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Spectrometric Gas Analysis (3.42)

and the DFM A/S

https://www.ptb.de/cms/en/ptb/fachabteilungen/abt3/fb-34/ag-342.html

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The TILSAM method adapted into Optical Gas Standards – complementing gaseous reference materials

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Abstract

TILSAM – **T**raceable **I**nfrared **L**aser **S**pectrometric **A**mount fraction **M**easurement - has been available since 2009 [1]. Onboarded by a EURAMET research project and validated by a comparison study of ambient level carbon dioxide gas standards [2], this method has been successfully applied for CO_2 and CO quantifications in greenhouse gas measurements, breath analysis studies, and industrial drying processes [3-6]. Facing new challenges in gas analysis related to an increasing number of critical analytes as well as an increasing demand from stakeholders in industry and atmospheric sciences for improved amount fraction sensitivity, the TILSAM method has been combined with appropriate spectroscopy techniques to form an instrument class of its own, called Optical Gas Standard (OGS).

TILSAM-compliant OGS systems are seen to advance and complement the use of gaseous reference materials. This is for example the case when the needed amount fractions cannot be supported by existing reference gases, or analyte definitions and combinations of species asked by customers do not allow them to be filled into pressurized cylinders because of their reactivity or instability. Furthermore, OGS systems can serve SI-traceability demands in applications where reference gases cannot be carried for and analyzer down times for individual calibrations are not economically tolerable.

In a collaborative approach DFM and PTB both have progressed their spectrometric gas metrology efforts towards more advanced individual OGSs for various species, including CO, H_2O, HCl, NH_3, NO_2. The TILSAM method has not yet been merged into an operational CMC-based service. However, ongoing work will advance the TILSAM protocol [1], providing an improved updated edition.

This contribution will introduce the TILSAM method, provide an outlook into the new edition, and discusses a suite of applications having advanced TILSAM and related instrumentation to finally become an OGS [7].

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[1] O. Werhahn, J.C. Petersen (eds.), “Traceable Infrared Laser Spectrometric Amount fraction Measurement”, TILSAM protocol V1, available from: https://www.euramet.org/Media/docs/projects/934_METCHEM_Interim_Report.pdf

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[5] Javis Anyangwe Nwaboh, Stefan Persijn, Kathrin Hein-rich, Marcus Sowa, Olav Werhahn, ‘QCLAS and CRDS-based CO quantification as aimed at in breath measurements’, In-ternational Journal of Spectroscopy (2012), dx.doi.org/10.1155/2012/894841

[6] Maija Ojanen-Saloranta, Final Report of EMPIR project ‘Metrology for humidity at high temperatures and transient conditions (HIT)’, 2018, https://www.euramet.org/research-innovation/search-research-projects/details/project/metrology-for-humidity-at-high-temperatures-and-transient-condi-tions/?L=0&tx_eurametctcp_project%5Baction%5D=show&tx_eurametctcp_project%5Bcontroller%5D=Project&cHash=9c59760299240cef5c348049d5abe4fd.

[7] N. Lüttschwager, A. Pogány, J. Nwaboh, A. Klein, B. Buchholz, O. Werhahn, V Ebert, ‘Traceable amount of sub-stance fraction measurements in gases through infrared spectroscopy at PTB’,17th International Congress of Metrolo-gy (2015), 07005-1-07005-5, dx.doi.org/10.1051/metrology/20150007005

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S4. GAS METROLGY

TILSAM method adapted into Optical Gas Standards
– complementing gaseous reference materials

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IN
MEASUREMENT
WE TRUST

Physikalisch-Technische Bundesanstalt
Braunschweig and Berlin
National Metrology Institute

The TILSAM method adapted to Optical Gas Standards – complementing gaseous reference materials

TILSAM

O. Werhahn (PTB), J.C. Petersen (DFM),
J. Nwaboh, A. Pogány, Z. Qu (PTB)

Author group and history of TILSAM

TILSAM:

Traceable Infrared Laser-Spectrometric Amount fraction Measurement

Originally by

O. Werhahn[1], J.C. Petersen[2],

[1] Physikalisch-Technische Bundesanstalt (PTB), Bundesallee 100, 38116 Braunschweig, Germany

[2] DFM A/S, Kogle Alle 5,2970 Hørsholm, Denmark

Author group and history of TILSAM

TILSAM: https://www.euramet.org/Media/docs/projects/934_METCHEM_Interim_Report.pdf

Traceable Infrared Laser-Spectrometric Amount fraction Measurement

TILSAM technical protocol, version 1.0 2010-09-29

TILSAM **– method**
– draft A of a technical protocol –

Author group and history of TILSAM

TILSAM: https://www.euramet.org/Media/docs/projects/934_METCHEM_Interim_Report.pdf

@ EURAMET project no. 934 in 2010

@ iMERA+ project, Breath Analysis in 2008-2011 (*BA-TILSAM*)

@ EMRP ENV06, Spectral Reference Data for Atmospheric Monitoring (2013)

@ EURAMET project no. 1280, Establishing equivalence of TILSAM and gravimetry-based analytical capabilities (2018)

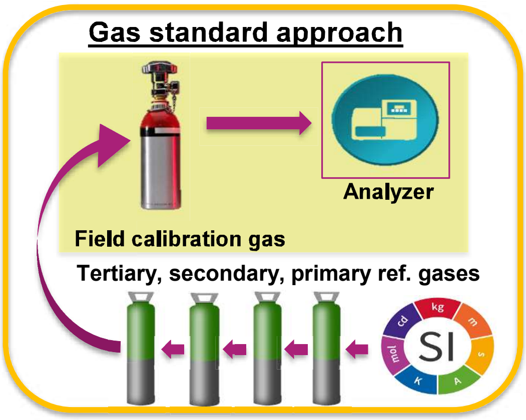
@ EURAMET 1498, bilateral comparison with KRISS on 100 µmol/mol HCl in nitrogen gas standards (2021) *by means of an Optical Gas Standard (OGS)*

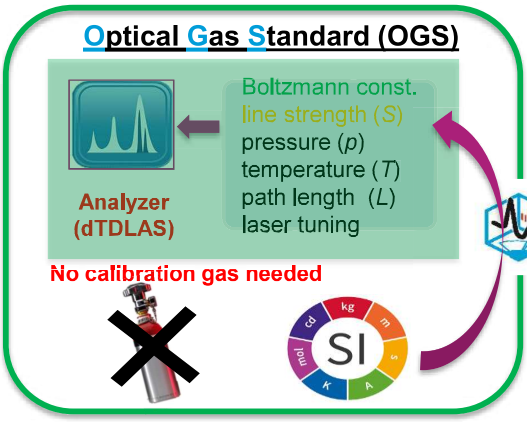
@ 2021, edition 2.0 of the TILSAM protocol available

TILSAM and Optical Gas Standard concepts

- *Measurement principle:* TILSAM
- *Spectroscopy technique:* dTDLAS (or CRDS, CEAS, etc.)
- *Spectrometer type:* Optical Gas Standard (OGS)
- *Target:* metrological traceability to the international systems of units (SI)

Concept of Optical Gas Standard (OGS)

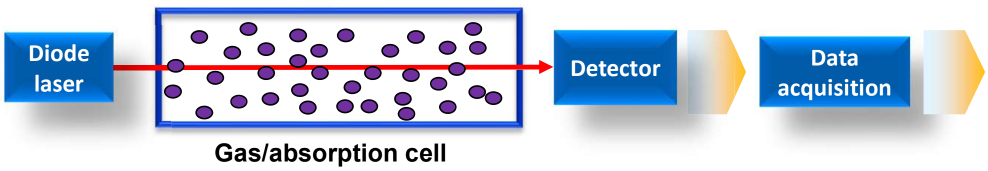


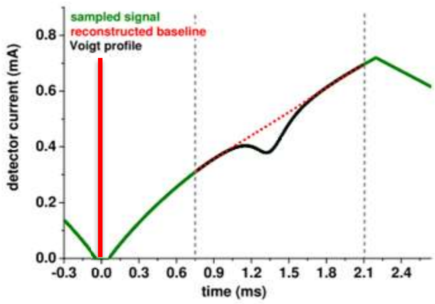


➲An **Optical Gas Standard** is a (laser) spectrometer providing amount of substance fractions **(concentrations)** that are **directly traceable to the SI**

TILSAM and Optical Gas Standard concepts

Combined with dTDLAS



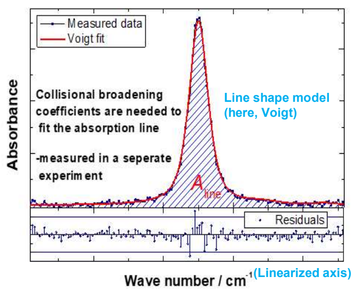


Amount fraction

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

measured, constants, molecular data:
→ SI - traceable → x_{HCl} SI - traceable

dTDLAS Advantages:
robust, linear, absolute, calibration-free, 1st principles model, in situ compatible



Time to frequency conversion via Etalon measurement

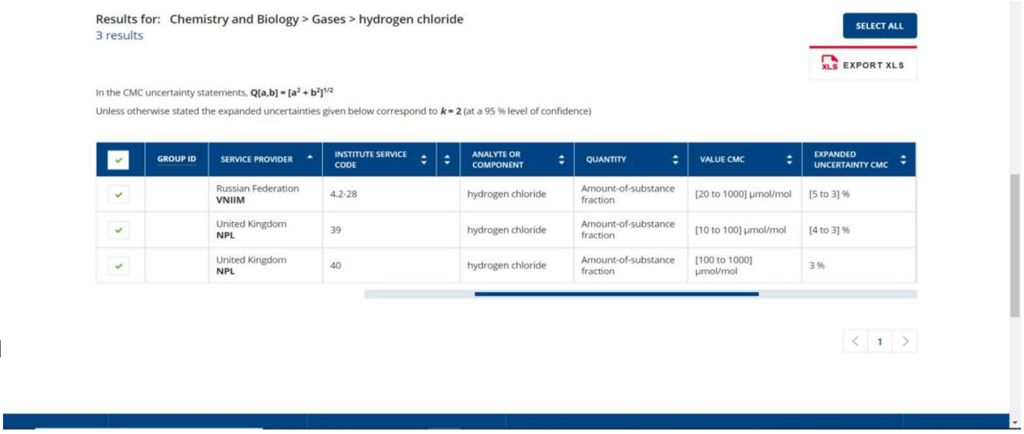
Traceable Infrared Laser-Spectrometric Amount fraction Measurement

Current pratice in gas metrology (KCDB)

- Examples from the KCDB* in terms of Calibration and Measurement Capabilities (CMCs) for HCl measurements in gas matrices:

- Only 3 matches in the KCDB for HCl gas mixtures with 3 % best uncertainty

- Before dissemination to the field



Results for: Chemistry and Biology > Gases > hydrogen chloride
3 results

SELECT ALL
EXPORT XLS

In the CMC uncertainty statements, **Q[a,b] = [a² + b²]^1/2**

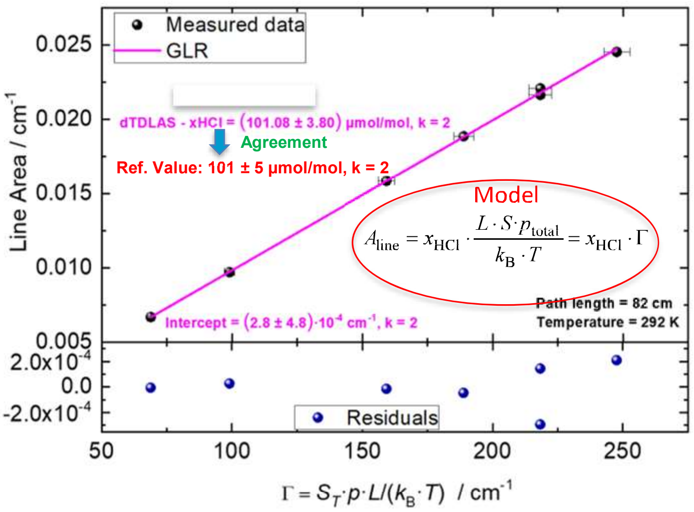
Unless otherwise stated the expanded uncertainties given below correspond to ***k* = 2** (at a 95 % level of confidence)

	GROUP ID	SERVICE PROVIDER	INSTITUTE SERVICE CODE		ANALYTE OR COMPONENT	QUANTITY	VALUE CMC	EXPANDED UNCERTAINTY CMC
✓		Russian Federation **VNIIM**	4.2-28		hydrogen chloride	Amount-of-substance fraction	[20 to 1000] µmol/mol	[5 to 3] %
✓		United Kingdom **NPL**	39		hydrogen chloride	Amount-of-substance fraction	[10 to 100] µmol/mol	[4 to 3] %
✓		United Kingdom **NPL**	40		hydrogen chloride	Amount-of-substance fraction	[100 to 1000] µmol/mol	3 %

* KCDB – Key Comparison Data Base, BIPM, https://www.bipm.org/kcdb/

Advancing OGS based gas metrology

Examples from Biogas, IMPRESS2 – HCl-OGS



Uncertainty budget

Parameter	Value	Relative standard uncertainty (k = 1) / %
Pressure	491.3 hPa	0.15
Temperature	292.2 K	0.10
Path length	0.82 cm	0.24
Line strength*	$1.895 \cdot 10^{-19}$ cm/ molecule	1.10
Line area	0.01911 cm^{-1}	1.00
HCl amount fraction	**100.97 µmol/mol**	**1.50 (combined uncertainty)**

*Value taken from the original publication up taken by the HITRAN 2016 database, G. Li et al., JQSRT 121 (2013) 78-90

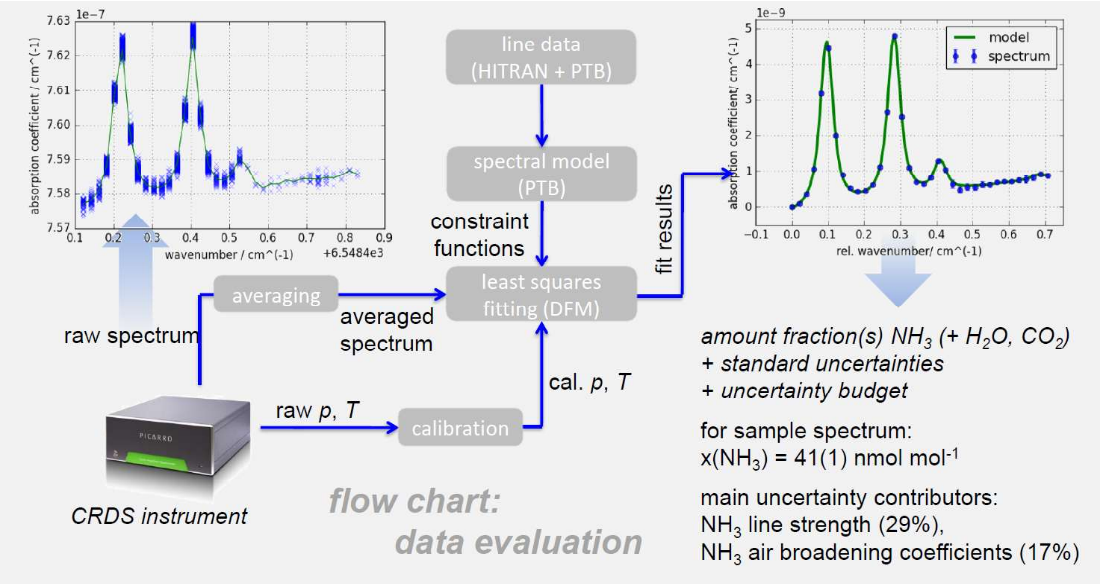
Traceability: Traceability of the results is addressed via the traceability of input paramaters such as the gas pressure and temperature that are traceable to respective PTB standards.

Advancing OGS based gas metrology

Examples from Metrology for Ammonia – NH3-OGS

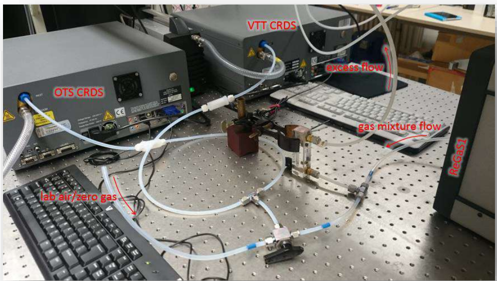
Fitting algorithm

- Generalized least squares fitting by DFM, accounts for uncertainty in line parameters
- Yields standard uncertainties, covariances, and uncertainty budget of amount fraction results
- Chi-square test to check consistency of data and fit

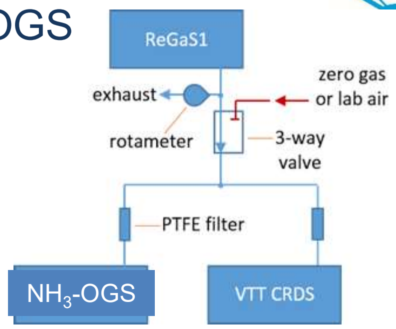


Advancing OGS based gas metrology

Examples from Metrology for Ammonia – NH3-OGS



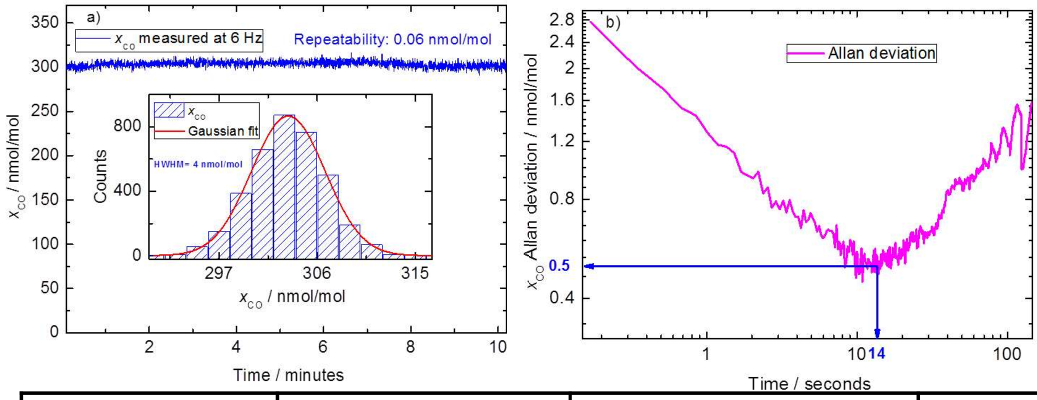
➲PTB
➲METAS
➲VTT



	$x_{nominal}$	x_{ReGaS1}	$u(x_{ReGaS1})$	x_{OGS}	$u(x_{OGS})$	$<xVTT>$	$s(<x_{VTT}>)$
NH_3 amount fractions in nmol mol^{-1}	200	201.8	2.55	215.9	2.3	212.85	0.25
	125	127.12	1.6	136.6	1.5	134.86	0.05
	10	10.27	0.13	11.10	0.16	10.58	0.09
	10	10.26	0.13	11.04	0.15	10.46	0.07
	50	50.892	0.65	52.02	0.58	51.81	0.02

Advancing OGS based gas metrology

Examples from HIGHGAS – CO-OGS



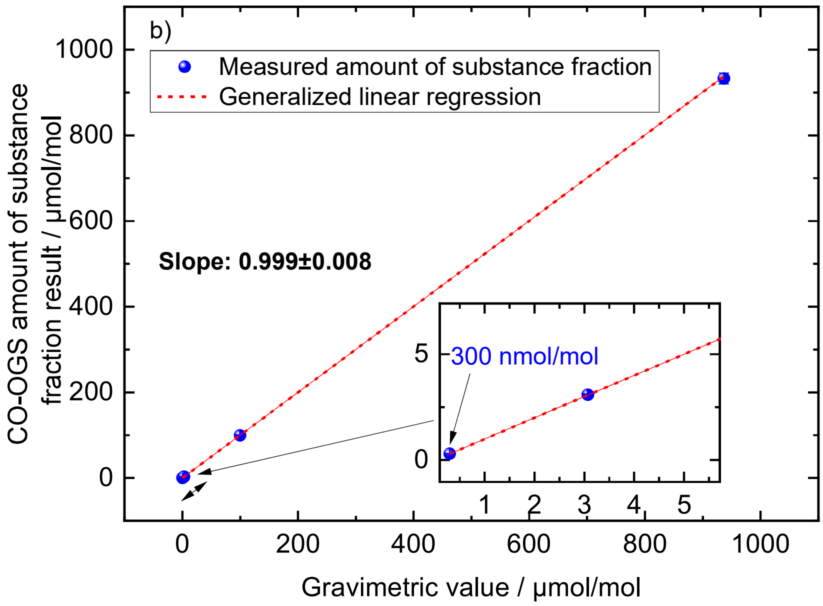
Repeatability: 0.06 nmol/mol
left: Static single scan concentration measurements versus time
right: Allan deviation of the concentration results on the left

Quantity	Value	Relative standard uncertainty / %	Index of contribution to the uncertainty of x_{CO} / %
L	76.643 cm	0.021	0.0
T	295.81 K	0.08	1.3
p	492.16 hPa	0.15	1.2
S	$271.80 \cdot 10^{-21}$ cm/molecule	0.96	**46.6**
A_{line}	$7.5634 \cdot 10^{-3}$ cm^{-1}	1.00	**50.9**
x_{CO}	**301.0 nmol/mol**	**1.4**	

J. Nwaboh, et al. Appl Opt. 56, 11, pp. E84-E93 (2017)

Advancing OGS based gas metrology

Examples from HIGHGAS – CO-OGS



- 4 primary gas standards used
- excellent agreement between OGS results and gravimetric values
- over nearly 3 orders of magnitude

TILSAM protocol 2.0 in view for 2021

Updated version with focus on:

- Providing users with insights to challenging applications;
- Recommendation and guidance on performing uncertainty budget estimates;
- Providing more details on estimating uncertainties from individual contributions;
- Providing additional cases based on actual measurments.

Conclusions

- TILSAM is an upcoming method suitable to be combined with spectroscopic techniques such as dTDLAS or CRDS to facilitate Optical Gas Standards (OGSs).
- OGSs will complement gaseous reference material in particular for challenging analytes, i.e., adsorbing or reacting species.
- Example applications for NH_3, HCl, and CO gas metrology proves its feasibility – up to new HCl-OGS-based CMC claims.
- TILSAM protocol 2.0 will provide new insights and more guidance to users.

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