The Role of Chemical Metrology in Decarbonisation and Renewable Energy

Annarita Baldan

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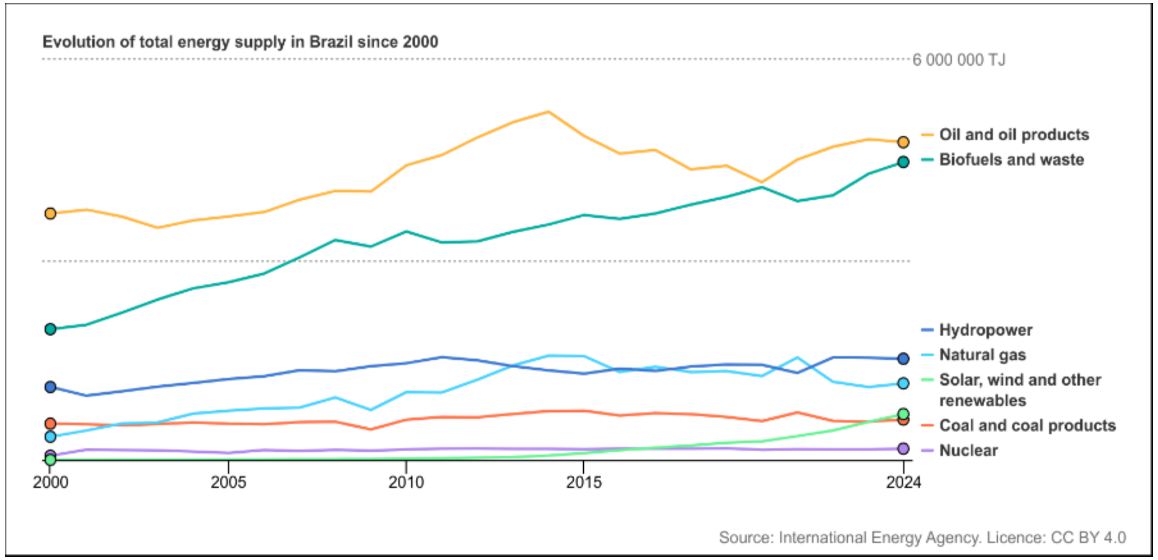
Renewable energy in Brazil



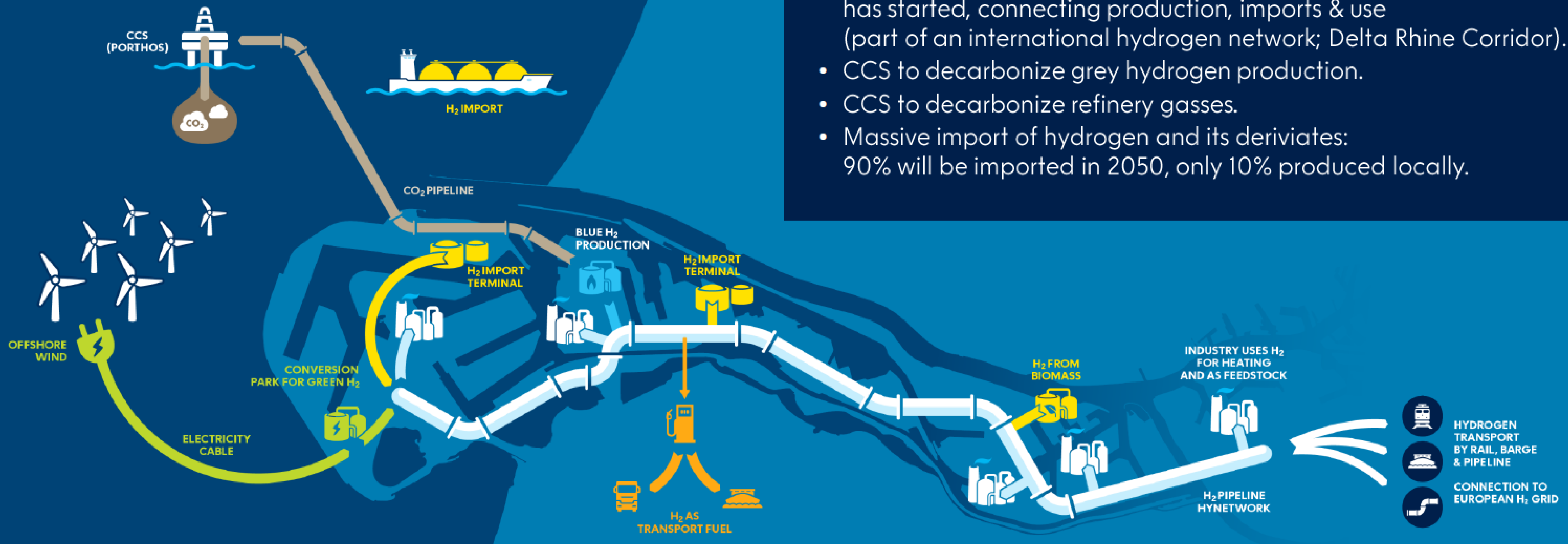
IEA 2024; https://www.iea.org/data-and-statistics/data-product/world-energy-statistics-and-balances, License CC BY 4.0

Share of modern renewables in final energy consumption (2022), Source IEA

Country	%
ISL	82.21
GAB	66.18
NOR	60.24
SWE	59.65
URY	51.39
FIN	49.59
LVA	47.23
BRA	**44.95**
PRY	44.84

Programa Nacional do Hidrogênio

ROTTERDAM'S HYDROGEN ECOSYSTEM IS BEING BUILT RIGHT NOW

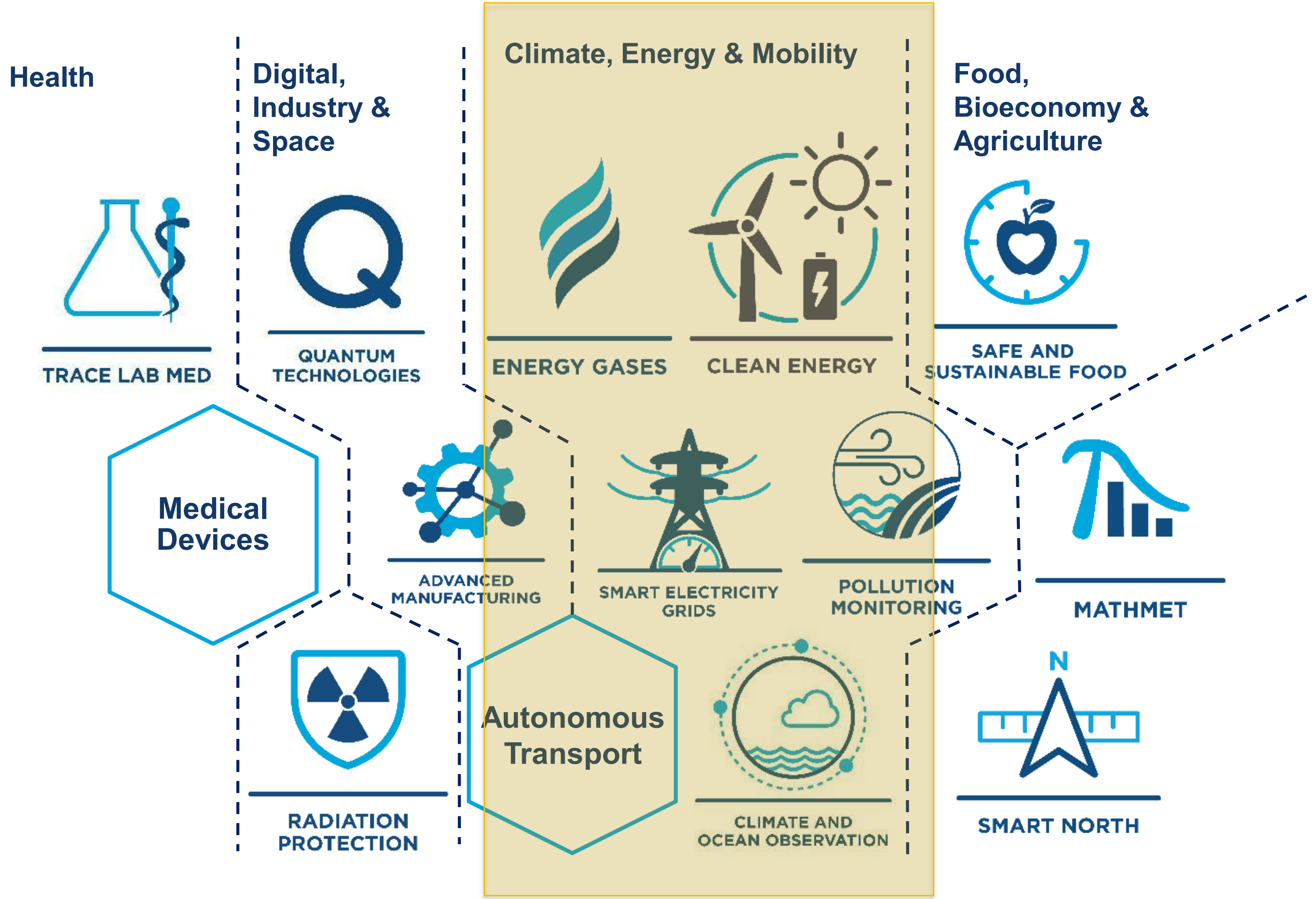


We are making this happen

- Offshore wind farms connected to Rotterdam: 7.4 GW in 2030.
- Production of green hydrogen (first 200 MW electrolyser under construction): 2-2.5 GW in 2030.
- Construction of open access Hydrogen pipeline across the port has started, connecting production, imports & use (part of an international hydrogen network; Delta Rhine Corridor).
- CCS to decarbonize grey hydrogen production.
- CCS to decarbonize refinery gasses.
- Massive import of hydrogen and its deriviates: 90% will be imported in 2050, only 10% produced locally.

European Metrology Networks (EMNs)

- ❑ Central role in achieving the objectives of EU Metrology Partnership
- ❑ Focus on specific sectors
- ❑ EMN members, partners, stakeholders



Proposed EMN

EMN for Energy Gases

Focus on accurate measurements for quality, regulation, trade, safety, interoperability AND Innovation

- ❖ **Engage** with stakeholders
- ❖ **Facilitate measurement research**

C

Method
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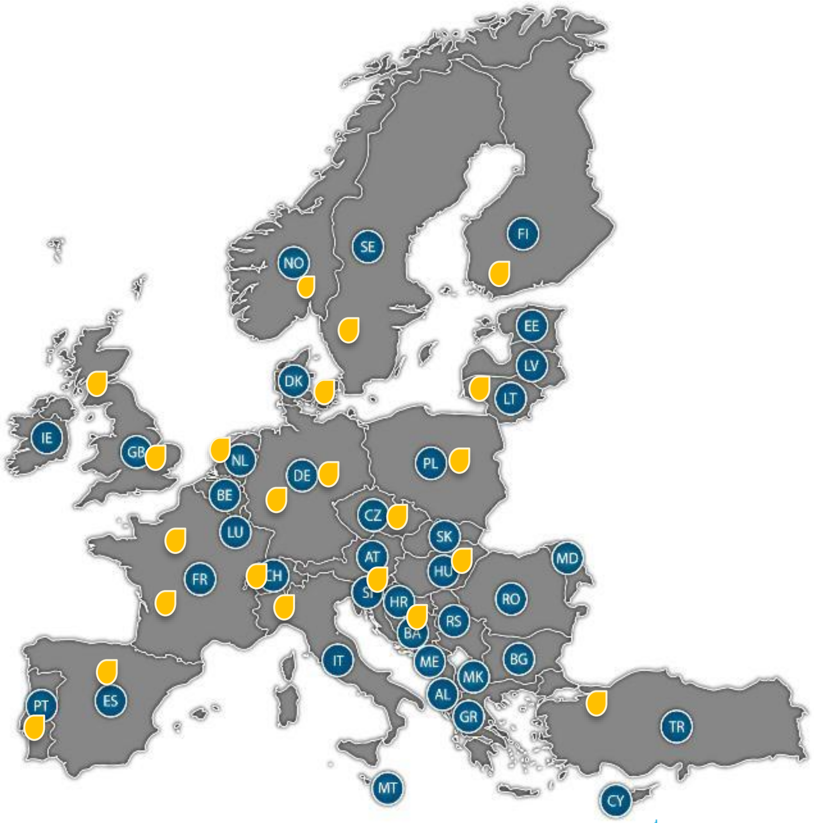
Flow
Pressur Temper
Calorim



ENERGY GASES

Chemical metrology (gas analysis) research

Energy gases

- Hydrogen
- Biomethane
- Other energy carriers
- CCUS

Environment & Climate

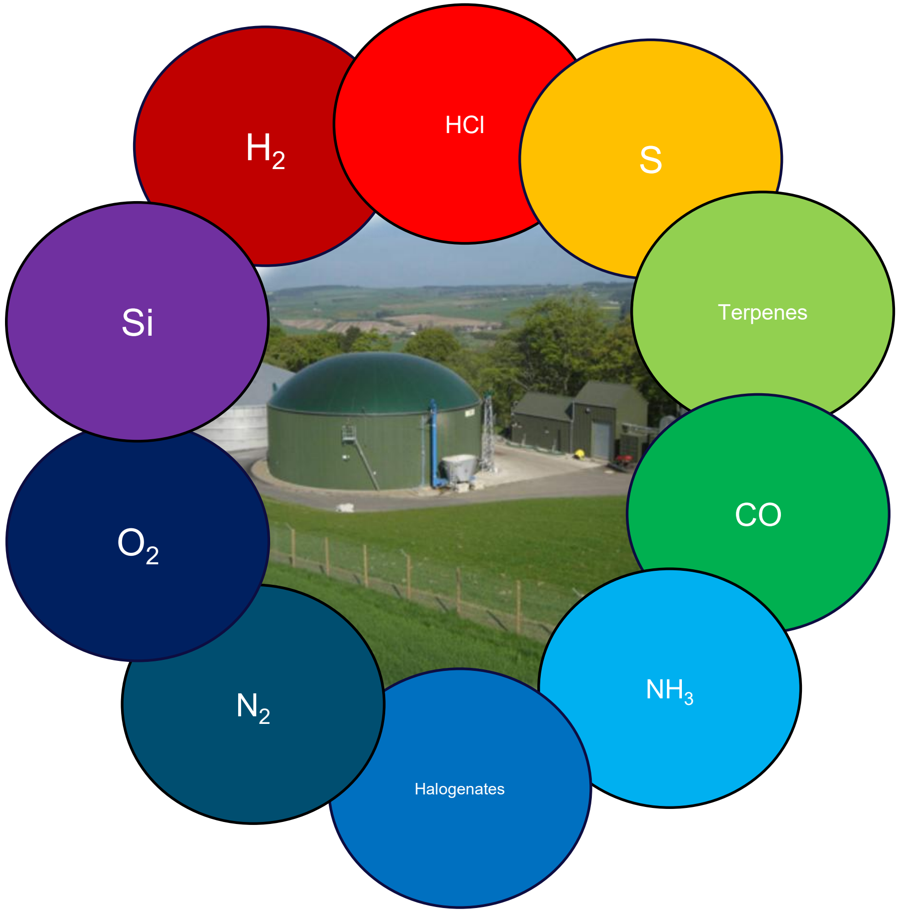
- GHG measurements
- Ambient air pollutants
- Emissions

Quality assessment of biogas and biomethane

- DRIVER

Compliance with **EN 16723-1 “Specifications for biomethane injection in the natural gas network”**

- Metrological research aimed at developing measurement methods and standards specific for the **quality assessment of biomethane/biogas**



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METROLOGY for BIOGAS

METROLOGY FOR BIOMETHANE

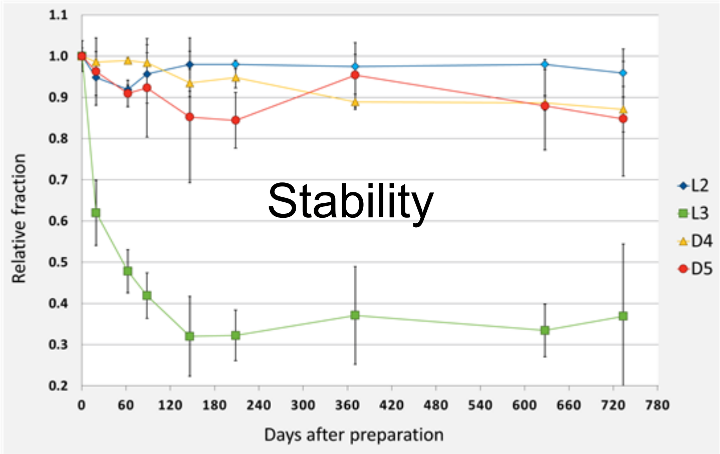
Quality assessment of biogas and biomethane

- IMPACT: **ISO/TC193 Natural Gas - SC1/WG25 Biomethane**
- 8 ISO standards published (ISO 2611 to ISO 2620) and 2 in draft phase covering analytical methods for biomethane conformity assessment

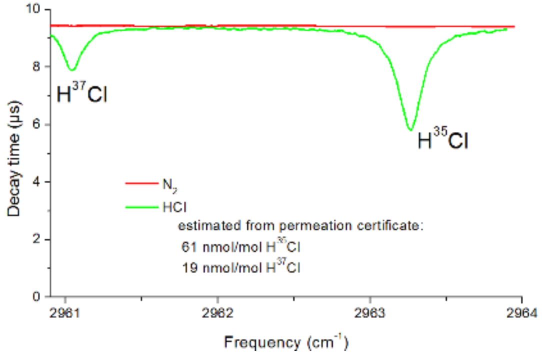
ISO/TS 2610:2022	Determination of amines content
ISO 2611-1:2024	Determination of halogenated compounds — Part 1: HCl and HF content by ion chromatography
ISO 2612:2023	Determination of ammonia content by tuneable Diode Laser Absorption Spectroscopy
ISO 2613-1:2023	Silicon content of biomethane — Part 1: Determination of total silicon content by AES
ISO 2613-2:2023	Silicon content of biomethane — Part 2: Determination of siloxane content by Gas Chromatography Ion Mobility Spectrometry
ISO 2614:2023	Determination of terpenes' content by micro gas chromatography
ISO 2615:2024	Determination of the content of compressor oil
ISO 2620:2024	Determination of VOCs by thermal desorption gas chromatography with flame ionization and/or mass spectrometry detectors (TD-GC-FID/MS)

VSL

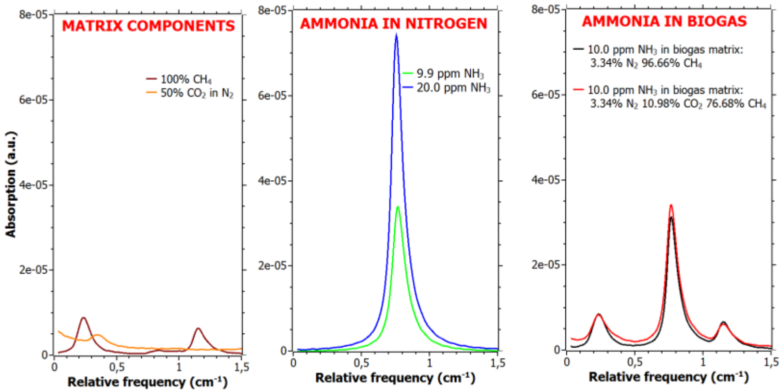
What were (are) the challenges?

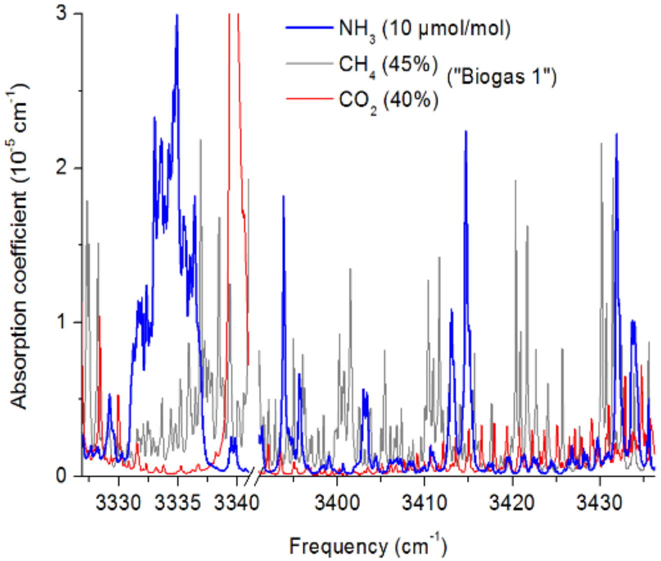


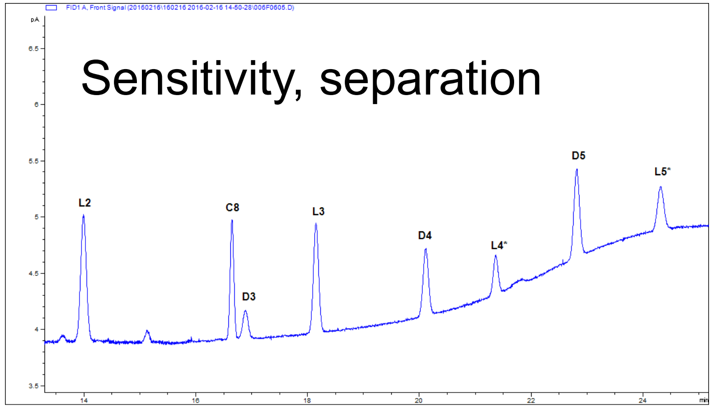
Isotopic composition



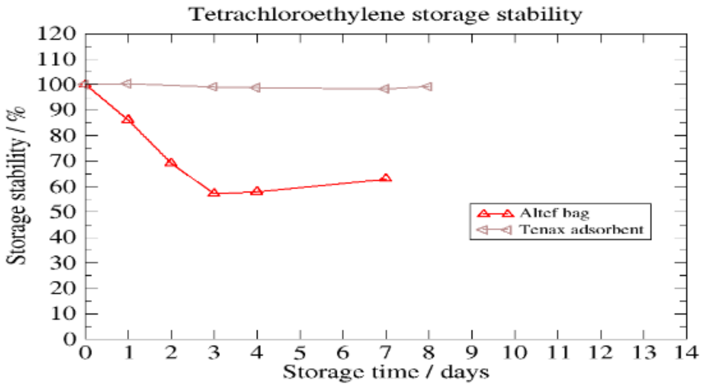
Spectral interferences







Sampling



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(gas) Hydrogen grade according to ISO 14687

Grade A: Residential/ commercial combustion appliances

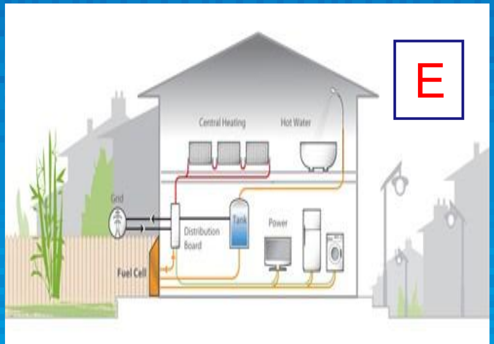
Grade B: Industrial fuel for power generation and heat generation except PEM fuel cell applications

Grade C: Aircraft and space-vehicle ground support systems

Grade D: PEM fuel cells for road vehicles

Grade E: PEM fuel cells for stationary appliances

Grade F: Internal combustion engine applications



Grade D Hydrogen (≥99.97 % mol/mol)

Impurities in Grade D hydrogen ISO14687:2025	Threshold, µmol/mol
Total non-hydrogen gases	300
Water	5
Total hydrocarbons non methane	2
Methane	100
Oxygen	5
Helium	300
Nitrogen	300
Argon	300
Carbon dioxide	2
Carbon monoxide	0.2
Total sulfur compounds	0.004
Formaldehyde	0.2
Ammonia	0.1
Halogenated compounds	0.05
Maximum particulate concentrations	1 mg/kg

With kind permission of Air Liquide

VSL

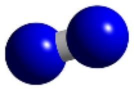
METROLOGY for HYDROGEN VEHICLES

Reference gas standards for hydrogen impurities

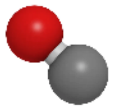
Gravimetric method (ISO 6142-1)

- Root of metrological traceability chain
- ‘Stable’ components
- Relatively “high” amount fractions

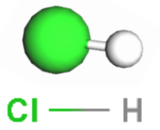
N_2



CO

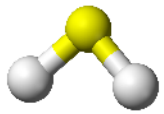


NH3

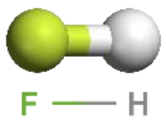


Dynamic methods (ISO 6145)

- Very low amount–of–substance fraction levels
- ‘Unstable’ components



H_2S



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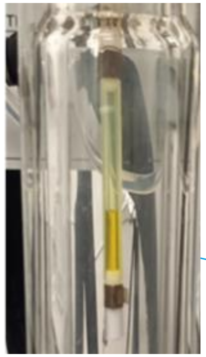
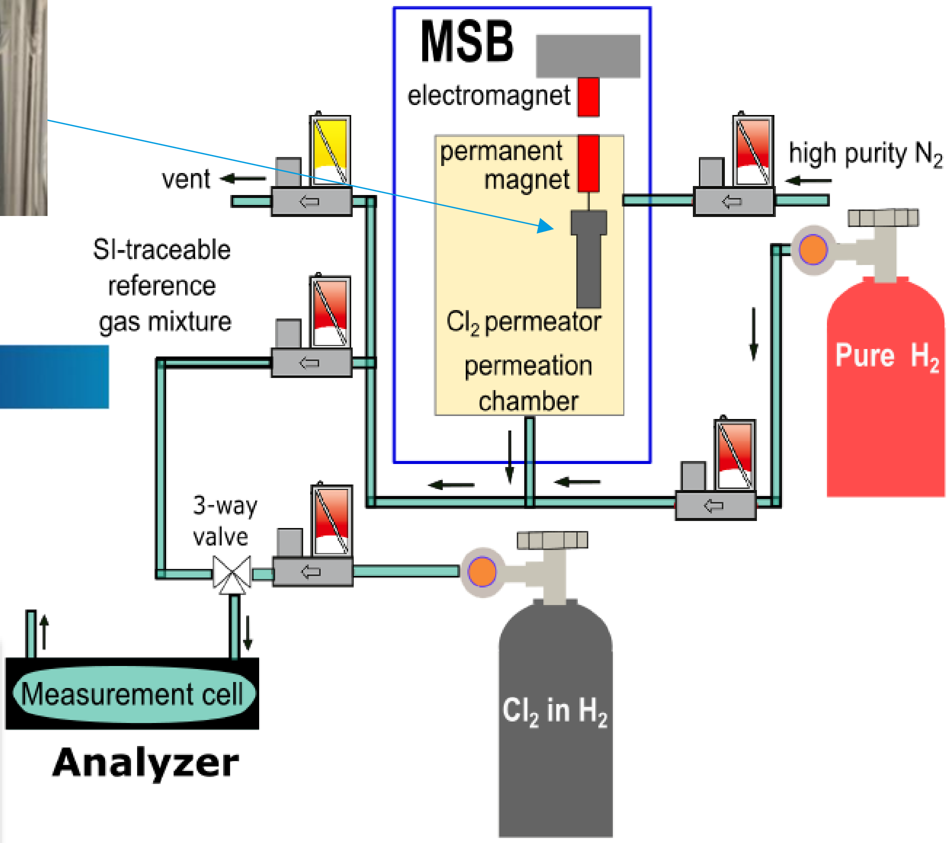
Evaluation of chlorine (Cl_2) reference gas standards

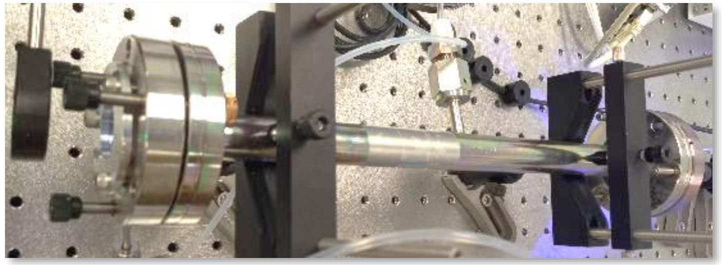
Gravimetric method

Grade D 0.05 µmol/mol

Dynamic method







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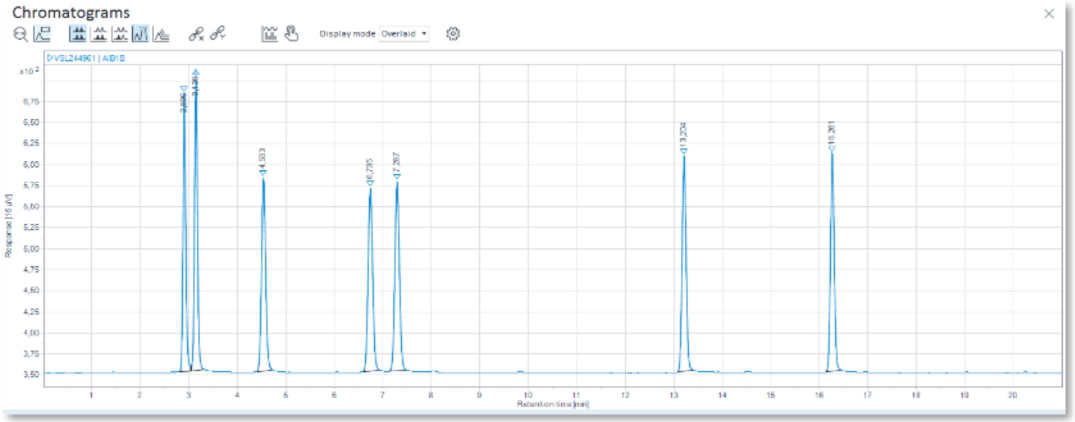
Standards and methods for sulfur-based impurities

- H_2S, COS, mercaptanes, DMS, DES, THT
- Method validation (TD-GC-SCD)
- Gravimetric reference standards (CRMs) at 0.01 µmol/mol Comparison gravimetric against dynamic dilution standards (Dilution to 0.004 µmol/mol) using 1 µmol/mol gravimetric standard in H_2
- Relative differences between 1- 5 % for all components with exception of H_2S (3-9%)

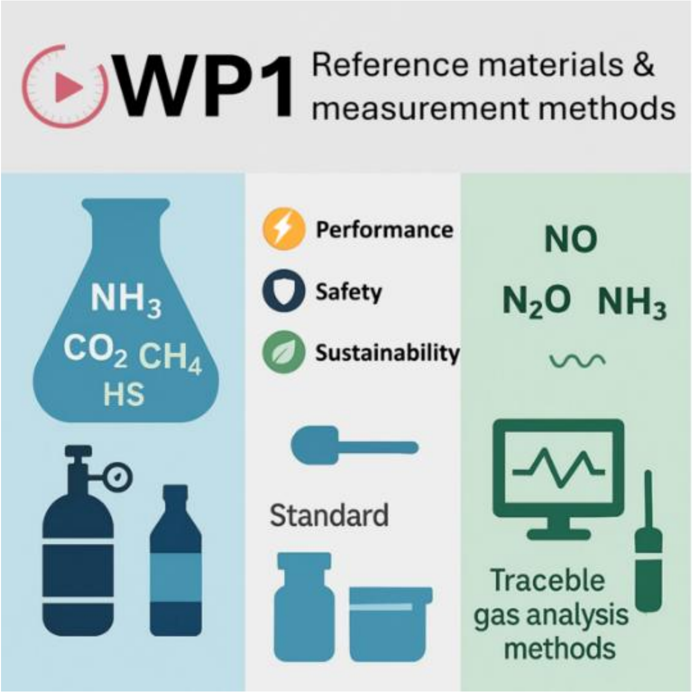

Grade D 0.004 µmol/mol



Hydrogen carriers: ammonia

- Focus on metrology for ammonia (NH_3) used for energy applications: as hydrogen carrier and fuel
- Metrology addressing quality, flow metering, leakage, emissions and Life Cycle Assessment

1. Reference materials for impurities in an ammonia matrix, such as H_2O and CO_2
2. Reference materials and gas analysis methods for emissions of N-gases (e.g. NH_3, NOx, N_2O)
3. Developing real-time emission monitoring methods



Website

MetNH3Energy

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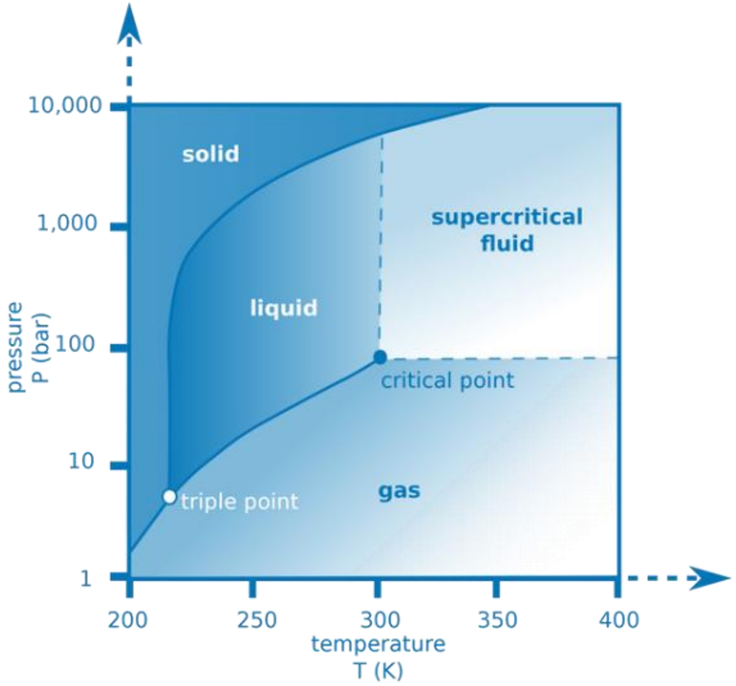
Chemical metrology for CCUS

- Development **novel reference gas standards** with impurities in CO_2 (water, nitrogen oxides, sulfur oxides, hydrocarbons, alcohols, permanent gases and amines)
- Performance evaluation of **commercial analysers** for O_2 and H_2O in CO_2
- Review current state-of-the-art of **vessels for sampling** captured CO_2
- **Good practice guide** for the sampling of CO_2 for CCUS



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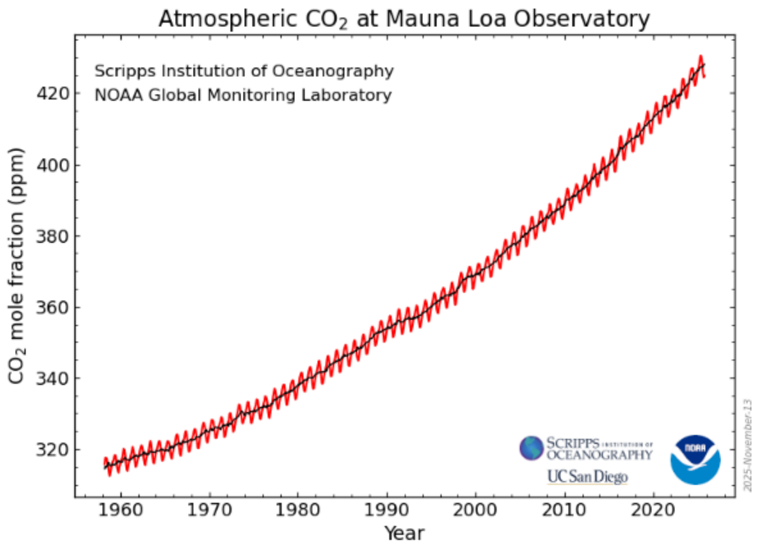
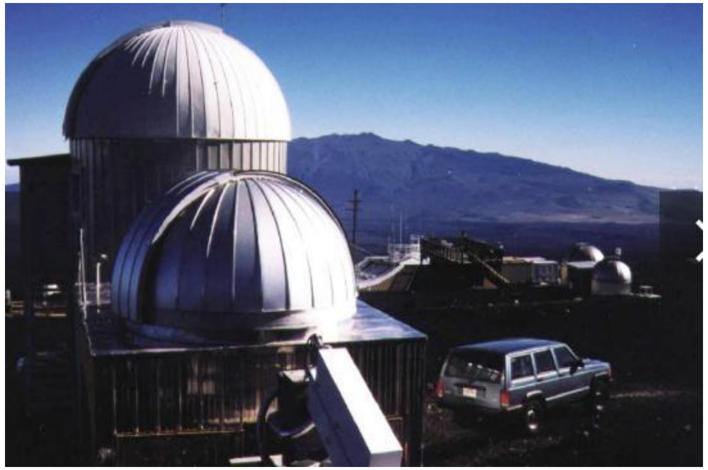
Material compatibility for CO_2 sampling – sampling bags

Component	Amount fraction (µmol/mol)	Restek Multifoil	Restek Altef	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 with time
	10-15	Stable at least 30 days (loss < 20% after D50)	Concentration decreases quickly with time	25-35% loss D1, then stable	Concentration decreases with time
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% loss D4, then stable	20-25% loss D50. Analysis before D10
	10-15	20-25% loss D50. Analysis before D10		35% loss D4, then stable	
Acetone	4-8	Max 15% loss D50	Concentration decreases quickly with time	Stable at least D7	Max 15% loss D50
	10-20	Max 15% loss D50		Stable at least D7	Max 15% loss D50
Benzene	0.3 – 2	Not compatible as benzene adsorbs on the walls	Stable at least D4		Stable at least D2 unknown
	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	

Trends of greenhouse gases in the atmosphere





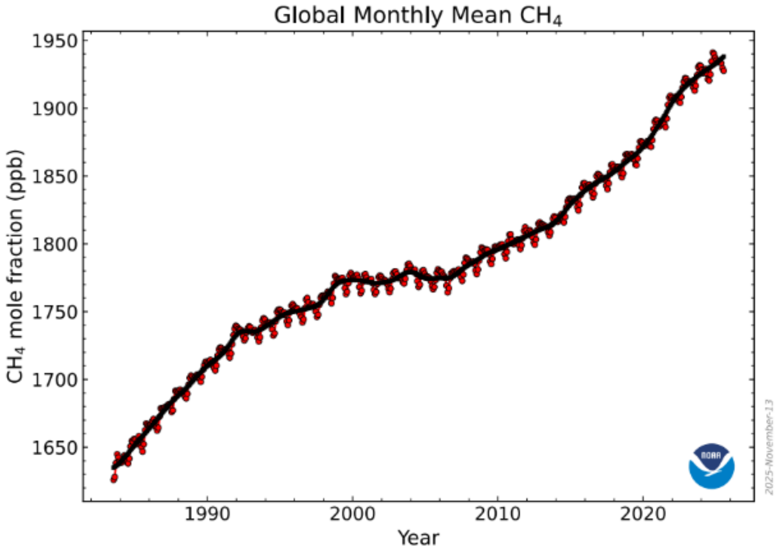
October 2025: 424.87 ppm

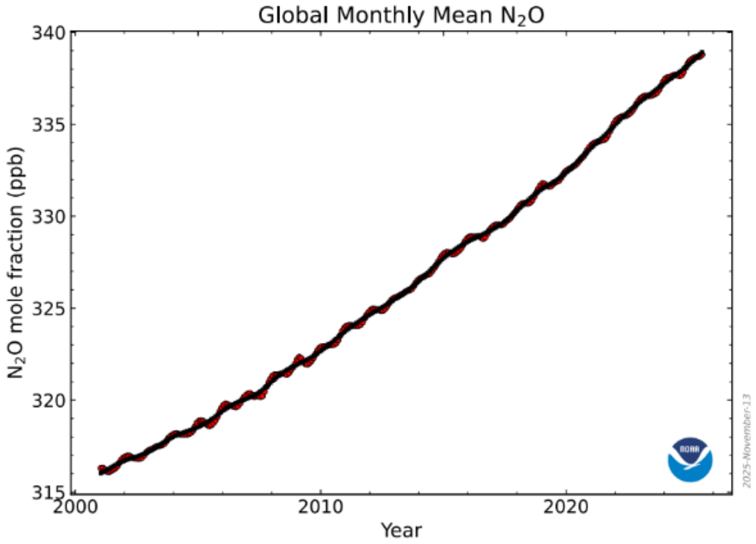
October 2024: 422.38 ppm

Last updated: Nov 13, 2025

Data source for CO_2:
NOAA Mauna Loa Observatory

Source: https://gml.noaa.gov/data/





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WMO participation in the CIPM MRA

WMO designated laboratories (since 2010): NOAA/ESRL, EMPA and PMOD/WRC

Comparison	Description	Measurement	Pilot institute	WMO Laborator
BIPM.QM-K1	Ozone at ambient level	2007 -	BIPM	EMPA
CCQM-K68.2019	Nitrous oxide in air	2019 - 2020	BIPM	NOAA/ESRL
CCQM-K82	Methane in air	2012	BIPM	NOAA/ESRL
CCQM-K120	Carbon dioxide in air	2017	BIPM	NOAA/ESRL
EURAMET.PR-S6	Total solar irradiance	2015	PMOD/WRC(CH)	PMOD/WRC(CH

Participation in currently active/planned comparisons:

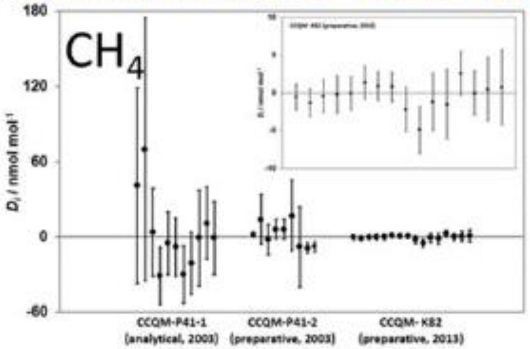
Surface Ozone Standards

BIPM.QM-K1

CO_2 in Air Standards

CCQM-P225 BIPM.QM-K2,5

Methane in Air Standards



CCQM-K82.2023

WMO OMM

Network compatibility objectives of Global Atmosphere Watch (GAW) of the WMO for Greenhouse gases

WMO

GAW

Recommended network compatibility of measurements within the scope of WMO-GAW

Component	*Network compatibility goal*[1]	*Extended network compatibility goal*[2]	*Range in unpolluted troposphere (approx. range for 2019)*
CO_2	0.1 ppm (NH) 0.05 ppm (SH)	0.2 ppm	380 - 450 ppm
CH_4	2 ppb	5 ppb	1750 – 2100 ppb
CO	2 ppb	5 ppb	30 – 300 ppb
N_2O	0.1 ppb	0.3 ppb	325 – 335 ppb
SF_6	0.02 ppt	0.05 ppt	9 – 11 ppt
H_2	2 ppb	5 ppb	400 – 600 ppb

Source: GAW Report No. 255

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Network compatibility objectives of Global Atmosphere Watch (GAW) of the WMO for Greenhouse gases

Recommended network compatibility of measurements within the scope of WMO-GAW

Compatibility goal Max troposphere
0.02% (NH) 0.01% (SH)
0.10%
0.67%
0.03%
0.18%
0.33%

challenge in purity analysis matrix gas

Component	*Network compatibility goal*[1]	*Extended network compatibility goal*[2]	*Range in unpolluted troposphere (approx. range for 2019)*
CO_2	0[illegible] ppm (NH) 0.[illegible] ppm (SH)	0.2 ppm	380 - 450 ppm
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SF_6	0.02 ppt	0.05 ppt	9 – 11 ppt
H_2	2 ppb	5 ppb	400 – 600 ppb

Source: GAW Report No. 255

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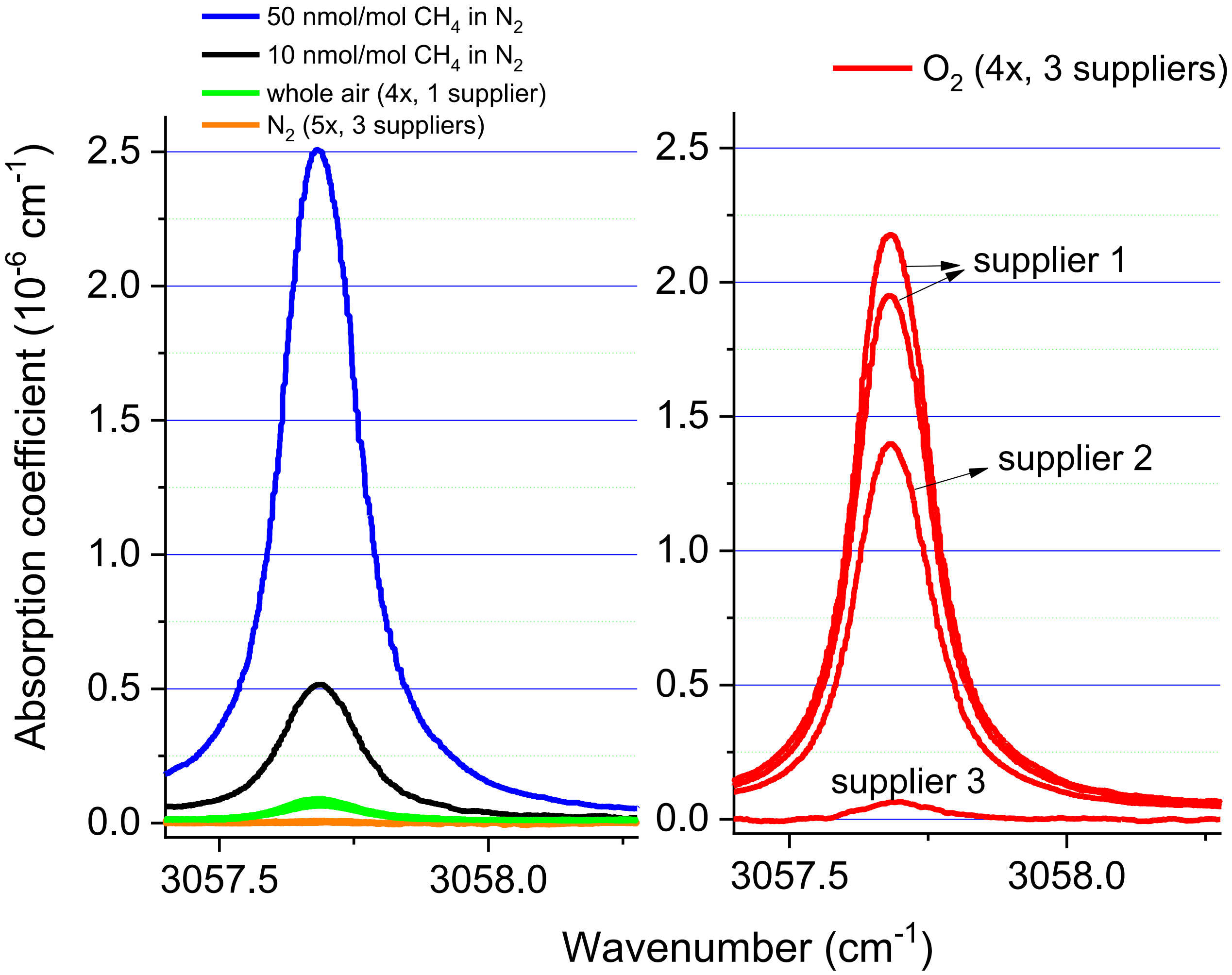
Methane (CH_4) purity of the matrix gas

Matrix gas	CH4 impurity, ppb
Nitrogen	< 0.5
Whole air	1.1 – 1.6
Oxygen (for synthetic air)	1.2 – 43 depending on supplier



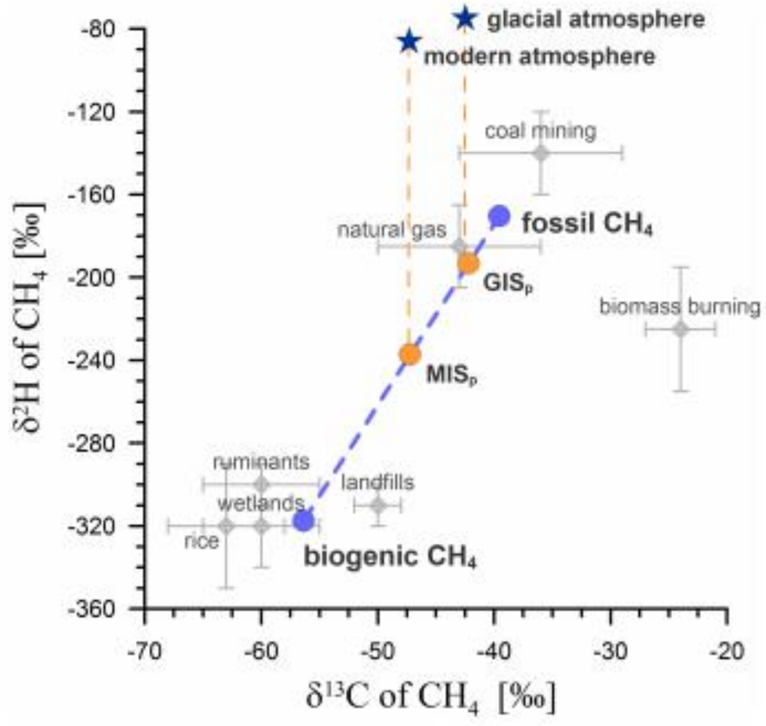
Reference: Purity analysis of gases used in the preparation of reference gas standards using a versatile OPO-based CRDS spectrometer. *Journal of Spectroscopy*, 2018. https://www.hindawi.com/journals/jspec/2018/9845608/

Methane isotopic standards

Measuring the isotopic composition can give insight in the source of the methane

Taking biogenic methane samples in a facility producing methane from food waste.

Isotope ratio gas reference materials for $\delta^{13}CH_4$ and δ^2H-CH_4 (both pure and at ambient level)



Sperlich et al., 2012

VSL

A metrological challenging air pollutant: nitrogen dioxide (NO_2)

- Hazardous gas for environment and health, present in ambient air, industrial emissions, exhaust from automotive, maritime shipping, etc.
- Metrology challenge: very reactive and unstable
- Gas standards for NO_x have commutability issues with NO_2- specific gas analyzers
- Calibration of such analyzers with NO_x standards induces a bias in the measurement results

World Health Organization

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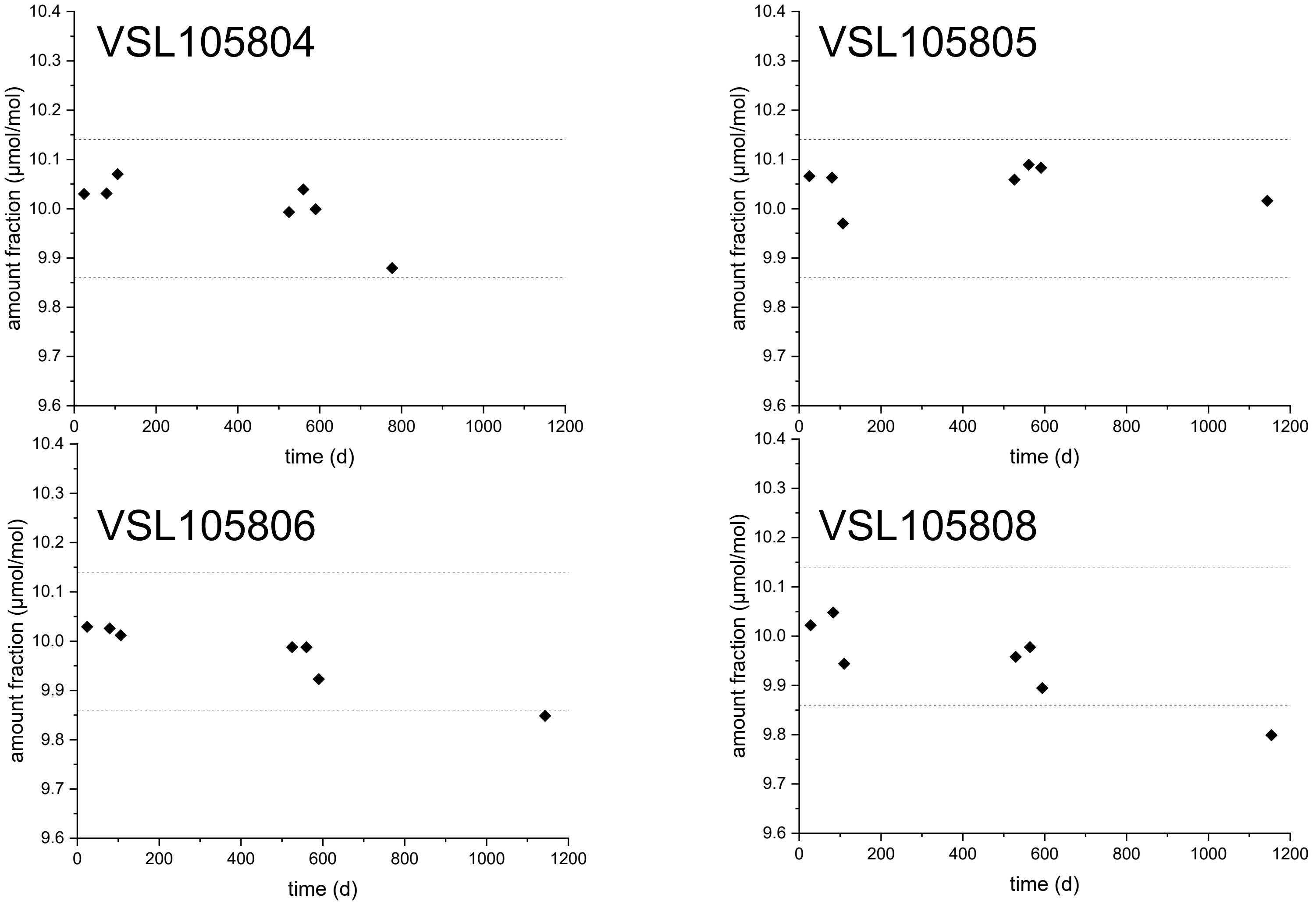
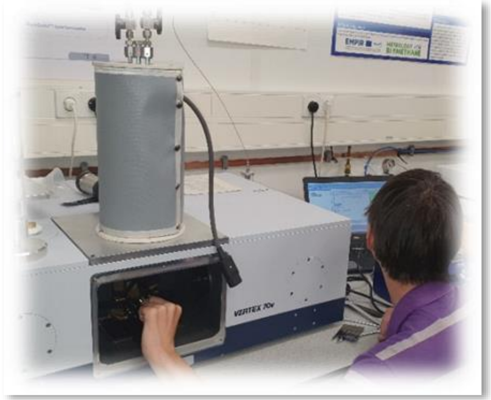
Between-cylinder effects



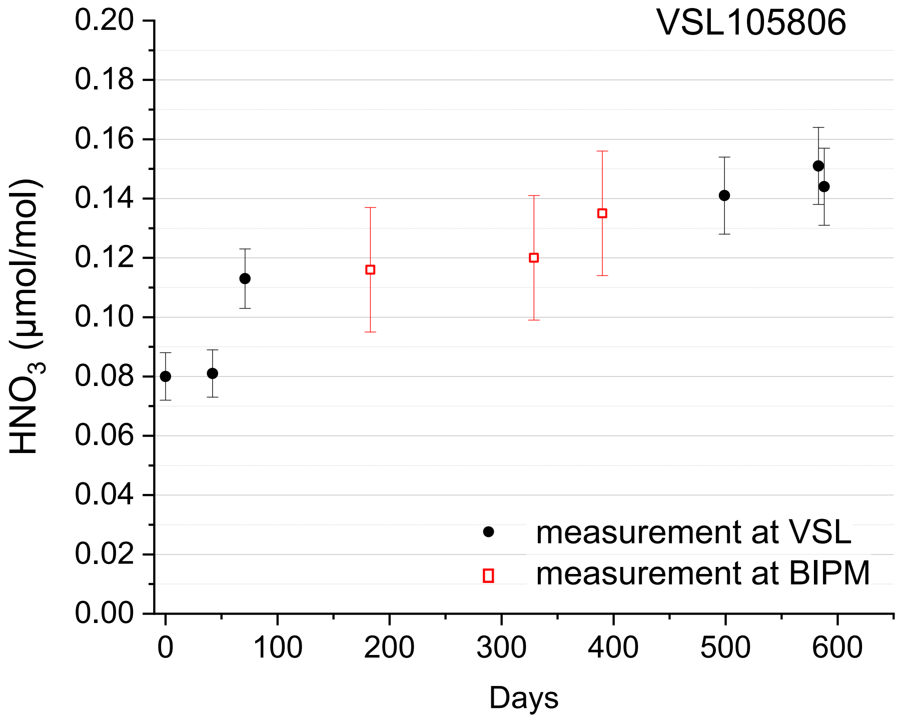
Dotted lines at ± 1.4 % (CMC)

Nitric acid formation



- Required: nitrogen dioxide, oxygen, water
- Water can be present in the gas phase and on the cylinder wall surface
- Reaction is thermodynamically favourable
- Reaction starts quickly
- Amount fraction gradually increases in time

- Right graph: source CCQM-P172
  - VSL quantification based on HNO_3 data from PNNL database
  - BIPM quantification based on permeation



NO_2 in N_2 at 10 µmol mol^{-1}

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Conclusion

Chemical (gas) metrology plays a key role in energy, climate and environment

Metrological traceability provided by gravimetric and dynamically prepared primary standards

Development of reliable and fit for purpose analytical methods in support regulation, standardisation and monitoring networks

Validation of sampling materials and methods as critical factor in chemical metrology

thank you for your attention

muito obrigada

Annarita Baldan
e-mail a.baldan@vsl.nl
Website www.vsl.nl

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The end