Publishable Summary for 16ENV06 SIRS
Metrology for stable isotope reference standards

Overview

Climate change is one of the greatest risks to society worldwide. The increase of greenhouse gas concentrations in the atmosphere from man-made emissions (CO_2 and N_2O are major contributors) is the main cause of global warming. There is a need to discriminate man-made from natural contributions in the atmosphere, to provide governments with emission inventory data to support verification of nationally determined emission targets and allow pledges of emissions reductions to be demonstrated. This cannot be achieved with existing metrological infrastructure, so new research to underpin measurements of stable isotopes of CO_2 and N_2O, which infers their origin, is vital. The project achieved the establishment of new measurement services for the production and provision of static reference materials for isotope ratio of CO_2, as well as new calibration services from the development of dynamic reference materials of CO_2. The project also achieved an optical Isotope ratio spectroscopy (OIRS) approach harmonised across the partners that advanced the previous state of the art in terms of rigorousness in uncertainty assessments, matrix and concentration artefact corrections and finally in terms of precession in delta value determinations in carbon dioxide and nitrous oxide.

Need

Immediate action is required to prevent irreversible changes to the Earth's climate from greenhouse gas emissions. Many of these components also influence the formation of tropospheric ozone and aerosols, so are relevant to air quality (directive 2008/50/EC) and climate. COP21 (Conference of the Parties) renewed and emphasised the agreement that each country would provide nationally determined contributions, pledges to reduce emissions. In Europe, the Covenant of Mayors New signatories now pledge to reduce CO_2 emissions by at least 40 % by 2030.

- To support governments to verify emissions and demonstrate national reduction targets the project need to discriminate between the natural and various manmade sources of greenhouse gases. Verifying emissions requires accurate measurements of baseline concentrations and contributions resulting from emission events. Separating man-made emissions from measured CO_2 (Objectives 1 and 2) and N_2O (Objective 3) concentrations is challenging and requires information on the stable isotopic composition.
- There is no infrastructure to deliver international gaseous CO_2 reference materials (Objectives 1, 2 and 5) to meet demand and no international gaseous N_2O reference materials (Objectives 3 and 5) with stated uncertainties to underpin isotope ratio measurements. This compromises the comparability of measurement data. It proved difficult until this project as the materials defining isotope scales were chosen decades ago with applications of that era (mainly geochemistry) and do not lend themselves to gas mixture preparation to meet high demand with tight uncertainty requirements.
- Advances in optical spectroscopy have made field deployable techniques that meet uncertainty requirements viable but metrological research is required to achieve this (Objective 4).

Objectives

The overall goal of this project was to fill a traceability gap by providing a new infrastructure for stable isotopes to deliver international gaseous CO_2 reference materials to meet the increasing demand and international gaseous N_2O reference materials with stated uncertainties to underpin measurements.

The project's specific objectives were:

1. To develop static and dynamic reference materials for pure CO_2 and at 400 µmol/mol in an air matrix with uncertainties (δ^{13}C-CO_2 0.1 ‰ and δ^{18}O-CO_2 0.5 ‰). Ensure traceability and consistency with VPDB

(primary scale) and work towards meeting the WMO compatibility goals ($\delta^{13}C-CO_2$ 0.01 ‰ and $\delta^{18}O-CO_2$ 0.05 ‰).

2. To re-measure the absolute CO_2 isotope ratios of the reference materials to provide the data necessary for SI traceability.
3. To develop static and dynamic reference materials for pure N_2O and at 300 nmol/mol – 1000 nmol/mol in an air matrix. The static and dynamic reference materials should meet the requirements for regionally focussed monitoring studies and have target uncertainties of 1.0 ‰ ($\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$) and 0.5 ‰ ($\delta^{15}N$, $\delta^{18}O$).
4. To develop spectroscopic methods for isotope ratio measurements of CO_2 with an uncertainty target of 0.1 ‰ for $\delta^{13}C-CO_2$ and 0.5 ‰ for $\delta^{18}O-CO_2$, and of N_2O, including site specific delta values in real time with a target precision of 0.1 ‰ for $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and $\delta^{18}O$ - N_2O. Methods will be suitable for use in the field and include spectral line data measurements to improve isotope-specific line parameters. Study the stability and fractionation of CO_2 and N_2O static reference materials.
5. To facilitate the uptake of the technology and measurement infrastructure developed in the project by industry, by standards developing organisations and end users.

Progress beyond the state of the art and results

CO_2 (pure and 400 µmol/mol in air) reference materials (uncertainties: $\delta^{13}C-CO_2$ 0.1 ‰, $\delta^{18}O-CO_2$ 0.5 ‰)

NBS19 (carbon and oxygen isotopes in carbonate), developed in 1982 at the National Institute of Standards and Technology (NIST), in U.S., from a white marble slab, was used to define the primary VPDB scale. It was nearly exhausted, and IAEA 603 was produced as a replacement. Transferring the scale to CO_2 in air as required for atmospheric monitoring, created problems of traceability and reproducibility. The Jena Reference Air Standard (JRAS) was a stable isotope standard consisting of CO_2 generated from a calcite and mixed into CO_2-free air. It was closely linked to the VPDB scale. However, production using this method was limited and prohibitively expensive, making it difficult to meet increasing demand and the metrological infrastructure is lacking. This project has developed reference materials of pure CO_2 and 400 µmol/mol in air matrix with uncertainties achieving $\delta^{13}C-CO_2$ 0.1 ‰, $\delta^{18}O-CO_2$ 0.5 ‰ and 100 nmol/mol (amount fraction) with production methods at several partner institutes to allow upscaling.

Re-measure absolute CO_2 isotope ratios to provide data for SI traceability

For CO_2, no absolute isotope ratio measurements traceable to the SI have been achieved with the desired uncertainty due to insufficient methods and instrumentation. Progress was required to put CO_2 isotope metrology on an SI basis to make existing infrastructure more robust. This project has published work towards testing and verifying new combined experimental and theoretical methods to determine absolute values of isotope ratios and the isotopic composition of CO_2 with potential to characterise existing reference gases and generate new reference gases traceable to the SI.

N_2O (pure and 300 nmol/mol – 1000 nmol/mol in air) reference materials (uncertainties 1.0 ‰ ($\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$) and 0.5 ‰ ($\delta^{15}N$, $\delta^{18}O$))

No international reference materials for isotopic composition in the form of gaseous N_2O with stated uncertainties were available. Instead, two independent approaches were developed which led to differences in the measured N_2O site preferences ($\delta^{15}N^{\alpha}$ – $\delta^{15}N^{\beta}$) in background air of almost 30 ‰. This project has created an infrastructure based on new international reference materials for $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$, $\delta^{15}N$ and $\delta^{18}O$ in N_2O which this project has produced within the target uncertainties of 1.0 ‰ ($\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$) and 0.5 ‰ ($\delta^{15}N$, $\delta^{18}O$), as well as 5 nmol/mol for amount fraction which is essential to improve inter-laboratory comparability.

Spectroscopic methods for isotope ratio measurements of CO_2 (uncertainty target 0.1 ‰ for $\delta^{13}C-CO_2$ and 0.5 ‰ for $\delta^{18}O-CO_2$) and N_2O (precision target 0.1 ‰ for $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and $\delta^{18}O-N_2O$)

Optical isotope ratio spectroscopy (OIRS) methods have advanced in recent years and this project has developed validation routines, recommendations and traceable field-deployable spectroscopy for CO_2 isotopes (with uncertainty targets demonstrated to reach 0.1 ‰ for $\delta^{13}C-CO_2$ and 0.5 ‰ for $\delta^{18}O-CO_2$) and for N_2O isotopes, including site specific delta values in real time, with a target precision of 0.1 ‰ for $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and $\delta^{18}O-N_2O$, an important step towards meeting the specification of IRMS and the WMO compatibility goals. Furthermore, an optimized and harmonized uncertainty assessment has been achieved and with the inside looks to the underlying spectroscopy, an optimized matrix and concentration dependency treatment was promoted for CO_2.

Results

CO_2 (pure and 400 µmol/mol in air) reference materials (uncertainties: $\delta^{13}C$-CO_2 0.1 ‰, $\delta^{18}O$-CO_2 0.5 ‰)

Pure carbon dioxide reference materials that span the range of isotope ratios most commonly found in the atmosphere have been produced at NPL, INRIM and TUBITAK with uncertainties below the stated targets (0.1 ‰ for $\delta^{13}C$-CO_2 and 0.5 ‰ for $\delta^{18}O$-CO_2). The reference materials are traceable to the international delta scale for measuring isotope ratios (VPDB scale) through measurement by isotope ratio mass spectrometry (IRMS) at MPI and JSI, and agreement in reference values for isotope ratio between the three NMIs (NPL, INRIM, TUBITAK) within the aforementioned uncertainties has been demonstrated.

An ambient amount fraction (400 µmol mol^{-1} in an air matrix) reference material with the same varying isotopic composition as the pure reference materials were prepared at the three NMIs. The reference materials were traceable to existing scales for amount fraction and have gravimetric uncertainties below the target of 100 $nmolmol^{-1}$. $\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2 values are traceable to the VPDB scale. A change in isotopic composition was observed when preparing the ambient amount fraction reference materials which has shown to be from the decanting process. The effects of contaminants from the matrix gas on the isotopic signature has been shown to be negligible.

The sampling of pure and ambient reference materials in low pressure vessels has been improved which will contribute to further reducing uncertainties in dissemination.

Storage and handling effects on the isotopic signature of the gaseous reference materials have been investigated, with the best practices reported. Pressure regulation, cylinder depletion and storage over one year have been shown to have no effect on the carbon and oxygen isotope ratios beyond the reference value uncertainties.

INRIM and TUBITAK constructed dynamic dilution systems with uncertainty in flow measurements below 0.1 % relative. The dynamic reference materials showed agreement in delta values for carbon and oxygen when compared to static reference materials and agreement to static reference materials from existing scales.

Reference materials with targeted isotopic signatures were prepared by gravimetric blending for carbon-13 and equilibration with enriched water for oxygen-18. The calculated delta values for blended reference materials showed agreement within the reference value uncertainties when compared to values assigned by IRMS.

This objective was fully achieved with uncertainty targets reached when implementing the best practice in handling the pure CO_2 and preparing the ambient amount fraction reference materials with an optimised method. The reference materials produced will allow end users of optical based instruments to measure isotope ratios with vastly improved comparability and uncertainties that approach the WMO-GAW data quality objectives.

Re-measure absolute CO2 isotope ratios to provide data for SI traceability

PTB has made significant progress towards determining the feasibility of absolute values of isotope ratio for CO_2 and realising measurements on an SI basis. A device for preparing gravimetric mixtures has been set up and, using two source gases highly enriched in carbon-12 and carbon-13 respectively, two mixtures have been prepared. Measurements of the source gases and the gravimetric blends show that for deriving the *K*-factors a new mathematical approach was required. A tool capable of solving a system of non-linear equations for deriving calibration factors (K factors) of gravimetric isotope mixtures has been developed, which can be used for any number of isotopes or isotopologues. An open access paper (with NPL and RUG) describing the tool has been published.

This objective was partially achieved, with the necessary data provided for an SI traceable delta scale, however further improvements are required to meet the uncertainty requirements.

N_2O (pure and 300 nmol/mol – 1000 nmol/mol in air) reference materials (uncertainties 1.0 ‰ ($\delta^{15}N^{\alpha}$ and $\delta^{15}N^{\beta}$) and 0.5 ‰ ($\delta^{15}N$, $\delta^{18}O$))

Seven pure nitrous oxide (N_2O) reference materials have been prepared by Empa from suitable nitrous oxide source gases (pure nitrous oxide, ^{15}N-enriched and depleted nitrous oxide, ^{18}O-enriched nitrous oxide). The reference materials have $\delta^{15}N$ values between 0 ‰ and 100 ‰, and $\delta^{18}O$ values between 40 ‰ and 150 ‰. The isotopic signatures were chosen to meet stakeholder expectations.

Empa and MPG reviewed current practices for characterisation of nitrous oxide for its isotopic composition and selected the most promising approaches. Based on this, Empa has developed a technique to characterise N_2O gases for their site-specific ^{15}N isotopic composition. As part of this work, an established approach, based on the thermal decomposition of ammonium nitrate to N_2O was refined with respect to reaction yield. In addition, isotopic analysis of NH_4NO_3 salts was provided by eight isotope laboratories including MPG, UEF, Tokyo Institute of Technology and an uncertainty budget calculated. The approach yielded nitrous oxide with defined isotopic composition, which was applied to analyse the established N_2O reference materials. MPG has developed a technique for $\delta^{15}N$-N_2O and $\delta^{18}O$-N_2O analysis including an uncertainty assessment, reviewed by Empa. The seven N_2O reference materials established within the project were analysed by Empa, MPG, Tokyo Institute of Technology and UEA to provide their isotopic composition and uncertainties.

Ambient amount fraction (300 – 1000 nmol/mol in an air matrix) reference material were prepared by NPL from the pure reference materials. The reference materials were compared to existing scales for amount fraction and have gravimetric uncertainties below 0.3 nmol mol^{-1}.

NPL studied the effects of the production and storage of ambient amount fraction N_2O in synthetic air reference materials in cylinders on the reported amount fraction and delta values were compared to reported values for dynamic reference materials produced from the same pure N_2O source. Agreement within 0.05 % (0.16 nmol mol^{-1}) was achieved between the static and dynamic reference materials at nominally 325 nmol mol^{-1}. No variation in reported delta values beyond the measurement uncertainty for N_2O amount fractions over the range of 300-1500 nmol mol^{-1} was observed between the analyser response of the static and dynamic reference materials.

This objective was fully achieved with respect to the established pure and diluted N_2O isotope reference material and their uncertainties and the provided reference materials are expected to be taken up by the scientific community.

Spectroscopic methods for isotope ratio measurements of CO_2 (uncertainty target 0.1 ‰ for $\delta^{13}C$-CO_2 and 0.5 ‰ for $\delta^{18}O$-CO_2) and N_2O (precision target 0.1 ‰ for $\delta^{15}N^{\alpha}$, $\delta^{15}N^{\beta}$ and $\delta^{18}O$-N_2O)

PTB characterised an OIRS system with relative expanded uncertainties of 0.10 ‰ and 0.14 ‰ for $\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2, respectively. RUG characterized a dual laser spectrometer with relative expanded uncertainties of 0.052 ‰ and 0.072 ‰ for $\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2 respectively. INRIM characterised a FTIR spectrometer for measurement of $\delta^{13}C$-CO_2 in air mixtures with relative expanded uncertainty of 0.6 ‰. PTB's system was field-deployable and investigated as a candidate optical isotope ratio standard. Based on this research and the underlying spectroscopy of CO_2 isotope lines, PTB demonstrated that the known matrix and concentration dependency artefacts could mostly been eliminated. VTT developed a carbon dioxide analyser for measurement of $\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2 under field deployable conditions. The sources of uncertainty for isotope ratio measurements of CO_2 using OIRS instruments were reproducibility; calibration; mole fraction dependency; and effects from the gas matrix.

A comparison of OIRS instruments developed in the project with Isotope Ration Mass Spectrometry (IRMS) measurements at MPI showed larger discrepancies than the uncertainties highlighted above. Further investigation needs to be undertaken to exclude potential sources of those discrepancies, including the use of sampling techniques (highlighted as part of objective 1) and matrix effects. Meanwhile, an ongoing EMPIR project has revealed that exactly the sampling issues suspected already in SIRS have been the reason for the discrepancies.

Suitable spectral regions for N_2O isotope analysis have been reviewed by Empa and VTT. Factors to enhance the performance of a Quantum Cascade Laser Spectroscopy (QCLAS) analyser to target precisions of 0.1 ‰ for $\delta\,^{15}N^{\alpha}$, $\delta\,^{15}N^{\beta}$ and $\delta\,^{18}O$ have been reported and implemented. The work in this activity was extended by testing four commercially available nitrous oxide OIRS systems. The laser spectrometers were metrologically characterised for spectral interferences (CO_2, CH_4, CO), gas matrix effects (N_2, O_2, Ar), non-linearities and temperature effects. An uncertainty budget has been prepared that included the aforementioned parameters and inter-comparison measurements to IRMS were performed to identify target applications.

This objective was fully achieved.

Impact

Ten peer reviewed, open access scientific publications have been written, including two in the Analytical and Bioanalytical Chemistry journal, titled "Gas weighing challenge" and "Solution to gas weighing challenge". A full list of publications is below. Twenty-one presentations/poster displays were conducted at conferences including: European Geosciences Union General Assembly (EGU-2018 and 2019); $19^{th}/20^{th}$ WMO/IAEA meetings on Carbon Dioxide, Other Greenhouse Gases, and Related Measurement Techniques (GGMT-2017/2019). An invited oral presentation on "SI Traceability of Isotope Ratios of CO2 - A Feasibility Study" was given at the CCQM Isotope Ratio Working Group Spring Meeting 2019 in April 2019. The development of reference materials for CO_2 and N_2O will support future Key Comparisons organised by the working group, for example (N_2O: CCQM-K68.2019), for global comparability, new calibration and measurement capability claims for amount fraction and isotopic composition. A pilot study for isotope ratio of CO_2 is currently in operation (CCQM-P.204). The project partners were also actively involved in the Subcommittees for Gas Analysis (SCGA) and Inorganic Analysis (SCIA) of the EURAMET Technical Committee for Metrology in Chemistry (TC-MC). Nine training courses based on project results were held during the project, for various scientific audiences.

Impact on industrial and other user communities

This project has developed new reference materials, instrumentation, methods and recommendations which are compiled as final reports and good practice guides. N_2O isotope reference materials have been requested by and provided to expert laboratories. This links to Objective 3. Gas metrology and external partners will benefit from enhanced capabilities and primary reference materials which will lead to increased revenue from measurement services. Instrument manufacturers will benefit from accurate calibration standards, ensuring their instruments are traceable and provide valid data for atmospheric monitoring. 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. The atmospheric monitoring community will have access to new traceable reference materials. A new range of stable ratio reference gases for Atmospheric monitoring analysis, which are available for purchase (e.g. Natural Air, CO_2 in Natural Air, Natural Air without CO_2) has been supplied to various customers which consist of universities, research institutes and NMIs. This will provide long-term impact and sustainability. End users (atmospheric monitoring) will benefit from traceable spectroscopic methods with improved specifications (e.g. CRDS) which is more cost effective and more portable for field use. They will also benefit from harmonised guidelines and instructions for commercial instrument validation and best practice guides for traceable reference standard measurements. This will lead to more isotopic measurements in the field and local source apportionment.

Impact on the metrology and scientific communities

The project partners were actively involved in the CIPM Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology - Working Group on Gas Analysis (CCQM-GAWG) and - Working Group on Inorganic Analysis (CCQM-IAWG), and one of the project partners (PTB) participated in the committee meetings of these working groups in April 2019. Outputs from this project will be presented to global experts. A new working group under the CCQM on isotope ratio measurement (CCQM-IRWG) has been created, and one of the project partners (PTB) participated in the committee meeting of this working group in April 2019. Partners of this project have been central to these developments and disseminating the output from this work in this forum. The achievements in this project have been transferred into PTB's participation in CCQM-P204, an international pilot study comparing global capabilities of gas metrology groups and stakeholder labs to perform isotope ratio determinations in CO_2.

Impact on relevant standards

The developments in this project will be used to update 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. In particular, there are new activities in ISO/TC158 WG2 on isotope ratio where the results from the SIRS project are have a direct input.

The vital infrastructure developed in the SIRS project will be maintained after completion of the project. This will be disseminated to key stakeholders via calibrations and reference materials. It will also provide the foundation for new research opportunities to provide a measurement infrastructure where isotope ratio measurements are realised on an SI basis and tackle new pressing components such as methane. Advances in the state of the art of reference materials will continue in the successor project STELLAR where the focus is to improve the uncertainty of CO_2 reference materials and target methane to address the requirements for global atmospheric observations.

List of Publications

- N2O isotopocule measurements using laser spectroscopy: analyzer characterization and intercomparison, article published in Atmospheric Measurement Techniques, https://doi.org/10.5194/amt-13-2797-2020

- Absolute isotope ratios – Analytical solution for the determination of calibration, article published in Spectrochimica Acta Part B: Atomic Spectroscopy, https://doi.org/10.1016/j.sab.2019.04.008

- Preliminary assessment of stable nitrogen and oxygen isotopic composition of USGS51 and USGS52 nitrous oxide reference gases and perspectives on calibration needs, article published in Rapid Communications in Mass Spectrometry, https://www.dora.lib4ri.ch/empa/islandora/object/empa:17210

- UncorK – A Monte Carlo simulation tool for calculating combined uncertainties associated, article published in Spectrochimica Acta Part B: Atomic Spectroscopy, https://doi.org/10.1016/j.sab.2020.105866

- Gas weighing challenge, article published in Analytical and Bioanalytical Chemistry, https://doi.org/10.1007/s00216-019-02168-4

- Solution to gas weighing challenge, article published in Analytical and Bioanalytical Chemistry, https://doi.org/10.1007/s00216-020-02697-3

- What can we learn from N2O isotope data? – Analytics, processes and modelling, article published in Rapid Communications in Mass Spectrometry, https://www.dora.lib4ri.ch/empa/islandora/object/empa:22957

- Absolute isotope ratios of carbon dioxide – a feasibility study, article published in Journal of Analytical Atomic Spectrometry, http://dx.doi.org/10.1039/d0ja00318b

The list is also available here: https://www.euramet.org/repository/research-publications-repository-link/?no_cache=1#c1384

Project start date and duration:	June 1st 2017, 42 months	
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Project website address: http://www.vtt.fi/sites/SIRS/		
Internal Funded Partners: 1. NPL, UK 2. DFM, Denmark 3. INRIM, Italy 4. PTB, Germany 5. TUBITAK, Turkey 6. VTT, Finland	External Funded Partners: 7. AL, Spain 8. JSI, Slovenia 9. MPG, Germany 10. RUG, Netherlands 11. UEF, Finland	Unfunded Partners: 12. EMPA, Switzerland