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Optical gas metrology – taking-up new challenges

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Abstract

Gas metrology is fundamental in facilitating the energy transition and assessing climate change mitigating strategies. Corresponding metrological developments can be extremely challenging. For instance, reference materials and standards for reactive gases need to be developed for applications like CCUS, and highly accurate reference measurement methods will be required to comply with the stringent data quality objectives for greenhouse gas monitoring set by the World Meteorological Organization (WMO), as for example for nitrous oxide set as 0.1 nmol/mol in air (0.03 % rel.).

To handle the increasing level of complexity and the stringent accuracy requirements, innovative solutions in gas metrology are called for: The use of artificial intelligence (AI), advanced analytical methods or novel reference gas standards. Optical measurement methods will play an increasingly important role in gas metrology, with two-fold potential: as analytical method and optical standard, e.g., the well-known Standard Reference Photometer for ozone or the optical gas standard for hydrogen chloride.

With both institutes having been exploring the use of optical methods in gas metrology and following a recently signed Memorandum of Understanding signed by VSL and PTB, each one's individual expertise in reference gas standards and optical methods have been combined to advance gas metrology. This contribution showcases examples from emerging fields in metrology for climate action and environmental monitoring to completed studies where foundations of optical gas metrology were provided jointly in the past. Optical gas standards for reactive gases like hydrogen chloride, purity assessments of reference materials, and new provisions of services to WMO GAW stations. Furthermore, we will outline new applications of optical methods and achievable accuracies, referring to uncertainties down to the sub-permille level. Finally, the applicability of optical gas standards as a complement to reference material-based gas standards, e.g., in combination with low-cost sensor networks, will be addressed.

Optical Methods in Gas Metrology: Ozone SRP as the Prototype of all

- Ozone being unstable and reactive, reference material-based gas standards cannot be maintained and used.
- So a spectrometric/photometric approach has been established since many years to provide metrological traceability to ozone amount fractions.
- The NIST Standard Reference Photometer (SRP) has been the most widespread measurement standard for ozone ever since.
- New cross section data measured at the BIPM HQ and in use worldwide since 2025.

Joint mission by VSL & PTB: Optical Methods in Gas Metrology

- Since early European metrology research programmes (iMERA+), VSL and PTB collaborated on optical methods employed to gas metrology
- Application driven projects have seen contributions by laser spectroscopic methods from both or our groups:
  - Breath gas diagnostics, metrology for chemical pollutants in air, molecular spectral line parameters, biogas, emissions monitoring, molecular airborne contaminants of clean room fascilities, carbon capture, utilization and storage.
- CIPM MRA-related activities followed as described here later on.

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Memorandum of Understanding VSL & PTB

- In 2025 a Memorandum of Understanding signed by the directors of both institutes additionally supported our longstanding collaboration in gas metrology.

- From gas metrology employing optical methods now also towards e-learning on metrology for climate action.

- More aspects include those of energy gas-related topics like standardization of biomethane, the hydrogen economy and quantum technology.

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As time goes by: EURAMET/CCQM studies with optical methods

- EUROMET 934 bringing-up the idea of background research for optical gas standards, 2008-2011, (the TILSAM method has been released, https://www.euramet.org/Media/docs/projects/934_METCHEM_Interim_Report.pdf).

- CCQM-K74, nitrogen dioxide in nitrogen, 2009 – 2010, https://www.bipm.org/kcdb/comparison?id=1299

- CCQM-K68.2019, nitrous oxide in nitrogen, 2019 - 2020, https://www.bipm.org/kcdb/comparison?id=340

- EURAMET 1498, hydrogen chloride in nitrogen, 2020 – 2021, https://www.euramet.org/technical-committees/tc-projects/details/project/comparison-of-100-umolmol-hcl-in-n2

- CCQM-K175, hydrogen chloride in nitrogen, 2021 – 2023, https://www.bipm.org/kcdb/comparison?id=1783

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- EURAMET 1498, hydrogen chloride in nitrogen, 2020 – 2021, https://www.euramet.org/technical-commit

Optical Gas Standard for HCl published in the KCDB

- CCQM-K175, hydrogen chloride in nitrogen, 2021 – 2023, https://www.bipm.org/kcdb/comparison?id=1783

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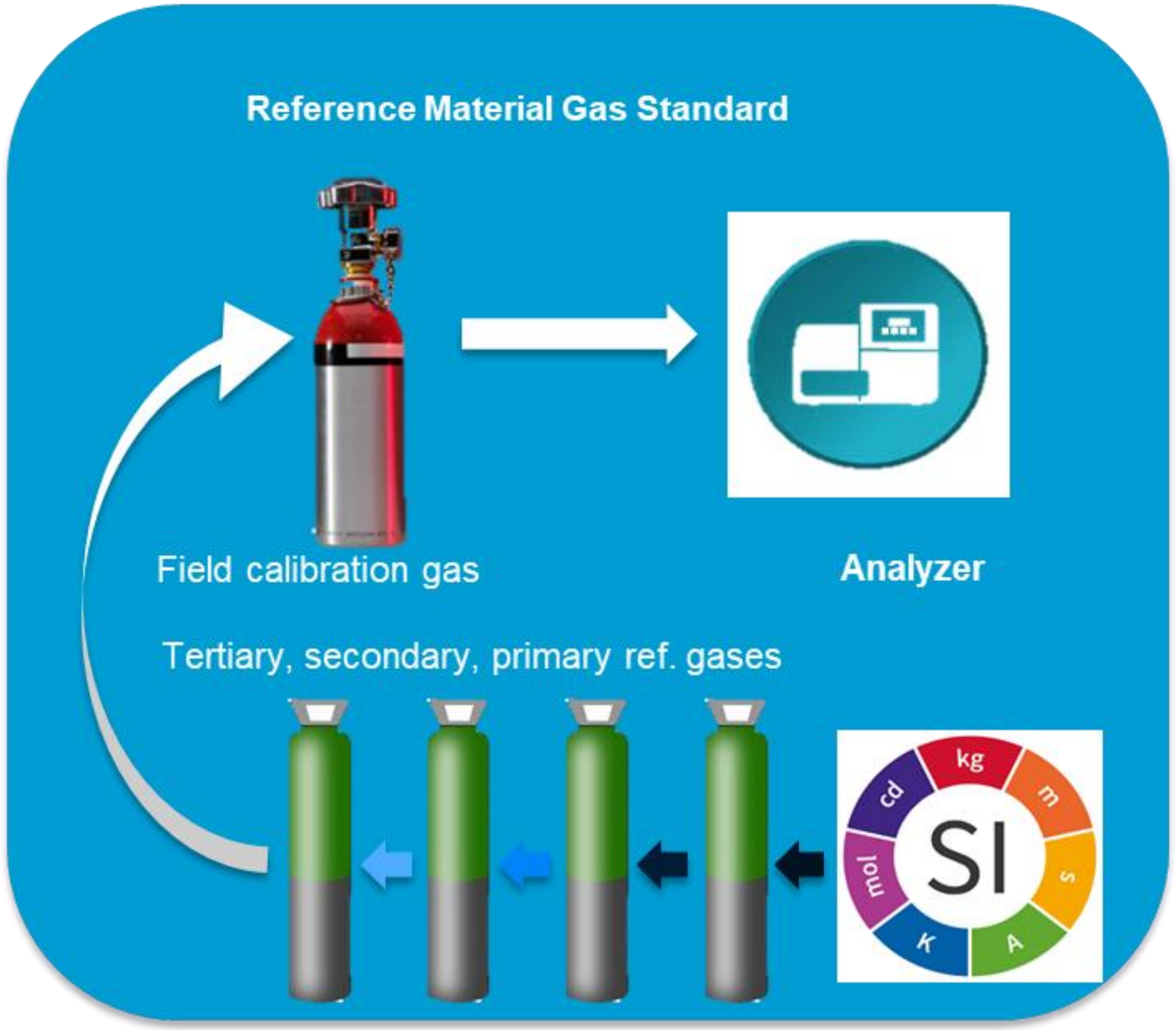
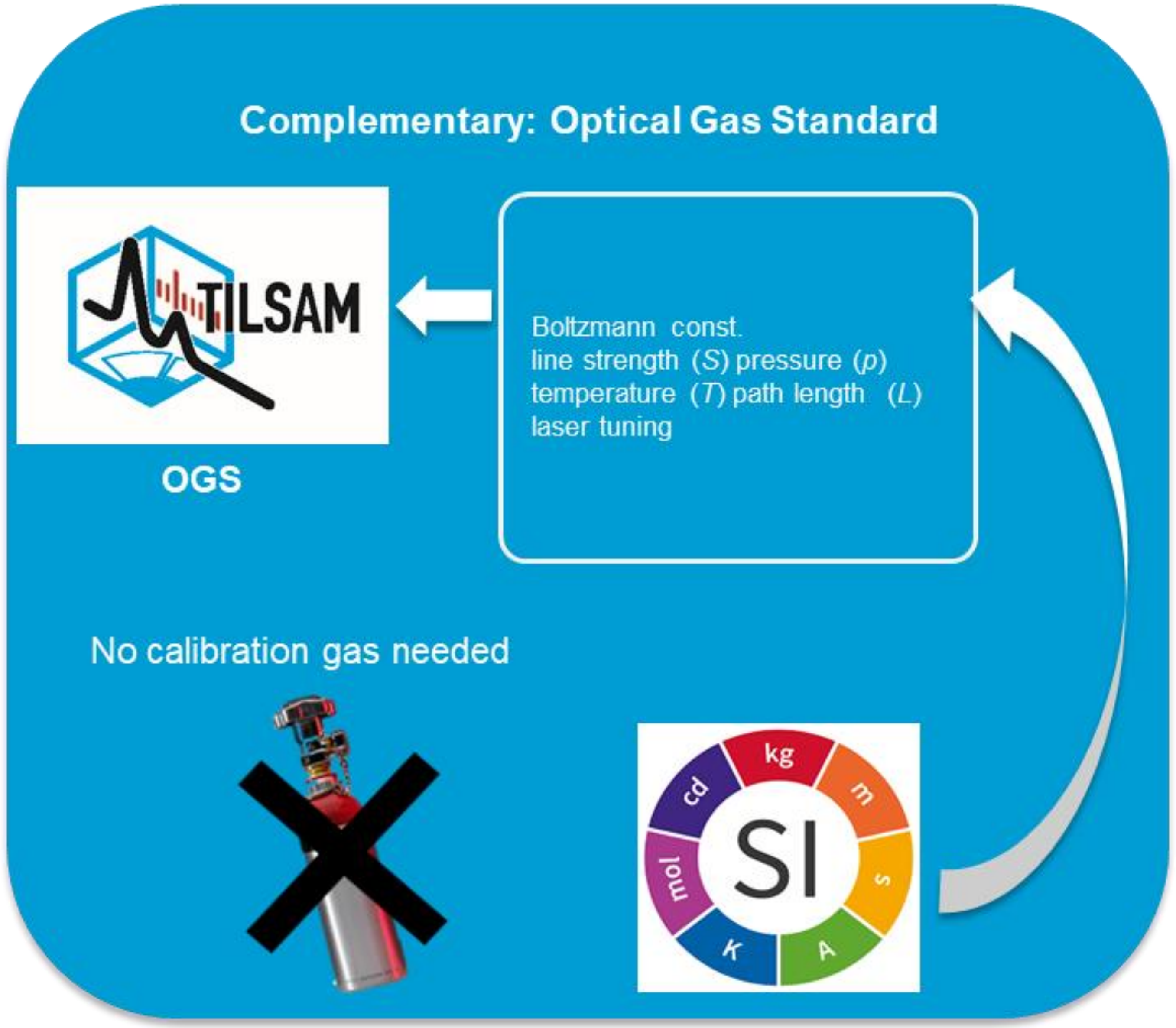
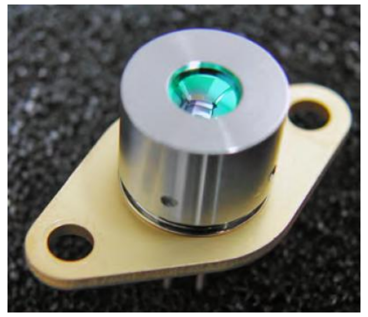
Optical Gas Standards

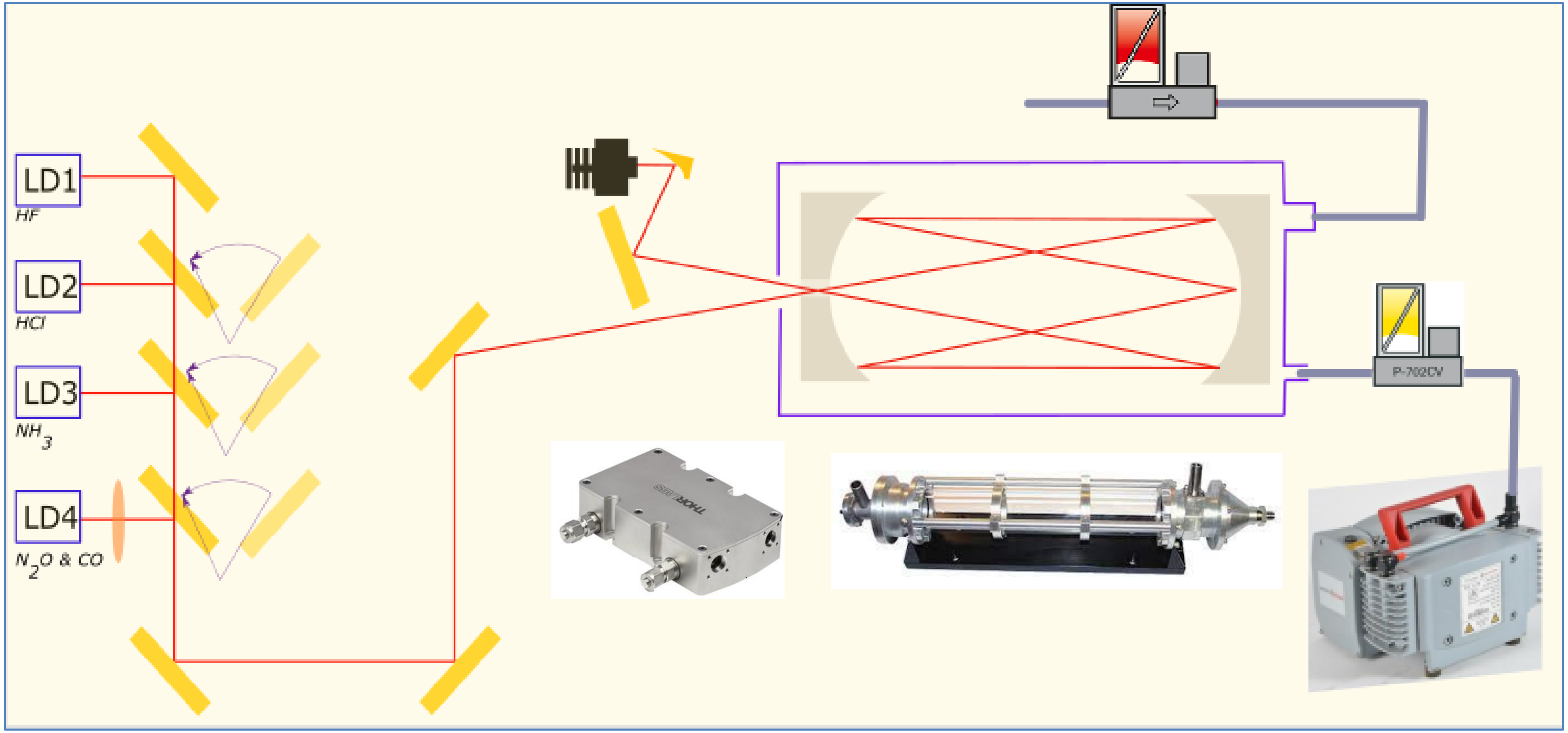




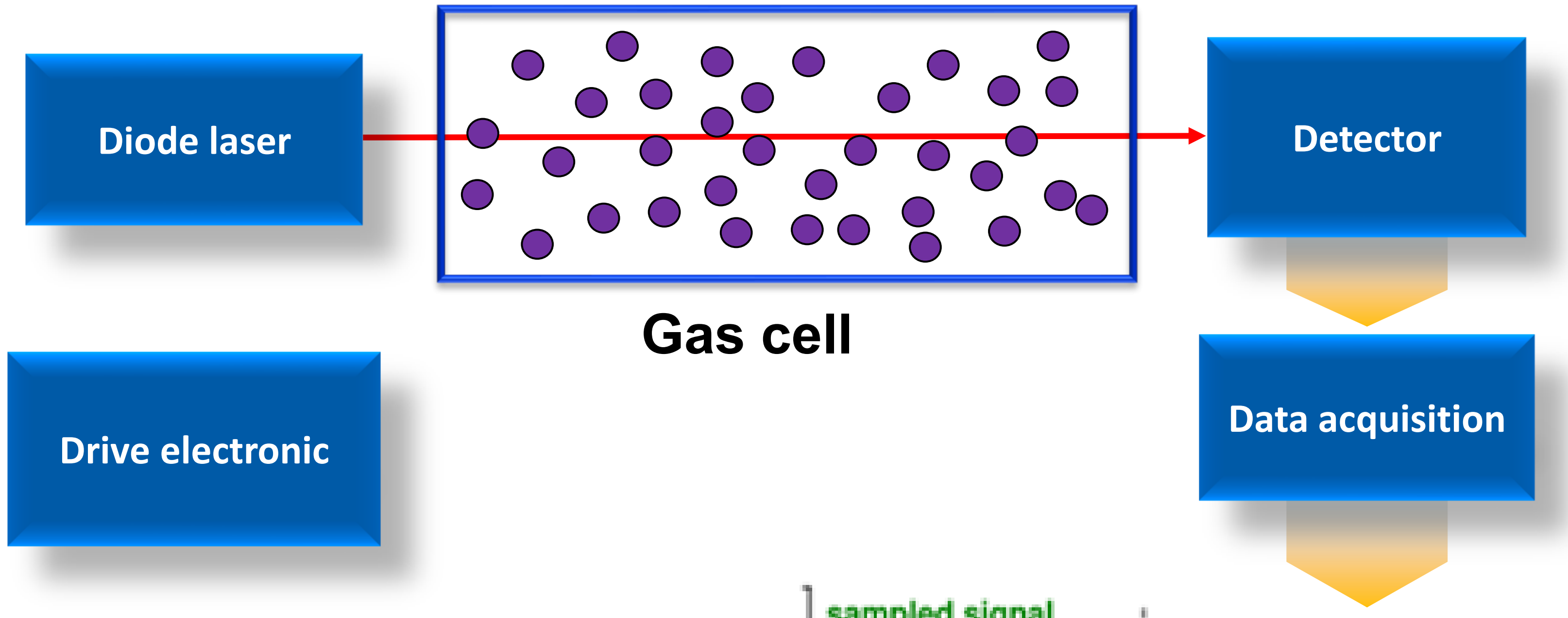
- To complement existing CRMs, especially for sticky and reactive gases which cannot be provided in static gas cylinders,
- alternative calibration and traceability strategies are required,
- and have been demonstrated based on instrumental standards.

Laser absorption spectroscopy set-up at VSL



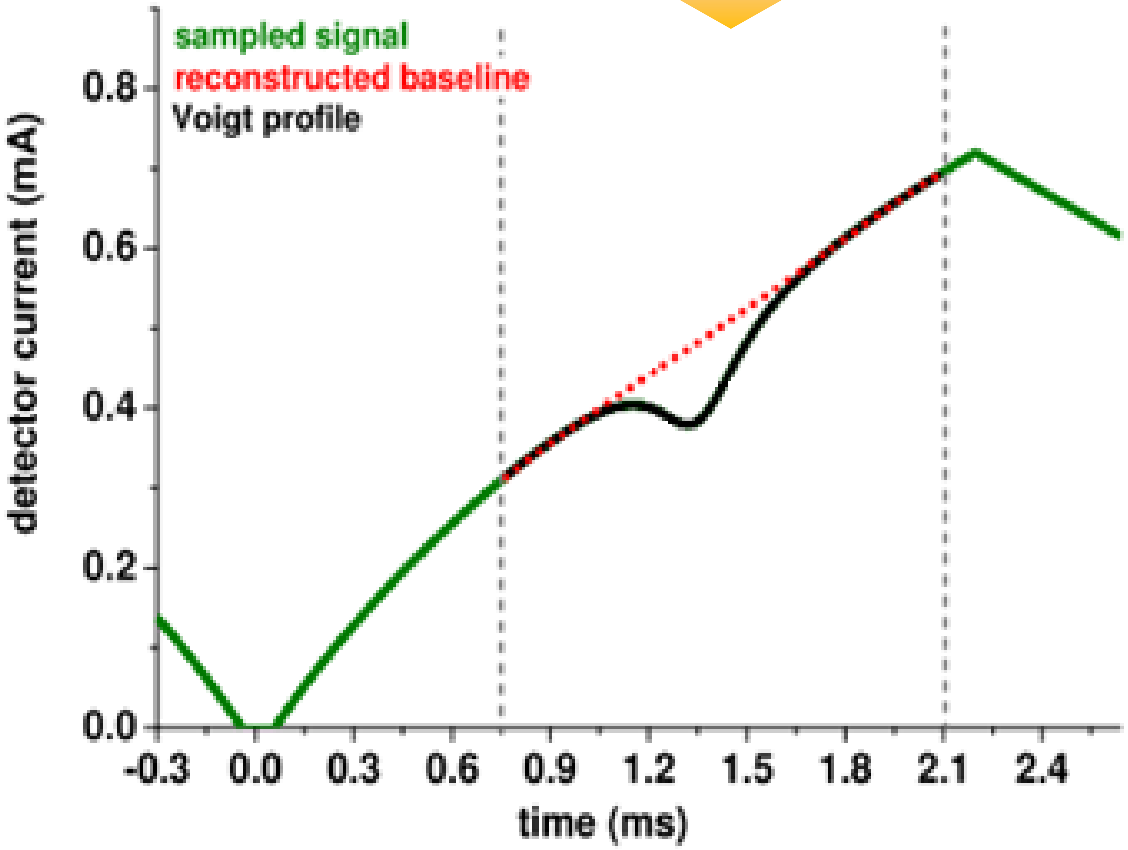


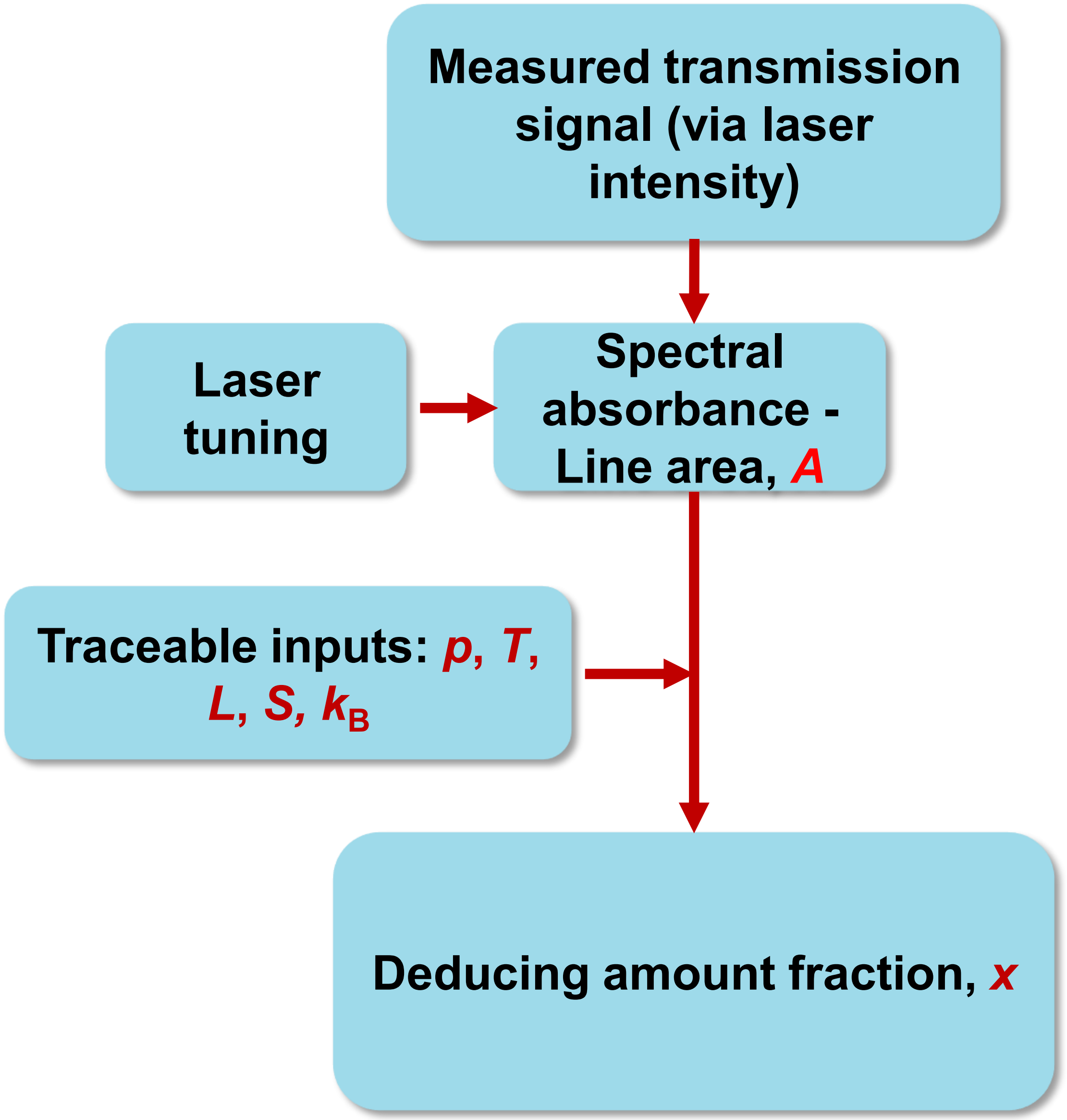
Traceable Infrared Laser-Spectrometric Amount fraction Measurement



$$x_{\mathrm{HCl}} = \frac{k_{\mathrm{B}} \cdot A \cdot T}{S \cdot p \cdot L}$$

measured parameters
constants
molecular line data





Laser absorption spectroscopy at PTB

Molecule	Wavelength range in µm	Laser type*	Concentration range validated in µmol/mol	Application	Relative uncertainty (OGS), (k = 1) in %+	Linearity (candidate OGS vs. certified or reference values)
H_2O	1.4 µm	DFB	10 - 18000	Atmospheric	2.2	0.993 ± 0.017
CO	4.6 µm	ICL	0.3 - 1000	Atmospheric	1.8	0.999 ± 0.008
NO_2	3.4 µm	ICL	100 - 1000	Air pollution	5.1	0.984 ± 0.094
HCl	3.6 µm	ICL	50 - 500	Biomethane quality control	2.3	1.038 ± 0.071

+relative uncertainties are calculated following the Guide to the expression of Uncertainty in Measurement (GUM)+ principles

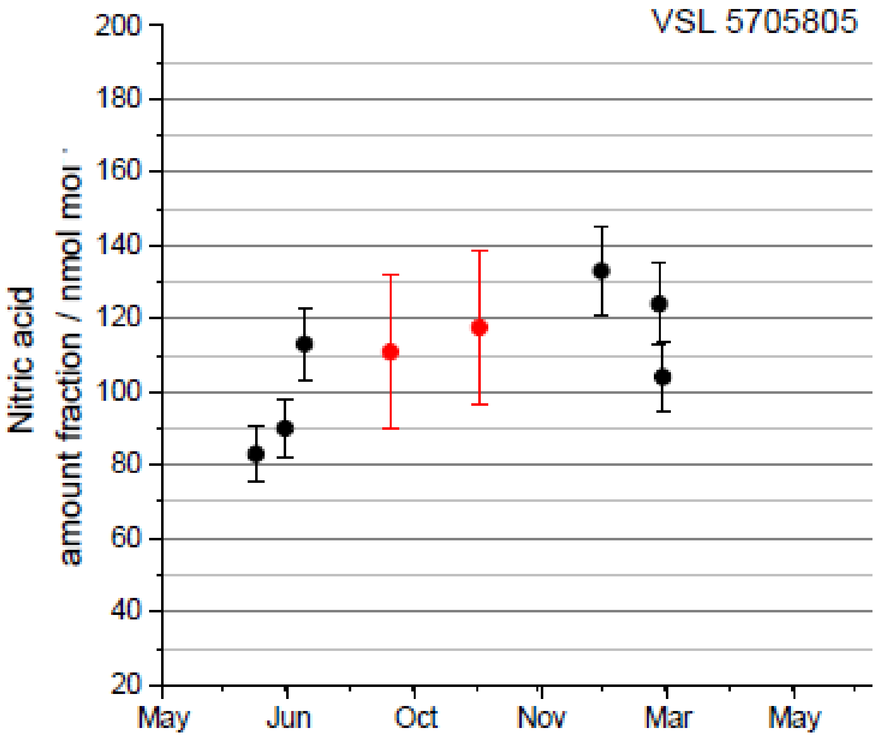
Optical Gas Metrology: spectroscopic line data and absorption cross-sections

- The number 1 requirement for Optical Gas Standards are spectroscopic data (line strengths, line-shape parameters, absorption cross-sections). Spectroscopic databases like HITRAN contain huge amount of data but these are typically not SI-traceable.

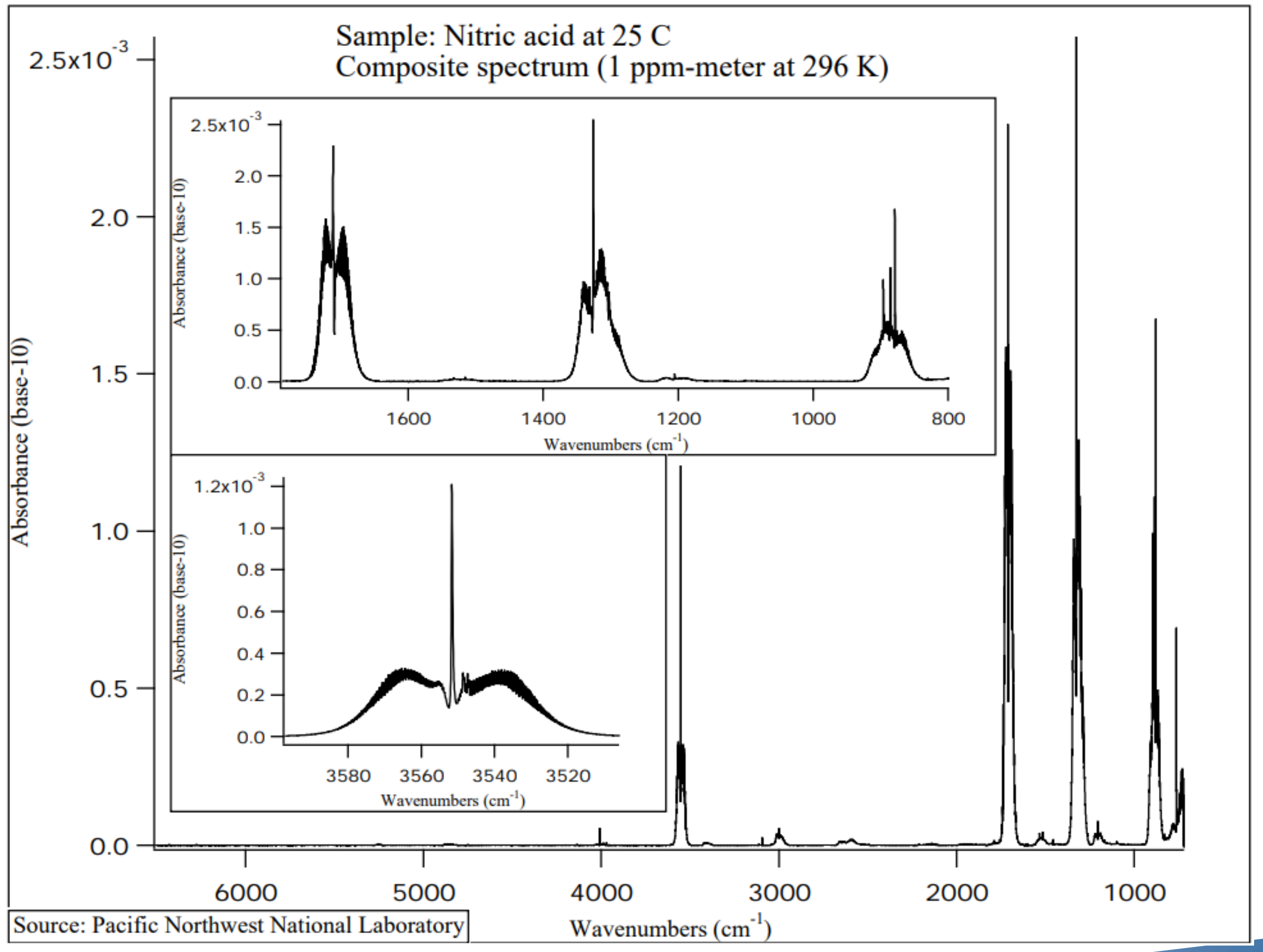
- In the spectroscopic community awareness on traceability is growing. Joined efforts between spectroscopic community and NMI's recently led to excellent results for simple di-atomics like CO (Bielska, et al. "Sub-permille measurements and calculations of CO (3–0) overtone line intensities." PRL 129 (4) 2022).

- In 2022 the CCQM GAWG Task Group on Advanced Spectroscopy (CCQM-GAWG-TG-ADV-SPEC, https://www.bipm.org/en/committees/cc/ccqm/wg/ccqm-gawg-tg-adv-spec) was established. This group sets out to provide SI-traceable spectroscopic reference data and develop measurement protocols for intercomparison of primary spectroscopic methods.

Comparisons: Pilot study CCQM-P17 spectroscopic methods for HNO_3 value ass



Nitric acid is the main impurity in NO_2 gas standards. HNO_3 was analyzed in 10 µmol/mol NO_2 gas standards. All labs used FTIR except VSL (CRDS).



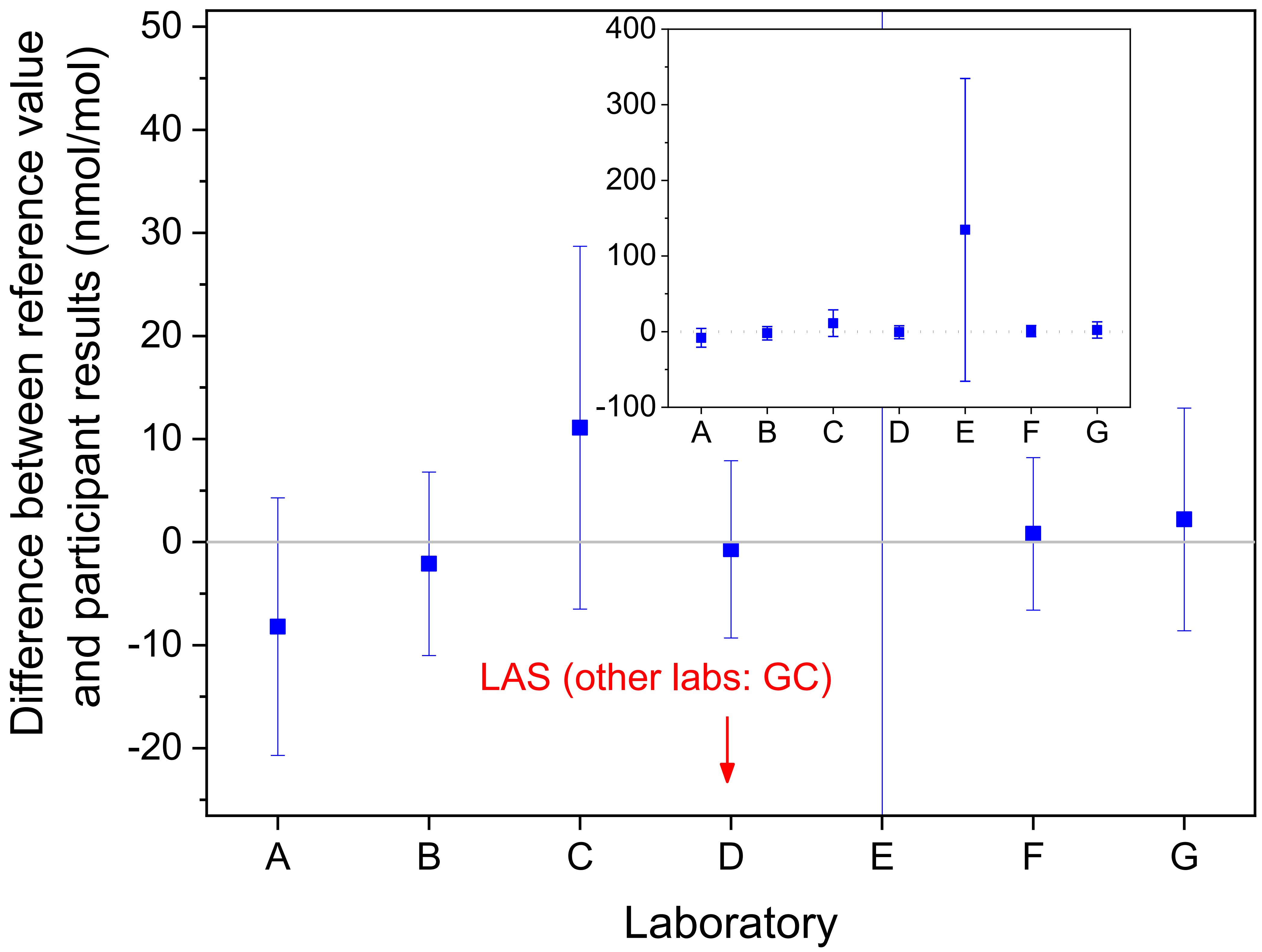
Lessons learned from this comparison:

1) Good agreement between CRDS (VSL) and FTIR measurements (BIPM) when based on the same spectroscopic data (in this case PNNL).

2) PNNL data HNO_3 consistent with permeation data (BIPM). HITRAN consistent with permeation for some HNO_3 absorption bands, others deviate up to 23%.

3) Do not underestimate the uncertainty of spectroscopic data.

Comparisons: CCQM-K164 – Hydrogen quality

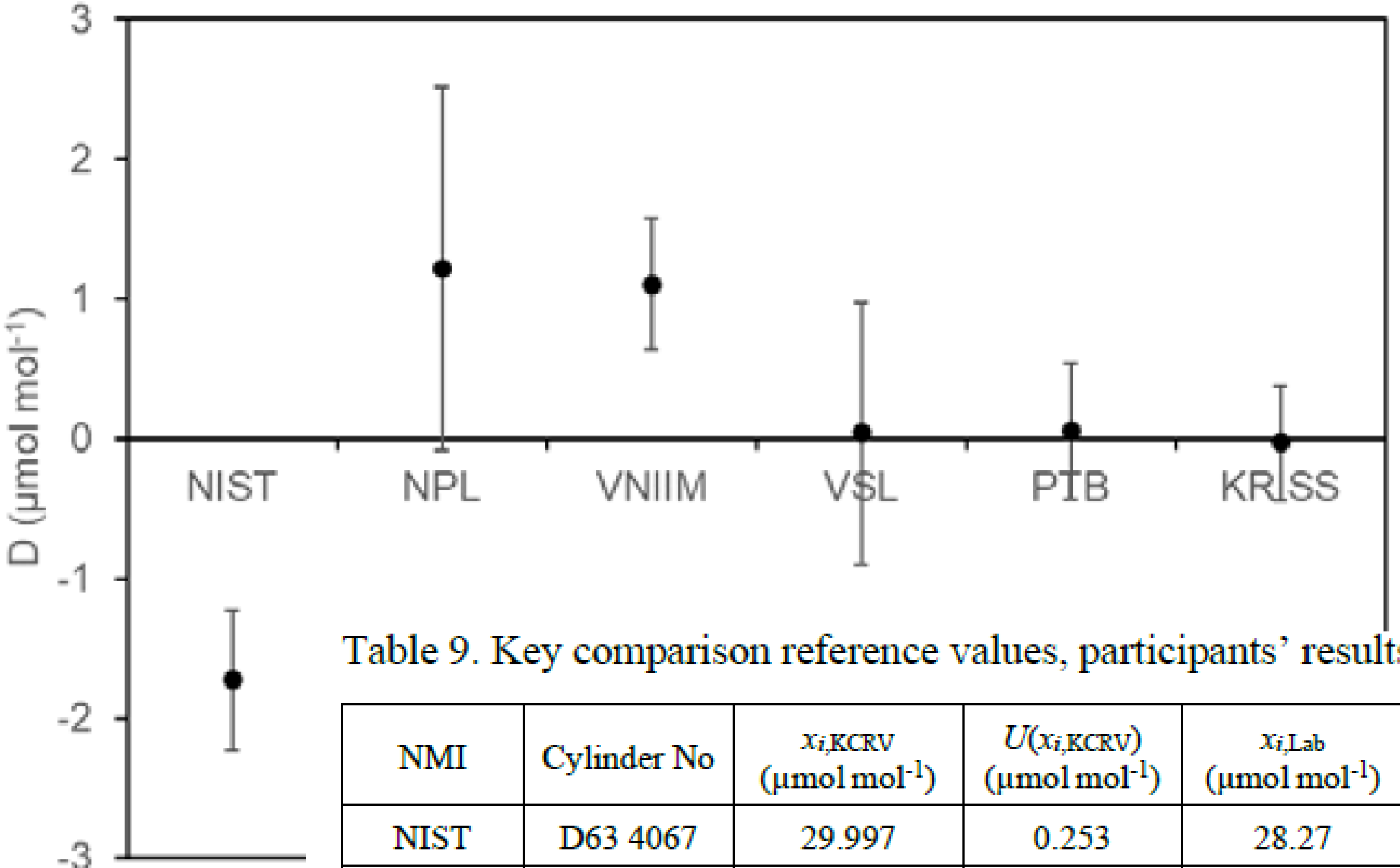


Carbon monoxide

ISO 14687 threshold : 200 nmol/mol

Gas standards sent around contained nominally 200 nmol/mol CO in H_2.

CCQM-K175, hydrogen chloride (HCl) in nitrogen, 30 µmol/mol

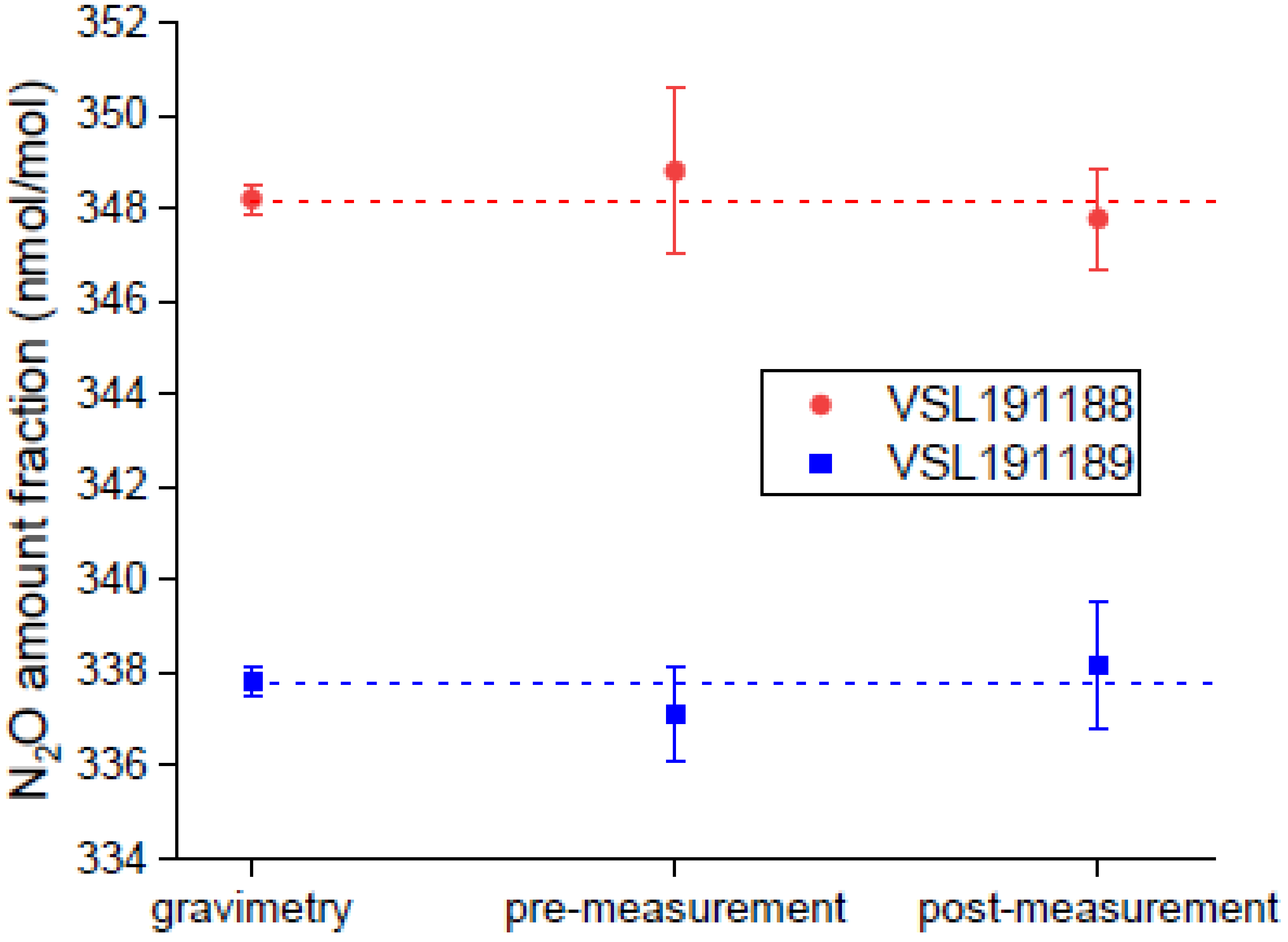


- Measurements all performed by optical methods, except of VNIIM.
- Metrological traceability of PTB to its HCl-OGS.

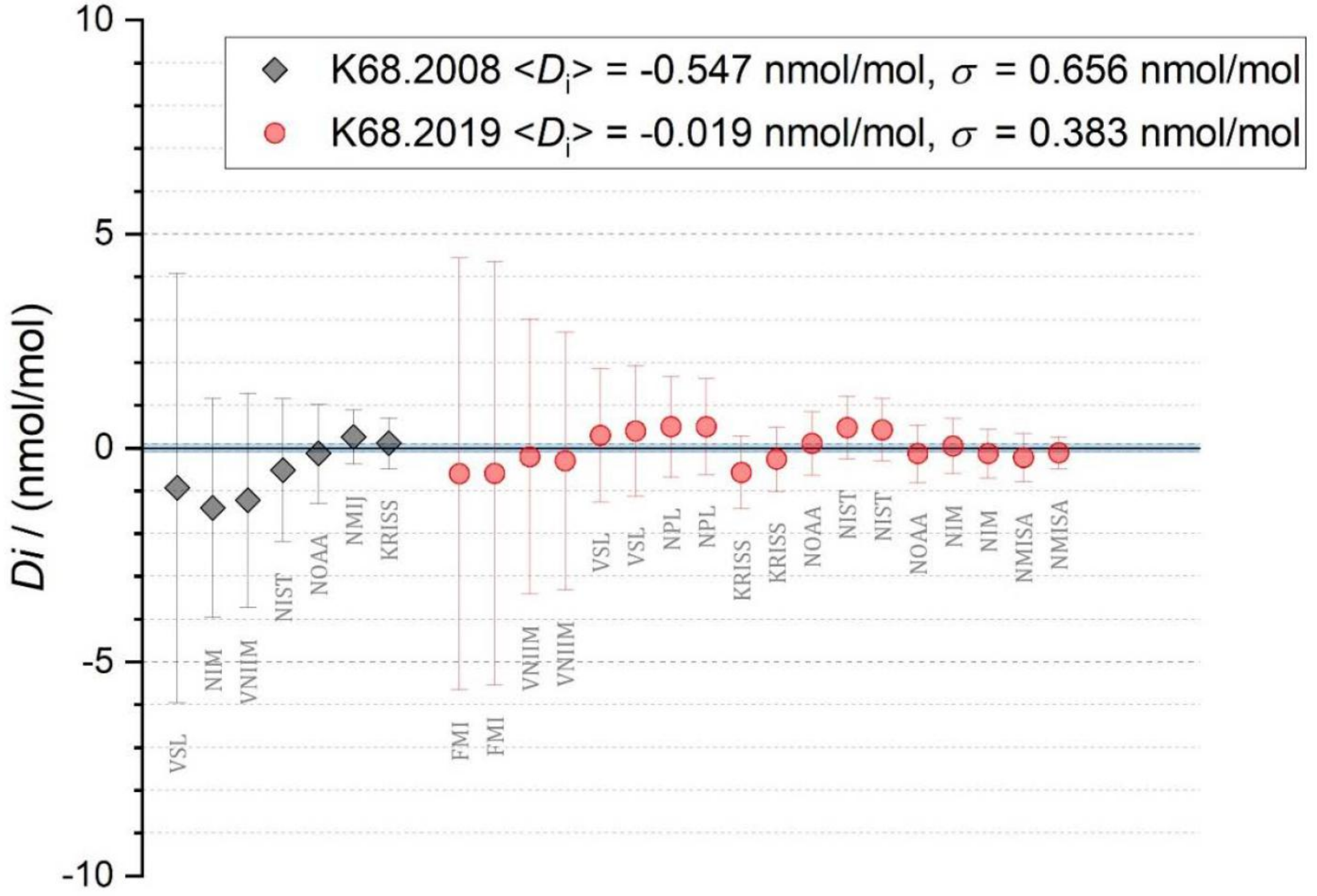
Table 9. Key comparison reference values, participants' results, and the degrees of equivalence.

NMI	Cylinder No	$x_{i,\mathrm{KCRV}}$ (µmol mol^{-1})	$U(x_{i,\mathrm{KCRV}})$ (µmol mol^{-1})	$x_{i,\mathrm{Lab}}$ (µmol mol^{-1})	$U(x_{i,\mathrm{Lab}})$ (µmol mol^{-1})	D_i (µmol mol^{-1})	$U(D_i)$ (µmol mol^{-1})
NIST	D63 4067	29.997	0.253	28.27	0.44	-1.73	0.51
NPL	D63 4090	30.057	0.253	31.27	1.28	1.21	1.30
VNIIM	D64 1531	29.996	0.253	31.10	0.40	1.10	0.47
VSL	D98 3267	30.061	0.253	30.10	0.90	0.04	0.93
PTB	D98 3274	30.056	0.253	30.11	0.42	0.05	0.49
KRISS	D98 3403	30.013	0.253	29.98	0.32	-0.03	0.41

CCQM-K68.2019, nitrous oxide (N_2O) in air, ambient level



Pre- and post-measurements at VSL of the 2 standards and the comparison of the QCLAS with the gravimetric value.



Methods participants: 3× GC-ECD, 6×optical (CRDS, CEAS, QCLAS)

Coordinating labs: GC-ECD & QCLAS

Source: J Viallon *et al* 2023 *Metrologia* **60** 08011
https://iopscience.iop.org/article/10.1088/0026-1394/60/1A/08011

Pilot study: EURAMET 1720, nitrous oxide (N_2O), comparing new OGS to established standards

- For European paths of metrological traceability for nitrous oxide, the development of new N_2O gas standards was proposed with the focus on climate related target applications. Here, the hope is to compare both optical N_2O standards and reference material-based N_2O standards in the range from 0.3 to 3 µmol/mol, https://www.euramet.org/technical-committees/tc-projects/details/project/pilot-study-comparing-nitrous-oxide-gas-standards-tackling-a-super-climate-pollutant-by-optical-and-reference-material-based-gas-standards-1 .

- To support N_2O CMCs and related services, the key comparison CCQM-K68.2019 has been run in 2019-2020. The corresponding data is now entering the 5-years age. Furthermore, the CCQM-K68.2019 has followed the model 2 comparison scheme – with the focus of the preparation of gas standards. The last model 1 key comparison on N_2O with the focus on the participants' analytical capabilities dates even back to 2008. At that time, only one EURAMET member institute participated (VSL).

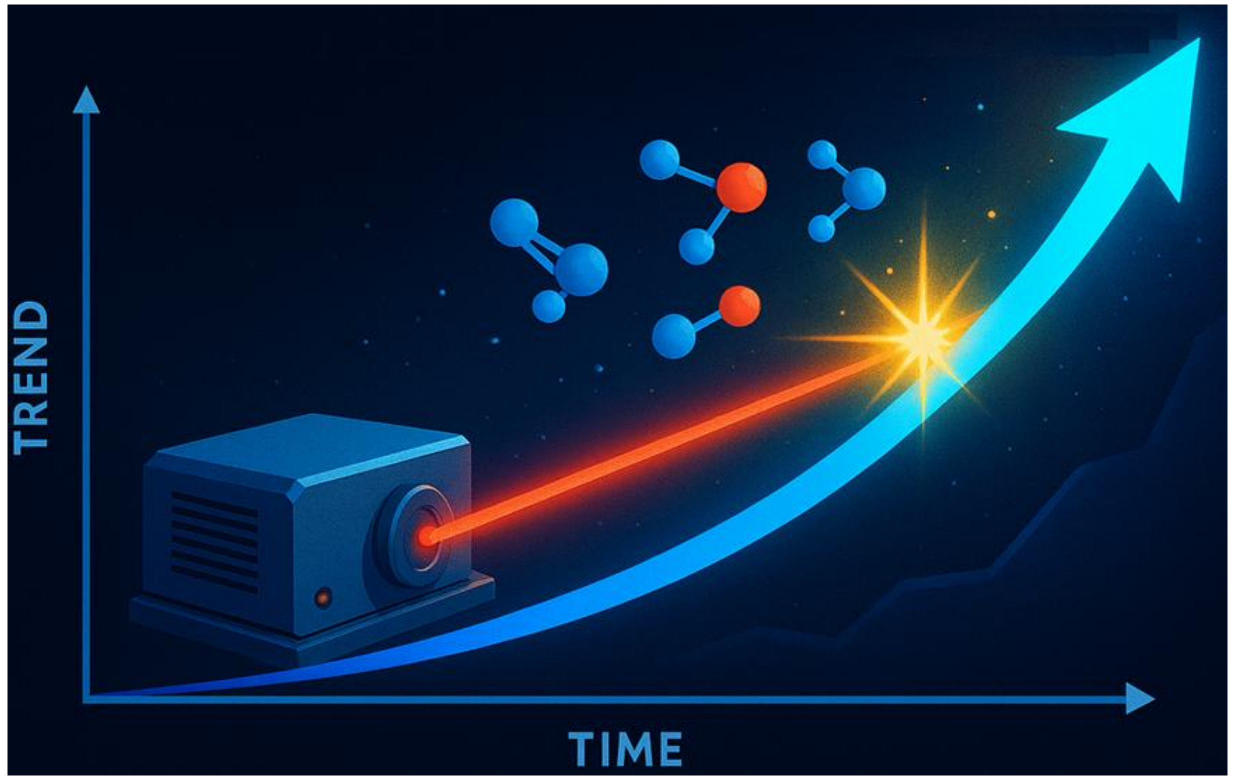
Future of optical methods in gas analysis

For certain analytes, optical methods have proven to be a great addition to conventional analytical methods.

When used as optical gas standards: Similar ‘rights & duties” should apply as for regular reference gas standards according to the CIPM MRA mechanisms, so

- taking part in key comparisons to povide
- supporting evidence for CMCs

as done, e.g. with EURAMET 1498 and CCQM-K175.



For the uptake of optical gas standards more traceable line data are needed.

Future is bright, in particular for analytes like diatomics (e.g., CO), greenhouse gases (CH_4, N_2O, CO_2) and small reactive gases (NH_3, HCl,….).

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Thanks for your attention.

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Measurements in Science and Technology