Will there be new options for PFAS quantifications based on optical gas standards?

Alexandra Domanskaya, Gang Li, Rainer Stosch, Zhechao Qu, Olav Werhahn*

Physikalisch-Technische Bundesanstalt (PTB), Braunschweig, Germany

*olav.werhahn@ptb.de

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Abstract

New regulations and the ban of PFAS in many circumstances proves metrological traceability for this type of species even more important. Reference material-based PFAS standards will become available from the Key Comparison Database (KCDB) of the International Bureau of Weights and Measure (BIPM). However, for many PFAS species, low numbers of standards are available, or for specific applications, the application of reference material-based gas standards are becoming very difficult.

In this contribution we report on ideas, options, and use-cases for new PFAS quantifications based on optical gas standards (OGS). OGS are to complement reference material-based gas standards where applications or species' peculiarities prevents the use or the production of these traditional type of gas standards.

To develop an OGS and provide metrological traceability by means of an OGS, spectroscopic molecular-specific data is required. This data is often not available or, if available, it comes with unclear uncertainty statements, not fit for purpose.

We discuss work arounds and provide an outlook of future possibilities for optical means to quantify PFAS species.

Limitations of Current Analytical Paradigms

- **Gold Standard:** LC-MS/MS (e.g., EPA Methods 537.1, 533, 1633)

  Pros: Excellent sensitivity and selectivity for target compounds.

  Cons: Costly, time-consuming, requires extensive sample prep and expertise.

- **The Reference Material (RM) Problem:**

  Thousands of PFAS compounds exist; RMs exist for only a fraction.

  RMs can be unstable, difficult to produce, and matrix-specific.

  The BIPM's Key Comparison Database (KCDB) has limited coverage for PFAS.

A Complementary Solution: OGS

Optical Gas Standards (OGS):

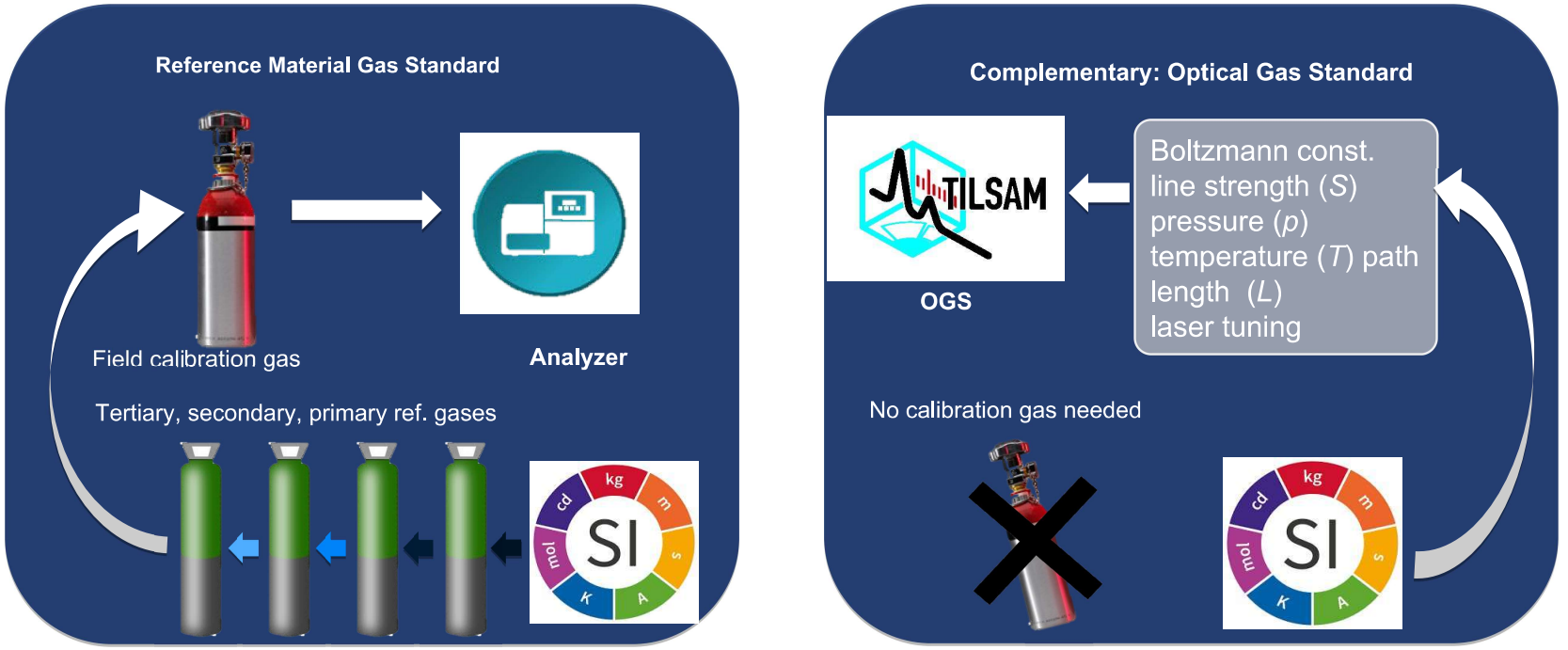
- **The Core Idea:** Establish metrological traceability through fundamental spectroscopic principles, not just physical reference materials.
- **How it Works:** An OGS determines concentration via:

  Precise measurement of molecular absorption features.

  Relating these measurements to fundamental physical constants.

  Comprehensive uncertainty quantification (following GUM guidelines).
- **Role:** OGS complements RM-based standards, especially where RMs are unavailable or impractical.

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.

Input knowledge for Optical Gas Standards

- **T**raceable **I**nfrared **S**pectra specific to each PFAS species;
- publicly available technical data on spectral parameters or cross sections;
- so far demonstrated for a number of species (H_2O, NO_2, CO_2, CO);
- underlying meta data including GUM compliant uncertainty information;
- to make use of first principle modelling of the absorption process by gas phase molecules.

FTIR spectroscopy for PFAS: Potential & Pitfalls

- **Key Advantage:**

  The strong C-F bond provides a unique & intense IR fingerprint (~1000-1300 cm^{-1}).

- **Benefits of FTIR:**

  Non-destructive analysis; Rapid measurement; No derivatization needed.

- **Critical Gaps for Quantification:**

  Spectral Overlap: Similar structures cause overlapping bands.

  Lack of Reference Data: Existing spectral libraries often lack the required uncertainty budgets.

  Sensitivity: Challenges in reaching low ppt levels for direct gas-phase analysis.

Bridging the Metrological Gap

PTB's Initiative on SI-Traceable FTIR Cross-Sections:

- **The Critical Need:** Reliable, quantitative infrared reference data with clear uncertainty statements for PFAS.
- **PTB's Work Addresses This By:**

  Creating a Database: Developing a public database of quantitative IR spectra for PFAS.

  High-Accuracy Measurement: Using advanced techniques (e.g., cavity-enhanced spectroscopy) to measure SI-traceable absorption cross-sections with uncertainties <1%.

  Providing Full Uncertainty Budgets: Enabling proper propagation of uncertainty for end-users.

<This provides the foundation for OGS approaches to PFAS quantification.>

Required experimental setup - FTIR

Journal of Quantitative Spectroscopy and Radiative Transfer
Volume 295, January 2023, 108420

An infrared spectral da… quantitation of volatile… polyfluoroalkyl substa…

Tracy J. Baker [a], Russell G. Tonkyn [a], Christopher J…
Paul G. Koster van Groos [b], Nikita A. Thakur [b], Mic…
Johnson [a]

Contents lists available at ScienceDirect

Journal of Quantitative Spectroscopy and Radiative Transfer

journal homepage: www.elsevier.com/locate/jqsrt

Check for updates

Spectral mosaics: Composite absorption cross sections of air-broadened tetrafluoromethane with comparable uncertainty in the measured intensity over orders of magnitude

A.V. Domanskaya [a,*], K. Berezkin [a], G. Li [a], H. Bohlius [a], M. Kim [a], J.J. Harrison [b,c], V. Ebert [a]

[a] Physikalisch-Technische Bundesanstalt (PTB), Bundesallee 100, Braunschweig 38116, Germany
[b] National Centre for Earth Observation, Space Park Leicester, Leicester LE4 5SP, United Kingdom
[c] School of Physics and Astronomy, University of Leicester, Leicester, United Kingdom

CF_4 bands with high accuracy

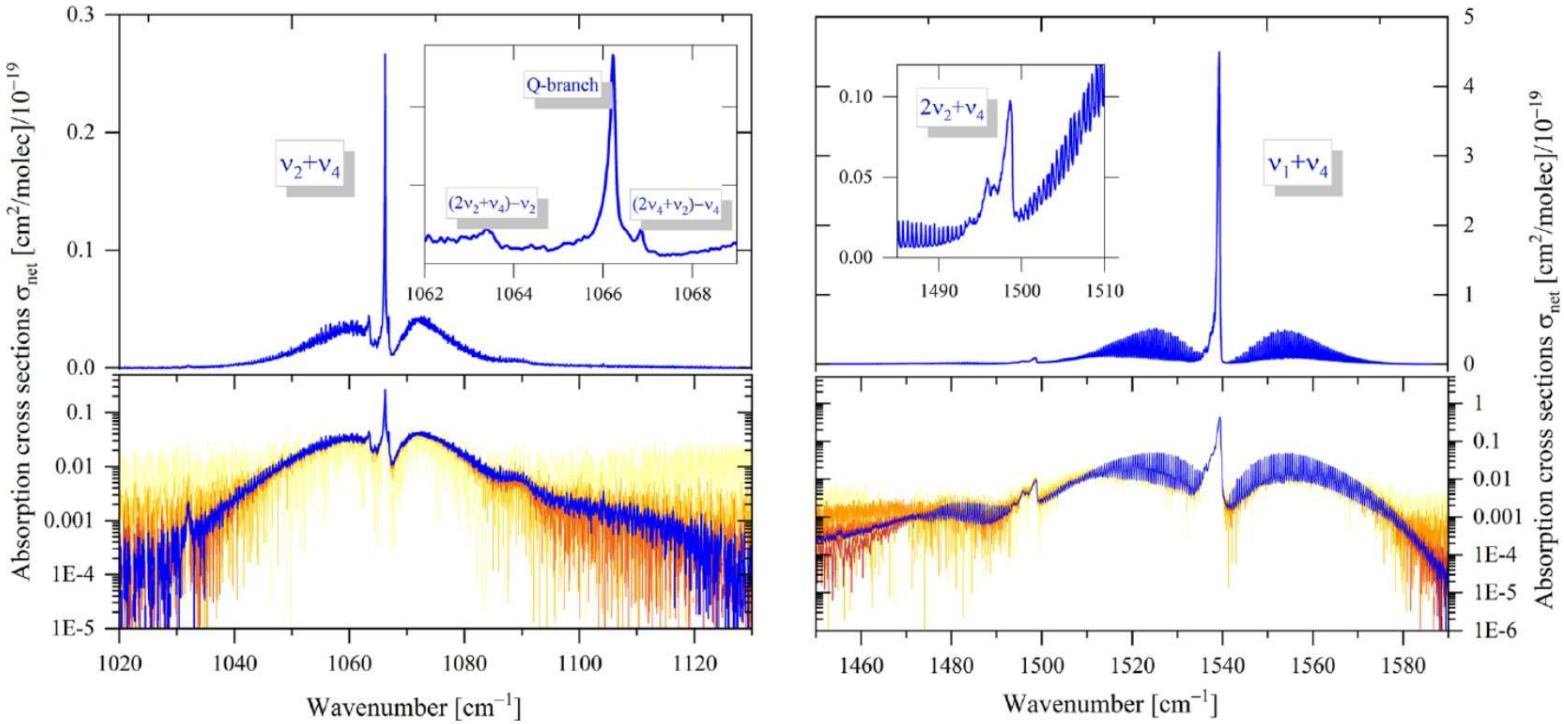


Fig. 10. Overview of the $\nu_2 + \nu_4$ (left side) and $\nu_1 + \nu_4$ (right side) bands. The thick blue line represents the composite air-broadened cross section at 500 mbar. The upper panels are on a linear scale, whereas the lower panels show the same bands on a logarithmic scale together with the individual components. The assignments follow [12,13].

Use Cases for OGS in PFAS Analysis

- **Industrial Emissions Monitoring:**

  Real-time, in-situ monitoring of PFAS stack emissions.

- **Validation of Destruction Technologies:**

  Verifying complete mineralization of PFAS in thermal treatment processes by quantifying gaseous products (HF, COF_2, etc.).

- **Process Control for Water Treatment:**

  Coupled with an interface system, could provide rapid feedback on treatment efficiency.

Future Research Directions & Challenges

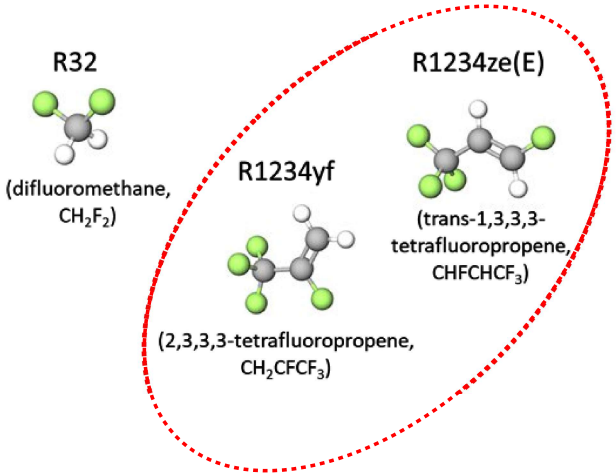
- **Priority:** Expand the library of PFAS with SI-traceable absorption cross-sections.
- **Technical Hurdles:** Developing efficient interfaces for transferring PFAS from water/soil to the gas phase for analysis.
- **Regulatory Acceptance:** Working with agencies to establish validation protocols for OGS-based methods.
- **Instrumentation:** Driving towards more robust, field-deployable OGS-capable instruments.

Metrology research on PFAS

Metrology to support zero pollution from industrial emissions

Short Name: MetZeroPol, Project Number: 24GRD02

Activities ongoing at PTB (refrigerants)



Conclusions: possible innovations by optical methods

- The ban and regulation of PFAS make metrological traceability more critical than ever.
- Optical Gas Standards (OGS) offer a powerful **complement** to traditional reference materials.
- **PTB's work on SI-traceable absorption cross-sections** is filling a crucial gap in the metrological infrastructure for PFAS.
- This paves the way for robust, calibration-free, and quantitative optical methods for PFAS detection and monitoring – i.e. **OGS.**
- To realize an OGS for PFAS several optical spectroscopy ressources can be investigated

Answering the title’s question

Yes

and there’s a lot to do!

Metrology for climate actions

Thanks for your attention.

Olav Werhahn
Executive Secretary Innovation Cluster
for Environment & Climate

IC-U@ptb.de

+49 531 592-2008