Publishable Summary for 19ENV05 STELLAR
Stable isotope metrology to enable climate action and regulation

Overview

This project has provided traceable isotopic reference materials of CO_2 and CH_4, good practice guides for measurements of the isotope ratio of CO_2, CH_4 and in-field calibration strategies, advanced understanding of the carbonate reaction which currently provides traceability to the VPDB scale for $\delta^{13}C$ and $\delta^{18}O$ and improved the SI traceability of $\delta^{13}C$ measurements. This improved infrastructure for traceable isotopic measurements of CO_2 and CH_4 in our atmosphere provides information to enable source apportionment of these most important greenhouse gases and thus allows governments to make informed policy decisions.

Need

Immediate action on greenhouse gas emissions mitigation is required to limit dangerous changes to Earth's climate. There is increasing international focus on meeting the United Nation's Paris Agreement signed by 197 countries in 2016, to prevent global temperatures from reaching 2 ˚C above pre-industrial levels by 2100, and ideally 1.5 ˚C. A report by the Intergovernmental Panel on Climate Change (IPCC) states that meeting this implies halving the annual global carbon emissions between now and 2030 and falling to zero by 2050. It is likely that even "negative emissions" (sinks of carbon dioxide) will have to be organised. Many of these components also influence the formation of tropospheric and depletion of stratospheric ozone, so are relevant to air quality (Directive 2008/50/EC) and climate.

To support governments verifying emissions and demonstrating national reduction targets, it is necessary to discriminate between the natural and various man-made sources of greenhouse gases. This requires accurate measurements of baseline concentrations and contributions resulting from emission events. Separating manmade emissions from measured carbon dioxide and methane amount fractions is challenging and requires information on the isotopic composition, especially if man-made negative emissions start to play a role.

Currently, there is no infrastructure to deliver carbon dioxide and methane gas reference materials with the required uncertainties to underpin global observations, compromising the comparability of measurement data. It is therefore necessary to address the existing traceability gap in the measurement of isotopes of carbon dioxide and methane by developing gas reference materials, calibration methods and dissemination mechanisms, which are traceable to existing scales (e.g. VPDB - Vienna Pee Dee Belemnite - and VSMOW/SLAP - Vienna Standard Mean Ocean Water/ Standard Light Antarctic Precipitation) and the SI.

Additionally, metrology is also required to ensure advances in optical spectroscopy result in field deployable techniques that meet uncertainty requirements.

Objectives

The overall objective of this project was to fill a traceability gap in the measurement of the isotopic composition of carbon dioxide and methane by providing a new infrastructure able to deliver gaseous carbon dioxide and methane reference materials to meet the increasing demand to underpin greenhouse gas measurements. This project also strived to validate existing and develop new and field-deployable spectroscopy. The specific objectives of the project were:

1. To develop gas reference materials of carbon dioxide (pure and 410 µmol mol^{-1} in an air matrix) with a repeatability of 0.01 ‰ for $\delta^{13}C$-CO_2 and 0.05 ‰ for $\delta^{18}O$-CO_2 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 stability of more than two years. In addition, to characterise IRMS scale contraction, establish the relation between the

VPDB-CO_2 and VSMOW-CO_2 scales for ^{18}O, and ^{17}O correction on carbon dioxide for methane isotope ratio measurements.

2. To develop gas reference materials of methane (pure and 1.85 µmol mol^{-1} in an air matrix) with a repeatability of 0.02 ‰ for $\delta^{13}C$-CH_4 and 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 one year.
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.
4. To develop and metrologically 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.
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, specialty gas industry).

Progress beyond the state of the art

Calibrating reference materials of carbon dioxide in air back to the reference standard (VPDB) as required for atmospheric monitoring, creates problems of traceability and reproducibility due to e.g., sampling. The Jena Reference Air Sets (JRAS) are stable isotope standards consisting of carbon dioxide generated from a calcite and mixed into CO_2-free air. These standards define the JRAS-06 scale that is closely linked to the VPDB-CO_2 scale. Currently, the production of gas reference materials using this method is limited and prohibitively expensive. This project has developed large volume traceable isotopic CO_2 reference materials.

This project built on the results of the EMPIR project SIRS (16ENV06) by developing independent capabilities for the whole traceability chain and an improved understanding of the influence of parameters in gravimetric preparation on isotopic fractionation. The improved method delivers reference materials of carbon dioxide with a target repeatability of 0.01 ‰ for $\delta^{13}C$-CO_2 and 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, traceable to the VPDB-CO_2 scale.

The use of different calibration approaches and standards have contributed to inter-laboratory measurement offsets of up to 0.5 ‰ for $\delta^{13}C$, and 13 ‰ for $\delta^{2}H$ measurements of atmospheric methane isotopes. Currently, no methane isotope ratio gas reference materials exist that provide traceability to the VPDB and VSMOW/SLAP scales for $\delta^{13}C$ and $\delta^{2}H$, respectively, which meet the uncertainty and high-volume requirements to underpin global measurements. There is also no Central Calibration Laboratory (CCL) at the WMO-GAW level to ensure compatibility of global observations. This project has delivered the first traceable isotopic CH_4 reference materials.

This project has developed SI traceable methods for absolute isotope ratio measurements of ^{13}C with uncertainties of 0.1 ‰

Introduction of relatively low-cost spectroscopic techniques has revolutionised the measurement of key greenhouse gas components in air by enabling continuous in-situ field measurements for quantifying sources and sinks at local, regional, and global levels. In tandem, existing validation routines, recommendations and traceability chains for field-deployable spectroscopic techniques that meet the precision specifications of IRMS have been developed in the project.

Results

Objective 1

Carbon dioxide gas reference materials (pure and 410 µmol mol^{-1} in air - The reference materials were produced from two pure CO_2 sources at nominal $\delta^{13}C$-CO_2 values of +1 and -42 ‰ with blends of the two pure sources producing intermediate $\delta^{13}C$-CO_2 values. These values span the range of emission sources of CO_2. The reference materials were assigned isotope ratio values relative to the VPDB scale. The uncertainty in $\delta^{13}C$-CO_2 value of the pure CO_2 reference materials is 0.03 ‰. The $\delta^{18}O$-CO_2 values of the pure sources were measured with an uncertainty of 0.04 ‰. Significant improvements in sampling the high pressure reference materials into glass flasks were made in this project however, the uncertainty in isotopic ratio values of the reference materials is still largely due to variation caused by flask sampling for IRMS measurements, with glass flasks shown to leak and cause variability in the reported isotope ratios measured by IRMS [Steur *et al*. 2023 Doi: 10.1080/10256016.2023.2234594].

The uncertainty in the $\delta^{13}C$-CO_2 and the $\delta^{18}O$-CO_2 of the ambient amount fraction reference materials is within the 0.5 ‰ and 1 ‰ target and are repeatable within the stated uncertainty. An offset towards more enriched isotopic values was observed for the ambient amount fraction reference materials compared to their corresponding pure values. The amount fraction of the ambient amount fraction reference materials with respect to their international scales with the reference materials mostly meeting the extended WMO GAW compatibility goals. The stability of the isotope ratio of the reference materials was demonstrated to be within the uncertainty of the isotope ratio of the reference materials.

Traceability to the VPDB scale - The calcite-phosphoric acid reaction, which is the basis of the VPDB-CO_2 scale, was thoroughly investigated by partners. CO_2, produced from calcite reference materials was exchanged and the calcite phosphoric acid reaction effects were studied separately from possible IRMS scale complications. Excellent agreement for $\delta^{13}C$, but a consistent difference of ≈ 0.14‰ for $\delta^{18}O$ was found with partners producing internally consistent scales. Intercomparisons using third party gas reference materials did not help decipher which of the two partners was closer to the true $\delta^{18}O$ values.

Objective 2

Methane gas reference materials (pure and 1.85 µmol mol^{-1} in air- Isotopic methane reference materials with a $\delta^{13}C$-CH_4 range of between ~ 39 and ~-57 ‰ and a $\delta\,^{2}H$-CH_4 range of between -189 and -324 ‰ were produced at pure and at ambient amount fractions in synthetic air. Isotopic analysis of the pure and ambient gas reference materials was carried out by MPI-BGC. The repeatability of the methane reference materials was within the target of 0.02 ‰ for $\delta^{13}C$-CH_4 and 1 ‰ for $\delta\,^{2}H$-CH_4 and meeting the required uncertainties of 0.2 ‰ for $\delta^{13}C$-CH_4 and 5 ‰ for $\delta\,^{2}H$-CH_4, with traceability to the VPDB and VSMOW scales. Isotope ratio was in agreement between pure and ambient amount fraction reference materials within the uncertainty of the measurements and stability was demonstrated with agreement in the isotope ratio of two ambient amount fraction reference materials made 5 months apart. The amount fraction of the reference materials was also measured against the WMO X2004A NOAA scale. Within the project we have achieved the first ambient methane reference materials at NMI level in high pressure (100 – 120 bar) cylinders of 5 or 10 L volume. The high volume and low uncertainty make these reference materials suitable for calibration of field operated optical isotope ratio spectrometers which require significantly larger volumes of gas than IRMS measurements. The suitability of the reference materials as calibration standards for OIRS has been demonstrated by agreement of the certified isotope ratio values of an ambient amount fraction CH_4 reference material by IRMS and by an OIRS calibrated using the CH_4 reference materials produced in the STELLAR project. CH_4 reference materials produced in the STELLAR project are already in use in EMPIR project IsoMET and at the Heathfield station of the UK DECC network.

Linking the $\delta^{13}C$ of methane to the existing established infrastructure for $\delta^{13}C$-CO_2 - A facility for linking the $\delta^{13}C$ of methane to the existing established infrastructure for $\delta^{13}C$-CO_2 has been complete. The conversion facility enables the quantitative combustion of methane from methane in synthetic air reference materials, to carbon dioxide at flow rates compatible with spectroscopic analysers. This provides a route to traceability of the $\delta^{13}C$-CH_4 of methane reference materials without the need for sampling and measurement using IRMS. The combustion facility provides real time certification of $\delta^{13}C$-CH_4 against carbon dioxide in synthetic air reference materials with traceability to the existing VPDB scale for $\delta^{13}C$-CO_2 using optical isotope ratio spectroscopy. The sensitivities of the conversion facility have been assessed along with the reproducibility of the $\delta^{13}C$-CH_4 certification. The $\delta^{13}C$-CH_4 of the nominally 410 µmol mol^{-1} methane in synthetic air reference materials have been certified with combined uncertainties (k=1) in the range of 0.4-0.6 ‰. The $\delta^{13}C$-CH_4 of three nominally 410 µmol mol^{-1} in synthetic air reference materials have been certified over a four-month period with demonstrated repeatability of 0.26 ‰.

Objective 3

Absolute carbon dioxide isotope ratio measurements towards SI traceability Work to determine the absolute 13/12 ratio of VPDB with an accuracy (k=1) of 0.1‰ in terms of $\delta^{13}C$-CO_2 was successful. Gravimetrically blended $^{13}CO_2$ and $^{12}CO_2$ reference materials were analysed for CO+ fraction by ICP-MS. Due to the complex behaviour of the CO_2 molecule this method did not lead to successful determination of the absolute isotope ratio. Gravimetrical mixing and ICP-MS and IRMS measurements of ^{13}C and ^{12}C glucose determined the $^{13}C/^{12}C$ ratio of the zero point of the VPDB scale. Results between partners were corroborated with an uncertainty of < 0.1 ‰. The goal of determination of the absolute 13C/12C ratio of VPDB with an accuracy of 0.1‰ (*k*=1) has been achieved.

Objective 4

Spectroscopic methods for in-field isotope ratio measurements of carbon dioxide and methane

Research into spectroscopic methods for in-field isotope ratio measurements of carbon dioxide and methane has led to the publication of three good practice guides.

carbon dioxide -The good practice guide includes practical recommendations on metrological characterization including instrument stability, calibration approaches and matrix effects. The GPG further includes a sample handling protocol and provides a comprehensive discussion on GUM compliant uncertainty evaluation including an example of uncertainty estimation for a calibration based OIRS system that is calibrated in the delta scale. Matrix effects were studied, concluding that significant differences between whole air, binary and ternary synthetic air occur. In the GPG discussions as to how these effects could be corrected and/or included into the uncertainty analysis. A novel isotopologue-based calibration approach was successfully implemented and validated with the observed differences between the implemented calibration approaches as well as general limitations of these implementations, which are partly related to the calibration material used, discussed.

Methane - The good practice guide details the measurement of isotope ratios in CH_4 by OIRS. The document includes discussions and examples of the characterization of a spectrometer's stability, the identification of interfering effects of matrix gases and different calibration approaches.

In-Field- The good practice guide focusses on field measurements of the isotopic composition of CO_2 and CH_4. This document contains minimal requirements for field measurements as well as recommendations for calibration routines and sample handling. It also includes examples for field measurements aiming at atmospheric monitoring and source characterization as well as literature-based work on OIRS-IRMS comparisons. The GPG further highlights practical aspects such as steps for remote monitoring and power supply considerations and factors to be considered to reduce uncertainties/ calibration routines for on-site measurements.

Impact

The key dissemination activities include a website featuring summary material on the project which can be found here: http://empir.npl.co.uk/stellarproject/. The project has regualrly updated it's stakeholders on progress through stakeholder events and news letters. The project had a committee of 16 stakeholders from organisations including CSIRO Oceans and Atmosphere, ABB LGR, BIPM, University of Wollongong, NOAA Global Monitoring Division, Max-Planck-Institute for Biogeochemistry, Licor, INSTAAR, University of Colorado and Institut fuer Umweltphysik and the University of Bristol. Over 30 presentations on aspects of the project were made at conferences and meetings and the work in the STELLAR project has informed a new joint Gas Analysis and Isotope Ratio working group (GAWG-IRWG). The partners attended meetings at 14 different standards/technical committees and provided training both on-line and in-person. Reference materials and calibration protocols developed in this project are already in use at monitoring sites, the reference materials are availiable for purchase and the caibration stratedies and good practice guides produced are availiable on the website alongside a training video.

Impact on industrial and other user communities

This project developed clear tangible outputs (i.e.new reference materials availiable for purchase, instrumentation, calibration methods and recommendations which are published on the project website). Partners who are members of the European Metrology Network (EMN) on Climate and Ocean Observation are in discussions to create an integrated European-based calibration service. Partners attended the European Metrology Network (EMN) on Climate and Ocean Observation meetings. The project was presented to the atmospheric monitoring community (e.g. the European ICOS and other networks, organisations such as WMO-GAW, Global Greenhouse Gas watch GGGW and academia) to promote the STELLAR project's new traceable reference materials and calibration techniques. Many partners are directly involved with greenhouse gas monitoring networks such as ICOS and the UK DECC network with reference materials produced in the STELLAR project already in use at the Heathfield UK DECC network site. The atmospheric monitoring community and instrument manufacturers will benefit from improved spectroscopy methods and calibration techniques, which provide traceable measurements and improved specifications to match those provided by mass spectrometry. Instrument manufacturers will benefit from the supply of the next generation of accurate calibration standards for isotopic composition and the good practice guides published on the STELLAR website. This will ensure their instruments are traceable and provide valid data for atmospheric monitoring. Stakeholders in the instrument manufacturing industry was kept informed of project progress through stakeholder meetings and publication and presentations at conferences and meetings. This increased market potential for their instruments. Speciality gas companies will benefit from traceability to support gas mixture production under accreditation, which will open new opportunities for reference mixtures for isotopic composition.

Impact on the metrology and scientific communities

Global comparability helps assess the real state-of-the-art in measurement. Metrology for stable isotopes of carbon dioxide and methane is a strategic priority for CCQM-GAWG, which the consortium has very good links with. Therefore, the research outputs (e.g., development of capabilities and reference materials) from this project were presented to global experts in gas metrology at the WMO-GAW and GGGW meetings to advance the state-of-the-art in measurement science. The NMIs and external partners involved in this project will benefit from enhanced capabilities and primary reference materials which will lead to increased revenue from measurement services.

Such is the importance of underpinning isotope ratio measurements to the metrology community that a new working group (CCQM-IRWG) has been established to advance measurement science and support stakeholders. The project partners actively involved in the activities of CCQM-GAWG and CCQM-IRWG. Outputs from this project were presented to global experts from a diverse range of sectors (e.g. metrology, academia and industry). The development of reference materials for carbon dioxide and methane will support future pilot studies and key comparisons for global comparability, new calibration and measurement capability claims for isotopic composition. The consortium was well connected with the WMO community, the IAEA and the IUPAC-CIAAW.

The STELLAR project was presented at the 43rd CCQM-GAWG meeting in April 2021, the last two joint CCQM-IRWG meetings held in April and November 2021.

Impact on relevant standards

The developments in this project will be used to revise existing standards by updating reference methods to allow isotopic analysis in documentary standards under ISO/TC158 (Gas Analysis) and CENTC/264 (Air Quality) and will improve comparability of atmospheric and stack measurements by end users.

Over the duration of the project, the partners attended meetings at 14 different standards/technical committees. The partners also presented the project through presentations and posters at 16 different conferences. Highlights are as follows; A presentation of the STELLAR project featured at a workshop organised by the EURAMET TC MC in February 2020. An ISO/TC 158 WG2 meeting took place in June 2021. At the meeting, a document to provide guidance on comparison methods was discussed with a particular focus on the impact of varying isotopic compositions on ISO/TC158 standards. Knowledge developed from this project will be used to inform the document. Developments and plans of this project were presented at the IAEA Technical Meeting on Development and Characterisation of IAEA Stable Isotope Reference Materials on 2nd September 2021. The project was presented at the 47th meeting of the Consultative Committee on Amount of Substance Gas Analysis Working Group (CCQM GAWG) at the BIPM in Paris, an overview of the STELLAR project was presented at the Meeting of the CCQM - Gas Analysis and Isotope Ratio Working Groups at the Bureau International des Poids et Mesures on the 25 April 2023.

Longer-term economic, social and environmental impacts

There are a variety of ways that climate change will have an economic impact. Some are gradual changes such as increased cooling costs for buildings, while others are more dramatic, related to the higher frequency of extreme weather events. The cost of inaction is vast. In a recent report, projections indicate that combined country-level costs (and benefits) add up to a global median of more than $400 in social costs per tonne of carbon dioxide. Based on the carbon dioxide emissions in 2017, that presents global impact of more than $16 trillion.

This project will have a direct impact on the environment and quality of life as it will underpin global monitoring, provide a greater understanding of the increasing influence of human activity on the global atmosphere and inform decisions on policy. It will allow European states to comply with current legislation requiring the measurement of components in ambient air which govern climate change and air quality. It will work towards meeting the requirements of the Kyoto Protocol and COP21 to reduce emissions of the most important greenhouse gases.

This project will have impact beyond the immediate community of laboratories concerned with monitoring long-term atmospheric trends. Examples include the impact on public health from future improvements in the accuracy and efficiency of the data acquired to meet the EU Air Quality Directives (e.g., 2008/50/EC).

List of publications

1. Rennick *et al*. Boreas: A Sample Preparation-Coupled Laser Spectrometer System for Simultaneous High-Precision In Situ Analysis of $\delta^{13}C$ and $\delta^{2}H$ from Ambient Air Methane, Analytical chemistry, https://doi.org/10.1021/acs.analchem.1c01103
2. Sega *et al*., Reference materials: gas mixtures to support measurements for climate change studies, J. Phys.: Conf. Ser. https://doi.org/10.1088/1742-6596/2192/1/012016
3. Rolle *et al.* Generation of CO_2 gas mixtures by dynamic dilution for the development of gaseous certified reference materials Measurement: Sensors https://doi.org/10.1016/j.measen.2022.100415
4. Steur *et al.* Preventing drift of oxygen isotopes of CO_2-in-air stored in glass sample flasks: new insights and recommendations, Isotopes in Environmental and Health Studies, https://doi.org/10.1080/10256016.2023.2234594
5. Francesca Rolle *et al*. Comparison of gravimetry and dynamic dilution for the generation of reference gas mixtures of CO_2 at atmospheric amount fraction, Measurement: Sensors https://doi.org/10.1016/j.measen.2023.100937

This list is also available here: https://www.euramet.org/repository/research-publications-repository-link/

<table>
<tr><td colspan="2">Project start date and duration:</td><td>1 September 2020, 36 months</td></tr>
<tr><td colspan="3">Coordinator: Paul Brewer, NPL Tel: +44 (0) 208 943 6007 E-mail: paul.brewer@npl.co.uk
Project website address: http://empir.npl.co.uk/stellarproject</td></tr>
<tr><td>Internal Funded Partners:
1 NPL, United Kingdom
2 DFM, Denmark
3 INRIM, Italy
4 LGC, United Kingdom
5 PTB, Germany
6 TUBITAK, Turkey
7 VSL, Netherlands
8 VTT, Finland</td><td>External Funded Partners:
9 AL, Spain
10 Empa, Switzerland,
11 JSI, Slovenia
12 MPG, Germany
13 RUG, Netherlands
14 UEF, Finland</td><td>Unfunded Partners:</td></tr>
<tr><td colspan="3">RMG: -</td></tr>
</table>