European Partnership on Metrology
Call 2022 – Digital Transformation, Health, Integrated European Metrology, Normative and Research Potential

Selected Research Topic number: **SRT-s14**
Version: 1.0

Title: Primary spectrometric thermometry for gases

Abstract

Accurate gas temperature measurements have numerous applications such as environmental science, industrial process control and combustion research. Spectrometric thermometry is particularly advantageous for these applications but often hampered by the uncertainties in molecular spectral parameters and their adoption to elevated temperatures. Recent advances in quantum mechanical calculations in combination with metrological comb/FT-based spectrometric techniques offer novel routes towards highly accurate spectral parameters. The proposed project aims to combine expertise in thermometry, spectrometry, and quantum-chemistry to enable the development of novel spectrometric gas thermometry.

Keywords

Spectrometric thermometry, primary temperature standard, molecular line parameter, quantum mechanical calculation, Fourier transform spectroscopy, comb-based FTS, comb-assisted cavity ring-down spectroscopy

Background to the Metrological Challenges

The spectroscopic temperature method works on the simple principle that the occupation probability of the initial state of a ro-vibrational molecular transition is temperature dependent. Variation in transition strength can be used to reveal thermodynamic temperature of gases. In contrast to platinum resistance thermometers (PRTs), spectroscopic methods are more rugged, stable under harsh conditions and more responsive for low density gases. Nevertheless, accurate spectroscopic methods have stringent requirements on the accuracy of the input spectral line parameters. New quantum mechanical models have been designed for the CO_2 molecule to reach a targeted accuracy better than 0.3 % for the absolute line intensity. Such high accuracy calculations will be further applied to other bands of CO_2, as well as other important molecules in a broader temperature range, e.g., for CO. Moreover, the calculation is not affected by random experimental noise and therefore has much better relative accuracy (approximately 0.03 %) for line intensity. This high relative accuracy could potentially be exploited by multi-line broadband methodology to further improve accuracy of spectroscopic thermometry.

Recent developments in spectroscopic measurement techniques allow for dramatically more accurate determination of line shape parameters: comb-assisted cavity ring-down spectroscopy (CA-CRDS) significantly improves the resolution and brings the highest signal-to-noise ratio (SNR > 10^5) whereas comb-based Fourier transform spectroscopy (FTS) allows for fast broadband measurements with high SNR. Both methods provide accurate frequency axis and no influence of instrumental line shape functions. Precise modelling of spectra measured with such high SNR requires line shape models beyond the Voigt profile, which typically leads to a systematic error of over 0.4 % in line intensity. By adopting the IUPAC recommended Hartmann-Tran profile, the line-shape related error for line intensity could probably be reduced to a negligible level. This would be compatible to the present accuracy target of 0.1 % for line intensity.

The current state of the art accuracies for experimental line intensities are typically 1 % - 3 %. The intensity accuracy of strong CO_2 bands has been improved to 0.3 % - 5 % using FTS. Single-line measurements of spectral shapes with the CA-CRDS technique could provide spectra for validation of FTS results, with high SNR and free from instrumental function.

Finally, the definition of air temperature is currently missing. Accurate thermodynamic temperature realised by non-contact methods in comparison to contact thermometry are crucial to pinpoint all the effects and parameters influencing the measurement process. Non-contact methods based on different physical principles (e.g. Doppler broadening thermometry (DBT), acoustic gas thermometry (AGT), refractive index gas thermometry (RIGT)) could improve the uncertainty evaluation.

Objectives

Proposers should address the objectives stated below, which are based on the PRT submissions. Proposers may identify amendments to the objectives or choose to address a subset of them in order to maximise the overall impact, or address budgetary or scientific / technical constraints, but the reasons for this should be clearly stated in the protocol.

The JRP shall focus on the traceable measurement and characterisation of primary spectroscopic thermometry.

The specific objectives are

1. To perform high accuracy quantum mechanical calculations on essential line parameters (line intensities and their rotational and vibrational dependence) of selected ro-vibrational bands of candidate “sensor” molecules (e.g., CO, CO_2) for temperatures in the range of 200 K to 400 K.
2. To perform high accuracy measurements of optimal selected molecular transitions (e.g. CO, CO_2) using high-resolution Fourier transform spectroscopy (FTS) infrastructure, comb-assisted cavity ring-down spectroscopy (CA-CRDS) and comb-based FTS techniques. To retrieve essential line parameters with high accuracy using refined line shape models (e.g. IUPAC recommended Hartmann-Tran profile). To compare and validate the *ab initio* results from objective 1 using the best experimental values
3. To develop the methodology of multi-line ro-vibrational spectrometric gas thermometry (RVSGT) and to evaluate its performance under metrologically controlled laboratory conditions in the range of 200 K to 400 K, adopting spectral parameters from objectives 1 and 2. To develop the infrastructure for primary gas temperature measurements by updating existing NMI FTS infrastructure with frequency comb technique with a target uncertainty of 25 mK, to correspond to 0.1 % accuracy in relative line intensities of the probed molecular absorption lines.
4. To cross-validate spectrometric gas thermometry from objective 3 against other methods for the determination of thermodynamic temperatures (e.g., Doppler broadening thermometry (DBT), noise thermometry, refractive index gas thermometry (RIGT), or via ITS-90 referenced SPRTs and $T-T_{90}$) maintained at NMIs. To adapt the NMIs’ optimum experimental capacities and proven test scenarios to identify further opportunities to improve the uncertainty to 10 mK.
5. To demonstrate the establishment of an integrated European metrology infrastructure for primary spectrometric thermometry for gases and to facilitate the take up of the technology and measurement infrastructure developed in the project by the measurement supply chain, European and international technical committees on thermometry (CCT, EURAMET and other RMOs TCs) and end users (remote sensing, automobile industry and aerospace industry).

These objectives will require large-scale approaches that are beyond the capabilities of single National Metrology Institutes and Designated Institutes. To enhance the impact of the research work, the involvement of the larger community of metrology R&D resources both within and outside Europe, plus engagement with existing European research infrastructures and European Partnerships is recommended. A strong industry involvement is expected in order to align the project with their needs and guarantee an efficient knowledge transfer into industry and end users.

Proposers should establish the current state of the art and explain how their proposed project goes beyond this. In particular, proposers should outline the achievements of the EMRP project ENV06 EUMETRISPEC and how their proposal will build on those.

EURAMET expects the average EU Contribution for the selected JRPs in this TP to be 1.9 M€ and has defined an upper limit of 2.6 M€ for this project.

EURAMET also expects the EU Contribution to the external funded beneficiaries to not exceed 25 % of the total EU Contribution across all selected projects in this TP.

Any industrial beneficiaries that will receive significant benefit from the results of the proposed project are expected to be beneficiaries without receiving funding or associated partners.

Potential Impact

Proposals must demonstrate adequate and appropriate participation/links to the ‘end user’ community, describing how the project partners will engage with relevant communities during the project to facilitate knowledge transfer and accelerate the uptake of project outputs. Evidence of support from the 'end user' community (e.g. letters of support) is also encouraged.

You should detail how your JRP results are going to:

- Address the SRT objectives and deliver solutions to the documented needs,
- Develop an integrated self-sustaining European metrology infrastructure,
- Feed into the development of urgent documentary standards through appropriate standards bodies,
- Transfer knowledge to the aerospace and automotive sector.

You should detail other impacts of your proposed JRP as specified in the document "Guide 4: Writing Joint Research Projects (JRPs)"

You should also detail how your approach to realising the objectives will further the aim of the Partnership to develop a coherent approach at the European level in the field of metrology and include the best available contributions from across the metrology community. Specifically, the opportunities for:

- improvement of the efficiency of use of available resources to better meet metrological needs and to assure the traceability of national standards
- the metrology capacity of EURAMET Member States whose metrology programmes are at an early stage of development to be increased
- organisations other than NMIs and DIs to be involved in the work.

Time-scale

The project should be of up to 3 years duration.