FINAL PUBLISHABLE REPORT

Grant Agreement number	19ENV05
Project short name	STELLAR
Project full title	Stable Isotope Metrology to Enable Climate Action and Regulation

Project start date and duration:	September 2020, 36 Months
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Internal Funded Partners:	External Funded Partners:	Unfunded 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	9. AL, Spain 10. Empa, Switzerland 11. JSI, Slovenia 12. MPG, Germany 13. RUG, Netherlands 14. UEF, Finland	n/a
RMG: -		

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1   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.

2   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.

3   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 δ^2H-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).

4 Results

## 4.1   Objective 1: Carbon dioxide gas reference materials - pure and 410 μmol mol^{-1} in air

The aim of this work was to considerably improve gas reference materials of carbon dioxide that were developed as part of the EMPIR funded SIRS project (16ENV06). This goal has been achieved, thanks to the fruitful cooperation between several NMI's experienced in gas handling and mixing (TUBITAK, INRIM and NPL), and expert laboratories capable of reliably calibrating $\delta^{13}C$ and $\delta^{18}O$ measurements to the international VPDB and VPDB-CO_2 scales (MPI-BGC, RUG and JSI). The consortium has calibrated and intercompared the $\delta^{13}C$ and $\delta^{18}O$ values for pure CO_2, with additional support from the IAEA, the custodian of stable isotope reference materials. For $\delta^{13}C$, agreement between the groups is very good, and the accuracy in the calibration of $\delta^{13}C$ values is ≤0.02‰. For $\delta^{18}O$ the agreement is less good. This is to be expected, as the realisation of the calibrated VPDB-CO_2 scale involves a critical, fractionating reaction. Still, agreement between the calibrated values for the four CO_2 gases is better than 0.04‰. For individual aliquots (flasks) of these gases, uncertainty due to the filling process increases the total uncertainty to 0.03 ‰ for $\delta^{13}C$, while for $\delta^{18}O$, the uncertainty is not significantly increased further.

These well-calibrated pure CO_2 gases were used to produce mixtures of carbon dioxide in CO_2-free air matrix at ambient amount fractions. These CO_2-in-air materials have subsequently been measured for the $\delta^{13}C$ and $\delta^{18}O$ values. Both the $\delta^{13}C$ and the $\delta^{18}O$ appeared to be more enriched than the pure CO_2 that which was diluted to make them, by ~0.1 ‰ for the depleted isotope ratio reference materials and ~0.7 ‰ for enriched reference materials. The offset appeared to be repeatable for reference materials made at all three participating NMIs. If the offset between pure and ambient amount fraction reference materials is not included in an uncertainty calculation, the ambient amount fraction reference materials also meet the target uncertainties of 0.05 ‰ for $\delta^{13}C$-CO_2 and 0.1 ‰ for $\delta^{18}O$-CO_2. Therefore, we may conclude that the work toward this deliverable has been successful and has paved the way for cheaper and more readily available ambient air CO_2 isotope reference materials.

Work undertaken and progress beyond the state of the art.

To date, the standard and associated VPDB scale for $\delta^{13}C_{VPDB}$ and $\delta^{18}O_{VPDB-CO2}$ in CO_2 are still artefact-based: they rely on the CO_2 production from carbonate material in a precisely described process. The so-called VPDB-scale is presently maintained using the calcite IAEA-603 developed by the IAEA. The original material that defined the VPDB scale was NBS19 which is now only used in some expert labs, but no longer commercially available.

The CO_2 release is based on the reaction of carbonate materials with (over)saturated phosphoric acid according to equation (1), and its description goes back to McCrea (1950).

$$CaCO_3 + 2H_3PO_4 \rightarrow Ca^{2+} + 2H_2PO_4^- + H_2O + CO_2 \qquad (1)$$
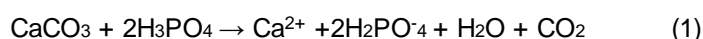
Whereas the transfer of C atoms from the carbonate to the CO_2 gas is 100%, on the oxygen side only 2/3 ends up as CO_2, the remaining fraction builds H_2O. This makes the scale realization for O more critical, and more sensitive to variations in the CO_2 formation process. Moreover, one should prevent the exchange of oxygen atoms between the formed H_2O and CO_2; to this end the phosphoric acid should be oversaturated, such that it immediately captures the formed H_2O.

To implement a more robust link between the carbon dioxide gas reference materials developed in the 16ENV06 SIRS project to both the VPDB $\delta^{13}C$ and VPDB-CO_2 $\delta^{18}O$ scales, the reaction of phosphoric acid with standard calcium carbonates (IAEA-603) has been conducted and studied by three laboratories of the Stellar consortium, and in addition by the IAEA laboratory who are the custodians of the primary reference material. Partners MPI-BGC and RUG have ample experience in this process (and so does the IAEA), whereas partner JSI developed the capability during the Stellar project period.

The four partners each developed CO_2 from a variety of calcium carbonates (tables 1 and 2), among them IAEA-603 (and/or the former scale definition material NBS-19). To be able to separate variability caused by the phosphoric acid reaction from differences in scale realization (and scale effects such as scale contraction) on the Isotope ratio mass spectrometers (IRMSs), batches of produced CO_2 were shipped back and forth between the laboratories. Where available, the diluted CO_2 reference materials have also been compared to the pure CO_2 gas reference materials.

For $\delta^{13}C$, the agreement between the CO_2's produced by the two labs is excellent (tables 1 and 2): their difference is zero within uncertainty. Figure 1 is an example in which CO_2 produced from IAEA-603 by RUG and by MPI-BGC are measured by IRMS both at RUG and at MPI-BGC. Also shown in figure 1 is the precision in the form of the variance between different portions of CO_2. Based on all materials, the uncertainty achieved for $\delta^{13}C$ of < 0.015‰ is much better than the target of 0.05‰. The reproducibility of the syntheses that was demonstrated was ≈ 0.015‰ for Groningen, for MPI-BGC it was 0.010‰. Finally, external partner IAEA demonstrated a reproducibility of ≈ 0.006‰.

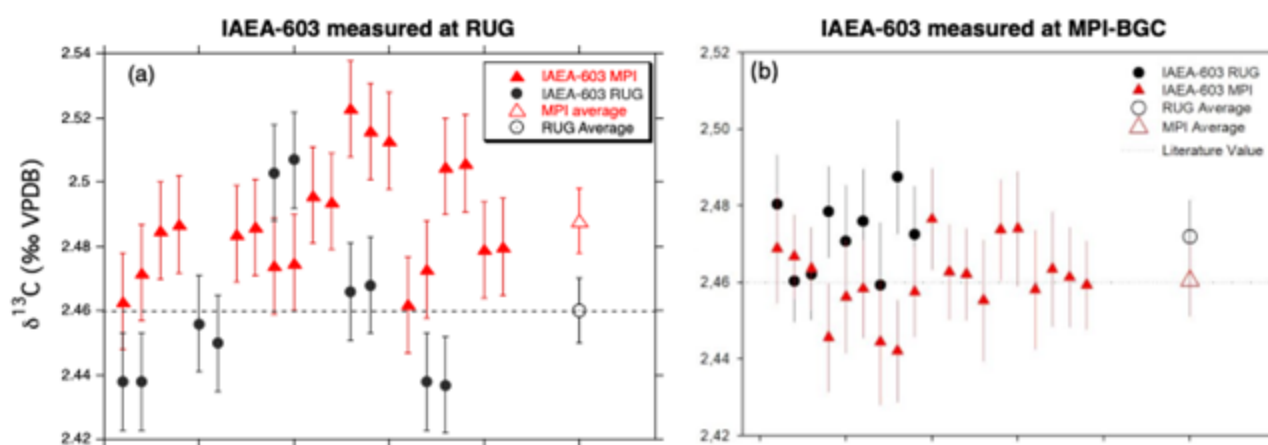

Figure 1. $\delta^{13}C$ Results for CO_2 samples from individual IAEA-603 calcite reactions performed at MPI-BGC and RUG, all measured in one batch at RUG (a), and MPI-BGC (b), respectively. The difference between the two preparation systems is not significant to within ±0.01‰

In conclusion, we can say that both the target uncertainty and reproducibility are met for $\delta^{13}C$.

Furthermore, all data scaled to NBS19, shows very good agreement with the literature values across the VPDB scale, as defined by standards from +1.95 ‰ (NBS19), to -42.08 ‰ (USGS44), indicating that the phosphoric acid reaction does not create biased results for calcium carbonates with different isotopic compositions and grain sizes.

For $\delta^{18}O$, the situation is more complicated, given the very characteristics of the formation process, in which kinetic fractionation occurs. Not only does the reaction have to be complete, but also the temperature (of 25.0°C) should be kept constant in spite of the exothermic reaction, and the phosphoric acid needs to be oversaturated (density ≥1.92 g/cm3) to avoid the post-reaction interaction between the CO_2 and the formed water.
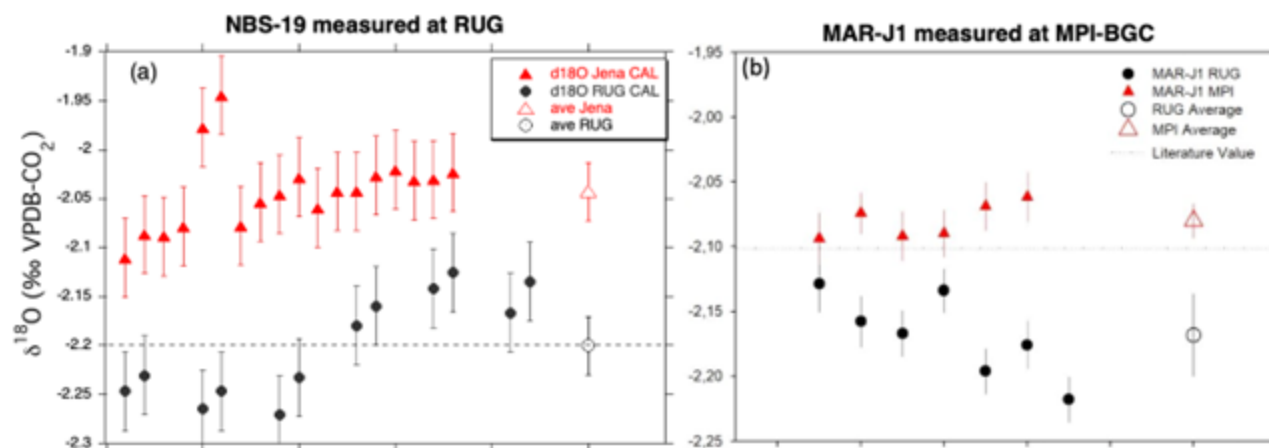

Figure 2. $\delta^{18}O$ Results for CO_2 samples from individual NBS-19 (a) and MAR-J1 (b) calcite reactions performed at MPI-BGC and RUG, all measured in one batch at RUG (a), and MPI-BGC (b), respectively. The difference between the two preparation systems is significant the RUG preparation being 0.10 to 0.15‰ more negative than the MPI-BGC one.

Using the same procedure as for $\delta^{13}C$, it became clear that the results of the three involved Stellar labs were significantly different beyond the reproducibility. While the latter was very satisfactory (≈ 0.03‰ for Groningen, ≈ 0.03‰ for MPI-BGC and ≈0.04‰ for JSI), the CO_2 produced at MPI-BGC was significantly, on average 0.14‰ more positive than that from RUG (figure 2).

At MPI-BGC, the temperature of the reaction vessel is continuously monitored. At RUG, the glass vessel is immersed in a temperature-controlled water bath. Nevertheless, due to the exothermic reaction and the poor heat conductivity of glass, one cannot exclude a certain, short-term temperature increase.

IRMS scales and normalization

Dual inlet IRMS's are designed for the high precision determination of small isotopic differences. They are, however, prone to effects that influence the exact quantification of these differences, in other words a per mil difference in the isotope content between two substances is not reproduced as a per mil (but usually slightly less). This scale contraction is caused by various effects, of which the cross contamination between sample and reference gas is the most prominent one.

Experienced groups, such as MPI-BGC and RUG, have been aware of this effect, and they have designed and applied strategies to minimize cross contamination and/or correct for it.

MPI-BGC and RUG have analysed a number of carbonate reference materials, and by these established the realisation of the VPDB (-CO_2) scale on their instruments. External partner IAEA was at the origin of these materials, and they also provided us with their best measurements.

SAll three labs reproduce the assigned values very well, and thereby can establish the VPDB scale to within ±0.01‰, and VPDB-CO_2 scale within ±0.02‰. while for RUG the deviations measured-assigned for the IAEA-603, 601, 611, 612 are all close to zero (the logical consequence of them being used together for the scale normalization), for the MPI-BGC results the IEAE-610, 611 and 612 show a negative deviation that scales with their $\delta^{13}C_{VPDB}$ value. This indicates that the assigned values (established by the IAEA, which lab reproduces its own assigned values very well) might be slightly too positive, caused by scale contraction that has not

completely be corrected for. The assigned value for USGS-44 on the other hand is corroborated by the MPI-BGC value, whereas the deviations for the RUG and IAEA are consistent with the reproduction of the assigned values for IAEA-610, 611 and 612.

Using the now well-calibrated DI-IRMS's, MPI-BGC and RUG analysed the four pure CO_2 gases from the previous project (SIRS-16ENV06) with the aim of reducing the uncertainties in their assigned values to 0.05‰ for $\delta^{13}C$ -CO_2 and 0.1 ‰ for $\delta^{18}O$ -CO_2. The pure gases were collected for NPL, INRIM and TUBITAK, and all gases were still undistinguishable. From the figure, it is clear that the assigned values can indeed be determined with the desired accuracies (or better).

Ion correction and oxygen isotope scale relations

The paper by Brand, Assonov, Coplen (2010, in short BAC) describes the way the "ion correction", that is the correction for the share of the isotopomere $^{12}C^{17}O^{16}O$ overlapping the desired $^{13}C^{16}O^{16}O$, is properly done. The correction is based upon the assumption that the ^{17}O abundance variation scales with that of the ^{18}O abundance according to a fixed relation:

$$\frac{R\left(^{17}O/^{16}O,\ sample\right)}{R\left(^{17}O/^{16}O,\ VPDB\text{-}CO2\right)} = \left(\frac{R\left(^{18}O/^{16}O,\ sample\right)}{R\left(^{18}O/^{16}O,\ VPDB\text{-}CO2\right)}\right)^{\lambda} (2)$$

Initially, λ was assumed to be 0.5 (Craig, 1961), and then all calculation steps could be performed analytically. Santrock *et al* (1985) were the first to postulate a λ different from 0.5 (namely 0.516) and that forced them to use a numerical process to obtain the final values for $\delta^{13}C$ and $\delta^{18}O$. BAC reproduced that iterative calculation, but used a newer set of values, both for the absolute ratios ^{13}R for VPDB, and ^{17}R and ^{18}R for VPDB-CO_2, and for λ. The current values as recommended by IUPAC-CIAAW are: $R_{VPDB}(^{13}C/^{12}C)$ = 0.01118, $R_{VPDB\text{-}CO2}(^{18}O/^{16}O)$ = 00208835 and $R_{VPDB}\text{-}CO2(^{17}O/^{16}O)$= 0.0003931, and finally λ= 0.528. (note that the $R_{VPDB}(^{13}C/^{12}C)$ applied is still the CIAAW recommended one, whereas the STELLAR project has led to a newer, and more accurate value, see Deliverable D2).

Next generation of CO_2-in-air gas reference materials
The aim of this task was to produce carbon dioxide gas reference materials in a carbon dioxide free air matrix that fulfil the requirements set out by the GAW-WMO. The carbon dioxide gas reference materials were measured on the JRAS-06 scale which is the WMO-GAW recommended scale for $\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2 measurements of atmospheric carbon dioxide. In addition, the amount fraction of the reference materials was calibrated on the NOAA/ESRL WMO carbon dioxide scale.
To reach the stringent uncertainty requirements for the reference materials, an air matrix was prepared ensuring that the amount fraction of carbon dioxide has a negligible influence on the isotopic composition of the final mixtures. The carbon dioxide and air matrix components were added gravimetrically in transportable high-pressure cylinders. Mixtures were also be prepared by dynamic dilution of the parent gases to investigate stability.
NPL, INRIM and TUBITAK independently prepared a suite of ambient amount fraction reference materials from the pure reference materials from the SIRS (16ENV06) project and synthetic air produced by NPL.
The enriched CO_2 source is from an underground well, and the depleted source is of industrial origin. The CO_2 within both of these batches of cylinders was shown to be homogenous between cylinders and stable for <4 years with a consistency of < 0.05 ‰, with respect to $\delta^{13}C$ and $\delta^{18}O$. A comparison of $\delta^{13}C$-VPDB and $\delta^{18}O$-VPDB for three cylinders each from both pure sources is shown in figure 3. Two cylinders from each source were sampled by INRIM and measured at MPI-BGC in 2019, and a third cylinder from each source was sampled at NPL and measured at MPI-BGC in 2023. Pure CO_2 was sampled again at INRiM in 2023 and confirmed the stability of the values, after verification at MPI-BGC.
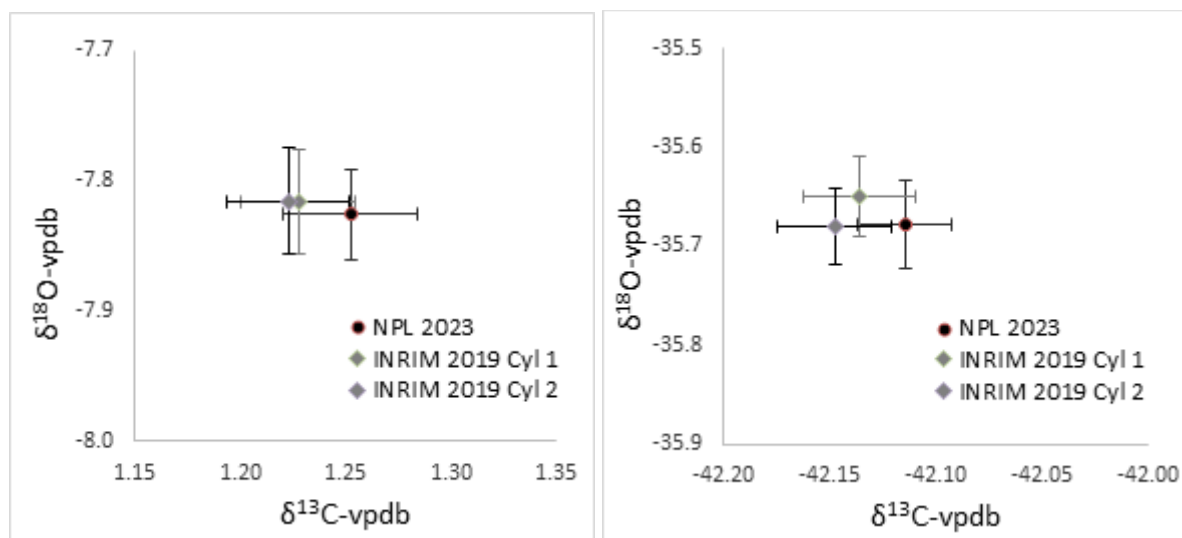
Figure 3: IRMS measurements of pure CO_2 from the enriched source (left) and depleted source (right) with δ^{13}C-VPDB on the x-axis and δ^{18}O-VPDB on the y-axis. A comparison is shown between samples taken in 2019 by INRIM and 2023 by NPL. All are sampled from different high-pressure cylinders but supplied from the same CO_2 source. Stability and homogeneity within measurement uncertainties is shown for δ^{13}C and δ^{18}O.

Certification of RMs (Reference Materials) on the VPDB scale

δ^{13}C-VPDB and δ^{18}O-VPDB-CO_2 value assignments for 410 µmol mol^{-1} CO_2 in air reference materials produced at NPL, INRIM and TUBITAK are shown in figures 4 and 5. Each point is the average of all the IRMS measurements on aliquots from a single 410 µmol mol^{-1} reference material. The aliquots were taken in evacuated 1L glass sample vessels (Normag) at 2 bar(a) and analysed at project partner MPI-BGC. The uncertainties are calculated by combining the standard deviation across the samples and the internal IRMS repeatability in quadrature. The dashed line in each graph shows the IRMS value assignment for the pure CO_2 source that the reference material was prepared from.

Figure 4 shows the ambient amount fraction reference materials produced from the enriched source and figure 5 shows the reference materials produced from the depleted source.

The uncertainty of the pure CO_2 isotope ratios due to sampling of the pure CO_2 gases and the uncertainty of the IRMS measurements is ~0.03 ‰ for δ^{13}C-CO_2 (k=2) and ~0.04 ‰ for δ^{18}O-CO_2 (k=2). The δ^{13}C-CO_2 and the δ^{18}O-CO_2 of INRIM's and NPL's ambient amount fraction reference materials are in agreement within the uncertainties and are reproducible between each cylinder of the reference materials produced from the same source of CO_2. The increased spread of values for TUBITAK's reference materials is thought to be due to air ingress caused during sampling into glass flasks.

An offset in the δ^{13}C and the δ^{18}O of the ambient amount fraction reference materials compared to the pure reference materials is observed towards more enriched values which, in several cases, is beyond the uncertainty in the measurements. The reason for this offset is not currently known but may be due to fractionation during preparation or sampling or due to differences in the IRMS measurement at pure and ambient amount fractions. Taking samples from the reference cylinders directly into an IRMS via a well flushed regulator would reduce the spread of results due to sampling into glass flasks at 2 bar and allow for a better characterisation of the offset between pure and ambient reference materials.
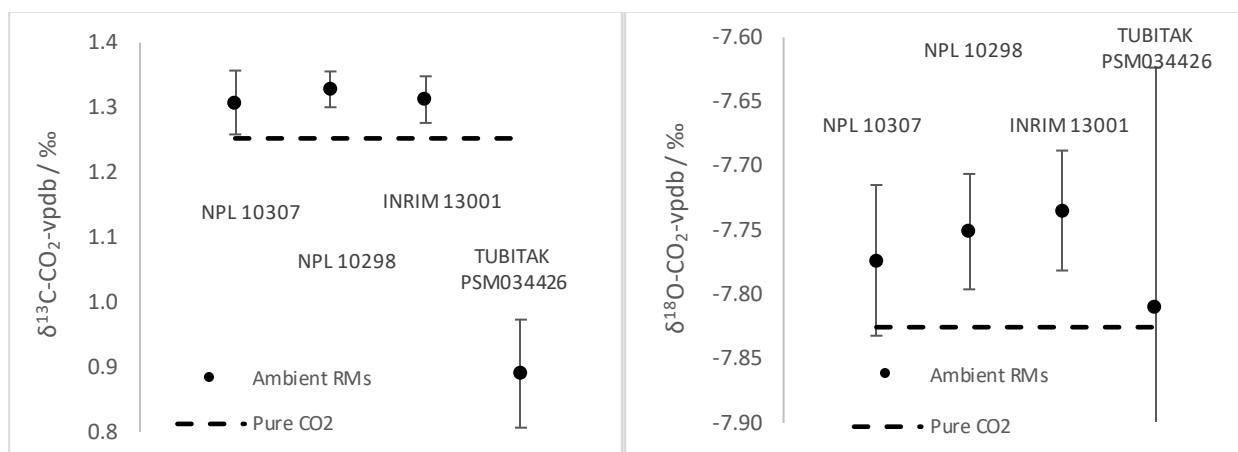
Figure 4: Isotope ratios assigned to reference materials prepared from the enriched CO_2 source; $\delta^{13}C$ left and $\delta^{18}O$-CO_2 right. Error bars show $k = 2$ uncertainty, with contributions from the IRMS measurement and the repeatability between sample flasks. The dashed line shows the isotope ratio values assignment of the pure CO_2 source.

Figure 5: Isotope ratios assigned to reference materials prepared from the depleted CO_2 source. $\delta^{13}C$ left and $\delta^{18}O$ right. Error bars show $k = 2$ uncertainty, with contributions from the IRMS measurement and the repeatability between sample flasks. The dashed line shows the isotope ratio values assignment of the pure CO_2 source.
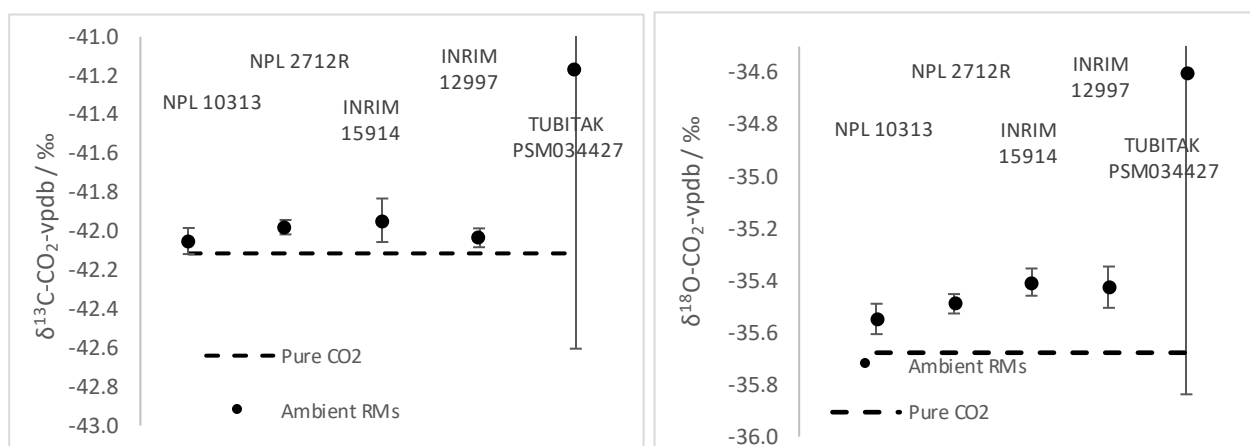
Summary and Key Results

The final reference materials were produced at pure and ambient amount fractions with a range of $\delta^{13}C$-CO_2 values of 43 ‰. The uncertainty associated with the gravimetric preparation for each reference material is ~0.08 µmol mol^{-1} (0.02 % relative) however, the gravimetric uncertainty is only one component of the final uncertainty of a reference material. The reproducibility in amount fraction is less for gravimetrically produced reference materials than for reference materials with values assigned via comparison to reference materials belonging to a scale, as can be seen in the comparison with the WMO-X2019 scale. No bias in results was observed between the gravimetrically assigned values and the scale assigned values however, while the majority of the values agreed within the WMO GAW compatibility goal of 0.1 µmol mol^{-1} or the extended goal of 0.2 µmol mol^{-1} for some reference materials, the difference between the gravimetric and scale values varies beyond that of the WMO GAW compatibility goals. There was no obvious trend in the difference between the gravimetric and scale assigned values with isotope ratio of the reference materials.

Isotope ratio measurements of the pure reference materials were undertaken by project partner MPI-BGC and RUG. The uncertainty in the isotope ratio of the pure CO_2 reference materials was dominated by spread due to sampling high pressure gas cylinders into glass flasks at 2bar(a). A process which, if not extremely carefully

undertaken, leads to fractionation. As the flasks are also prone to leaking there is a resultant spreading of the isotope ratio values due to air ingress. The uncertainty in isotope ratio for the pure materials was ~0.03 ‰ for $\delta^{13}C$-CO_2 and ~0.04‰ for $\delta^{18}O$-CO_2. These uncertainties are within the target uncertainties of 0.05 ‰ for $\delta^{13}C$-CO_2 and 0.1 ‰ for $\delta^{18}O$ -CO_2. The pure and ambient reference materials were shown to be homogenous with respect to isotope ratio between cylinders produced at all NMIs with a repeatability within the uncertainties of 0.03 ‰ and 0.04 ‰, for $\delta^{13}C$ and $\delta^{18}O$, respectively for the pure CO_2 reference materials. The isotope ratios of the pure reference materials were demonstrated to be stable for 4 years by IRMS measurements sampled at INRIM and NPL.

An offset in the $\delta^{13}C$ and the $\delta^{18}O$ of the pure and ambient amount fraction reference materials is observed with the ambient amount fraction reference materials having more enriched values which, in several cases, is beyond the uncertainty in the measurements. The offset is ~0.1 ‰ for the depleted isotope ratio reference materials and ~0.7 ‰ for enriched reference materials. The offset is repeatable for reference materials made at all three participating NMIs. It is not presently known if the offset is caused by fractionation on production of the reference materials, on sampling of the reference materials for IRMS measurements or is an artifact of the IRMS measurements. The uncertainty in the isotope ratio of the ambient amount fraction reference material is dominated by sampling the high-pressure cylinders into glass flasks for IRMS measurements. If the offset between pure and ambient amount fraction reference materials is not included in an uncertainty calculation, the ambient amount fraction reference materials also meet the target uncertainties of 0.05 ‰ for $\delta^{13}C$-CO_2 and 0.1 ‰ for $\delta^{18}O$-CO_2. The stability of the ambient amount fraction reference materials was measured against dynamically produced reference materials and shown to be stable over a 12 month period.

4.2   Objective 2: Methane gas reference materials - pure and 1.85 µmol mol^{-1} in air

Isotopic methane reference materials were produced at both pure and at ambient amount fractions in synthetic air. Most of the development presented here was done by VSL and NPL but important contributions came from project partners MPG (isotopic analysis of a large set of pure and ambient gas reference materials) and Air Liquide (supply of pure gases and cylinders).

Reducing methane (CH_4) emissions is one of the key priorities of the European Green Deal and the EU's methane strategy, published in October 2020. The focus lies on reducing CH_4 emissions in the sectors responsible for most of the anthropogenic methane emissions, i.e., energy, agriculture and waste. One method to trace CH_4 is by measuring the ratio of isotopes in atmospheric samples, a value characteristic of different formation and transportation processes.

The aim to reduce CH_4 emissions is one of the drivers for the increased requirement for CH_4 in air isotopic reference materials. A need further amplified by the significant increase in the use of (commercial) optical isotope ratio spectroscopy (OIRS), which is dependent on frequent calibrations of amount fraction and isotope ratio with CH_4 in air mixtures.

There are currently no commercially available gas reference materials that meet the emergent demand for $\delta^{13}CH_4$ and δ^2H-CH_4 calibration gases. These should be traceable to international isotope ratio scales to underpin global measurements at the required volumes and with the required uncertainties.

At the 17th WMO/IAEA meeting in 2013, experts outlined a set of recommendations to achieve the adopted WMO goals for Global Atmosphere Watch (GAW) network compatibility. These include the recommendations for the CH_4 amount fraction and isotopic δ-values.

Component	Compatibility goal	Extended compatibility goal
CH_4	±2 ppb	±5 ppb
$\delta^{13}C$-CH_4	0.02 ‰	0.2 ‰

δ^2H-CH$_4$	1 ‰	5 ‰

Recommended compatibility of measurement for the WMO-GAW network.

The compatibility goals set for the isotopic δ-values and amount fractions are challenging. Ideally, the reference materials developed in STELLAR should support these goals. This means that the target uncertainty of the reference materials should be even smaller as additional uncertainty is introduced by e.g., sampling or the analytical instrumentation.

Note that typical variations of the isotopic signature observed in CH$_4$ reference materials do not influence the measurement of CH$_4$ amount fraction significantly. In other words, for amount fraction CH$_4$ measurements, it is not necessary to have an accurate knowledge of the isotopic signature of the CH$_4$.

A world-wide inter-laboratory comparison revealed discrepancies of up to 0.5 ‰ for δ^{13}C and 13 ‰ for δ^{2}H-CH$_4$ isotopic measurements of ambient air samples which are 25 and 13 times their respective WMO-GAW network compatibility goals. This is due to different calibration approaches and calibration propagations in the various labs. A new infrastructure based on gas reference materials of pure methane as well as methane in air mixtures will enable direct dissemination of unified standards and metrological traceability to meet the wide demand and improve international comparability.

The aim of the work covered in this report is to develop the required infrastructure through the preparation of gas reference materials of pure CH$_4$ and at ambient amount fractions (about 1.9 µmol mol^{-1}) in an air matrix on a large scale suitable for dissemination to measurement networks. The gas reference materials require a repeatability in the preparation process of 0.02 ‰ for δ^{13}C-CH$_4$ and of 1 ‰ for δ^{2}H-CH$_4$ and uncertainties of 0.2 ‰ for δ^{13}C-CH$_4$ and 5 ‰ for δ^{2}H-CH$_4$. The stability of the isotopic composition reference materials should be more than one year. It is necessary that the δ^{13}C-CH$_4$ and δ^{2}H-CH$_4$ isotope ratio reference materials will be traceable to the VPDB and VSMOW/SLAP scales, respectively.

The first step towards realising the required methane gas reference materials is to identify suitable sources of methane and then to develop pure gas reference materials with a range of isotopic compositions in high pressure cylinders for underpinning measurements of δ^{13}C-CH$_4$ and δ^{2}H-CH$_4$. These sources of methane are required to be made traceable to the existing VPDB and VSMOW/SLAP scales via IRMS measurements. The STELLAR Annex 1 states that commercially available sources of pure CH$_4$, covering as wide a range as possible (suggested -20 ‰ to -80 ‰ for δ^{13}C-CH$_4$ and -75 ‰ to -400 ‰ for δ^{2}H-CH$_4$) which are relevant for underpinning atmospheric measurements for source apportionment will be identified. These sources will be used to prepare gas reference materials of pure methane for underpinning measurements of δ^{13}C-CH$_4$ and δ^{2}H-CH$_4$. The target repeatability is 0.02 ‰ for δ^{13}C-CH$_4$ and 1 ‰ for δ^{2}H-CH$_4$. The target uncertainties are 0.2 ‰ for δ^{13}C-CH$_4$ and 5 ‰ for δ^{2}H-CH$_4$.

Diluted reference materials at ambient amount fractions (1.9 µmol mol^{-1}) in air are required from the pure CH$_4$ sources for distribution to monitoring networks. A study of repeatability of isotope ratio with production and a study of potential fractionation causes in the production of ambient isotopic CH$_4$ reference materials is necessary to demonstrate the uncertainties are suitable for their intended application.

To achieve this aim, key challenges will need to be overcome in the preparation and validation of the gas reference materials and establishing traceability to the VPDB and VSMOW/SLAP scales for δ^{13}C-CH$_4$ and δ^{2}H-CH$_4$ respectively. Monitoring networks require ambient amount fraction methane reference materials with

a matrix which matches ambient air or, which comprises the key elements of atmospheric air. For calibration of measurement instruments at least two different isotope ratios are required (see for example report A3.1.4 of the Stellar project for more information on the calibration approaches).

To achieve the required unprecedented uncertainties and long-term stability, use of suitable cylinder passivation chemistries is needed to assure long term stability and minimise fractionation. Trace amount fraction methane in the zero-air used to prepare the reference materials has a significant effect on the final amount fraction and associated uncertainty of the reference materials due to the relatively low amount fraction of the reference materials (1.9 µmol mol^{-1}). A full characterisation of the zero-air used in the preparation enables lower uncertainties on the amount fractions assigned to the reference materials produced. If the isotope ratio of the residual CH_4 gas in the zero-air is significantly different to that of the CH_4 added to the reference material the isotope ratio of the final reference materials may also be affected.

Most of the research on isotopic reference gas standards has so far been devoted to CO_2. For example, in the SIRS 16ENV06 and ENV52 HIGHGAS projects, the development of pure and ambient CO_2 isotopic reference materials was begun at the NMI level and this work was significantly progressed in the STELLAR project. In the ongoing pilot comparison, CCQM-P204, CO_2 isotope ratios (δ^{13}C and δ^{18}O) in pure CO_2 are determined. Further, commercial isotopic CO_2 gas standards are now also available. Another example is the development of isotopic reference materials for helium at the Korean NMI, KRISS].

In contrast, for CH_4, much less research has been carried out to date. The lack of suitable isotopic reference materials for CH_4 was recognised at a very early stage. Due to a lack of suitable reference materials for isotopic CH_4 measurements, several laboratories have developed methods to calibrate purified CH_4 against certified reference materials.

Preparation of reference materials
Within the project, VSL and NPL worked on the preparation of isotopic methane gas standards, both pure and at ambient amount fractions in an air matrix. This section describes the different steps made to obtain the pure methane and prepare with these the various gas standards.

Selection of pure CH_4 sources
The start of the traceability chain starts with obtaining pure CH_4 gases of suitable purity level and with a suitable isotopic ratio signature. CH_4 is emitted into the atmosphere by a range of processes including anthropogenic activities and biological processes. Each emission source of CH_4 has a different isotopic signature enabling source apportionment of the CH_4 emitted. To make reference materials with a wide range of isotope ratios and thus allow optimum calibration of OIRS spectrometers for source apportionment, pure sources of CH_4 were sought from fossil sources and biogenic sources. Methane from fossil sources, primarily from natural gas tends to have a more positive δ^{13}C-CH_4 and δ^{2}H-CH_4 than biogenic process (see Figure 6). Biogenic processes which emit CH_4, including ruminants, wetlands, rice growing and emissions from landfill, favour lighter isotopologues. Atmospheric CH_4 has a δ^{13}C-CH_4 intermediate to these two main groups but closer to that of natural gas. Gas reference materials with intermediate isotopic compositions can be produced via blending fossil and biogenic sources however, blending CH_4 sources would not give ambient δ^{2}H-CH_4 values (the current atmosphere has a δ^{2}H value of around -90 ‰ due to processes in the atmosphere which affect the δ^{2}H-CH_4 of atmospheric methane). However, very few OIRS can measure δ^{2}H-CH_4, most can only measure δ^{13}C-CH_4.
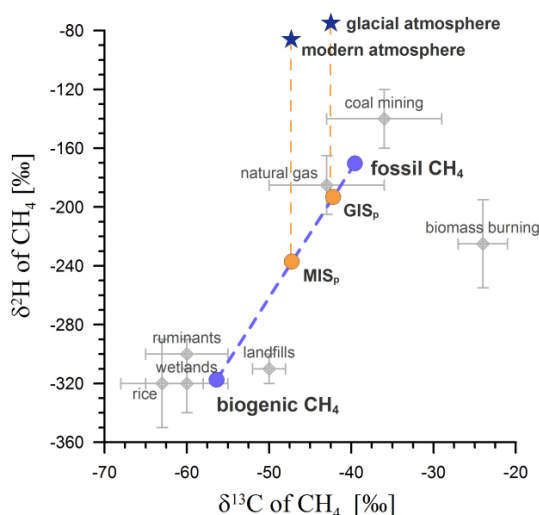
Figure 6: Isotope signature of CH_4 from different origins. Graph taken from Sperlich *et al.*

A cylinder of fossil methane supplied by Air Liquide and one with biogenic methane from Nordstrom, were sent to project partner MPI BGC for IRMS measurements. NPL screened commercially available methane fossil sources by optical isotope ratio measurements. On finding a second source with a sufficiently different $\delta^{13}C$-CH_4 value to that of the fossil source supplied by Air Liquide, samples of this methane were sampled into 1 L glass flasks (Normag) and also sent to project partner MPI BGC for IRMS measurement.

All IRMS measurements were made relative to internationally accepted standards or in-house standards that have been scaled to internationally accepted standards. Each isotopic measurement was done twice, on two separate occasions. A two-point linear normalisation scheme was used to scale all measurements to the respective isotope scale. Combined uncertainties (standard deviations, SD) are calculated using the "NIST uncertainty machine" (https://uncertainty.nist.gov).

The results of the IRMS measurements are shown below

CH_4 source	$\delta^{13}C$ VPDB [‰]	δD	$\delta^{2}H$ VSMOW-SLAP [‰]	δD
STELLAR Fossil 1	-39.07	0.09	-194.52	1.45
STELLAR Fossil 2	-51.87	0.08	-189.06	1.55
STELLAR Biogenic	-56.82	0.04	-323.9	1.9

IRMS results of the STELLAR pure CH_4 sources

The fossil sources, which are available in large volume and at high purity, span the ambient $\delta^{13}C$-CH_4 range for isotope ratio, as such, these reference materials have a range ideal for calibration of instruments which measure atmospheric $\delta^{13}C$-CH_4.

For the preparation of diluted gravimetric gas standards, the purity of the matrix gas must be known to prepare accurate reference gas standards]. For CH_4 isotopic reference materials at ambient level, even small traces of CH_4 in the matrix gas result in a significant change of both the CH_4 amount fraction and the isotopic signature of the mixture. As the matrix gas consists of nearly 80% nitrogen, one might think that the CH_4 impurity in N_2

contributes most to the CH$_4$ impurity of the matrix gas. However, typically the CH$_4$ impurity in O$_2$ is the main contributor. STELLAR project partner Air Liquide supplied cylinders (50 L Alphagaz, 200 bar) with pure gases (in total 34x N$_2$, 4x O$_2$ and 1 x Argon) to VSL and NPL.

Both VSL and NPL prepared a set of isotopic CH$_4$ gas standards at CH$_4$ amount fractions close to the ambient level (in April 2023 the global CH$_4$ monthly mean was 1922.20 nmol/mol. Gravimetric preparation following ISO 6142:2015 was used at both VSL and NPL.

NPL sent samples of four ambient amount fraction CH$_4$ reference materials for IRMS measurements at project partner MPI-BGC. Two ambient amount fraction reference materials were prepared from STELLAR fossil CH$_4$ sources 1 and 2. The four reference materials were sampled into 1 L glass sampling vessels (Normag) after evacuating and flushing three times before filling to 1.8 bar(a) as described in STELLAR deliverable 1. The glass vessels were then shipped to project partner MPI BGC for certification of δ^{13}C-CH$_4$ and δ^{2}H vs VPDB and VSMOW/SLAP.

Significant work has been undertaken on sampling procedures for isotopic reference materials of CO$_2$ within the SIRS and STELLAR projects however, studies of sampling of isotopic CH$_4$ have not been undertaken to the same extent. The best sampling practice for isotopic CO$_2$ has been applied to sampling of isotopic CH$_4$ with excellent results. Within the SIRS project, poor IRMS sampling practice was shown to cause large deviations in the reported isotope ratios of isotopic reference materials. Figure 7 shows that there is no deviation of assigned isotope ratio values beyond the uncertainty of the IRMS measurements for each of the reference materials samples.
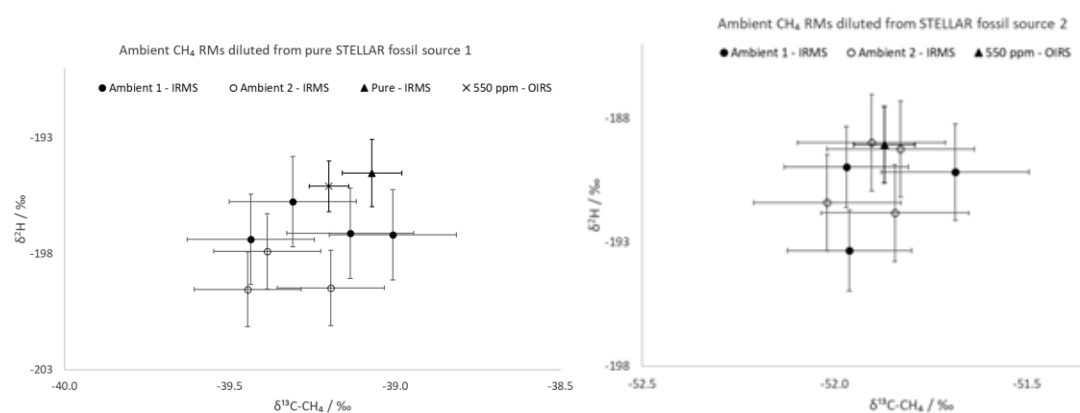

Figure 7: Comparison of isotope ratio of pure and diluted CH$_4$ reference materials measured by IRMS and OIRS prepared from the two NPL fossil sources (left panel: source 1, right panel: source 2).

Figure 7 shows the excellent reproducibility of the production methods of isotopic CH$_4$ reference materials; the overlap in delta values of the two ambient amount fraction reference materials produced from each STELLAR source with each other and, with the pure STELLAR sources, demonstrates that there is no obvious fractionation caused by the dilution of the pure sources.

Stability of isotope ratio

Figure 8 shows the average isotope ratio values of two ambient amount fraction reference materials produced nominally 6 months apart. Both reference materials were prepared from STELLAR fossil source 1, sampled in glass flasks and measured by IRMS at project partner MPI-BGC. Agreement within the uncertainties (the sum

in quadrature of the measurement uncertainty and the standard deviation of the isotope ratio values of each sample flask) demonstrates the isotope ratio stability of the reference materials.
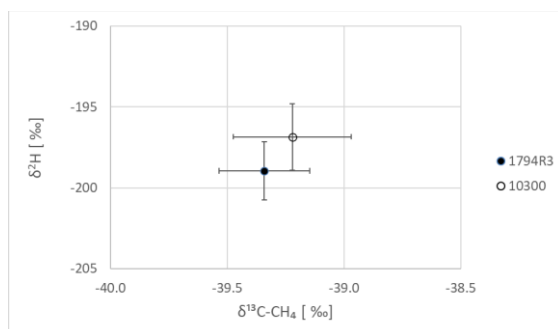

Figure 8: Stability of ambient amount fraction reference materials demonstrated by agreement within the uncertainty of two ambient amount fraction reference materials prepared from STELLAR fossil source 1 and measured by IRMS at nominally month 8 (10300) and month 2 (1794R3) after preparation.

Further, two ambient amount fraction reference materials were produced nominally 5 months apart from the same methane source (Fossil source 2), using the same preparation techniques and matrix components as described earlier. Both reference materials were measured using the Boreas preconcentration system at NPL with isotope ratios assigned via comparison to reference materials at 550 mmol mol^{-1} produced from the same source of CH_4 diluted in N_2 (Air products, BIP plus) at NPL. The reference materials were measured 12 months after the first reference materials was produced and 7 months after the second reference material was produced. Figure 9 shows that there is no measurable difference between the isotope ratio of the mixtures prepared five months apart. The error bars are uncertainty propagated from the isotope ratio assignment to the reference materials at 550 mmol mol^{-1}, and the amount fraction calibration.
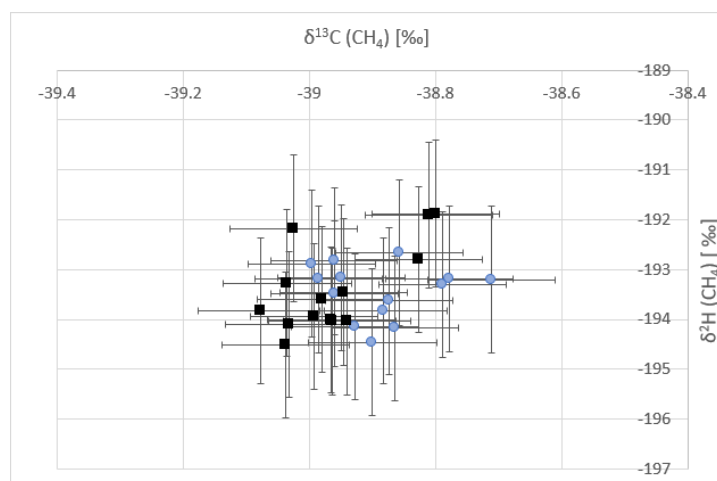

Figure 9: Comparison of $\delta^{13}C$ and $\delta^2H - CH_4$ for two reference materials prepared nominally 5 months apart. Black squares: reference material produced 1 year before the measurement, blue circles: reference material produced 7 months before the measurement.

A summary of the latter data is shown in below. This shows that for both isotopes the standards are stable.

Cylinder prep. Date	Cylinder number	$\delta^{13}C$ (CH_4) ‰	s.d.	δ^2H (CH_4) ‰	s.d.
Sep-22	10300	-38.89	0.08	-193.44	0.54
Jan-23	1794R3	-38.95	0.09	-193.39	0.87

Summary of the isotope stability measurements

Acknowledgements

Summary and Key Results

This report demonstrates the important work that has been undertaken to achieve the first ambient methane reference materials at NMI level. While Sperlich and co-workers performed similar work with excellent results some important advances have been made within the STELLAR project:

- Improved purity analysis of CH_4 in the dilution gases leading to a smaller impact on both the amount fraction and the isotopic signature of the final reference materials. An excellent agreement was demonstrated for the CH_4 impurity analysis between VSL and NPL in the synthetic air (both found 0.3 nmol/mol CH_4).
- In this work the ambient gas mixtures were prepared in 5 L glass flasks and a final filling pressure of 1.8 bar (i.e., 9 L gas). The ambient gas standards produced within STELLAR have been prepared in 5 L or 10 L aluminium cylinders with a filling pressure of 120 bar (i.e., 600 L tot 1200 L gas). Therefore, a much larger quantity of gas is available. Further, aluminium cylinders are likely to provide a better long-term stability for storage of reference gases as compared to glass flasks.
- The repeatability of isotope ratio during the dilution of the pure CH_4 sources to produce the ambient reference materials has been shown to be excellent with agreement within the uncertainty of the IRMS measurements demonstrated. This is critical if large volumes of these reference materials are to be produced for networks of monitoring stations using OIRS techniques to measure the isotope ratio of atmospheric methane where large volumes of reference materials are required for calibration. The suitability of the reference materials as calibration standards for OIRS has been demonstrated by agreement of certified isotope ratio values. These reference materials are already in use in EMPIR project IsoMET and at the Heathfield station of the UK DECC network.

While the fossil sources have high purity and are available in large quantities, it would be beneficial if larger quantities of high purity sources of biogenic methane become available allowing for a larger span for $\delta^2H–CH_4$ and $\delta^{13}C–CH_4$. With the increasing production of Bio-LNG used as a fuel for transportation, this should be a viable route for future CH_4 sources. Although the grades (voluntary) specified for biomethane in EN167223-2 are quite relaxed (e.g., $CO_2 + O_2 + N_2$ <5 cmol/mol), most Bio-LNG is expected to be of relative much higher purity as was shown within the STELLAR project for the gas samples obtained from Nordsol.

Finally, more research on spiking is needed as to produce gas standards with an isotopic signature close to atmospheric $\delta^2H–CH_4$. Spiking offers the most flexible route to isotopic gas standards with a wide range of isotopic signatures, yet there are still various hurdles that must be overcome including the formation of clumped isotopes during the processes which enrich the isotopologues used. The aforementioned challenges, identified within the STELLAR project are being addressed within the ongoing IsoMET project.

4.3 Objective 3: Absolute carbon dioxide isotope ratio measurements towards SI traceability

Gravimetric mixtures of carbon isotope enriched D-glucoses to allow correction for instrumental mass bias. The absolute carbon isotope ratios of the prepared mixtures together with two natural carbon isotopic composition glucoses could therefore be determined my multicollector-ICP-MS. The carbon isotope delta

values for these materials were also determined by calibration against RMs traceable to VPDB. Regression of isotope ratio against isotope delta allowed determination of ratio where delta was exactly equal to zero (i.e. the absolute carbon isotope ratio for the virtual VPDB material).

Background

The isotope amount ratio for the internationally agreed but virtual zero-point of the carbon isotope delta scale, Vienna Peedee Belemnite (VPDB) plays a critical role in linking carbon isotope delta to the SI. It is also a quantity used for various data processing procedures including $\delta^{17}O$ correction," clumped isotope analysis and conversion of carbon isotope delta into other expressions of isotopic composition.

Carbon isotope delta values are relative differences in carbon isotope amount ratio, $R(^{13}C/^{12}C)$, between a sample and an internationally agreed standard as defined in equation 1:

$$\delta_{standard}(^{13}C/^{12}C) = \frac{R_{sample}(^{13}C/^{12}C) - R_{standard}(^{13}C/^{12}C)}{R_{standard}(^{13}C/^{12}C)} \qquad 1$$

The isotope delta value of the standard relative to itself is zero exactly by definition, while positive and negative isotope delta values indicate proportionately more or less ^{13}C within the sample than the reference, respectively.

The value of $R_{VPDB}(^{13}C/^{12}C)$ was determined by errors-in-variables regression of isotope delta traceable to VPDB measured by isotope ratio mass spectrometry against isotope amount ratio traceable to the SI by use of gravimetric mixtures of ^{12}C- and ^{13}C-enriched D-glucose measured by multicollector-inductively coupled plasma mass spectrometry.

Results

A value of $R_{VPDB}(^{13}C/^{12}C)$ = 0.0111115 ± 0.0000040 (expanded uncertainty, k = 2) was obtained when using carbon isotope delta values traceable to the recent suite of IAEA carbonate reference materials.

The significant reduction in uncertainty by a factor of ten over our previous best efforts was achieved through a combination of factors: The molar masses of D-glucoses A and B could be determined with smaller relative uncertainty than for their glycine equivalents as (i) there was no potential co-enrichment of nitrogen isotopes to consider; (ii) use of a mass spectrometer with equal amplification on two Faraday cups allowed direct measurement of the enriched glucose materials for oxygen isotopic composition, rather than requiring dilution with natural isotopic composition material before analysis; (iii) the D-glucoses A and B had significantly less co-enrichment with ^2H than the glycines we had previously used: the former had hydrogen isotope delta values of $\delta_{VSMOW}(^2H/^1H)$ = (+1408 ± 12) ‰ and $\delta_{VSMOW}(^2H/^1H)$ = (+287 ± 3) ‰, respectively (combined standard uncertainties), while the glycine equivalents were $d_{VSMOW}(^2H/^1H)$ = (+22 808 ± 50) ‰ and $d_{VSMOW}(^2H/^1H)$ = (+47 828 ± 50) ‰, respectively (combined standard uncertainties); and (iv) more of the carbon isotope-enriched glucoses were available for measurements and therefore a larger number of replicate analyses could be performed.

The determination of water content was also achieved with lower relative uncertainty for the D-glucoses A and B than for their glycine equivalents. The latter contained approximately four-fold less water and as a result the water content was more challenging to determine with a small uncertainty as it approached the method limit of quantification.

Finally, the optimization of balance use, particularly the use of the Mettler-Toledo XP6 where possible, also contributed to the improvement uncertainty for the preparation of gravimetric mixtures of glucose. Given the limitations imposed by MC-ICP-MS analysis of carbon in the form of solutions of glucose where high concentrations are desirable to minimize the blank contribution and maximize the $^{13}C^+$ signal and relatively large volumes of solution are needed for measurement when compared to FIA-CO-IRMS, it was not possible

to use the more precise balance for all weighing operations, but nevertheless a reduction in uncertainty compared to our work with glycine was possible.

As a result of the changes to reporting guidelines for the VPDB carbon isotope delta scale, there are two calibration approaches that could be applied. Firstly, two or more RMs with assigned isotope delta values traceable to both NBS 19 and LSVEC could be used for calibration which would produce carbon isotope delta values on the so-called VPDB-2006 scale realization. Alternatively, two or more of the new IAEA carbonates and/or NBS 19 could be used to realise the VPDB-2020 scale for calibration. As it is known that these two realisations of VPDB are biased against each other, particularly as carbon isotope delta values become more negative, we applied both calibration approaches separately to investigate how the obtained value for $R_{VPDB}(^{13}C/^{12}C)$ might be affected. It was expected that the bias between VPDB-2006 and VPDB-2020 at the zero-point for carbon isotope delta would be minimal as both VPDB-2006 and VPDB-2020 realisations use NBS 19 with assigned $\delta_{VPDB}(^{13}C/^{12}C)$ of +1.95 ‰. Indeed, the function between VPDB-2006 and VPDB-2020 derived by Hélie *et al* (2021) has very small bias at isotope-delta values close to zero.

Comparison between VPDB-2006 and VPDB-2020

For fair comparison between the $R_{VPDB}(^{13}C/^{12}C)$ values obtained by regression of carbon isotope delta values obtained using the two different realisations the same set of materials should be considered. As a result, the ^{12}C-enriched glucose was not included. The values, associated standard and expanded uncertainties for $R_{VPDB}(^{13}C/^{12}C)$ can be found in the table below. There is no significant difference between these values, indicating that the bias between the VPDB-2006 and VPDB-2020 scale realisations is indeed minimal at isotope delta values approaching zero. Given the issues surrounding the VPDB-2006 scale relating to the instability of the LSVEC material, we suggest that the VPDB-2020 value from the table below is our best estimate for the isotope amount ratio for VPDB.

	$R_{VPDB}(^{13}C/^{12}C)$			
	value	u	U(95%)	k
VPDB-2006	0.0111095	0.0000018	0.0000036	2
VPDB-2020	0.0111115	0.0000020	0.0000040	2

$R_{VPDB}(^{13}C/^{12}C)$ values derived by errors-in-variables regression of carbon isotope delta against carbon isotope amount ratio.

There have been several previous determinations of $R_{VPDB}(^{13}C/^{12}C)$
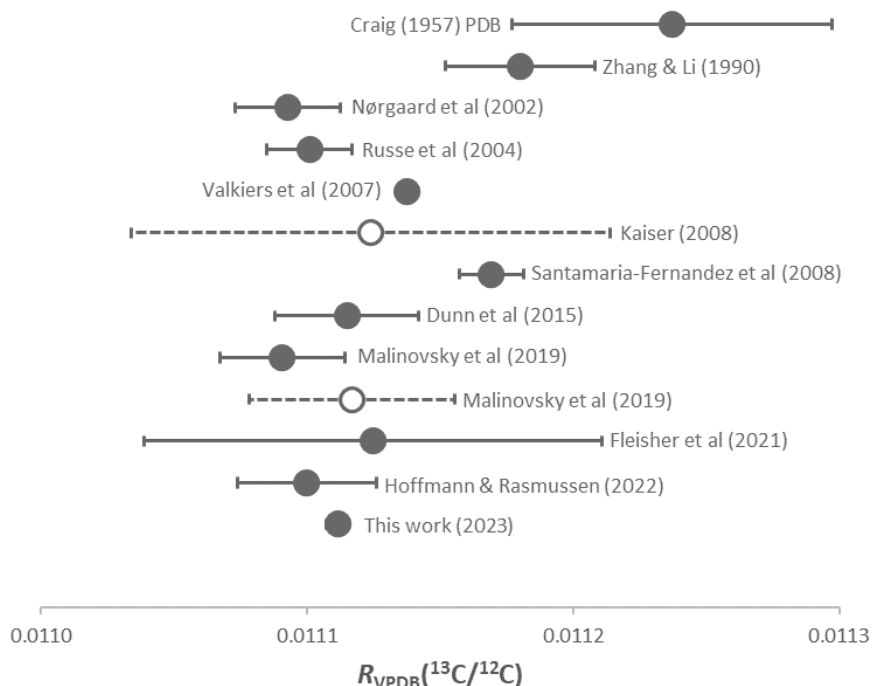
Figure 10: Previous values reported for $R_{VPDB}(^{13}C/^{12}C)$. Filled circles represent measurement results. Open circles represent calculated consensus values that are derived from a subset of the measurement results. Craig's original value for $R_{PDB}(^{13}C/^{12}C)$ has also been provided for completeness. Error bars show the expanded uncertainties and in two instances are smaller than the symbol.

Summary and Key Results

The new value for $R_{VPDB}(^{13}C/^{12}C)$ agrees very well with the consensus values calculated from previous measurement results proposed by Kaiser and by ourselves, as well as recent determinations independent of mass spectrometry. It has an expanded uncertainty of 0.4 ‰ when expressed as an isotope delta which is a ten-fold improvement over the previous best measurement of the isotopic composition of carbon.

Implications for ^{17}O corrections

As noted in the introduction, "^{17}O algorithms" applied to correct carbon dioxide isotopologue ratios rely either on a value for $R_{VPDB}(^{13}C/^{12}C)$ or for the ratio between $R_{VPDB-CO2}(^{17}O/^{16}O)$ and $R_{VPDB}(^{13}C/^{12}C)$. The IUPAC-recommended parameter set contains $R_{VPDB}(^{13}C/^{12}C) = 0.011180(28)$ and $R_{VPDB-CO2}(^{17}O/^{16}O) = 0.0003931(9)$ and the $R_{VPDB-CO2}(^{17}O/^{16}O)$ / $R_{VPDB}(^{13}C/^{12}C)$ ratio of 0.03516(8).[25–27,38] Changing the value of $R_{VPDB}(^{13}C/^{12}C)$ to that determined in this work yields $R_{VPDB-2006-CO2}(^{17}O/^{16}O) = 0.00039061(89)$ and $R_{VPDB-2020-CO2}(^{17}O/^{16}O) = 0.00039068(89)$ from the recommended $R_{VPDB-CO2}(^{17}O/^{16}O)$ / $R_{VPDB}(^{13}C/^{12}C)$ ratio. These agree well within measurement uncertainty.

Implications for SI traceability and delta scale maintenance

As with previous determinations of carbon isotope amount ratio rather than isotope delta, the work herein does not depend on any pre-existing RM for carbon isotope amount ratio. This work can therefore be repeated or replicated independently, which is of great benefit for long-term comparability of data as there is no need for careful preparation and calibration of "replacement" primary RMs in ever-lengthening calibration chains. This is a general feature of measurements that are traceable to the SI rather than to specific artefacts chosen by convention.

One means to make carbon isotope delta relative to VPDB traceable to the SI, would be to define VPDB not only by the exact isotope delta value assigned to NBS 19, but to fix $R_{VPDB}(^{13}C/^{12}C)$ to an exact value. This would mirror the re-definition of the kilogram within the SI that no longer relies on the international prototype

of the kilogram artefact held by the International Bureau of Weights and Measures (French: Bureau *International des Poids et Mesures*, BIPM) in Paris but rather the fixed value assigned to the Planck constant of $h = 6.62607015 \times 10^{-34}$ kg m^2 s^{-1}. For this to be useful, measurements of $R(^{13}C/^{12}C)$ would need to be made with a small enough uncertainty such that they could be converted into isotope delta values using equation 1 without imparting too much uncertainty. For EA-IRMS, FIA-CO-IRMS and other continuous flow approaches, an uncertainty of 0.1 ‰ in isotope delta is desirable, while for dual-inlet at least an order of magnitude lower uncertainty is required in the region of 0.01 ‰ to support atmospheric gas measurements. These would require measurement of isotope amount ratios with associated uncertainty of a similar order of magnitude; while the isotope amount ratios obtained herein have associated expanded uncertainties of between 0.38 ‰ and 0.73 ‰ and therefore tethering of the VPDB carbon isotope scale to the SI in this way requires further reduction uncertainty. The value for $R_{VPDB}(^{13}C/^{12}C)$ determined herein does, however, link the carbon isotope delta scale to the SI more securely than previous efforts.

Implications for the standard atomic weight of carbon

While we have only measured isotope amount ratios for natural D-glucoses and gravimetric mixtures prepared from isotopically enriched D-glucoses, the $R_{VPDB}(^{13}C/^{12}C)$ value we have determined relates directly to $R_{NBS\ 19}(^{13}C/^{12}C)$ through equation 1 as for NBS 19 $\delta_{VPDB}(^{13}C/^{12}C) = +1.95$ ‰ exactly. We can therefore derive $R_{NBS\ 19}(^{13}C/^{12}C) = 0.0111332 \pm 0.0000020$ from $R_{VPDB-2020}(^{13}C/^{12}C)$. Isotope amount ratios for VPDB and for NBS 19 can then be used to derive the atomic weight of carbon within the virtual VPDB and in the extant NBS 19 calcium carbonates from the masses of the ^{12}C and ^{13}C isotopes. We find that $A_r(C, NBS\ 19) = 12.0110475 \pm 0.0000040$ with $A_r(C, VPDB) = 12.0110263 \pm 0.0000040$. The standard atomic weight of carbon applicable to all normal materials is given as an interval, $A_r°(C) = [12.0096\ 12.0116]$, due to natural variations in the atomic weight of carbon between materials resulting from variations in carbon isotopic composition. More precise estimates of the atomic weight of carbon in particular materials may be derived from a $R_{VPDB}(^{13}C/^{12}C)$ value together with a measured carbon isotope-delta value.

A new best measurement of $R_{VPDB}(^{13}C/^{12}C) = 0.0111115 \pm 0.0000040$ (expanded uncertainty, $k = 2$) has been obtained my MC-ICP-MS measurements calibrated with gravimetric mixtures of ^{13}C- and ^{12}C-enriched D-glucose mixtures. This represents a significant improvement to our previous work in terms of measurement uncertainty by approximately an order of magnitude and agrees with *ab initio* measurement results reported recently using fully independent measurement techniques.

4.4 Objective 4: Spectroscopic methods for in-field isotope ratio measurements of carbon dioxide and methane

The fourth objective focused on the development and metrological characterisation of field deployable spectroscopic methods, and on 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 δ^2H-CH_4. The aim of this objective was to advance optical isotope ratio spectroscopy (OIRS) for CO_2 and CH_4 through new and improved laboratory and field deployable spectroscopic methods and calibration approaches for isotope ratio measurements of CO_2 and CH_4, aiming to achieve the required precision for in-field monitoring. This work formed the basis of three good practice guides, published on the STELLAR project website https://empir.npl.co.uk/stellarproject/documents/. The good practice guides are entitled; Specification and application of OIRS for atmospheric measurements, including sample handling protocol, optimised analytical procedures, traceability to the international standards and target uncertainties (0.05 ‰ for $\delta^{13}C$-CO_2 and $\delta^{18}O$-CO_2), Good practice guide for accurate methane isotope ratio measurements using laser spectroscopy: analyser characterization and statement of uncertainty with a target precision of 0.2 ‰ for $\delta^{13}C$-CH_4 and 1 ‰ for δ^2H-CH_4, and Good practice guide for accurate methane isotope ratio measurements using laser spectroscopy: analyser characterization and statement of uncertainty with a target precision of 0.2 ‰ for $\delta^{13}C$-CH_4 and 1 ‰ for δ^2H-CH_4.

Results

The good practice guide for specification and application of OIRS for atmospheric measurements, includes sample handling protocol, optimised analytical procedures, traceability to the international standards and target uncertainties (0.05 ‰ for δ^{13}C-CO_2 and δ^{18}O-CO_2).

In brief, the partners' work covers the metrological characterization of OIRS analysers and their uncertainty evaluation. The partners' further worked on detailed experiments and data evaluation on matrix effects; the implementation and validation of the novel isotopologue-based calibration approach; technical implementations and the optimization of analytical procedures to FTIR and laser-based spectrometers that improved the respective uncertainties below or close to the respective target precisions. The GPG also contains a series of suggested steps to metrologically characterize an instrument. For the different characterization steps, practical recommendations, background information and example measurements are presented. Further, the good practice guide contains a sample handling protocol to avoid fractionation as well as traceability considerations. Recommendations for a GUM-compliant uncertainty evaluation is given, as well as an example for such an uncertainty estimation.

This document addresses scientists who work with an optical isotope ratio spectrometer (OIRS) to measure δ^{13}C and δ^{18}O in ambient CO_2. This document outlines a series of steps to be taken into account when a spectroscopic isotope analyser is to be metrologically characterized. For each characterization step, we give background information to clarify the underlying definitions and to enable the user to interpret the resulting data. Further we suggest a set of specific experiments to provide robust characterization with limited time and gas consumption to fit the needs of the isotope ratio measurement community. In this document, we discuss traceability and uncertainty evaluation compliant to the 'Guide to the Expression of Uncertainty' (BIPM *et al.*, 2008). Further this document contains a sample handling protocol to avoid fractionation and suggestions to optimize analytical procedures. We want to emphasize that gas and cylinder handling (including the tubing used, the choice and storage of cylinders, the choice and usage of regulators and valve seals) is crucial to optimise the experiment.

A highlight of the good practice guide is the descriptions of calibration approaches; different calibration approaches can be applied to calibration OIRS analysers, most common calibration approaches are the isotope ratio and isotopologue based calibration approach. Those approaches differ in assuming a certain shape (most commonly a linear shape) of the analyser's response either in delta space or in isotopologue amount fraction space. Some other calibration approaches[2] have been discussed e.g., by (Wen *et al.*, 2013).
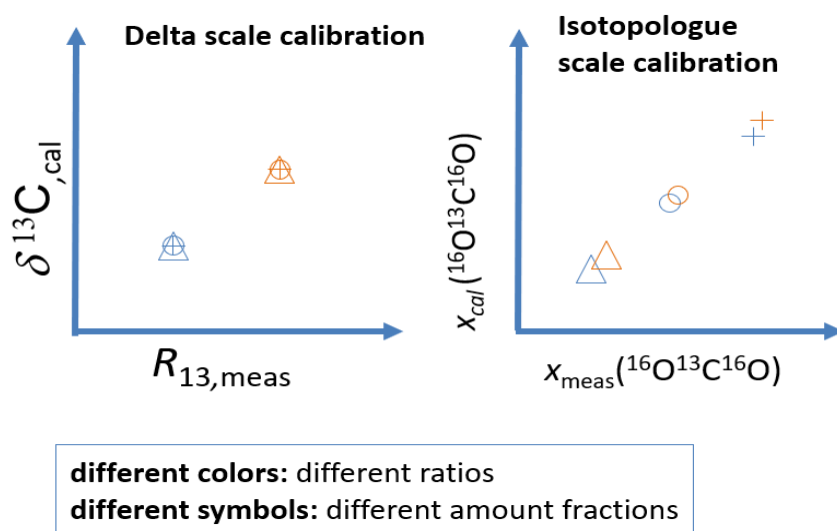
Schematic drawing of the two most common calibration approaches that can be used for OIRS measurements for delta scale calibration (left panel).

Limitations of the calibration approaches can be related to linearity (or a different assumed nonlinear calibration curve, e.g., polynomial) of the analyser in delta space and/or in isotopologue space within the application range, but also to the availability and uncertainty of reference material. For delta scale calibration, additional uncertainty is typically added by the applied correction for concentration dependency of the measured isotopologue ratio.

The good practice guide for accurate methane isotope ratio measurements using laser spectroscopy: analyser characterization and statement of uncertainty with a target precision of 0.2 ‰ for δ^{13}C-CH$_4$ and 1 ‰ for δ^2H-CH$_4$. The partners collated information into the good practice guide aimed towards measurement of isotope ratios in CH$_4$ by OIRS. In brief, the partners' work covers the implementation of modifications to the different OIRS analysers, measurement procedures and preconcentration devices yielding precisions better than the target precision. Further, the partners worked on characterising matrix effects and spectral interferences, implementing and validating an isotopologue-based calibration approach and evaluating the need for improved line data. The good practice guide also includes characterising the spectrometer stability and quantifying the interfering effects of matrix gases. Two calibration methods in use by the partners are described which use the mixtures prepared for objective 2.

Methane (CH4) is the second most important anthropogenic greenhouse gas after carbon dioxide (CO2) (Canadell *et al.*, 2021). The amount fraction in the atmosphere is growing with the rate of change varying over the observation record and a more rapid growth starting in 2007 (Nisbet *et al.*, 2019). Simultaneous measurement of the stable isotope ratios can provide insight into the relative magnitudes of the various sources and sinks and have been performed at global background sites (Nisbet *et al.*, 2016; Miller *et al.*, 2002) and regional atmospheric monitoring stations (Röckmann *et al.,* 2016). These measurements have been performed by isotope ratio mass spectrometry (IRMS), but ease of use, sampling frequency and improving precision has led to a growth in deployment of optical isotope ratio spectrometers (OIRS) based on techniques such as Fourier transform spectroscopy (FTIR) (Griffith *et al.*, 2012; Flores *et al.*, 2017), cavity ringdown spectroscopy (CRDS) (Rella *et al.*, 2015; Miles *et al.*, 2018; Saboya *et al.*, 2022), and tuneable infrared laser direct absorption spectroscopy (TILDAS) (Santoni et al., 2012; Eyer *et al.*, 2016; Rennick *et al.,* 2021).

The absorption of infrared light by molecular gases is a well-established method to quantify the amount fraction of these gases in a mixture. Different species absorb light in distinctive regions of the spectrum, providing selectivity, and the absorbance is in proportion to the abundance, providing quantification. This technique to quantify stable isotope ratios in CH$_4$ by direct measurement of the amount fraction of individual isotopologues – ^{12}CH$_4$, ^{13}CH$_4$ and ^{12}CH$_3$D – then taking the ratio of these amount fractions in a similar manner to isotope ratio mass spectrometry (IRMS). The isotope ratios are calculated as:

$$\delta^{13}\text{C}\,(\text{CH}_4) = \frac{Y_{311}^{samp}/Y_{211}^{samp}}{{}^{13}r_{\text{ref}}} - 1 \qquad (1)$$

$$\delta^2\text{H}\,(\text{CH}_4) = \frac{Y_{212}^{samp}/Y_{211}^{samp}}{4\,{}^2r_{\text{ref}}} - 1 \qquad (2)$$

where the amount fraction Y of the isotopologues are labelled by the AFGL notation

$Y_{211} \equiv Y\left({}^{12}\text{CH}_4\right)$, $Y_{311} \equiv Y\left({}^{13}\text{CH}_4\right)$ and $Y_{212} \equiv Y\left({}^{12}\text{CH}_3\text{D}\right)$ (Gordon et al., 2022).

${}^{13}r_{\text{ref}} = 0.011180$ and ${}^2r_{\text{ref}} = 0.00015575$ are the reference isotope ratios of VPDB and VSMOW respectively (Werner and Brand, 2001).

A requirement for the atmospheric measurements is that the calibrated isotope ratios are traceable to the same reference materials as IRMS measurements to allow comparison between sites and across time series. Targeted precisions have been identified by the Global Atmospheric Watch (GAW) for well-mixed background

air and source studies, where this is a measure of the bias between different measurement networks. From this for the STELLAR project target precisions of 0.2‰ for δ ^{13}C and 1‰ for δ ^{2}H, were derived.

A highlight of this good practice guide is the description of matrix gas effects; Changes in the gas matrix (O_2, N_2, Ar, H_2O, etc.) from standard ambient air composition that is reported in the HITRAN database causes variations in the pressure broadening coefficient effectively acting on the spectrum. This often results in a bias when fitting the spectrum with standard commercial fitting software or typical spectrometers' firmware (an effect sometimes called 'gas matrix effect'). Matrix effects cancel out when the sample and the reference gas have similar gas matrix composition but are relevant when one or both deviates. One example is incomplete separation of a non-target gas species in CH_4 preconcentration. Therefore, incomplete gas species separation should be tested during instrumental developments and critical levels of gas matrix changes should be evaluated.

Within STELLAR matrix effects of oxygen (O_2 from 0% to around 20%), argon (Ar from 0% to around 1%) and krypton (Kr from 0 µmol mol^{1} to around 4000 µmol mol^{1}) on apparent δ^{13}C(CH_4) and δ^{2}H(CH_4) values were tested for the TILDAS spectrometer at Empa. The experimental setup is shown in Figure 4 and exemplary results are provided in Figure 5. Findings of our study demonstrate, that in order to limit effects on δ ^{13}C (CH_4) and δ ^{2}H (CH_4) below 0.2‰ and 5‰, respectively, the following preventions have to be met: O_2 has to be removed to better than 1.4% in order to limit effects to 0.2‰ for δ ^{13}C (CH_4), while the O_2 gas matrix effect is less severe for δ ^{2}H (CH_4). For both Ar and Kr, effects are strongest on δ ^{2}H (CH_4), where 17% of Ar or 24% of Kr result in deviations of 5‰, while observed changes were lower for δ ^{13}C (CH_4).
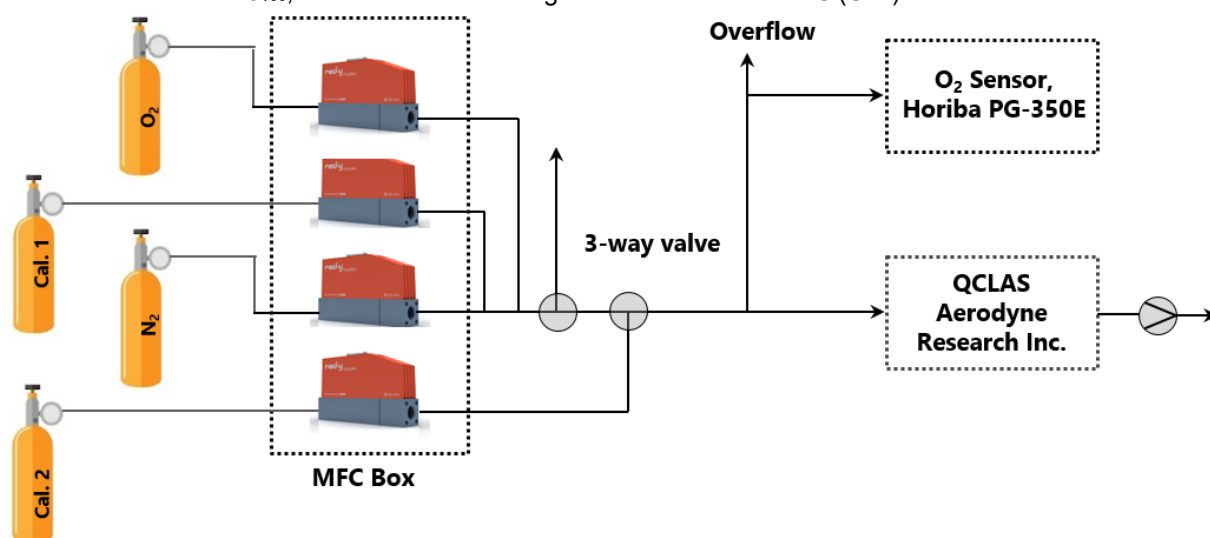
Setup established at Empa to characterise O_2, Ar, and Kr gas matrix effects on apparent δ ^{13}C (CH_4) and δ ^{2}H (CH_4) values. An additional oxygen sensor was applied to verify dynamic O_2 dilution using mass flow controllers (MFC). The following gases were applied: Calibration gas 1 with C(CH_4) = 10,000 µmol mol^{1}, Calibration gas 2 with C(CH_4) = 569 µmol mol^{1}, N_2 purity 99.9999%, O_2 purity 99.9999%. For the Ar and Kr experiments the O_2 cylinder was replaced by 1.999 % Ar in N_2 or 5005 ± 50 µmol mol^{1} Kr in N_2.
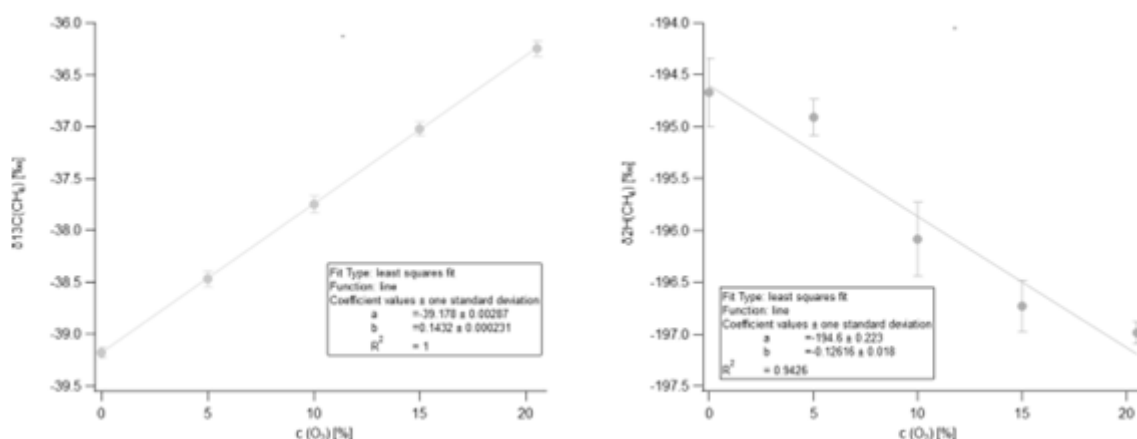
Changes of apparent δ ^{13}C(CH$_4$) (left) and δ ^{2}H(CH$_4$) (right) values as a function of O$_2$ concentration in the N$_2$ gas matrix.

The presence of additional trace gases, which are not spectrally resolved, can yield changes in the apparent isotopologue concentrations and delta values if they are not separated prior to analysis. Interfering substances can be identified using the HITRAN or other spectral databases. A database survey was conducted for the spectral regions used by partners in the Stellar project and potential interfering species are listed in Appendix B of the good practice guide.

For the specific Empa TILDAS analyser, critical levels of major interferences, nitrous oxide (N$_2$O) and water vapour (H$_2$O), were determined. For N$_2$O interference tests, a gaseous standard (480 ± 42 nmol mol^1 N$_2$O in N$_2$) in a setup similar to Figure 4 was used, while for H$_2$O a VOC calibration device (HovaCAL N424-VOC4) was used and H$_2$O concentration confirmed with a dew point meter. N$_2$O interferences are shown in Figure 6, indicating that 50 nmol mol^{-1} N$_2$O result in a 5‰ deviation for δ ^{2}H (CH$_4$), while the effect on δ ^{13}C (CH$_4$) is less pronounced. Water vapour must be removed to below 1200 µmol mol^{-1} to reach the extended WMO-GAW compatibility goals. The effect is more pronounced for δ ^{2}H (CH$_4$) than for δ ^{13}C (CH$_4$).
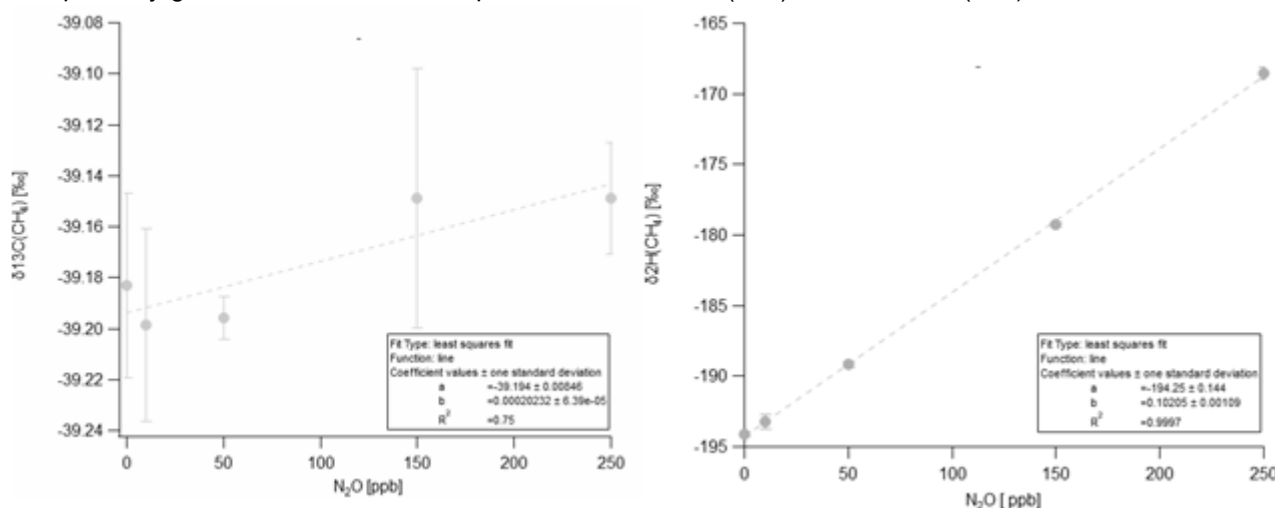
Apparent δ ^{13}C (CH$_4$) (left) and δ ^{2}H (CH$_4$) (right) values as a function of N$_2$O concentration in the gas mixture.

The OIRS spectrometers must be calibrated using reference materials that are traceable to the international standard isotope references of VPDB for $^{13}C/_{12}C$ and VSMOW for $^2H/_1H$ (Werner and Brand, 2001).

For most CH$_4$ samples with naturally-occurring abundances of all isotopologues these isotope ratios are equal to the isotopologue ratios – e.g.,

$$^{13}C\big/_{12}C \approx Y(^{13}CH_4)\big/Y(^{12}CH_4)$$

– to the limit of precision of OIRS or IRMS, so the calibration procedures here calibrate the spectrometer response.

For the good practice guide on monitoring stations / gas handling for carbon dioxide and methane isotope analysis and achieved in-field compatibility between different OIRS and IRMS with a target precision of 0.05 ‰ for δ^3C-CO_2 and $\delta^{18}O$-CO_2, the partners collated information into a good practice guide aimed towards measurement of isotope ratios in CO_2 and CH_4 by OIRS. The partners' work covers carrying out field measurements including continues measurements at a monitoring station and a Keeling-plot approach to evaluate the isotopic composition of a CH_4 source. Further, the partners worked on demonstrating field capability of their OIRS analyser for CO_2 and CH_4; performing instrument tests of the temperature stability of the analyser under field and laboratory conditions; and performing an evaluation of the feasibility of different monitoring sites for an extended campaign. The good practice guide focusses on field measurements of CO_2 and CH_4 isotopic compositions. This document contains minimal requirements for field measurements, recommendations for calibration and sample handling and examples for field measurements. The good practice guide 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.

This document addresses NMIs and the end-users who carry out OIRS measurements at monitoring stations. The report includes minimal requirements for field measurements, calibration routines of the instrument and sample handling. The field measurements process and achieved sensitivities are also included. It highlights the steps for remote monitoring and factors to be considered to reduce uncertainties/ calibration routines for on-site measurements. Comparison measurements for OIRS and IRMS are also added.

The aforementioned guideline reports have covered the application of OIRS for atmospheric measurements, including sample handling protocol, optimized analytical procedures, traceability to the international standards and target uncertainties for both carbon dioxide and methane (Braden-Behrens *et al* 2023, Rennick *et al* 2023) while here, the focus is on field measurements. The good practice guide highlights the OIRS instruments used for field measurements, the minimum requirements for operating these instruments, recommendations for reducing measurement uncertainties and results. An excerpt from the good practice guide is detailed below.

Planning and setting up field campaigns: OIRS instrument requirements,
Evaluating minimal requirements for monitoring stations.
When planning an OIRS based field campaign, an evaluation of the minimal requirements of the experimental setup can help in achieving a comprehensive dataset and to reduce uncertainties. The minimum requirements will include:
1.   Infrastructure requirements
such as remote-control options, rain protection and stability of the power supply including options to handle differently long power supply failures,
2.   Maintenance requirements
such as replacement of drying material, calibration cylinders or filters
3.   Instrumental requirements
such as required temperature stability, required flow rates and pressures as well as operational ranges (pressure p, temperature T and flow rate Φ)
4.   Expected measurement ranges (amount fraction χ and delta value δ), instrument ranges (χ and δ) & detection limits (χ)

such as expected variability of χ and δ during the experiment and guaranteed specification ranges of the instrument .

5. Consumables

such as purging and calibration gases, filters

6. Sample preparation systems

such as dryers and preconcentration setups (see e.g., the setup used by NPL and EMPA, in this report, for dual isotope analysis of CH_4)

7. Auxiliary measurements

such as temperature and humidity sensors or additional CO_2/CH_4/H_2O analysers.

Further information is provided by station specifications of monitoring networks such as ICOS or WMO GAW.

Summary and Key Results

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.

5 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 strategies 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).

6   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 δ^2H 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/