EMPIR Call 2019 – Energy, Environment, Normative and Research Potential

Selected Research Topic number: **SRT-v02**
Version: 1.0

Title: Stable isotope metrology to enable climate action and regulation

Abstract

Climate change is one of the greatest risks to society worldwide. The increase of greenhouse gas concentrations in the atmosphere from anthropogenic emissions is the main cause of global warming. Carbon dioxide and methane are the major contributors. There is a need to discriminate anthropogenic from natural contributions and discern emissions from different industrial sectors. To provide governments with the data required to support inventory verification of nationally determined emission targets and allow pledges of emissions reductions to be demonstrated, vital new research is required to underpin measurements of stable isotopes of carbon dioxide and methane, which infers their origin.

Keywords

Climate change, stable isotopes, reference materials, greenhouse gas, SI traceability, scale realisation, gas metrology.

Background to the Metrological Challenges

Industrial and domestic activities have been recognised by the Kyoto Protocol and more recently by the Conference of Parties (COP21) as being major contributing sources to one of the greatest risks to society, climate change. To prevent stark changes to the Earth's climate, emissions of the major contributing greenhouse gases, such as carbon dioxide and methane, must be reduced. Abundances of carbon dioxide and methane in the atmosphere are at the highest they have been in the past 3 million years and this is mainly attributable to human activities. In 2015, the World Meteorological Organisation (WMO) reported that the global average amount-of-substance fraction of carbon dioxide exceeded the symbolic 400 µmol mol^{-1} threshold and it is unlikely to return to this in our lifetimes. Current levels of methane are nearly triple the pre-industrial value. The Intergovernmental Panel on Climate Change (IPCC) stated that to keep to the 1.5 °C goal, governments would have to slash emissions of greenhouse gases by 45 % by 2030. Action must be taken and can only be achieved with a better understanding of the global atmosphere to inform policy and control the increasing influence of human activity. The Paris agreement (COP21) outlined that each country would provide nationally determined contributions, pledges to reduce emissions from each individual country. Verification of these pledges by independent measurement is viewed as best practice by IPCC and an activity being adopted within Europe. However, verifying emissions requires accurate measurement both of baseline concentrations and contributions resulting from emission events. Measurements of isotopic composition discriminate anthropogenic emissions from natural contributions and provide important information about the transformations involved in the sources and sinks processes of these components. The anthropogenic component of these processes is very difficult to assess because of the very significant, temporally and spatially varying natural sources and sinks. Abundance ratios of isotopologues are regarded as useful parameters to infer the origin and production-consumption mechanisms of these substances and to estimate their global budget, but the signals are small and thus an accurate and long-term stable calibration scheme is required.

There has been a significant research effort to set up a metrological infrastructure to provide traceable measurements of carbon dioxide isotope ratios to the delta scale. The stable isotope standard for oxygen and carbon, NBS19, was developed in 1982 at NIST from a white marble slab of unknown origin and was used to define the primary VPDB scale. In 2006 new guidelines were published for $\delta^{13}C$ calibration, including a recommendation to additionally use an assigned $\delta^{13}C$ value for the LSVEC (lithium carbonate) reference material to obtain an improved two-point calibration. NBS19 is nearly exhausted, and LSVEC has suffered stability issues, both posing serious challenges to maintaining continuity to the primary scale and reducing offsets between laboratories from calibration. The IAEA has taken great care to maintain continuity to the primary scale by producing IAEA-603 (replacement of the highest, $\delta^{13}C$ scale-defining NBS19), but the procedure still depends upon consensus among several specialised labs about differences in $\delta^{13}C$ for a second scale anchor to replace LSVEC. The Jena Reference Air Standard (JRAS), produced by the stable isotope laboratory at the Max Planck Institute for Biogeochemistry in Jena (BGC-IsoLab), is a stable isotope standard consisting of carbon dioxide generated from a calcite and mixed into carbon dioxide free air. It is closely linked to the VPDB-scale and is well suited to serve as a primary scale anchor for CO_2–in-air measurements. The BGC-IsoLab serves as the WMO-GAW Central Calibration Laboratory (CCL) for carbon dioxide isotope ratio measurements. However, there is no CCL for methane isotope ratio. Measurements of methane ($\delta^{13}C$ -CH_4 and ^{2}H-CH_4) are reported on the VPDB and the VSMOW scales, respectively. Most laboratories have developed their own laboratory standards and associated protocols to link $\delta^{13}C$ and $\delta^{2}H$ methane isotope data to the VPDB and VSMOW scale. The use of different calibration approaches and standards, inconsistent use of the ^{17}O correction and not correcting for instrumental memory and cross-contamination have contributed to inter-laboratory measurement offset of up to 0.5 ‰ for $\delta^{13}C$, and up to 13 ‰ for $\delta^{2}H$ measurements of atmospheric methane isotopes. These offsets clearly indicate that a unified effort is required to improve calibrations. Many of these issues relate to the primary scale realisation. When probing the isotopic composition of gases, usually relative methods are applied with the necessity of a well-characterised reference gas. For carbon dioxide, no absolute isotope ratio measurements traceable to the SI have been achieved with the desired uncertainty due to insufficient methods and instrumentation. Work to progress beyond the state of the art by testing and verifying new methods to determine absolute values of isotope ratios for $\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2 are of paramount importance to put measurements on an SI-basis for the first time. This will lead to a more robust measurement infrastructure, ensuring results are comparable, stable and coherent.

Stable Isotope-Ratio Mass Spectrometry (IRMS) remains the most precise technique for these measurements. However, the introduction of spectroscopic techniques has revolutionised the measurement of key greenhouse gas components in air by enabling real time, in-situ field measurements for quantifying sources and sinks at local, regional, and global scales. Instruments typically report values as amount fractions of individual isotopologues, and for the most accurate measurements of isotope ratio, require calibration gases that have their isotope ratios assigned to at least the analytical precision of the technique. These developments have led to an urgent need for gas reference materials for carbon dioxide and methane isotope ratio. However, production of reference materials using current methods is limited and prohibitively expensive and it is not possible to meet the large volume requirements for calibrating these instruments. With the advances made in optical spectroscopy for isotope ratio methods, an urgent requirement also exists to develop validation routines, recommendations and traceable field-deployable spectroscopy. Ideally, the development of such routines goes hand in hand with the establishment of SI traceability.

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 stable isotopes for CO_2 and CH_4 to enable climate action and regulation.

The specific objectives are

1. To develop gas reference materials of pure CO_2 at 410 µmol/mol in an air matrix with a repeatability of 0.01 ‰ for $\delta^{13}C$-CO_2 and of 0.05 ‰ for $\delta^{18}O$-CO_2 and with target uncertainties of 0.05 ‰ for $\delta^{13}C$- CO_2 and 0.1 ‰ for $\delta^{18}O$-CO_2, ensuring traceability to the primary VPDB scale with a stability of more than two years.
2. To develop gas reference materials of pure CH_4 at 1.85 µmol/mol in an air matrix with a repeatability of 0.02 ‰ for $\delta^{13}C$-CH_4 and of 1 ‰ for $\delta^{2}H$-CH_4 and with target uncertainties of 0.2 ‰ for $\delta^{13}C$-CH_4 and 5 ‰ for $\delta^{2}H$-CH_4, ensuring traceability to the VPDB and VSMOW scales with stability of more than two years. In addition, to characterise IRMS scale contraction and ^{17}O correction on CO_2 for methane isotope ratio measurements.
3. To develop SI traceable methods for absolute isotope ratio measurements of carbon dioxide with uncertainties of 0.1 ‰ for $\delta^{13}C$-CO_2 and 0.1 ‰ for $\delta^{18}O$-CO_2.
4. To develop and characterise field deployable spectroscopic methods and calibration approaches for isotope ratio measurements of carbon dioxide and methane with a target precision of 0.05 ‰ for

$\delta^{13}C-CO_2$ and $\delta^{18}O-CO_2$, 0.2 ‰ for $\delta^{13}C-CH_4$ and 1 ‰ for $\delta^{2}H-CH_4$, improving on isotope-specific line parameters.

5. To facilitate the take-up of the technology and measurement infrastructure developed in the project by the measurement supply chain (accredited laboratories, CCQM), standards developing organisations (CEN, ISO) and end users (WMO-GAW, IAEA, instrument manufacturers, speciality gas 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, the involvement of the appropriate user community such as industry, standardisation and regulatory bodies is strongly recommended, both prior to and during methodology development.

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 projects ENV52 HIGHGAS and 16ENV06 SIRS and how their proposal will build on those.

EURAMET expects the average EU Contribution for the selected JRPs in this TP to be 2.0 M€, and has defined an upper limit of 2.3 M€ for this project.

EURAMET also expects the EU Contribution to the external funded partners to not exceed 35 % of the total EU Contribution across all selected projects in this TP.

Any industrial partners that will receive significant benefit from the results of the proposed project are expected to be unfunded 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,
- Feed into the development of urgent documentary standards through appropriate standards bodies,
- Transfer knowledge to the Environmental 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 EMPIR 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.