene, Ethane, Ethanol, Heptane, Isobutane, isopropyl alcohol, Propene, Propane, Methanol, Octane, Toluene etc.

Hydrogen sulphide
Carbonyl sulphide
Dimethyl sulphide
Methyl mercaptan Ethyl mercaptan Tert-butyl mercaptan
Tetrahydrothiophene

+ Acetaldehyde

Chloroethane
Dichloromethane 1,1-Dichloroethane
Tetrachloroethylene
Tetrachlorohexafluorobutane
Dichlorobenzene
Chloroform

Hydrogen Standard Test Methods

Fuel Quality Assurance R&D and Impurity Testing

- **ASTM D7892** Standard Test Method for Determination of Total Organic Halides, Total Non-Methane Hydrocarbons, and Formaldehyde in Hydrogen Fuel by Gas Chromatography/Mass Spectrometry.
- **ASTM D7675** Standard Test Method for Determination of Total Hydrocarbons in Hydrogen by FID Based Total Hydrocarbon (THC) Analyzer
- **ASTM D7676** Standard Practice for Screening Organic Halides Contained in Hydrogen or Other Gaseous Fuels
- **ISO 21087** Gas analysis - Analytical methods for hydrogen fuel - Proton exchange membrane (PEM) fuel cell applications for road vehicles
- **ISO 19880** Gaseous hydrogen- Fuelling stations
- **ASTM D7166** Standard Practice for Total Sulfur Analyzer Based On-line/At-line for Sulfur Content of Gaseous Fuels

Relevant Hydrogen Standards & Practice

ASTM 7892 Method Amendments

Determination of Total Organic Halides, Total Non-Methane Hydrocarbons, and Formaldehyde in Hydrogen Fuel by Gas Chromatography/Mass Spectrometry

ASTM 7892-22

4. Summary of Test Method Cryogen Based

4.1 The target compounds in Table 1 and Table 2, which may be contained in a 400 mL hydrogen sample, are cryogenically frozen or concentrated onto a glass bead trap at -150 °C. The target compounds are slowly desorbed by warming to 10 °C and transferred to a Tenax trap cooled to -60 °C using desorption flow rate of 10 mL/min. This process leaves water in the glass bead trap and dehydrates the sample. The Tenax trap is then desorbed by heating to 180 °C and the target compounds cyro-focused at -170 °C at the entrance to a GC column (see 6.5). The cyro-focusing section is then rapidly heated up to 80 °C to release the cryo-focused target compounds, which are eventually eluted from the column and analyzed using a mass spectrometer scanning from m/e 23 to 100 for initial 4.5 min and from m/e 34 to 550 the remaining analytical time. The retention times of the target compounds are listed in Table 1 and Table 2 under the chromatographic conditions in 6.5.

ASTM 7892-25

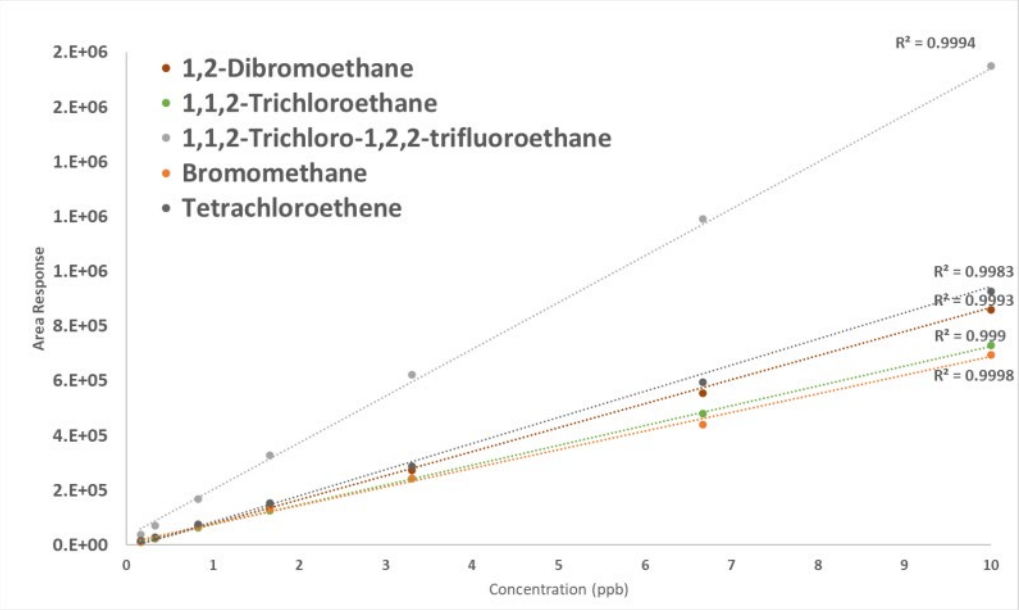
Cryogen Based

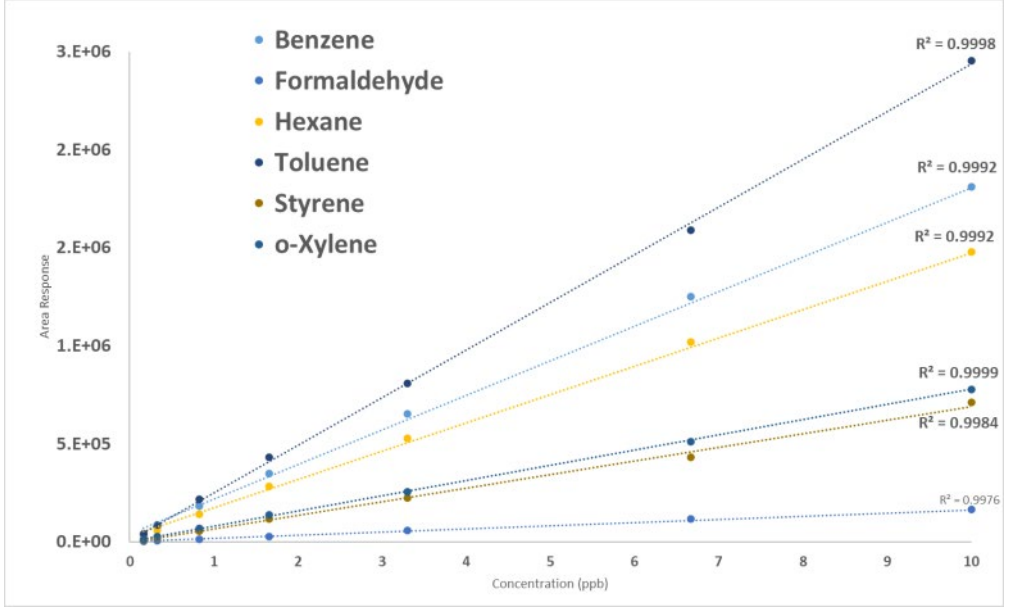
4.1.1 *Cryogen System*—The target compounds in Table 1 and Table 2, which may be contained typically in a 400 mL hydrogen sample, are cryogenically frozen or concentrated onto a glass bead trap at -150 °C. The target compounds are slowly desorbed by warming to 10 °C and transferred to a porous polymer trap cooled to -60 °C using a desorption flow rate of typically 10 mL/min. This process leaves water in the glass bead trap and dehydrates the sample. The polymer trap is then desorbed by heating to 180 °C and the target compounds cryo-focused at -170 °C at the head of the GC column (see 6.5). The cryo-focusing section is then rapidly heated up to 80 °C to release the cryo-focused target compounds, which are then eluted from the column and analyzed using a mass spectrometer scanning from m/e 23 to 100 for typically 4.5 min and from m/e 34 to 550 the remaining analytical time. The retention times of the target compounds are listed in Table 1 and Table 2 under the chromatographic conditions in 6.5.

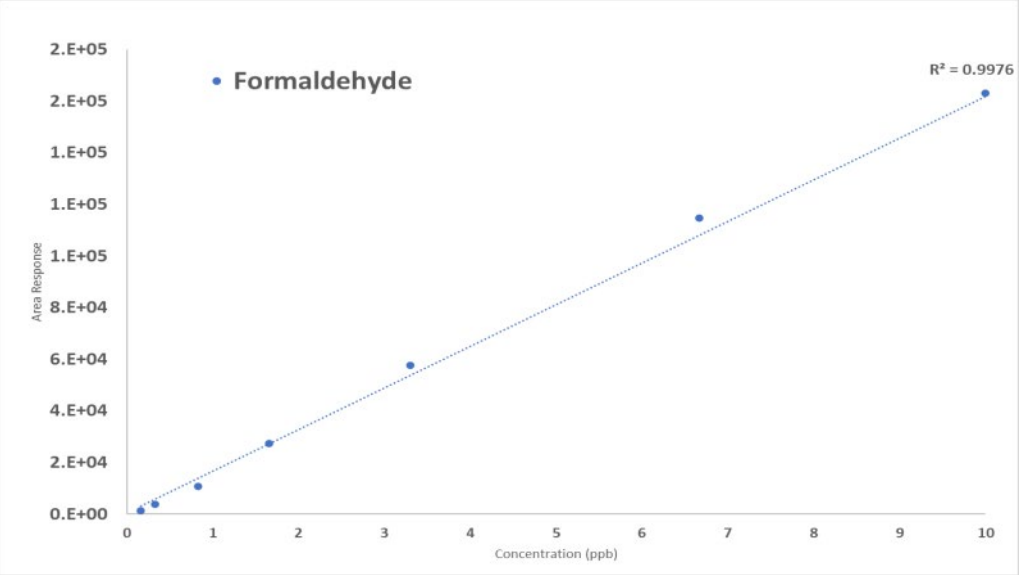
Non-Cryogen Based

4.1.2 Cryogen-free systems contains a water abstraction device and sorbent filled focusing trap. In these systems, the sample is drawn through an thermoelectric (Peltier) cooled empty glass trap held at -30 °C, in which water is removed, without the need for liquid cryogen, while target organic vapours pass through without loss. A second thermoelectric cooled sorbent focusing trap containing multiple sorbents ranging from weak to strong (see 6.7) is used to retain organic analytes over thea wide volatility and polarity range while any residual water is purged to vent. The sorbent trap is then heated rapidly to release the target analytes onto the GC column using a reverse flow of carrier gas, without the need to cryo-focus analytes at the head of the GC capillary column.

Single Lab Precision Study







Compound	Linearity: R2
1,1,2-Trichloro-1,2,2-trifluoroethane	0.9995
1,1,2-Trichloroethane	0.9999
1,2-Dibromoethane	0.9993
Bromomethane	0.9990
Tetrachloroethene	0.9982
Benzene	0.9992
Formaldehyde	0.9977
Hexane	0.9993
Styrene	0.9984
Toluene	0.9998
o-Xylene	0.9999

ASTM 7892-25 revised Standard

- Method has been reviewed using non-cryogen pre-concentration technology
- Single Lab precision study was carried out to support standard method amendments
- Linearity: 0.25ppb standard all shown compounds R^2>0.997
- Reproducibility: 10 replicate 0.25 ppb RSD shown ~2.87% for Organic Halides and ~2.34& for Non-methane Hydrocarbons compounds

D7892 – 25

TABLE 5 Estimated Repeatability At (@) Average (ppb(v)) of Non-Halogenated Non-Methane Hydrocarbons using a Cryo-TD System and Cryo-Free Pre-concentration System

	Cryogen preconcentration system	Cryogen-free preconcentration system
Non-Methane Hydrocarbons	Estimated Repeatability At (@) Average (ppb(v))	Estimated Repeatability At (@) Average (ppb(v)) n=10
1,2,4-Trimethylbenzene	0.1 @ 1	0.02 @ 0.25
1,3,5-Trimethylbenzene	0.1 @ 1	0.02 @ 0.25
1,3-Butadiene	0.1 @ 1	0.01 @ 0.25
1,4-Dioxane	0.3 @ 1	0.01 @ 0.25
2-Butanone	0.3 @ 1	0.01 @ 0.25
2-Hexanone	0.3 @ 1	0.41 @ 0.25
4-Ethyltoluene	0.2 @ 1	0.02 @ 0.25
4-Methyl-2-Pentanone	0.5 @ 1	0.02 @ 0.25
Acetone	0.5 @ 1	0.01 @ 0.25
Ethene	0.7 @ 2	No data
Benzene	0.1 @ 1	0.01 @ 0.25
Cyclohexane	0.04 @ 1	0.02 @ 0.25
Ethane	0.7 @ 3	No data
Ethanol	0.8 @ 1	0.03 @ 0.25
Ethyl Acetate	0.1 @ 1	0.02 @ 0.25
Ethylbenzene	0.1 @ 1	0.02 @ 0.25
Formaldehyde	2.3 @ 5	0.04 @ 0.25
Heptane	0.5 @ 1	0.02 @ 0.25
Hexane	0.1 @ 1	0.02 @ 0.25
Isopropyl Alcohol	0.4 @ 1	0.02 @ 0.25
Methyl tert-Butyl Ether	0.2 @ 1	0.02 @ 0.25
Propane	0.6 @ 3	No data
Propene	0.4 @ 1	0.02 @ 0.25
Styrene	0.1 @ 1	0.02 @ 0.25
Tetrahydrofuran	0.1 @ 1	0.01 @ 0.25
Toluene	0.2 @ 1	0.02 @ 0.25
Vinyl acetate	0.4 @ 1	0.15 @ 0.25
Xylenes, m&p-	0.1 @ 1	0.02 @ 0.25
Xylenes, o-	0.1 @ 1	0.02 @ 0.25

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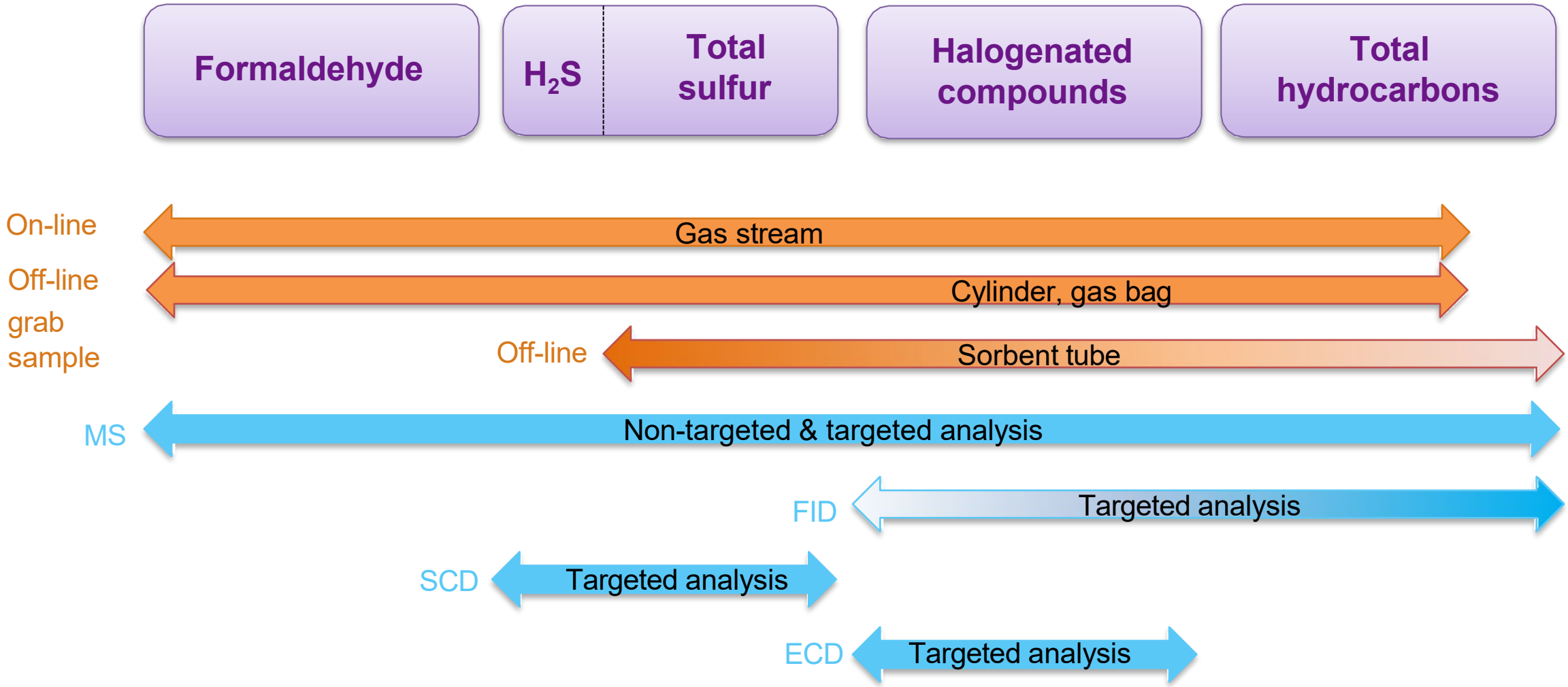
How TD can be applied ?
Thermal Desorption
Pre-concentration technique

Sampling and analytical options

Profiling or targeted analysis

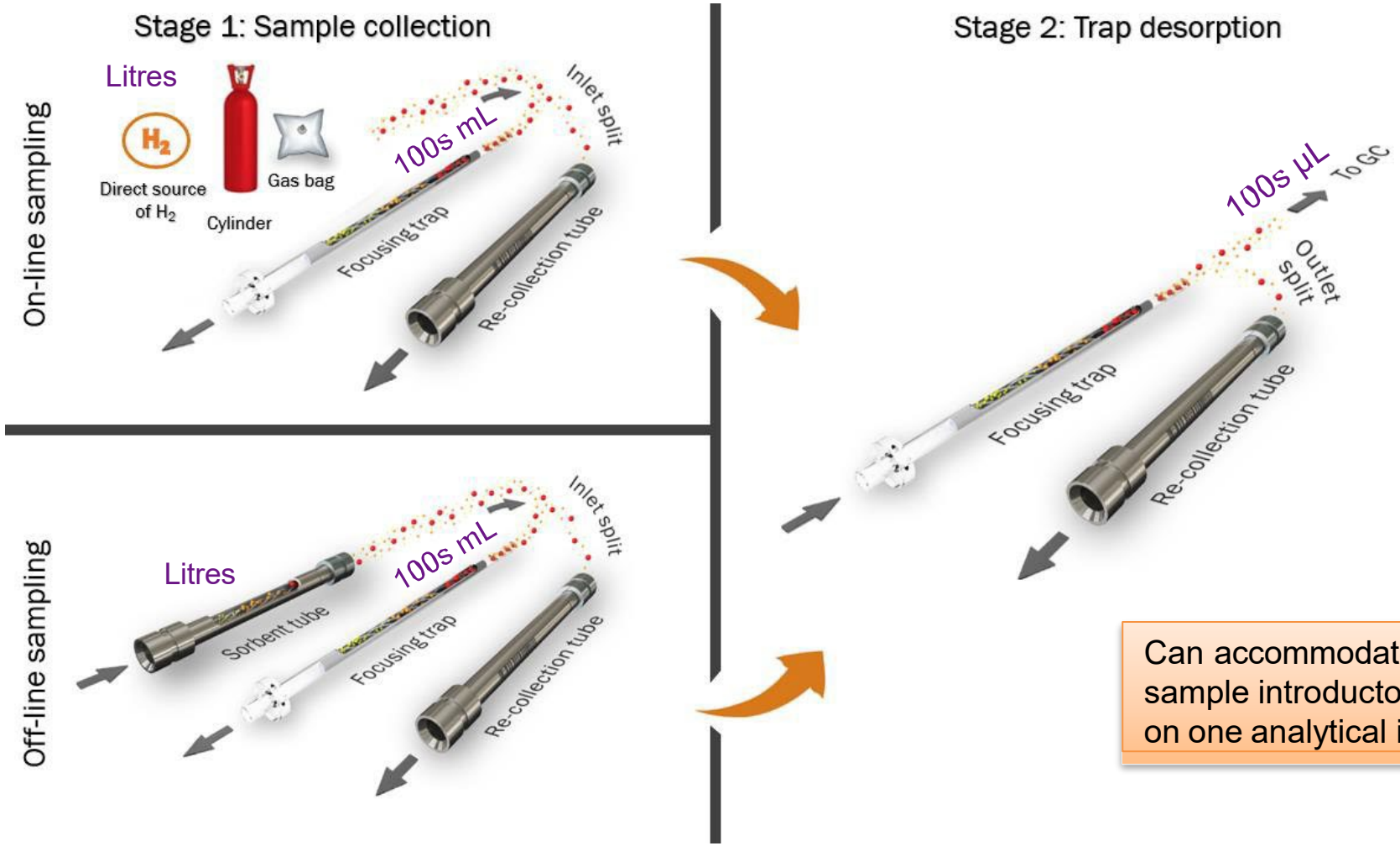


Pre-concentration of Hydrogen impurities by TD

Schematic of on-line and off-line preconcentration of hydrogen sample

Hydrogen production Fuel cell stack

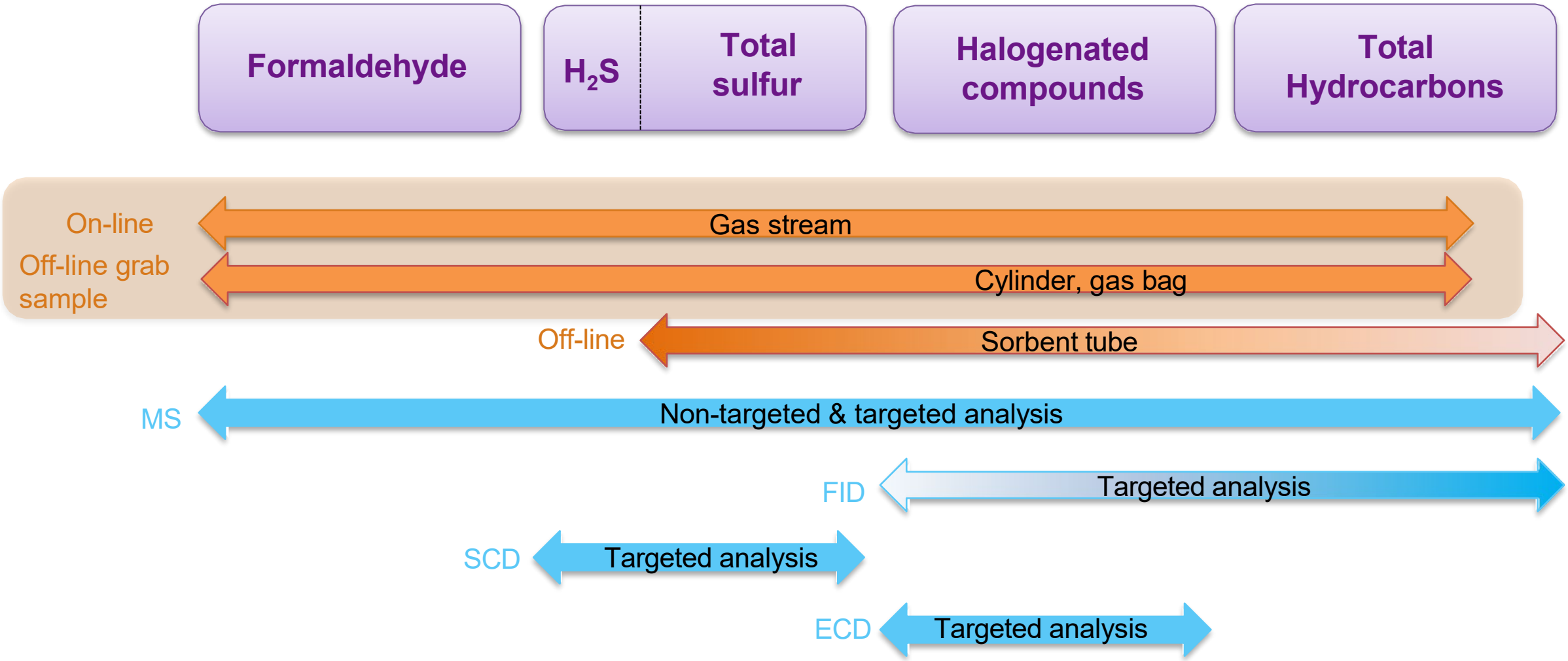
Hydrogen refuelling Stations



Can accommodate both sample introductory techniques on one analytical instrument

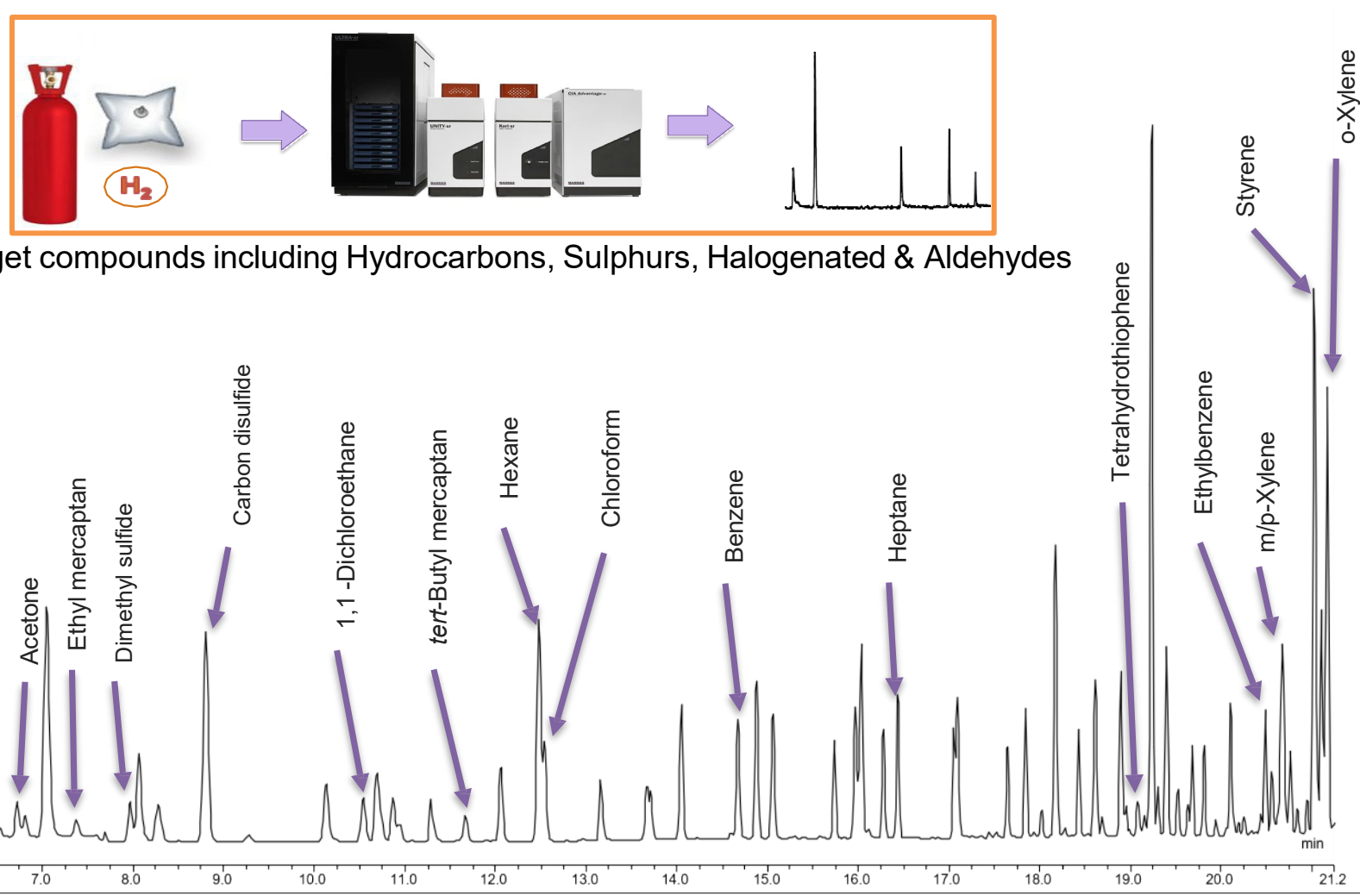
Sampling and analytical options

Profiling or targeted analysis



Data quality assessment for on-line samples TD–GC–MS

Broad range of analytes in single analytical run



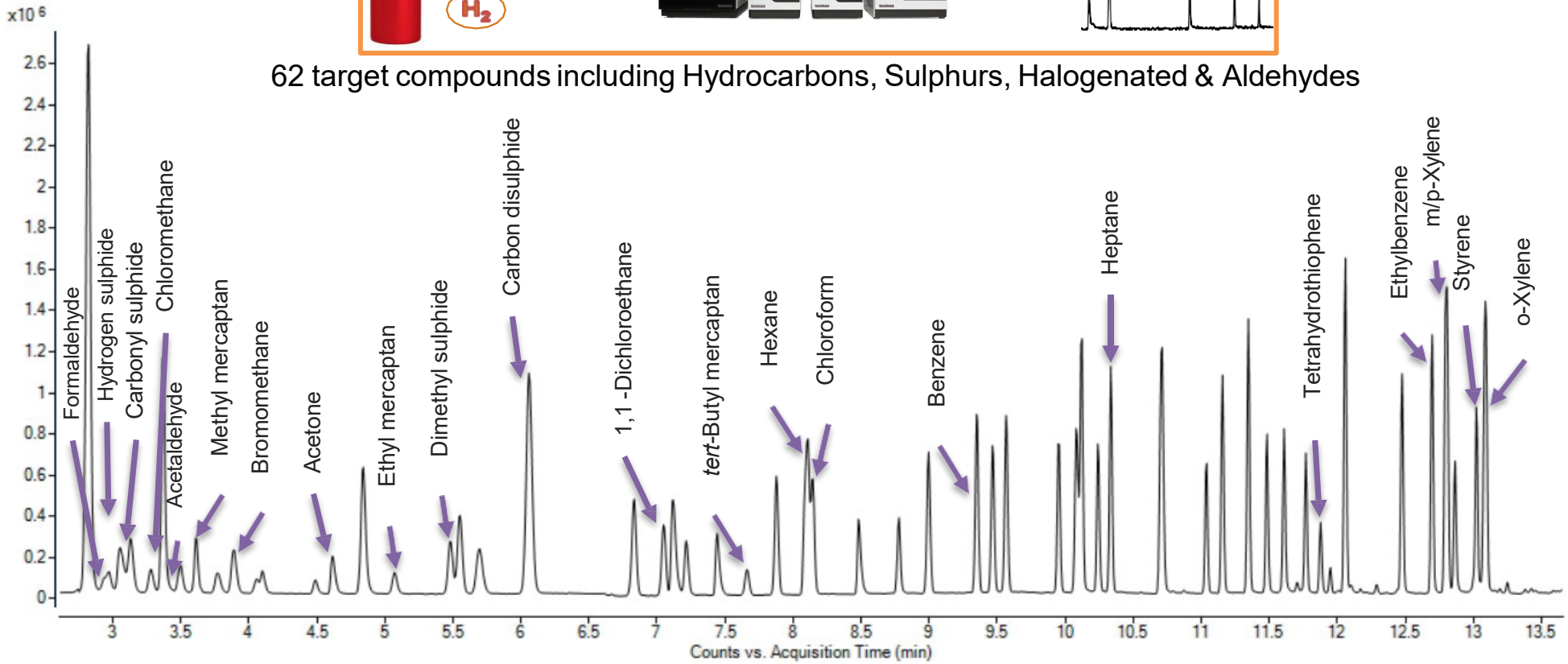
Helium as carrier gas

Future proofing with sustainable carrier gases

MULTI-GAS ENABLED

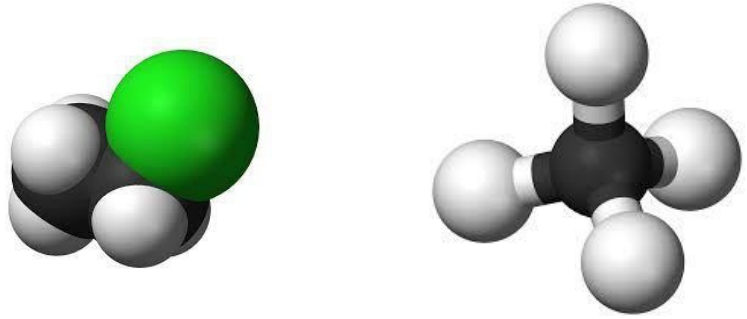
Hydrogen carrier gas – renewable and energy efficient

62 target compounds including Hydrocarbons, Sulphurs, Halogenated & Aldehydes

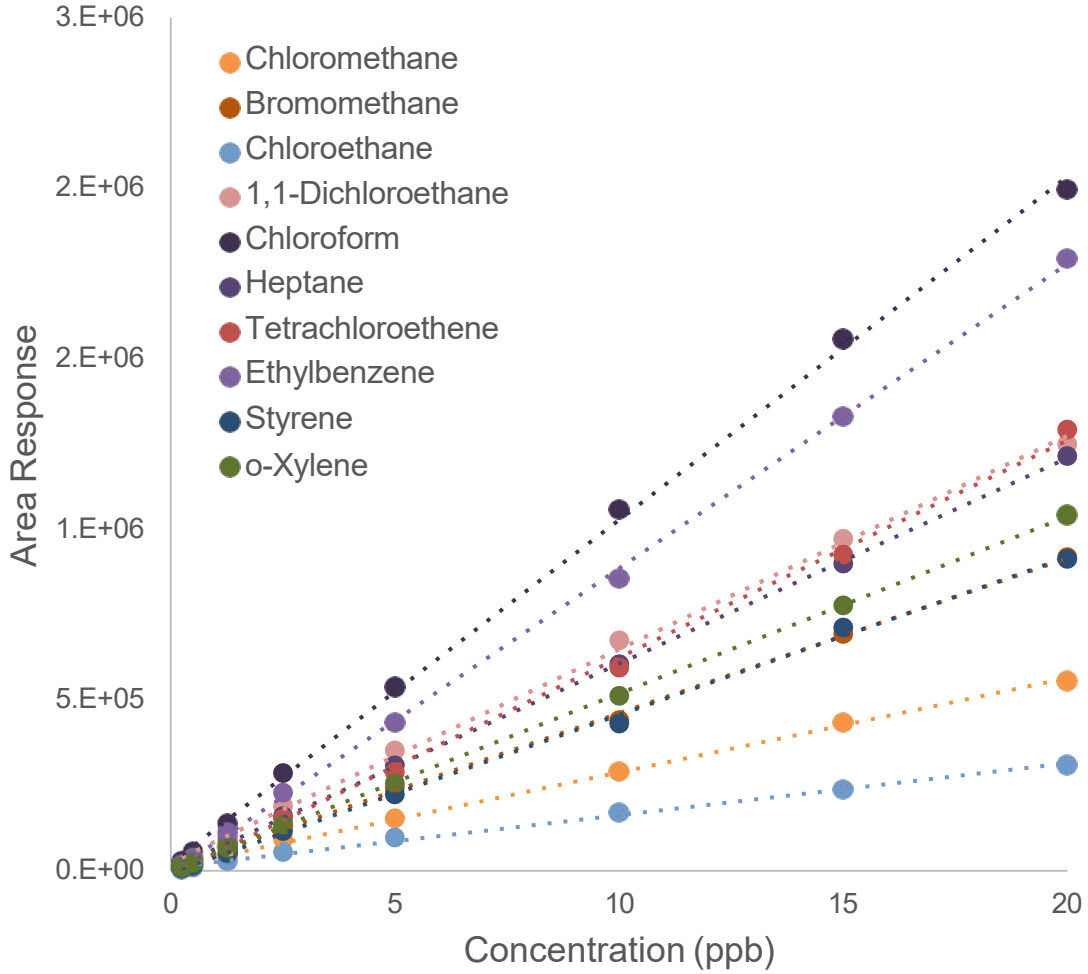


Data quality assessment for on-line samples by TD–GC–MS

Key impurities – halogenated and hydrocarbon compounds

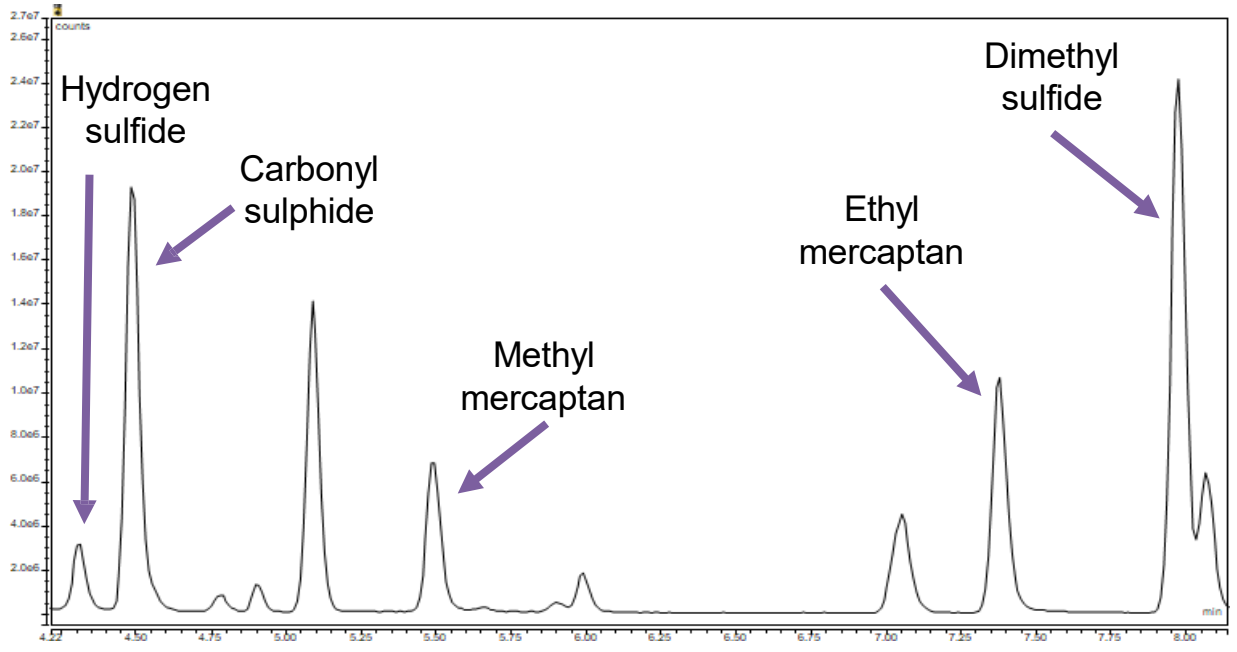


- Halogenated and hydrocarbon compounds in mix from 0.25 to 20 ppb
- Linearity: Average R^2 0.999 across the shown compounds
- Reproducibility: 9 replicates of 2.5 ppb halogenated and hydrocarbon standard <2.37% RSD for same compounds

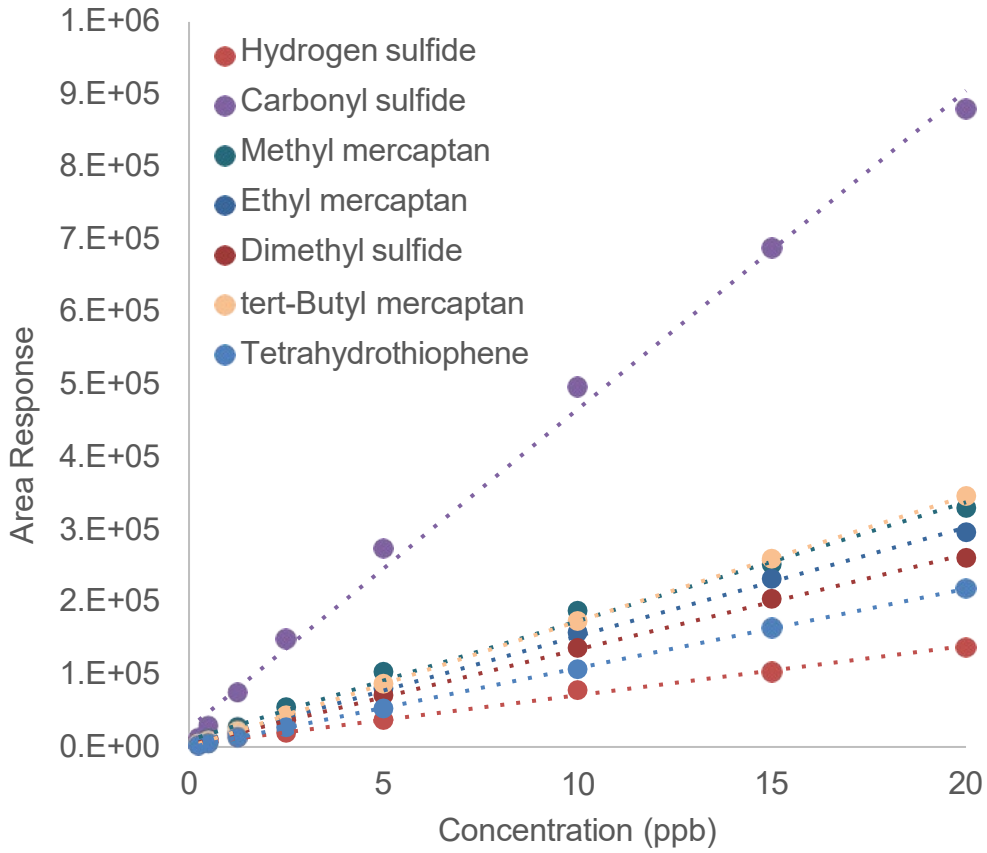


Data quality assessment for on-line samples using GC–MS

Sulphur Species: Inert flow path enables quantitative analysis of reactive species



Combined SIM windows for sulfur standard

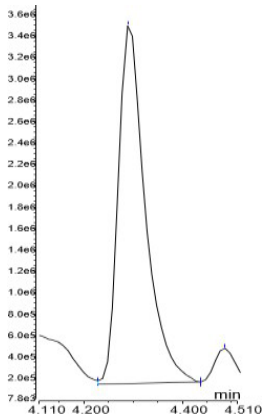


- Linearity: 0.25-20 ppb standard all of shown compounds R^2>0.994
- Reproducibility: 9 replicate 2.5 ppb RSD <3.57% for all shown compounds

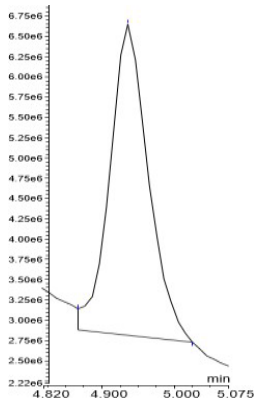
Data quality assessment for on-line samples by TD–GC–MS

Aldehydes: formaldehyde and acetaldehyde

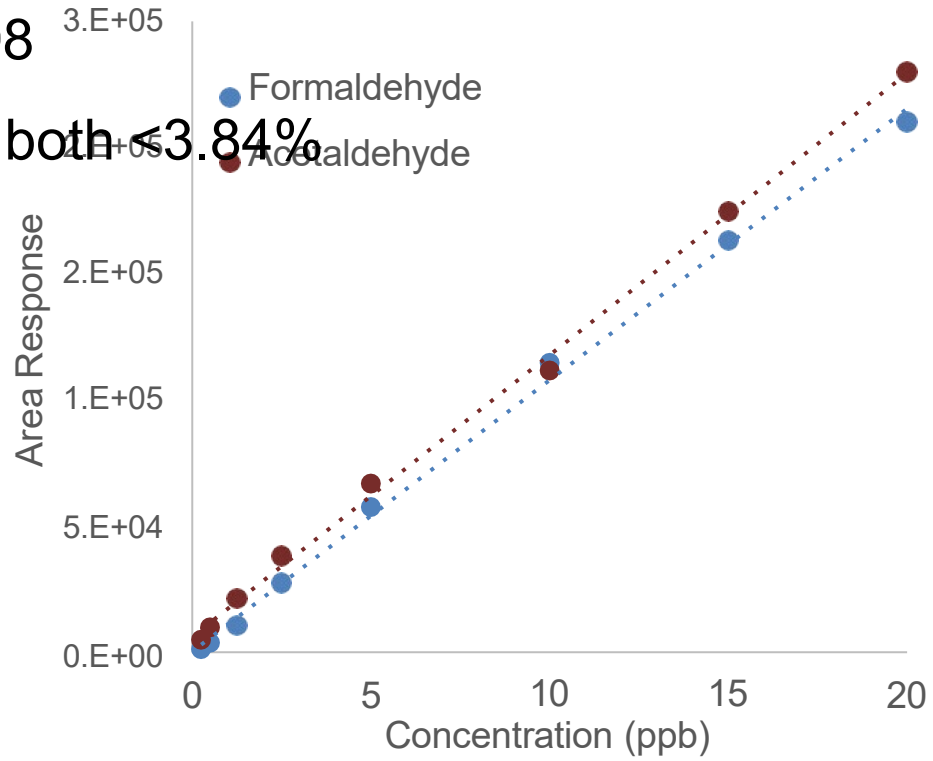
- Linearity: 0.25 to 20 ppb standard both R^2>0.998
- Reproducibility: 9 replicates of 2.5 ppb sample, both <3.84% RSD
- Excellent peak shape



Formaldehyde



Acetaldehyde



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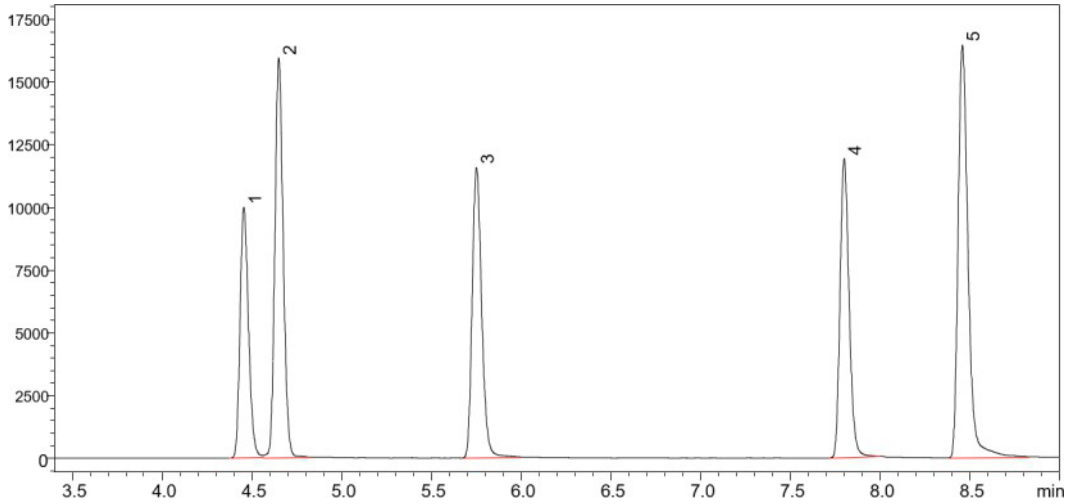
Alternative detectors

Thermal Desorption–Gas Chromatography with Sulfur Chemiluminescence Detection (TD–GC–SCD)

Validation of system using alternative detectors

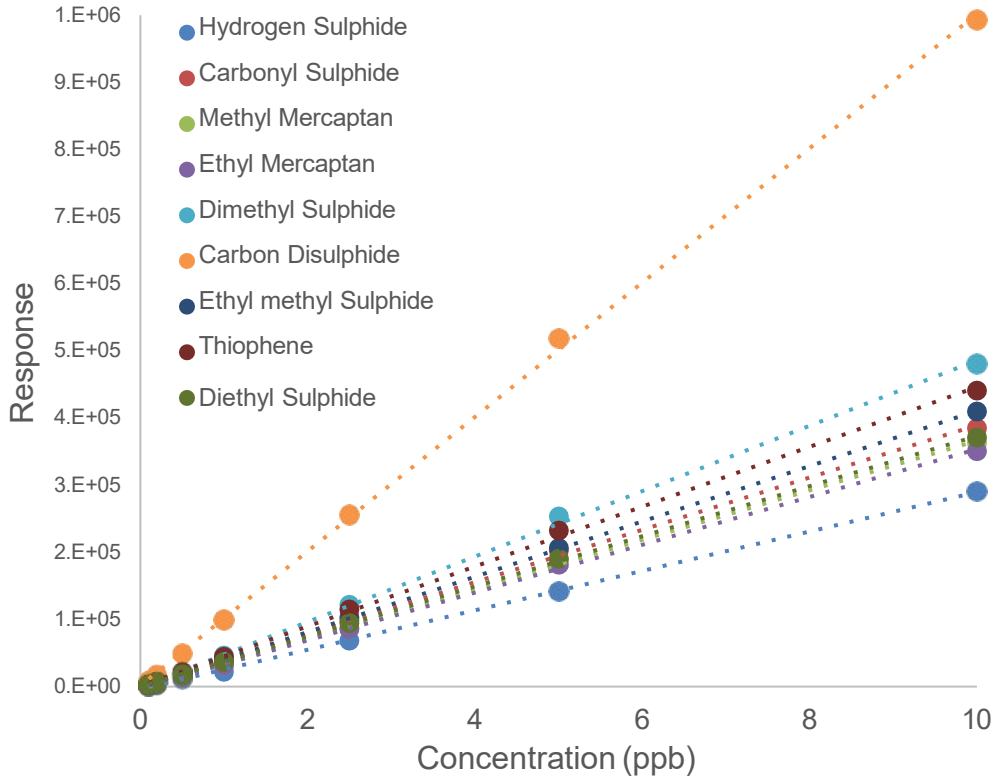
High quality data achieved with TD–GC–SCD

Excellent peak shape for early eluting compounds at low concentrations of 1 ppb



1. Hydrogen sulfide 2.Carbonyl sulfide 3.Methanethiol 4.Ethanethiol 5.Dimethyl sulfide

Linearity plot showing concentrations from 0.1 – 10 ppb for a range of sulfur compounds

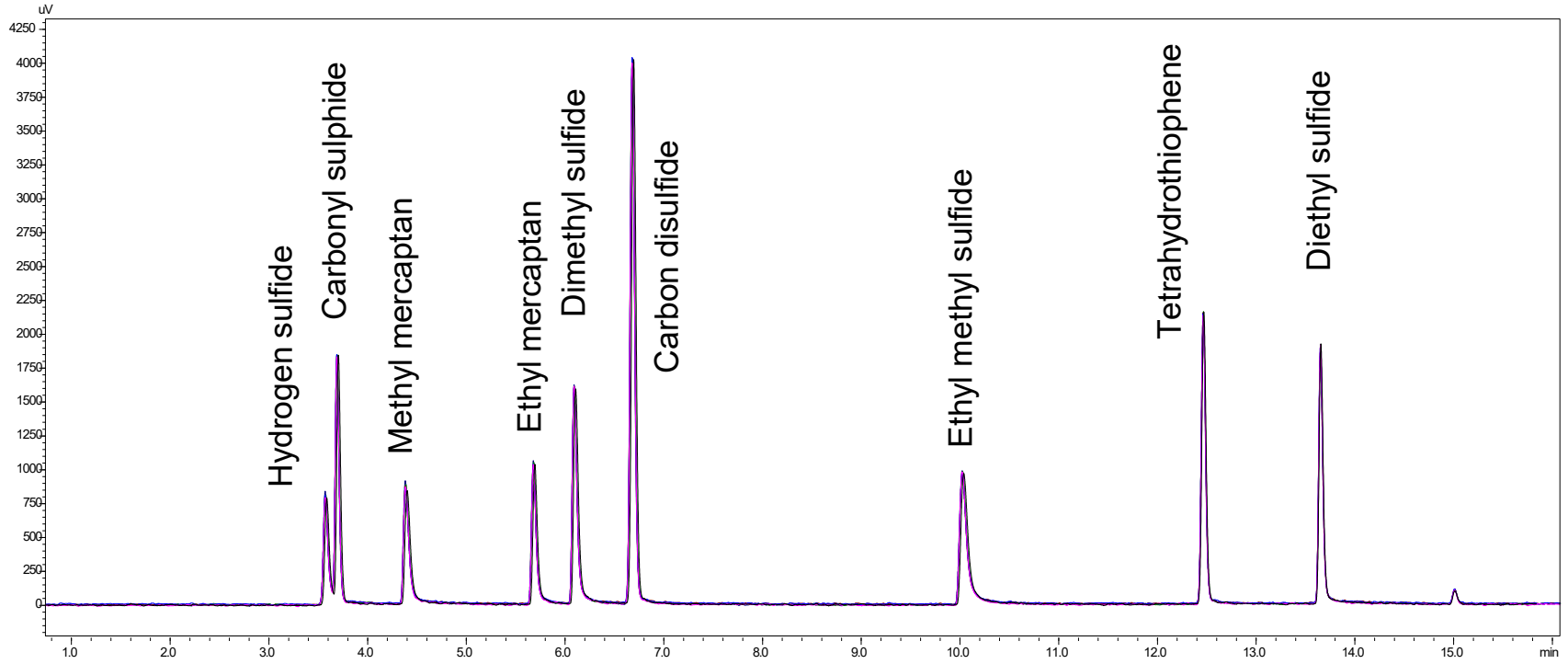


Linearity: R^2>0.999 for all sulfur compounds

Reproducibility: 6 replicates of 0.1 ppb standard <2.8% RSD

Targeted measurement of trace level sulfur using GC–SCD

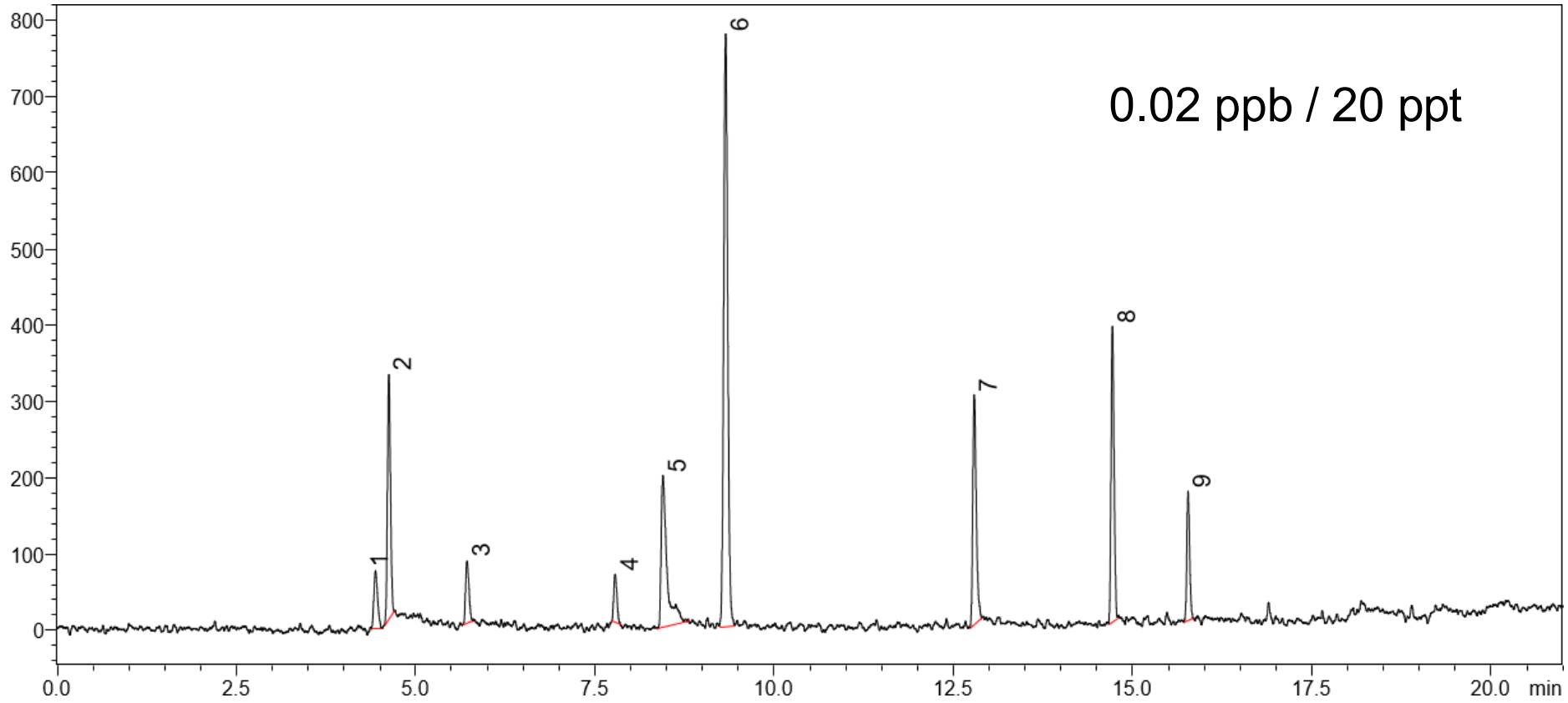
- Selective detector mitigates impact from interferences in GC–MS.
- Allows larger sample volumes up to 800 mL.
- Highly sensitive and reproducible sulfur quantitation.



Six overlaid replicates of sulfurs in hydrogen at 50 ppt.

Validation of system using alternative detectors

Using TD–GC–SCD for sulfur compounds at trace level concentrations

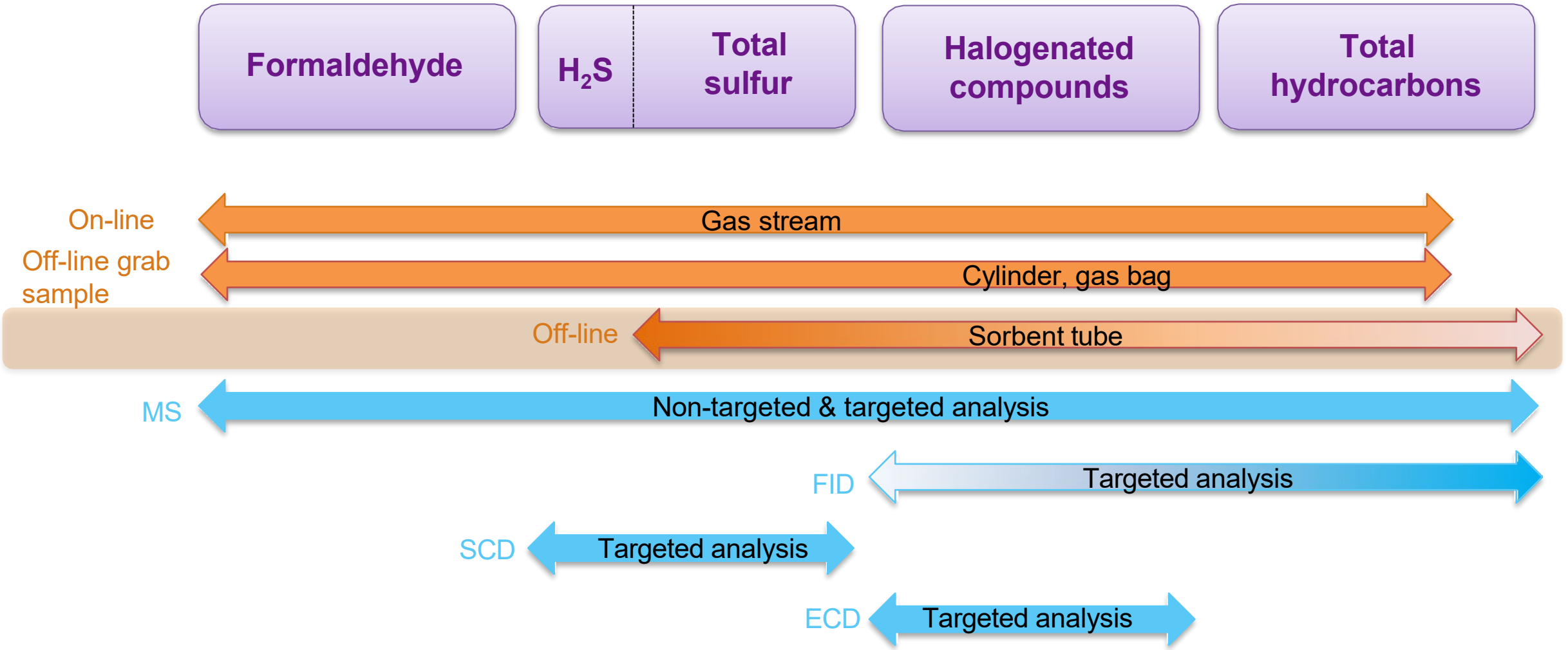


1. Hydrogen sulfide
2. Carbonyl sulfide
3. Methanethiol
4. Ethanethiol
5. Dimethyl sulfide
6. Carbon disulfide
7. Ethyl methyl sulfide
8. Thiophene
9. Diethyl sulfide

Specific detectors enable detection down to trace level concentrations such as 20 ppt

Sampling and analytical options

Profiling or targeted analysis



Off-line sorbent tube samples

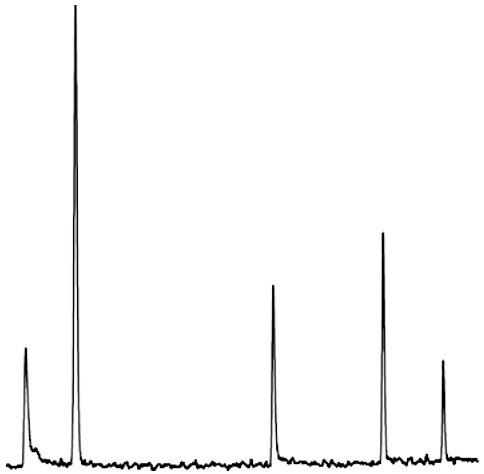
Sampling procedure

Several litres of Hydrogen

Sorbent Tube

Capped & shipped to lab

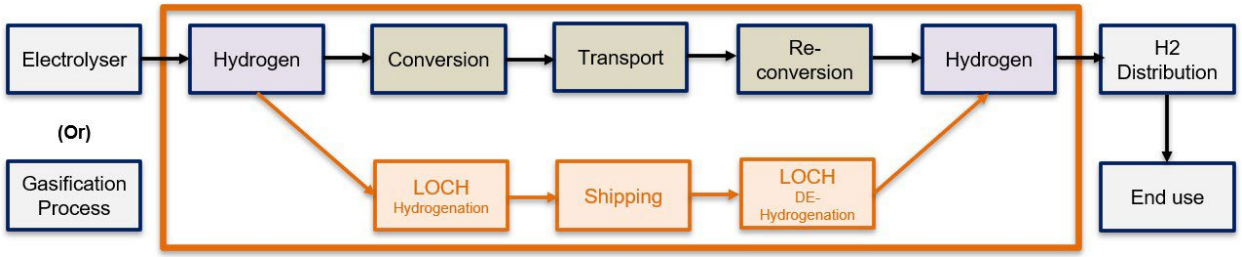
TD instrumentation

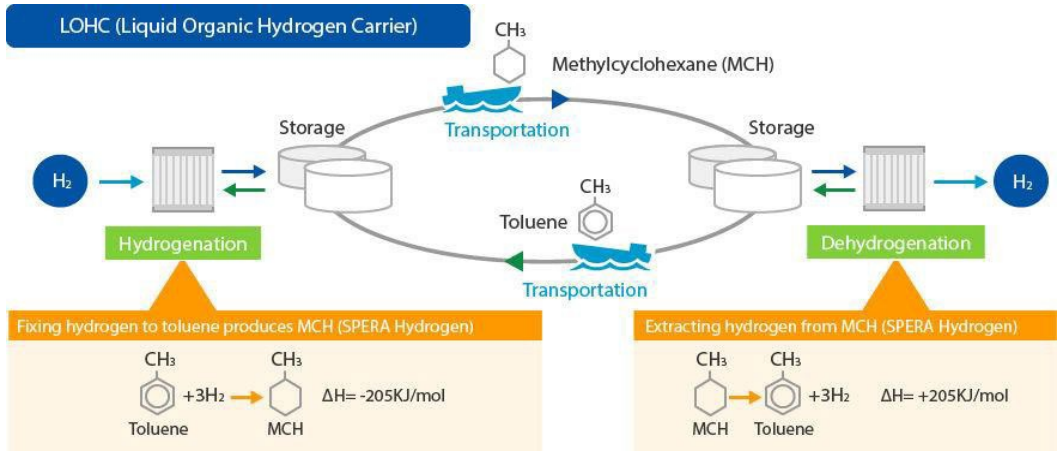


Impurities screening

Off-line Analysis of Hydrogen: Sorbent Tube approach

What's best for Hydrogen transport: ammonia, liquid hydrogen, LOHC or pipelines?



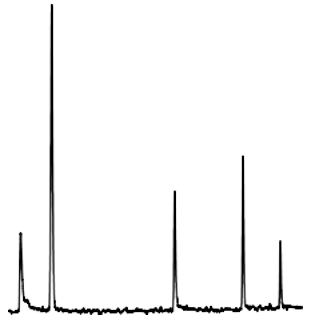


Several litres of Hydrogen

Sorbent Tube

Capped & shipped to lab

TD instrumentation

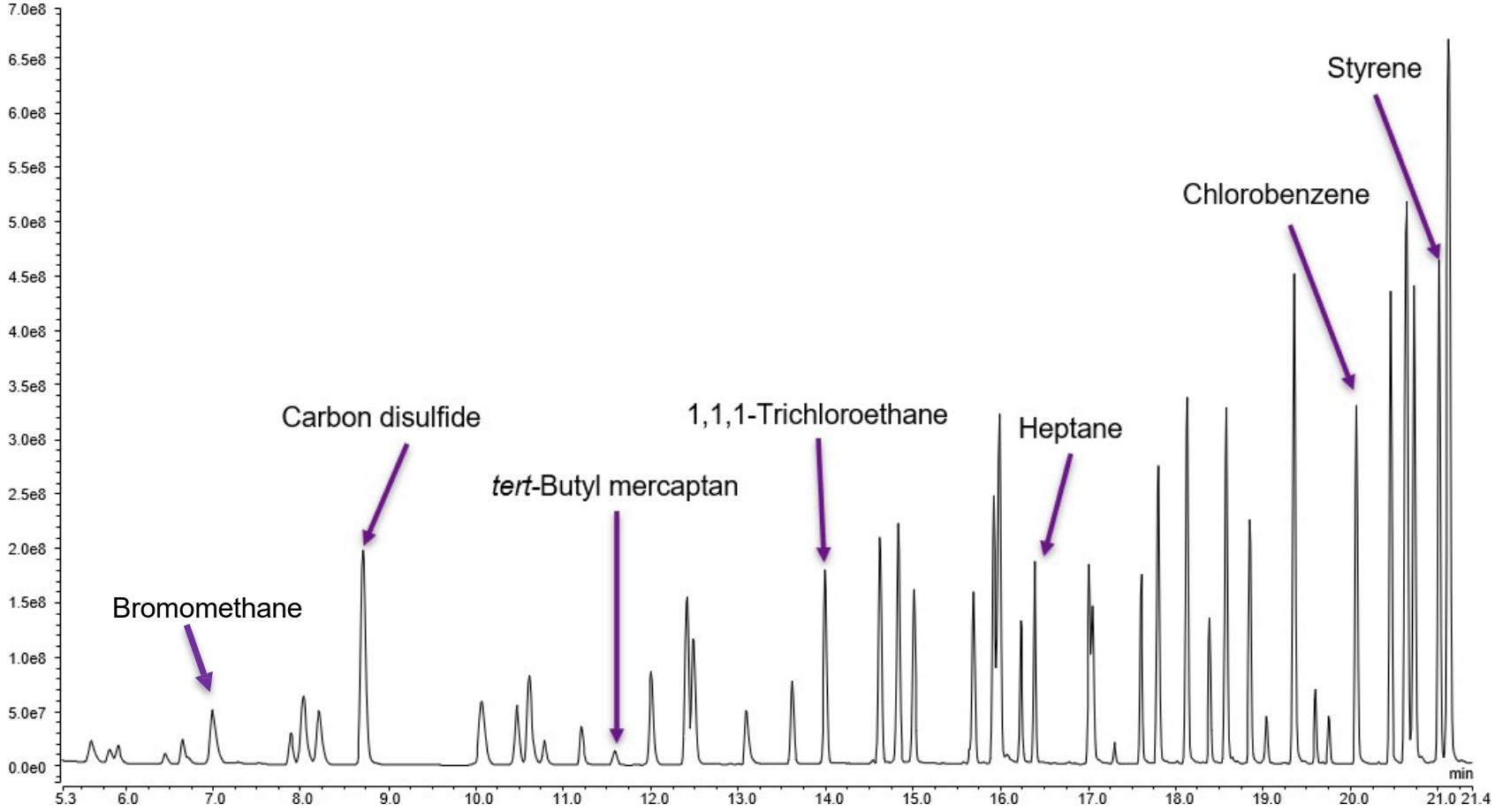


Impurities screening

Tube-based hydrogen impurities testing

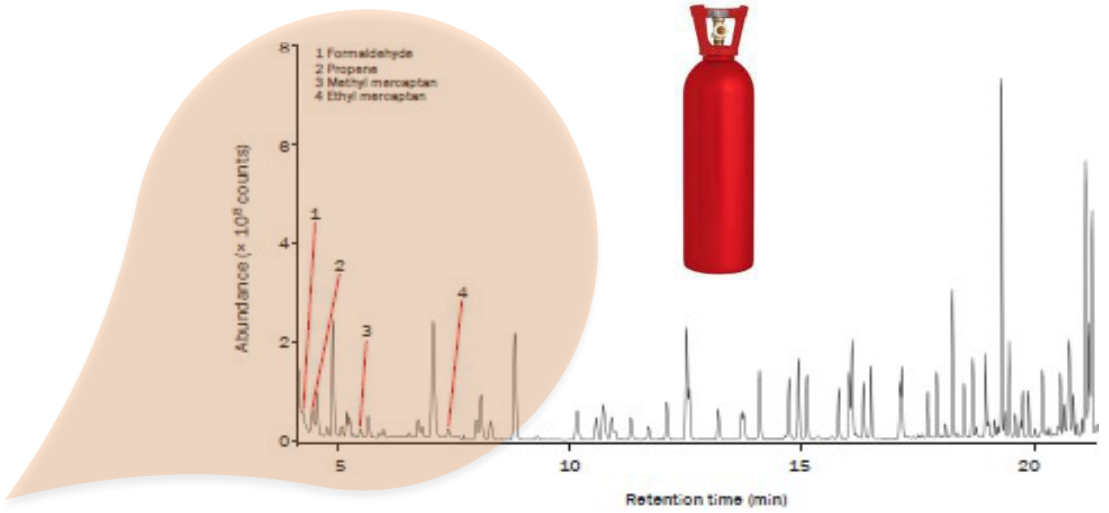
Not only ‘on-line’ but also ‘off-line’ analysis of hydrogen sample

- Remote sampling at multiple sites.
- Optimal for shipping.
- Extend storage stability especially for sulfurs.
- Enhance sensitivity with extended sample volumes.



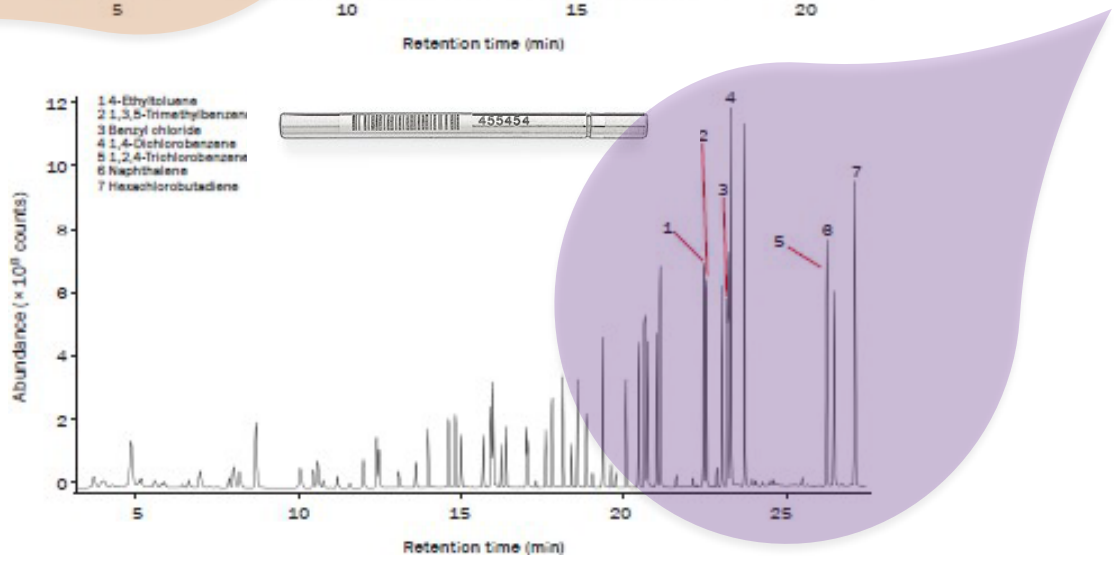
Sampling strategies deliver complementary information

Important for discovery and characterisation phases



Sorbent tube samples extend the range to heavier VOC impurities including tri-chlorobenzenes, naphthalene and hexachlorobutadiene.

Online or Cylinder grab are best for ultra volatile impurities including formaldehyde and hydrogen sulfide.



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Instrument configuration and data evaluation for hydrogen fuel impurities

Instrument Configuration

Multi-Gas hydrogen certified UNITY–Kori–CIA *Advantage*-xr ™ automated system

- Accommodates numerous sample types for the ultimate flexibility – on-line, sampling bags, canisters (cylinders) and has the option to upgrade with an autosampler for sorbent tube analysis
- '-xr series' can be installed onto multiple platforms, including GC–MS, GC–FID, GC–SCD – dual detectors
- Configuration enables simultaneous targeted and untargeted analysis for specified analytes and screening of samples

UNITY–Kori–CIA Advantage-xr

MULTI-GAS ENABLED

Single Instrument for analysing key impurities in Energy Gases

U-T14 H2S-2S

Hydrogen Fuels

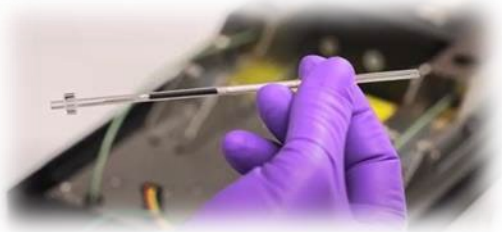
CCSU

U-T6 SUL-2S

U-T11 GPC-2S

Biogas

Focusing Trap



Multi-Gas-xr TD instruments

Not only can you analyse Hydrogen itself, but also WITH Hydrogen

UNITY-xr

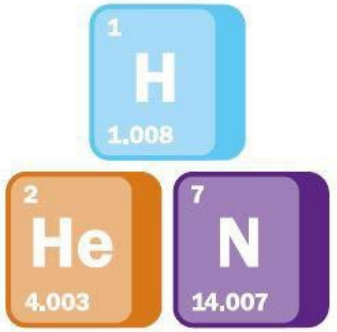
UNITY–ULTRA-xr

TD100-xr

MULTI-GAS ENABLED

UNITY–Air Server-xr

UNITY–Kori–CIA *Advantage*-xr



Conclusions

Optimised solutions for targeted or untargeted analysis

- Pre-concentration by TD delivers exceptional sensitivity for measuring total impurity classes and simultaneous speciation.
- TD couple with GC/MS/FID can be applied to multiple applications (H2, CO_2 and Biogas) with a simple swapping of focusing trap.
- Sampling strategies can be optimised for workflow and target analyte considerations.
- Both On-line and Off-line sampling can be carried out in a single sequence.
- Inert flow paths deliver reliable performance for even highly reactive hydrogen sulfide and formaldehyde.
- Couple TD with GC–SCD for targeted sulfur compound analysis at ultra trace levels (ppt).
- Couple TD with GC–MS for untargeted characterisation and quantitative measurement.
- Comply with relevant standards (ISO 14687, DIN EN 17124, SAE J2719 and ASTM D7892).

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