Nitrous oxide emissions - monitoring a critical aspect of energy source diversification

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Abstract

Introduction: In the context of hydrogen, N_2O will become crucial to monitor and urgently avoid an excess of emissions following the emerging ammonia use as hydrogen-based fuel. This work describes the current situation with respect to measurements of N_2O in terms of its metrological traceability. We report on the outlined development of new N_2O gas standards and compare them to the needs in emissions monitoring applications and greenhouse gas measurements.

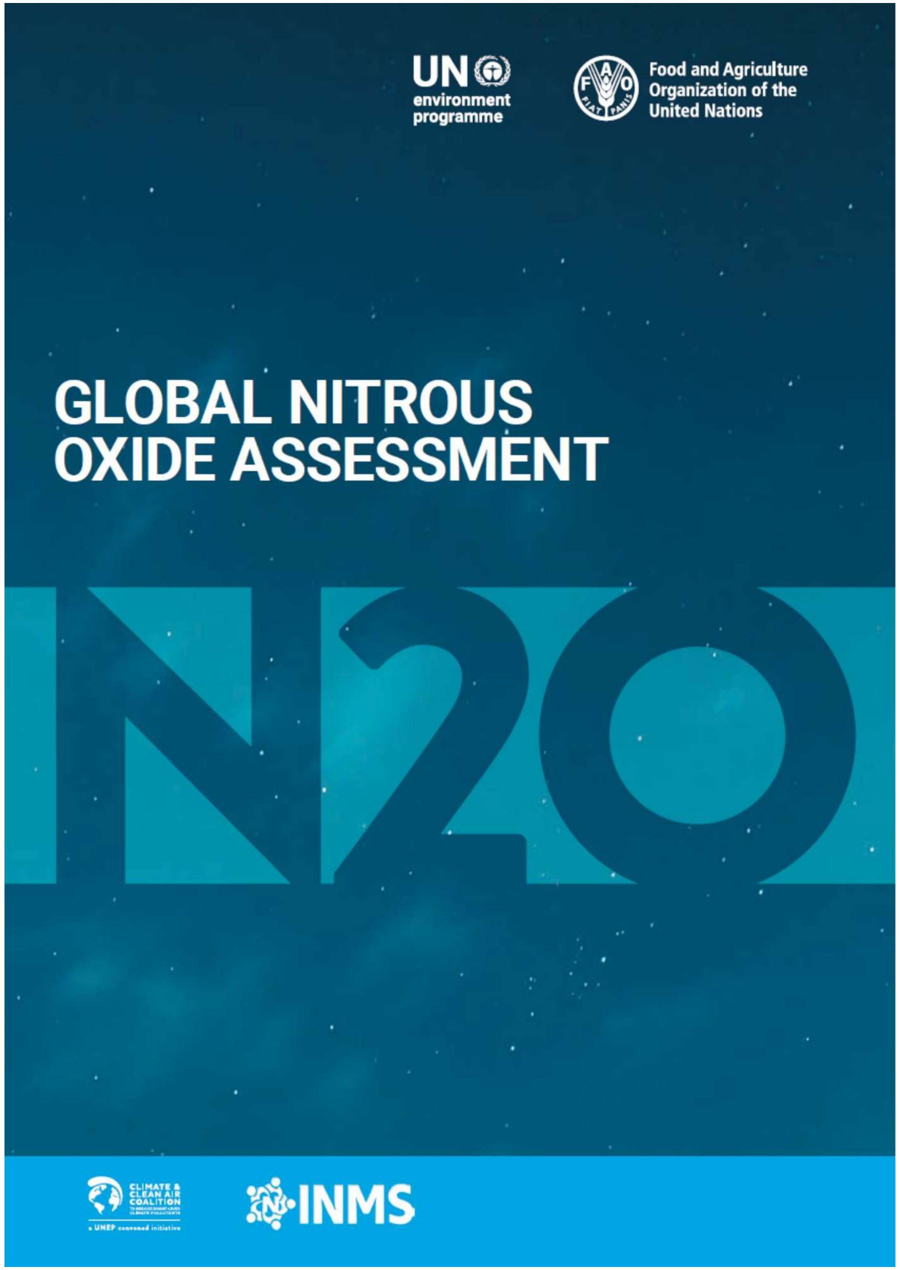
Methodology: We investigated the present situation on available gas standards applicable to calibrate continuous emission measurements (CEMs) of N_2O as an emission from hydrogen's derivative ammonia (NH_3) used as fuel. While real-world data on N_2O emissions of maritime ammonia engine tests is not available, a maximum emission factor of 0.06 g N_2O per kWh (0.158 g N_2O per kg NH_3 consumed) is targeted by the industry. This performance value would guarantee a negligible effect on green ammonia trade and consumption as a fuel. The Key Comparison Database of the International Bureau of Weights and Measures reveals only eight institutes worldwide who can offer N_2O standards, needed for accurate measurements aiming at metrological traceability. Of them, each calibration and measurement capability is related to a reference material-based gas standard, i.e. a certified reference material (CRM).

An alternative concept to CRM-based gas standards is given by optical gas standards (OGS). Yielding gas concentrations that are directly metrological traceable, OGS offer a flexible alternative to CRM-based gas standards, particularly where CRMs are less stable and difficult to be carried to the field, as, e.g., for CEM.

Experimental Evaluation: Experimental collaborations have been started on nitrous oxide spectroscopy in the 1.65 mm near infrared wavelength range for N_2O emissions and the mid infrared range around 4.5 µm wavelength for background N_2O quantifications. This underlying spectroscopy work is required for the development of new optical N_2O standards as sketched in Fig. 1. In cases a thorough spectroscopic line selection is crucial to customize the optical gas standard for a specific application – or to have it available for general purpose N_2O certification and calibration for example. Metrological characterization and comparisons to available CRM-based N2O standards are underway.

Why bothering with nitrous oxide?

Nitrous oxide, considered to be a **super pollutant**, is the **third most important greenhouse gas** and the most significant ozone-layer depleting substance emitted today. Its **human-induced emissions**, which primarily originate from the agricultural use of synthetic fertilisers and manure, **are increasing faster than previously projected.**



Nitrous oxide is a long-lived greenhouse gas **approximately 270 times more powerful than carbon dioxide per tonne of emission at warming the Earth**. Its anthropogenic emissions are responsible for approximately 10 per cent (around 0.1° Celsius) of net global warming to date since the industrial revolution. It is also an ozone-layer depleting substance. Although nitrous oxide is not controlled under the Montreal Protocol, its current **anthropogenic emissions are a larger threat to the ozone layer than any chemical** controlled under this protocol.

Hydrogen metrology mirrored by CIPM MRA activities

PTB

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Measurement

Volume 235, August 2024, 115041

CIPM MRA support for hydrogen metrology – A case study

A. Krietsch, O. Werhahn

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Highlights

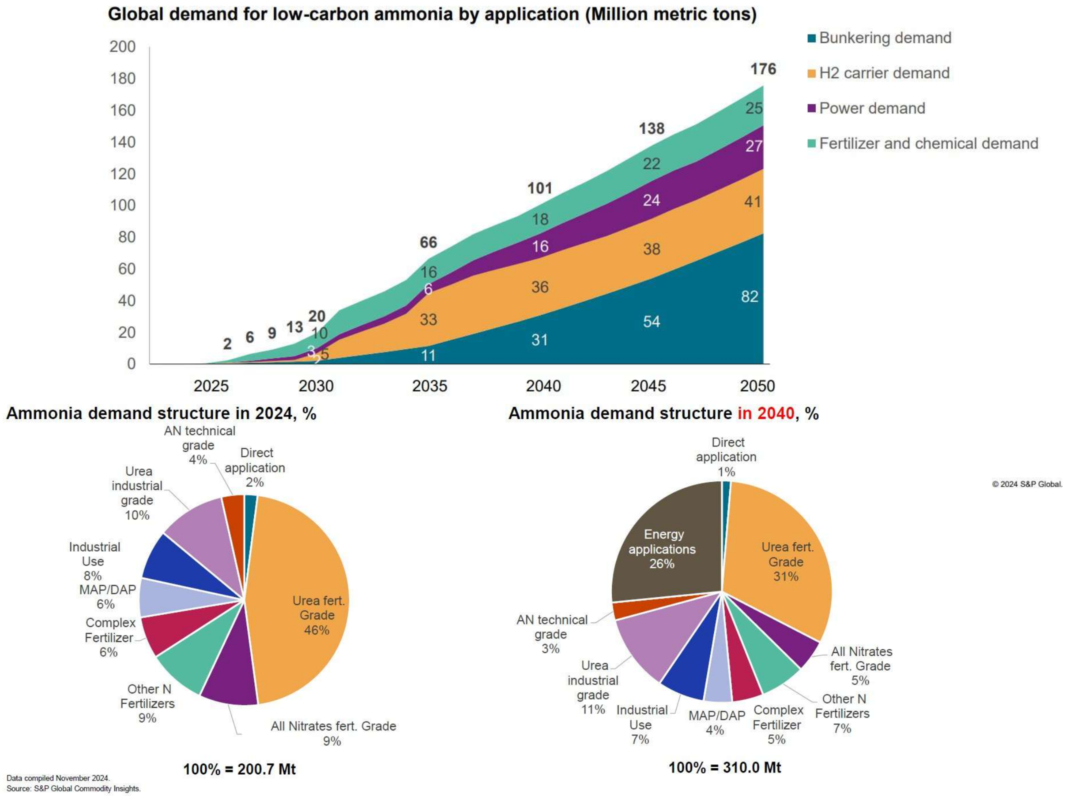
Outlook of low-carbon ammonia demand

Ammonia demand is expected to grow by 54% until 2040

- **Global ammonia consumption** is estimated to reach **310 million tonnes by 2040** from 201 Mt in 2024 (+54%) due to emerging clean energy applications (26% of demand in 2040) [1]

- New low-carbon energy applications are **marine fuel consumption**, **hydrogen supply chains** based on ammonia cracking (ammonia as a H_2 carrier) and **power generation** [1]

- Ammonia could enable the **global trade of green hydrogen** as it is considered as the **lowest cost hydrogen carrier option** for short and long distance **seaborne trade** [2]



Source: [1] G. Eliseev 2024, The Ammonia Market Today and a Bridge to the Future, Ammonia Market, [2] Scheffler et al. 2025 https://doi.org/10.1016/j.apenergy.2024.125073

Ammonia as Hydrogen Carrier

PNAS RESEARCH ARTICLE | EARTH, ATMOSPHERIC, AND PLANETARY SCIENCES OPEN ACCESS

Minimizing the impacts of the ammonia economy on the nitrogen cycle and climate

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Ammonia as Hydrogen Carrier

$$4\ NH_3 + 3\ O_2 \longrightarrow 2\ N_2 + 6\ H_2O$$

$$NO + NH \longrightarrow N_2O + H$$

Ammonia as Hydrogen Carrier

$$4\,NH_3 + 3\,O_2 \longrightarrow 2\,N_2 + 6\,H_2O$$

"With ***a 1% nitrogen conversion into*** $\boldsymbol{N_2O}$*, an ammonia economy of 1,600 Mt* NH_3*/y would result in 20 Mt* N_2O*/y, around three times current anthropogenic emissions (31). With a GWP of 265, 20 Mt* N_2O*/y is equivalent to 6 Gt* CO_2*eq/y, about 15% of the global greenhouse emissions rate per year (Fig. 3A). The GHG intensity of* ***such an ammonia economy*** *(0.2 Gt*CO_2*e/EJ)* ***is about twice as high as the current fossil fuel economy*** *(~0.1 Gt*CO_2*e/EJ), even without considering all upstream emissions related to ammonia production."*

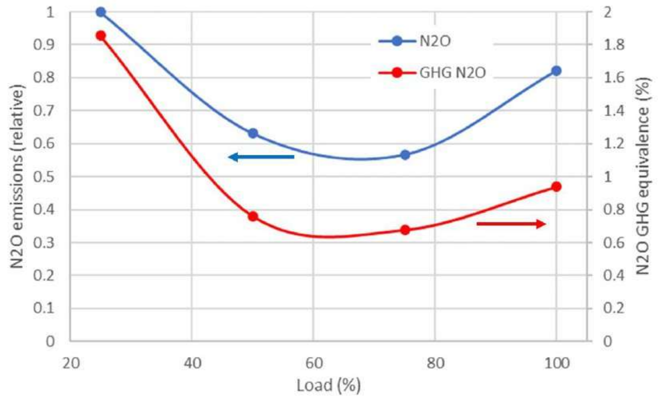
Ammonia as Hydrogen Carrier

$$4\ NH_3 + 3\ O_2 \longrightarrow 2\ N_2 + 6\ H_2O$$

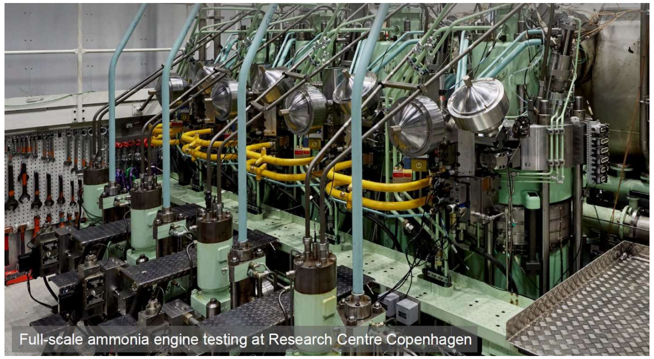
"The ammonia economy would have the ***same climate impact as the fossil-fuel*** *energy system* ***in the case of a 0.4% nitrogen conversion*** *from NH3 to N2O. The same critical rate has recently been obtained in the specific analysis of* ***shipping emissions*** *(16)."*

Test results for N_2O emissions from MAN B&W ammonia engine
Status Quo of marine dual-fuel ammonia engine tests

- MAN achieved 100% engine load on ammonia on full-scale dual-fuel ammonia research engine at Research Centre Copenhagen (2025) [1]
- First commercial engine on testbed in Mitsui, Japan (Feb 2025) [1]
- MAN reports very low N_2O emissions below a **typical reference value of 5 ppm** resulting in a N_2O emission impact less than 2% GHG equivalence [1]
- In total more than 90% saving of GHG emission with commercial ammonia engine (ME-LGIA) considering both fossil pilot oil consumption (~5% at 100% engine load) and N_2O emissions [1]
- Industry emission target of 0.06 g N_2O / kWh refers to 42 kg CO_2(e) / t NH_3 (2,3 g CO_2(e) / MJ NH_3) [2]
- MAN estimate for sales release of two-stroke marine ammmonia engine by **end of 2026** [1]



Test engine measurements relative to typical reported value of N_2O (less than 5 ppm)



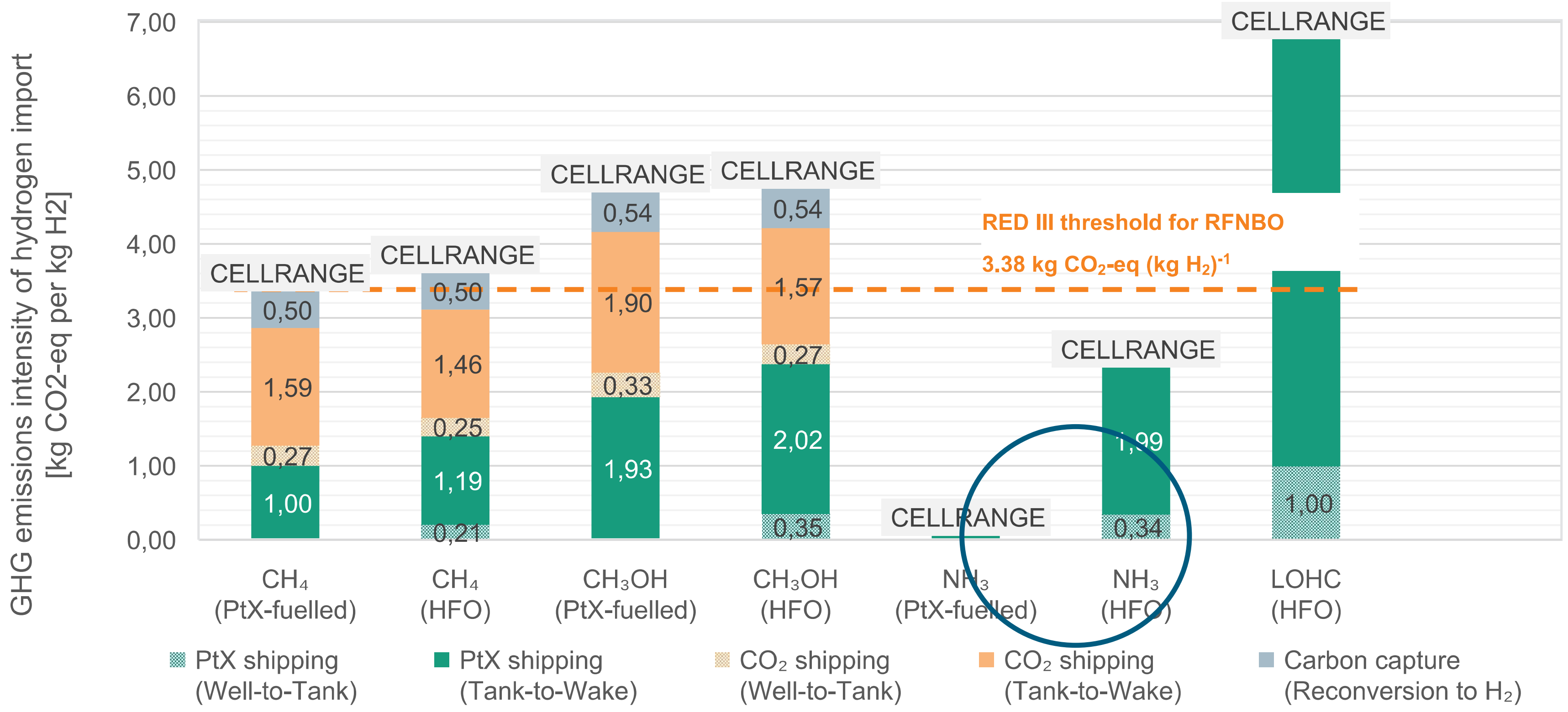
Full-scale ammonia engine testing at Research Centre Copenhagen

Source: [1] MAN ExpertTalk 2025, MAN B&W ammonia engine development, [2] Mærsk Mc-Kinney Møller Center for Zero Carbon Shipping 2023 Managing Emissions from Ammonia-Fueled Vessels

Fraunhofer IST

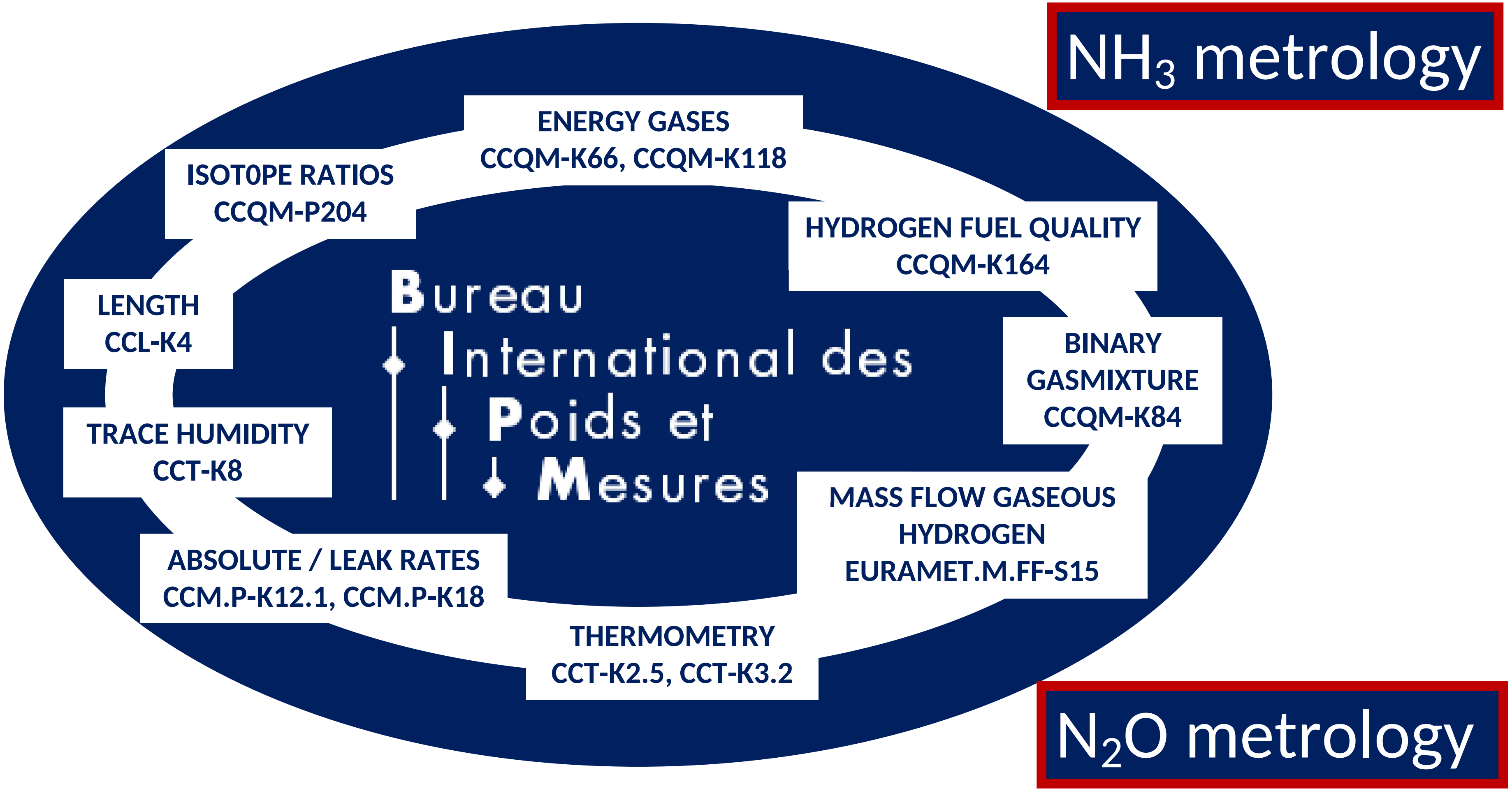
GHG emissions intensity of hydrogen import from Australia

Ammonia-fuelled vessels enable zero emissions hydrogen ship transport



Source: Scheffler et al. 2025 https://doi.org/10.1016/j.apenergy.2024.125073, GHG emission factor for ammonia engine with 0.06 g N_2O / kWh refers to 42 kg CO_2(e) / t NH_3

Hydrogen metrology mirrored by CIPM MRA activities

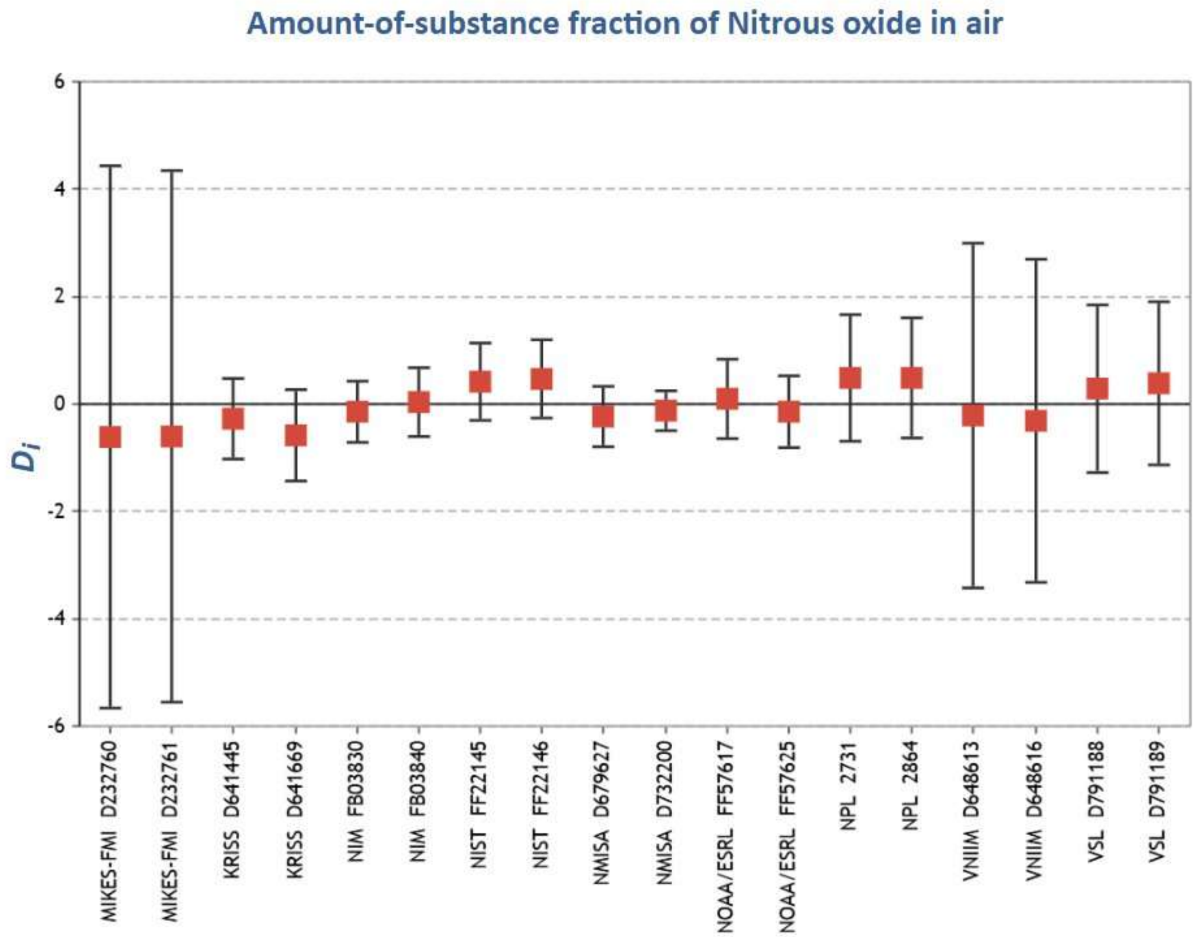


Current situation with N_2O gas standards

N_2O in Atmosphere	337.91 nmol/mol		
Service-Provider	Matrix	CMC	Expanded Uncertainty CMC
China, NIM	nitrogen or air	[200 to 400] nmol/mol	[0.3 to 0.15] %
Japan, NMIJ AIST	nitrogen or air	[200 to 2.00E7] nmol/mol	[0.2 to 0.1] %
Korea Republic of, KRISS	air	[200 to 2.00E4] nmol/mol	[0.2]%
Netherlands, VSL	synthetic air	[100 to 3.00E4] nmol/mol	[2 to 1] %
Russian Federation, VNIIM	synthetic or real air	[200 to 400] nmol/mol	[1]%
United Kingdom, NPL	nitrogen or air	[50 to 1.00E4] nmol/mol	[2 to 0.34] %
United States, NIST	synthetic air	[200 to 2.00E4] nmol/mol	[3.5 to 2] %
WMO - International Organization, NOAA/ESRL	natural air	[260 to 370] nmol/mol	[1 t **[0.4 to 0.3] %** l

Current situation with N_2O metrological traceability

Degrees of equivalence represented by D_i and its expanded uncertainty U_i at a 95 % level of confidence, both expressed in nmol/mol.



comparability within 0.3 %

Current situation with N_2O gas standards

Table 1. 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)*	*Range covered by the WMO scale*
CO_2	0.1 ppm (NH) 0.05 ppm (SH)	0.2 ppm	380 - 450 ppm	250 – 800 ppm
CH_4	2 ppb	5 ppb	1750 – 2100 ppb	300 – 5900 ppb
CO	2 ppb	5 ppb	30 – 300 ppb	30 – 500 ppb
N_2O	0.1 ppb	0.3 ppb	325 – 335 ppb	260 – 370 ppb
SF_6	0.02 ppt	0.05 ppt	9 – 11 ppt	2.0 – 20 ppt
H_2	2 ppb	5 ppb	400 – 600 ppb	140 –1200 ppb
$\delta^{13}C\text{-}CO_2$	0.01‰	0.1‰	-9.5 to -7.5‰ (VPDB)	
$\delta^{18}O\text{-}CO_2$	0.05‰	0.1‰	-2 to +2‰ (VPDB-CO_2)	
$\delta^{13}C\text{-}CH_4$	0.02‰	0.2‰	-51 to -46‰ (VPDB)	
$\delta^{2}H\text{-}CH_4$	1‰	5‰	-120 to -63‰ (VSMOW)	
$\Delta^{14}C\text{-}CO_2$	0.5‰	3‰	-80 to 20‰	
$\Delta^{14}C\text{-}CH4$	0.5‰		50-350‰	
$\Delta^{14}C\text{-}CO$	2 molecules cm^{-3}		0-25 molecules cm^{-3}	
O_2/N_2	2 per meg	10 per meg	-900 to -400 per meg (vs. SIO scale)	

0.03 %

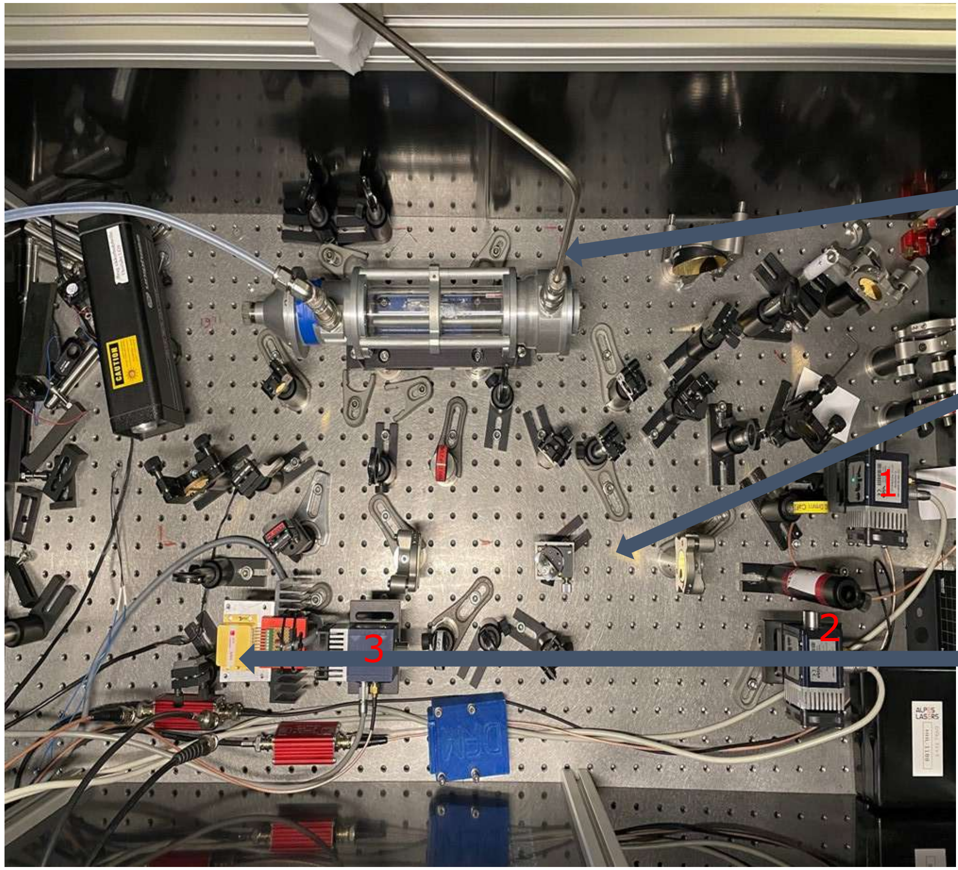
TILSAM and Optical Gas Standards

- To complement existing CRMs, especially for sticky and reactive gases, or applications which cannot be provided with static gas cylinders,
- alternative calibration and traceability strategies are required,
- and have been demonstrated based on instrumental standards.

TILSAM and Optical Gas Standards

- **T**raceable **I**nfrared **L**aser-**S**pectrometric **A**mount fraction **M**easurement;
- publicly available technical protocol for the TILSAM method;
- has been demonstrated based on realised instrumental standards for a number of species (H_2O, NO_2, CO_2, CO);
- underlying method of a published CMC on HCl (https://si-digital-framework.org/kcdb-cmc/EURAMET-QM-DE-00000OIY-1)
- makes use of first principle modelling of the linear absorption process by gas phase molecules.

Work-in-progress 1.65 µm wavelength range



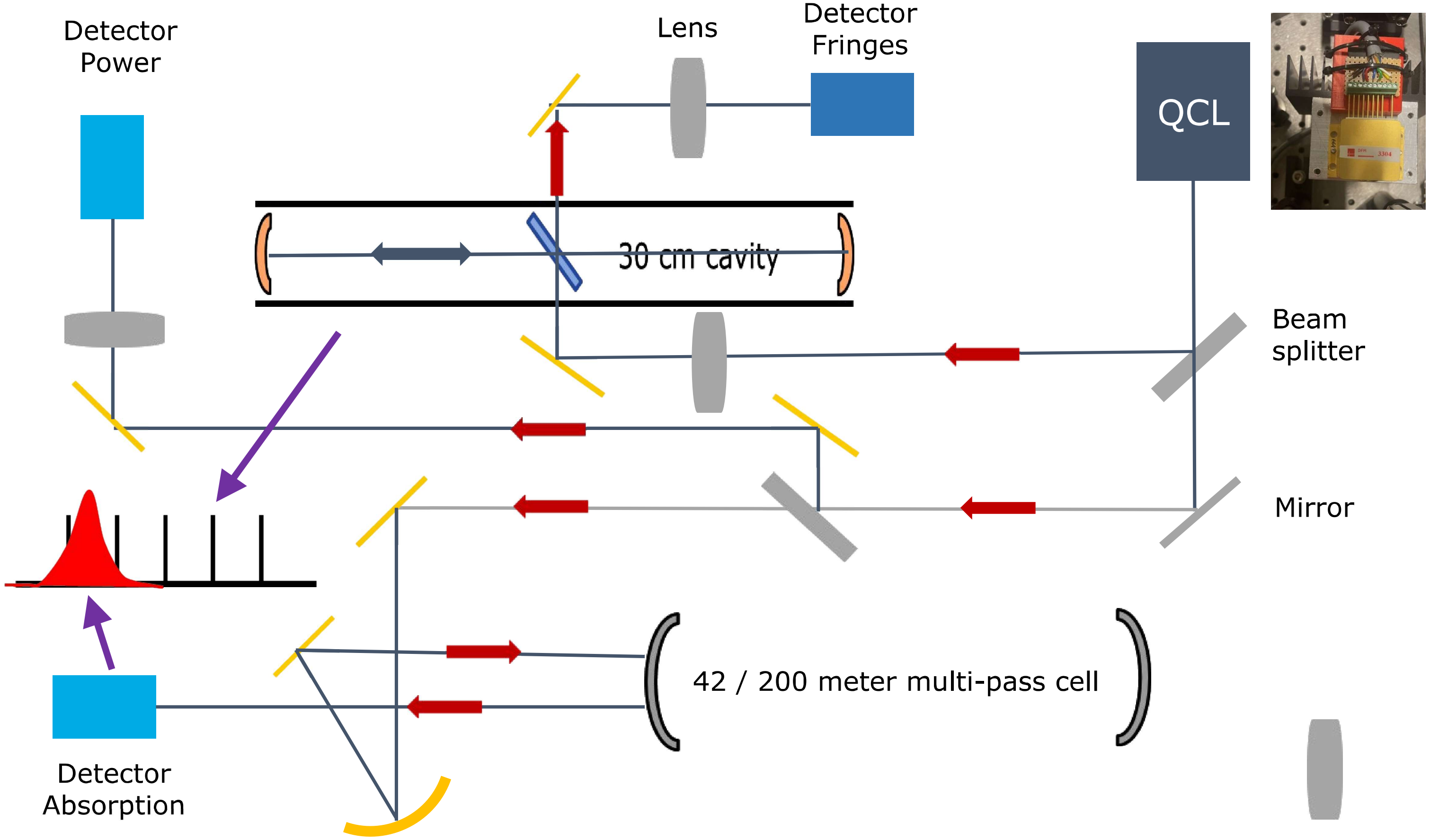
Multipass gas cell
42 m

Frequency
reference cavity

Detectors 1, 2 and 3 monitor absorption, power and reference fringes, respectively.

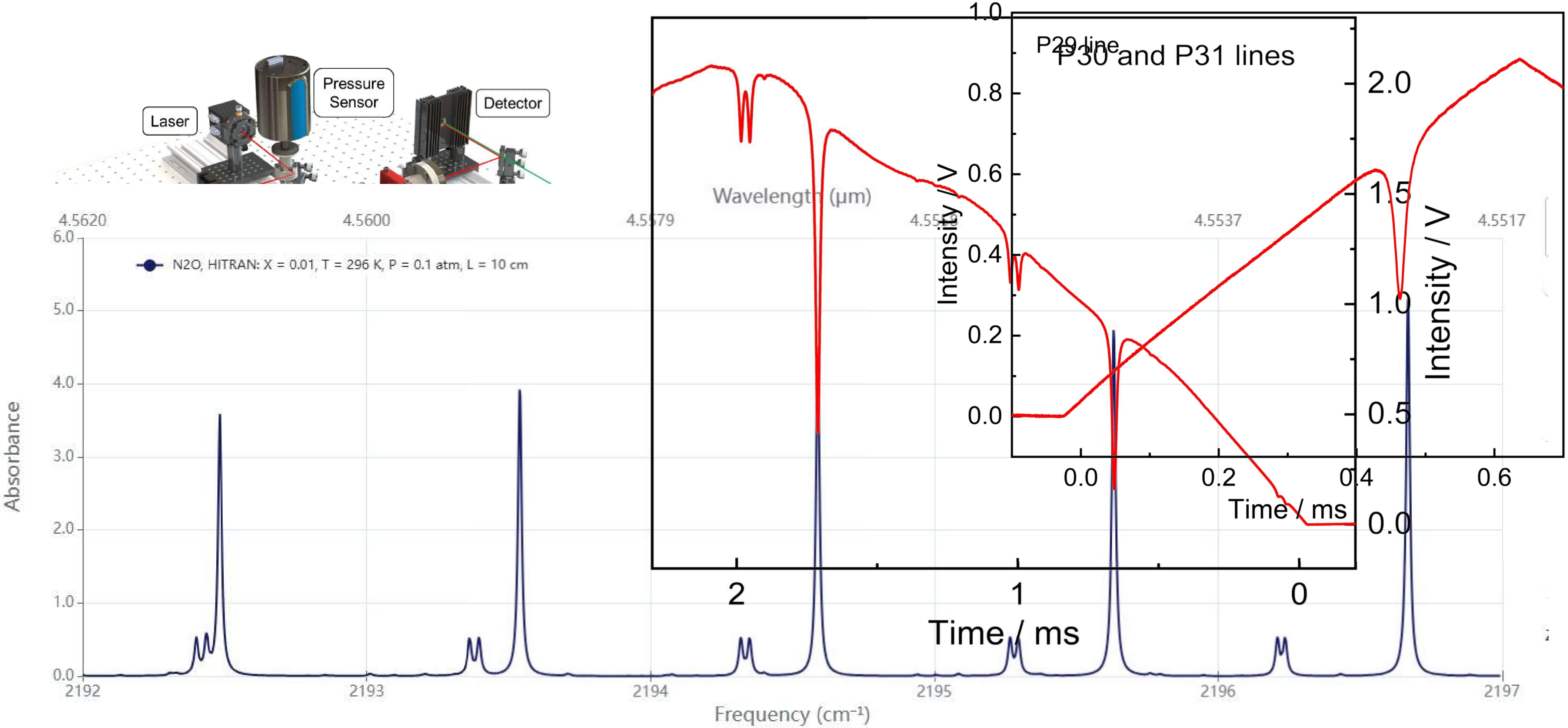
QCL laser for monitoring N_2O in the MIR region.
(Tunable diode laser for monitoring in the NIR region available)

Work-in-progress 1.65 µm wavelength ra

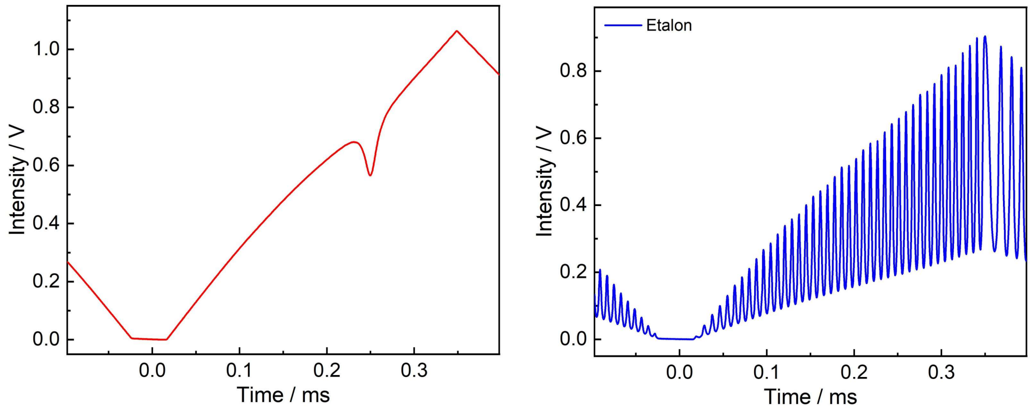


DFM
Danmarks Nationale Metrologiinstitut

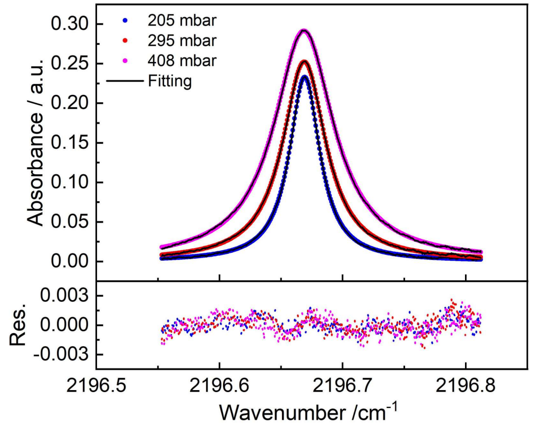
Work-in-progress 4.5 µm wavelength rang



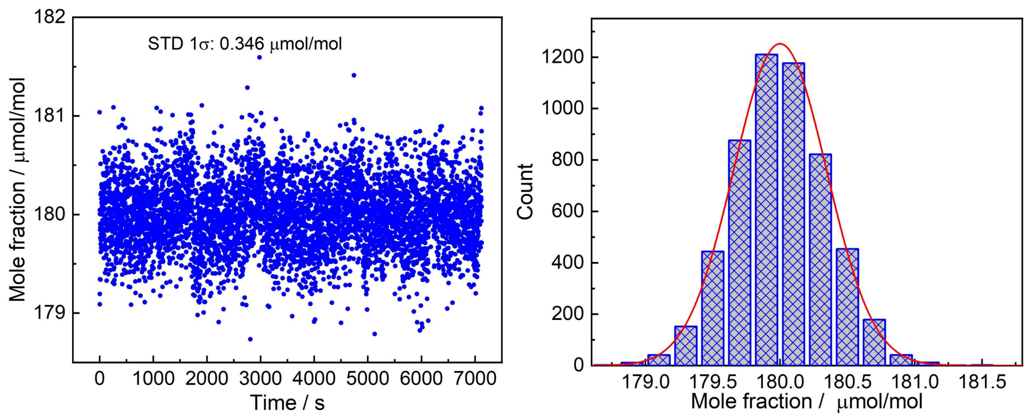
Work-in-progress 4.5 µm wavelength range



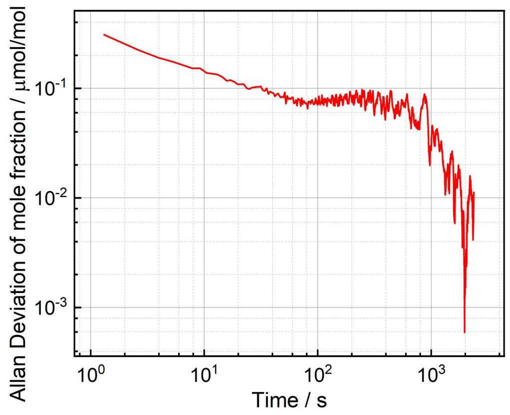
Left: the measured typical laser intensity with N_2O absorption peak; Right: the measured Etalon signal.



Measured N_2O absorption spectra (10 scan averaged) in air mixture at pressures from 205 mbar to 408 mbar. The fitting residuals between measured and fitted data are shown below



Left: Long term mole fraction measurement results under the equilibrium condition. Right: Histogram of the measured mole fractions distribution and the Gaussian fit contour.



Allan deviation plot

Proposed comparison study of N_2O gas standards

- The latest Key Comparison: CCQM-K68.2019 (model 2)
  - Measurand: 325-350 nmol/mol N_2O in air.
  - Approach: Standards sent to the BIPM headquarters for analysis.
  - The corresponding data to the Key Comparison is now entering the 5-year ago state, and there is no active plan for the next one at the moment.

- Study: comparison in the range of 300 to 3000 nmol/mol N_2O in N_2
  - Beginning in summer / autumn 2026, running 1 year.
  - Potential participants: PTB (optical gas standard), KRISS? (reference material-based gas standard), DFM? (optical gas standard), *NN*.

- Purpose
  - To evaluate the level of comparability of newly developed optical N_2O gas standards and classical reference material-based N_2O gas standards.
  - To prepare and support potential participation in future key comparisons.

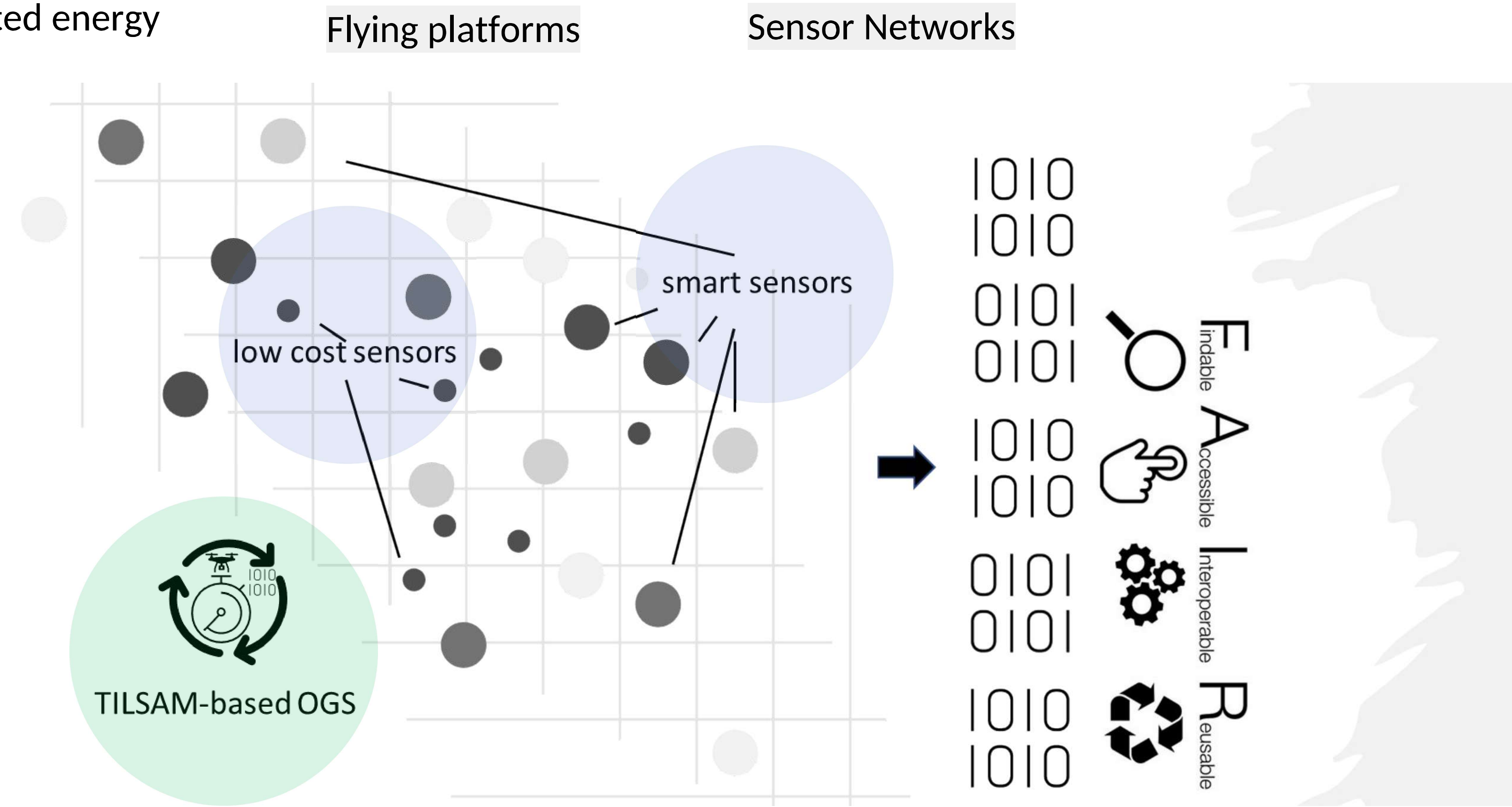
Outlined Applications

Ammonia as hydrogen-related energy carrier

Metrology Study

Flying Platforms

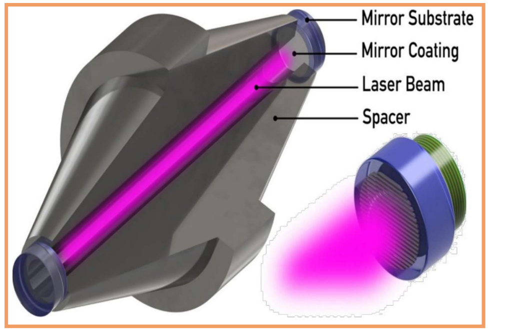
Air quality sensor networks

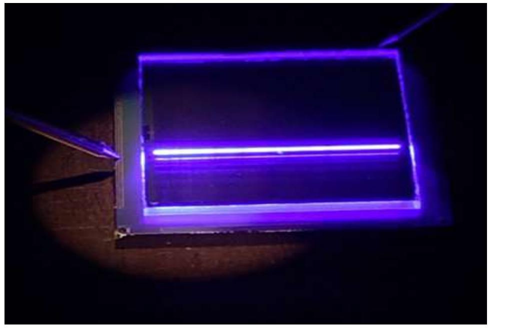


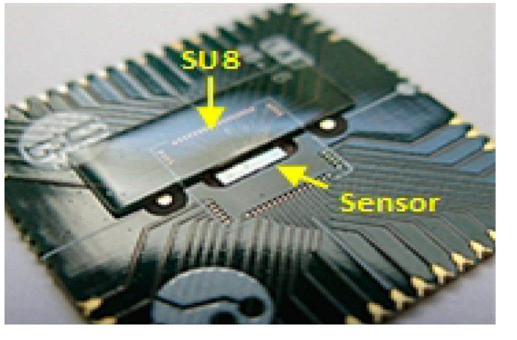
Quantum Technology-based implementations
(by courtesy of D. J. Prades, TU-Braunschweig, Germany)

Progress:

- Prototype instruments with optical measurement methods available.
- Inhouse QT-hardware and software development with TU-Braunschweig.
- Micro-cavities on chip for modern spectroscopy techniques with smallest footprint projected.
- Sizes of a modern mobile phones.
- Communication protocols and DCCs for data transport.
- Outline: calibration at PTB's new optical gas standards.







Conclusions

Metrology for environment and climate is worth to get combined with energy metrology as see by the example of nitrous oxide (N_2O)

- it is an interdisciplinary topic best tackled with expertise from very different scientific areas

- Fraunhofer, PTB, DFM , and TU-Braunschweig have set out to address this by combining forces within a joint-N_2O-project

New optical gas standards for N_2O

- at PTB: metrology @ 4.5 µm laser wavelength – OGS development – sensor networks

- at DFM: metrology @ 1.65 µm laser wavelength – OGS development – maritime emission monitoring applications

- at TU-BS: quantum technology-based instrument development for micro-sensors

Thank you.

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