



# FINAL PUBLISHABLE REPORT

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2. DFM, Denmark	8. JSI, Slovenia	
3. INRIM, Italy	9. MPG, Germany	
4. PTB, Germany	10. RUG, Netherlands	
5. TUBITAK, Turkey	11. UEF, Finland	
6. VTT, Finland		

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## 1 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 ( $\text{CO}_2$  and  $\text{N}_2\text{O}$  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  $\text{CO}_2$  and  $\text{N}_2\text{O}$ , 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  $\text{CO}_2$ , as well as new calibration services from the development of dynamic reference materials of  $\text{CO}_2$ . 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 precision in delta value determinations in carbon dioxide and nitrous oxide.

## 2 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  $\text{CO}_2$  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  $\text{CO}_2$  (Objectives 1 and 2) and  $\text{N}_2\text{O}$  (Objective 3) concentrations is challenging and requires information on the stable isotopic composition.
- There is no infrastructure to deliver international gaseous  $\text{CO}_2$  reference materials (Objectives 1, 2 and 5) to meet demand and no international gaseous  $\text{N}_2\text{O}$  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).

## 3 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  $\text{CO}_2$  reference materials to meet the increasing demand and international gaseous  $\text{N}_2\text{O}$  reference materials with stated uncertainties to underpin measurements.

The project's specific objectives were:

1. To develop static and dynamic reference materials for pure  $\text{CO}_2$  and at 400  $\mu\text{mol/mol}$  in an air matrix with uncertainties ( $\delta^{13}\text{C}-\text{CO}_2$  0.1 ‰ and  $\delta^{18}\text{O}-\text{CO}_2$  0.5 ‰). Ensure traceability and consistency with VPDB (primary scale) and work towards meeting the WMO compatibility goals ( $\delta^{13}\text{C}-\text{CO}_2$  0.01 ‰ and  $\delta^{18}\text{O}-\text{CO}_2$  0.05 ‰).
2. To re-measure the absolute  $\text{CO}_2$  isotope ratios of the reference materials to provide the data necessary for SI traceability.
3. To develop static and dynamic reference materials for pure  $\text{N}_2\text{O}$  and at 300  $\text{nmol/mol}$  – 1000  $\text{nmol/mol}$  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 ‰ ( $\delta^{15}\text{N}^a$  and  $\delta^{15}\text{N}^b$ ) and 0.5 ‰ ( $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$ ).

4. To develop spectroscopic methods for isotope ratio measurements of CO<sub>2</sub> with an uncertainty target of 0.1 ‰ for δ<sup>13</sup>C-CO<sub>2</sub> and 0.5 ‰ for δ<sup>18</sup>O-CO<sub>2</sub>, and of N<sub>2</sub>O, including site specific delta values in real time with a target precision of 0.1 ‰ for δ<sup>15</sup>N<sup>α</sup>, δ<sup>15</sup>N<sup>β</sup> and δ<sup>18</sup>O - N<sub>2</sub>O. 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<sub>2</sub> and N<sub>2</sub>O 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.

## 4 Results

The SIRS project developed the key infrastructure required to upscale the production of isotopic CO<sub>2</sub> and N<sub>2</sub>O reference materials for the greenhouse gas monitoring community by providing traceability for stable isotopes. Additionally, the project validated existing and developed new field-deployable spectroscopy for CO<sub>2</sub> and N<sub>2</sub>O and initiated SI traceability of the international CO<sub>2</sub> isotope ratio scale by re-measuring the absolute isotope ratios by gas-source isotope ratio mass spectrometry.

The research work was split into four main objectives:

- 1 – New reference materials for δ<sup>13</sup>C-CO<sub>2</sub> and δ<sup>18</sup>O-CO<sub>2</sub> to uphold the global measurement infrastructure
- 2 – Exploratory absolute measurements
- 3 – New international reference materials and scale for δ<sup>15</sup>N<sup>α</sup>, δ<sup>15</sup>N<sup>β</sup> and δ<sup>18</sup>O-N<sub>2</sub>O
- 4 – Advancing optical isotope ratio spectroscopy for CO<sub>2</sub> and N<sub>2</sub>O

### Objective 1: New reference materials for δ<sup>13</sup>C-CO<sub>2</sub> and δ<sup>18</sup>O-CO<sub>2</sub> to uphold the global measurement infrastructure

#### Reference materials of pure CO<sub>2</sub> with assigned δ<sup>13</sup>C-CO<sub>2</sub> and δ<sup>18</sup>O-CO<sub>2</sub> values

Pure CO<sub>2</sub> reference materials were produced at three National Metrology Institutes (NMIs) (INRIM, NPL and TUBITAK) to investigate if reference materials were comparable for δ<sup>13</sup>C-CO<sub>2</sub> and δ<sup>18</sup>O-CO<sub>2</sub> with the required uncertainties. Each NMI produced a range of gas reference materials in high pressure gas cylinders and sampled aliquots for δ<sup>13</sup>C-CO<sub>2</sub> and δ<sup>18</sup>O-CO<sub>2</sub> assignment using Isotope Ratio Mass Spectroscopy (IRMS) to provide traceability to the international VPDB scale at MPI, RUG and JSI. The repeatability and stability of the amount fraction of the reference materials produced was assessed at MPI and is shown in tables 1 and 2. The aliquots of reference materials were sampled in different cylinder types after either flushing or evacuating and flushing the sample vessels for IRMS measurements.

The associated standard uncertainties shown in table 1 was calculated by summing in quadrature the spread of delta values across all samples and the largest assigned standard uncertainty in IRMS measurement of a single sample (equation 1).

$$u = \sqrt{\text{spread}^2 + \sigma^2} \quad (1)$$

Depleted CO <sub>2</sub>	δ <sup>13</sup> C Average	δ <sup>13</sup> C uncertainty (k=1)	δ <sup>18</sup> O Average	δ <sup>18</sup> O uncertainty (k=1)
NMI 1 glass	-42.18	0.067	-35.77	0.091
NMI 2 glass	-42.14	0.026	-35.66	0.046
NMI 3 glass	-42.17	0.032	-35.76	0.044
NMI 1 metal	-42.15	0.014	-35.73	0.020
Combined	-42.15	0.079	-35.71	0.166

Table 1: IRMS measurements for the depleted CO<sub>2</sub> source, showing results from different laboratories.

Enriched CO <sub>2</sub>	δ <sup>13</sup> C Average	δ <sup>13</sup> C uncertainty (k=1)	δ <sup>18</sup> O Average	δ <sup>18</sup> O uncertainty (k=1)
NMI 1 glass	1.21	0.035	-7.84	0.070
NMI 2 glass	1.23	0.018	-7.82	0.025
NMI 3 glass	1.20	0.014	-7.86	0.051
NMI 1 metal	1.22	0.013	-7.85	0.019
Combined	1.23	0.057	-7.82	0.088

Table 2: IRMS measurements for the enriched CO<sub>2</sub> source, showing results from different laboratories.

Additional reference materials were produced through blending to target intermediate isotopic signatures, such as that of clean atmospheric air. The uncertainty in  $\delta^{13}\text{C}_{\text{vpdb}}\text{-CO}_2$  and  $\delta^{18}\text{O}\text{-CO}_2$  of the blended reference materials is dominated by the reproducibility in delta values of the sampled aliquots of the  $\text{CO}_2$  with variation linked to poor sampling technique. Variability in the assigned delta value of aliquots of  $\text{CO}_2$  due to air contamination and kinetic fractionation during the fast release of  $\text{CO}_2$  were identified and best practice for the sampling procedure was determined to require evacuation and flushing of the sample vessels rather than flushing alone.

The delta value has shown to be consistent throughout the entire depletion of a gaseous reference material and consistent within the uncertainty in IRMS analysis for over one year of use by AL [ACS Omega 5, 17926–17930 (2020)].

This work is summarised in a good practice guide “Good practice guide on selection of suitable source gases for  $\text{CO}_2$  reference materials, including an uncertainty budget for upholding and upscaling the existing VPDB scale with target uncertainties of 0.1 ‰ for  $\delta^{13}\text{C}\text{-CO}_2$  and 0.5 ‰ for  $\delta^{18}\text{O}\text{-CO}_2$ ”

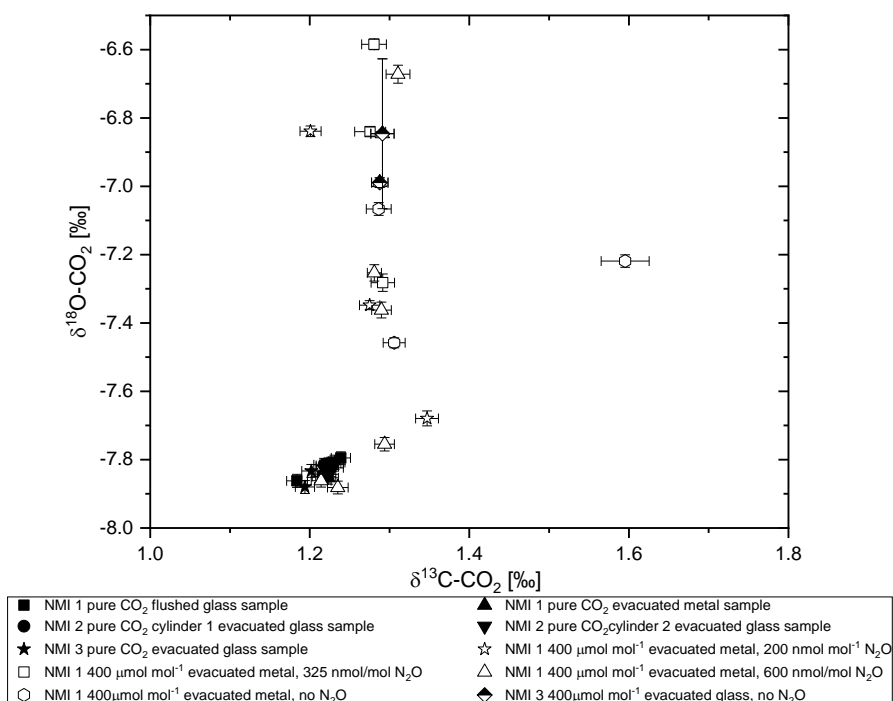
**Static and dynamic stable isotope reference gas mixtures of  $\text{CO}_2$  at  $400\ \mu\text{mol mol}^{-1}$  compared to the VPDB scale for  $\text{CO}_2$  in air mixtures** - Develop static and dynamic reference materials for pure  $\text{CO}_2$  at  $400\ \mu\text{mol/mol}$  in an air matrix with uncertainties of  $\delta^{13}\text{C}\text{-CO}_2$  0.1 ‰ and  $\delta^{18}\text{O}\text{-CO}_2$  0.5 ‰. Ensure traceability and consistency with the VPDB primary standard and to work to meet the WMO compatibility goals ( $\delta^{13}\text{C}\text{-CO}_2$  0.01 ‰ and  $\delta^{18}\text{O}\text{-CO}_2$  0.05 ‰).

The measurement community requires ambient amount fraction reference materials with assigned delta values linked to the current VPDB scale. The pure reference materials produced were diluted to ambient amount fraction by the NMIs (NPL, INRIM and TUBITAK) by a range of different gravimetric methods to assess comparability and repeatability in amount fraction and delta value. An uncertainty budget for amount fraction at each NMI showed the  $k=2$  uncertainty to be lower than the  $0.1\ \mu\text{mol mol}^{-1}$  required by the project. The amount fraction was compared by EMPA to existing amount fraction scales.

As was found for pure  $\text{CO}_2$  reference materials, sampling technique for IRMS measurements is the largest factor in the uncertainty of assigned delta values of the reference materials. Figure 1 shows pure (filled shapes) and ambient (open shapes) amount fraction reference materials produced at three different NMIs. Some of the samples of the ambient reference materials agree well with the values of the pure samples while some samples are shifted to more enriched isotopologues. A range of sampling techniques were used for the aliquots sent for IRMS with non-optimised sampling techniques for ambient  $\text{CO}_2$  reference materials leading to varying shifts to in  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  values.

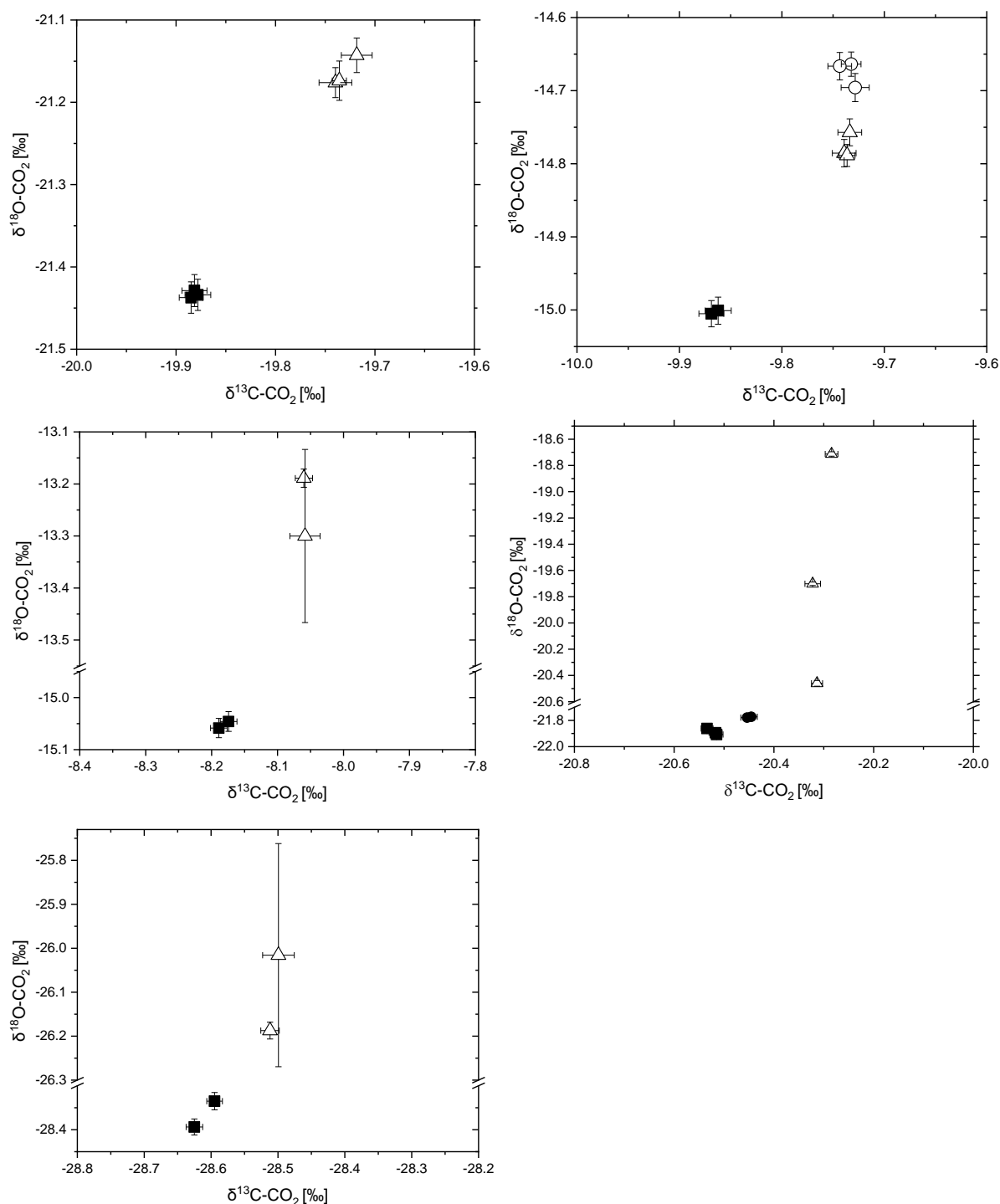
Using the most optimised sampling procedure gravimetric uncertainties ( $k=2$ ) of 0.036 ‰ and 0.05 ‰ for  $\delta^{13}\text{C}_{\text{vpdb}}\text{-CO}_2$  and  $\delta^{18}\text{O}_{\text{vpdb}}\text{-CO}_2$  were achieved for ambient reference materials blended to atmospheric  $\delta^{13}\text{C}_{\text{vpdb}}\text{-CO}_2$  values. This is within the targeted uncertainties for the project of 0.1 ‰ for  $\delta^{13}\text{C}_{\text{vpdb}}\text{-CO}_2$  and 0.5 ‰ for  $\delta^{18}\text{O}_{\text{vpdb}}\text{-CO}_2$ .

The agreement of amount fraction and  $\delta^{13}\text{C}_{\text{vpdb}}\text{-CO}_2$  and  $\delta^{18}\text{O}_{\text{vpdb}}\text{-CO}_2$  of the reference materials with that of atmospheric  $\text{CO}_2$  is important for the monitoring community. As  $\delta^{18}\text{O}_{\text{vpdb}}\text{-CO}_2$  values of the reference materials couldn't be blended to match that of  $\text{CO}_2$  in the atmosphere an equilibration process for tuning the  $\delta^{18}\text{O}$  value towards that of atmospheric  $\text{CO}_2$  was achieved at RUG. The obtained results for  $\delta^{18}\text{O}$  agreed within 0.1 ‰ of the intended values. The stability of  $\delta^{13}\text{C}_{\text{vpdb}}\text{-CO}_2$  and  $\delta^{18}\text{O}_{\text{vpdb}}\text{-CO}_2$  in ambient amount fraction reference materials was demonstrated to be within the measurement uncertainty of  $\pm 0.5$  ‰, upon depletion of the reference materials.



**Figure 1: IRMS assigned values for enriched CO<sub>2</sub> reference materials at pure (closed shapes) and ambient amount fraction (open shapes).**

A shift to more enriched  $\delta^{13}\text{C}_{\text{vpdb}}\text{-CO}_2$  and  $\delta^{18}\text{O}_{\text{vpdb}}\text{-CO}_2$  values was observed for most of the ambient reference materials compared to the pure reference materials (Figure 2). This may be due errors in following best practice for taking aliquots of the reference materials for IRMS measurements or due to preparation technique where dilution may cause fractionation or contamination. The effects of contaminant CO<sub>2</sub> in the matrix gas was calculated to be very small ( $\pm 0.001$  ‰) and thus unlikely to cause the observed differences in  $\delta^{13}\text{C}_{\text{vpdb}}\text{-CO}_2$  and  $\delta^{18}\text{O}_{\text{vpdb}}\text{-CO}_2$ . Agreement between pure and ambient amount fraction reference materials may be improved with optimised production methods.



**Figure 2: Agreement between IRMS assigned values for samples of blended reference materials at pure and ambient amount fraction  $\text{CO}_2$  in synthetic air, error bars on the y-axis are not always visible. a) black squares, pure  $\text{CO}_2$ , open triangles, nominally  $390 \mu\text{mol mol}^{-1}$  for evacuated glass flasks b) black squares, pure  $\text{CO}_2$ , open triangles, nominally  $412 \mu\text{mol mol}^{-1}$ , open circles nominally  $390 \mu\text{mol mol}^{-1}$  for evacuated glass flasks c) black squares, pure  $\text{CO}_2$ , open triangles, nominally  $400 \mu\text{mol mol}^{-1}$  for flushed glass flasks d) filled squares, flushed glass samples of pure  $\text{CO}_2$ , filled circles, evacuated metal samples of pure  $\text{CO}_2$ , open triangles pressure reduction sampling at nominally  $400 \mu\text{mol mol}^{-1}$  e) black squares, pure  $\text{CO}_2$ , open triangles, nominally  $400 \mu\text{mol mol}^{-1}$  for flushed glass flasks.**



Further details can be found in the report on this work:

*“At least three gas mixtures of pure CO<sub>2</sub> and three in air at ambient amount fractions (400 μmol mol<sup>-1</sup>) of varied isotopic composition will be developed which are value assigned for isotope ratio and amount fraction with a target stability period of at least 2 years. Expanded uncertainties of 0.1 ‰ for δ<sup>13</sup>C-CO<sub>2</sub> and 0.5 ‰ for δ<sup>18</sup>O-CO<sub>2</sub> for isotope ratio and 100 nmol mol<sup>-1</sup> for amount fraction. Reference materials compared to existing infrastructure.”*

Objective 1 was fully achieved with uncertainty targets reached when implementing the best practice in handling the pure carbon dioxide 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.

**Objective 2: Exploratory absolute measurements** - Re-measure the absolute CO<sub>2</sub> isotope ratios of the reference materials, in order to provide the data necessary for SI traceability.

Isotopic measurements of CO<sub>2</sub> are currently linked to a scale rather than having SI traceability. This work aimed to re-measure the absolute CO<sub>2</sub> isotope ratios of reference materials in order to provide the data necessary for SI traceability.

Significant progress has been made on determining the feasibility of absolute values of isotope ratios for CO<sub>2</sub> and realising measurements on an SI basis: PTB has developed a mathematical tool capable of solving a system of linear equations to derive correction factors (*K*-factors) of gravimetric isotope mixtures. The tool can be used for any number of isotopes. An open access paper about the tool was published. In a second open access publication PTB described the calculation of the uncertainties associated with the correction factors via a Monte Carlo simulation. This is an important metrological contribution to the field of isotope reference materials.

A fundamental study on potential sources of mass bias has been conducted. It investigates the impact of the ion source, the ion lenses, adsorption and desorption effects and the fragmentation of carbon dioxide in the ion source. PTB has designed and built a gas mixing apparatus to mix highly enriched and depleted CO<sub>2</sub>. As a prerequisite for its successful operation, PTB has developed a mathematical approach for correcting the masses of gas for air buoyancy. This approach has been published in two open access papers. PTB, RUG and NPL published jointly an open access paper describing first attempts of applying an adopted version of the gravimetric mixture approach to derive absolute isotope ratios of carbon dioxide.

Objective 2 was partially achieved, with the necessary data provided for an SI traceable delta scale, however further improvements are required to meet the uncertainty requirements.

**Objective 3: New international reference materials and scale for δ<sup>15</sup>N<sup>α</sup>, δ<sup>15</sup>N<sup>β</sup> and δ<sup>18</sup>O-N<sub>2</sub>O** - Develop static and dynamic reference materials for pure N<sub>2</sub>O and at 300 nmol mol<sup>-1</sup> – 1000 nmol mol<sup>-1</sup> in an air matrix. The static and dynamic reference materials should meet the requirements for regionally focused monitoring studies and have target uncertainties of 1.0 ‰ (δ<sup>15</sup>N<sup>α</sup> and δ<sup>15</sup>N<sup>β</sup>) and 0.5 ‰ (δ<sup>15</sup>N, δ<sup>18</sup>O).

In contrast to CO<sub>2</sub>, no Central Calibration Laboratory (CCL) exists to provide N<sub>2</sub>O reference materials as a unifying scale anchor to the international isotope ratio scales AIR-N<sub>2</sub> for δ<sup>15</sup>N<sup>α</sup> as well as δ<sup>15</sup>N<sup>β</sup> and Vienna Standard Mean Ocean Water (VSMOW) for δ<sup>18</sup>O-N<sub>2</sub>O. Also, no international reference materials in the form of gaseous N<sub>2</sub>O with stated uncertainties are available.

Pure N<sub>2</sub>O reference materials were developed at EMPA after discussion with stakeholders on their expectations of the isotopic composition of future nitrous oxide reference materials. Ambient (300 nmol/mol – 1000 nmol/mol) reference materials were developed in an air matrix at NPL. Static and dynamic reference materials were compared for amount fraction and delta values at NPL.

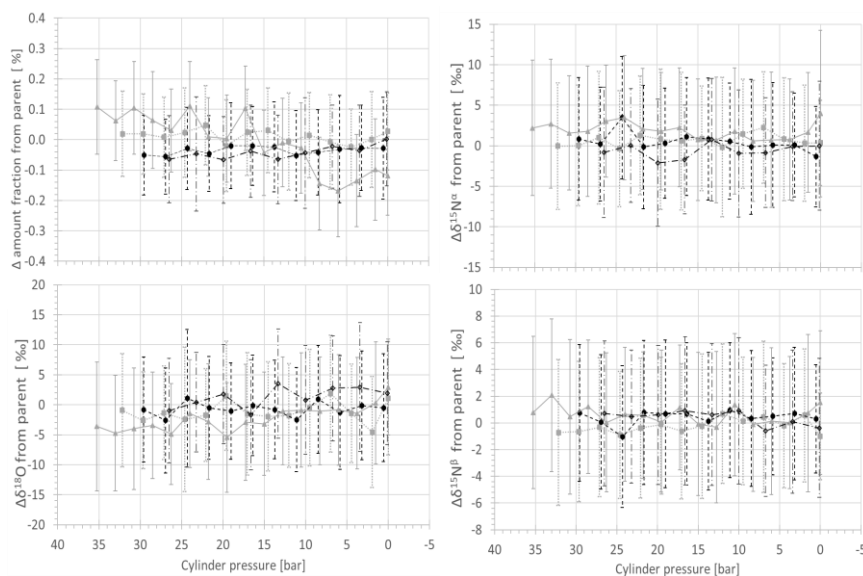
A set of seven pure N<sub>2</sub>O isotope RMs anchored to international isotope ratio scales were developed via the use of a gas mixing line. As currently available commercial N<sub>2</sub>O gases offer only limited isotopic variability, high purity N<sub>2</sub>O (99.999%, Linde, Germany) was supplemented with defined amounts of <sup>15</sup>N-enriched / <sup>15</sup>N-depleted and <sup>18</sup>O-enriched N<sub>2</sub>O. The dopant gases were commercial <sup>15</sup>N<sup>14</sup>NO, <sup>14</sup>N<sup>15</sup>NO (isotopic purity of > 98%, Cambridge Isotope Laboratories Inc., USA), and <sup>18</sup>O-enriched N<sub>2</sub>O (36.25 ± 0.10 ‰ NN<sup>16</sup>O, 63.75 ± 0.76 ‰ NN<sup>18</sup>O) as well as <sup>15</sup>N<sup>β</sup>-depleted N<sub>2</sub>O (δ<sup>15</sup>N<sup>α</sup> = -2.54 ± 0.005 ‰, δ<sup>15</sup>N<sup>β</sup> = -162.21 ± 0.03 ‰, δ<sup>18</sup>O = 38.92 ±



0.003 ‰), both produced and characterized at Empa. Homogeneity of the prepared salts by repetitive IRMS analysis of sub samples has been confirmed.  $\text{NH}_4\text{NO}_3$  salts were sent out to different laboratories for  $\delta^{15}\text{N}^{\text{bulk}}$  and  $\delta^{15}\text{N}\text{-NH}_4$  as well as  $\delta^{15}\text{N}\text{-NO}_3$  analysis. Based on these  $\text{NH}_4\text{NO}_3$  salts a technique to characterise  $\text{N}_2\text{O}$  gases for their  $^{15}\text{N}$  site preference with reference to the AIR- $\text{N}_2$  scale has been developed by EMPA. A technique for  $\delta^{15}\text{N}\text{-N}_2\text{O}$  and  $\delta^{18}\text{O}\text{-N}_2\text{O}$  analysis including an uncertainty assessment has been developed by MPI-BGC. The seven newly established  $\text{N}_2\text{O}$  isotope RMs were analysed by EMPA, MPI-BGC, Tokyo Institute of Technology and UEA to provide their isotopic composition and uncertainties. The confirmed spread in isotopic composition of the  $\text{N}_2\text{O}$  isotope reference materials with  $\delta^{15}\text{N}$  values between 0 ‰ and 100 ‰, and  $\delta^{18}\text{O}$  values between 40 ‰ and 150 ‰ meets stakeholder expectations.

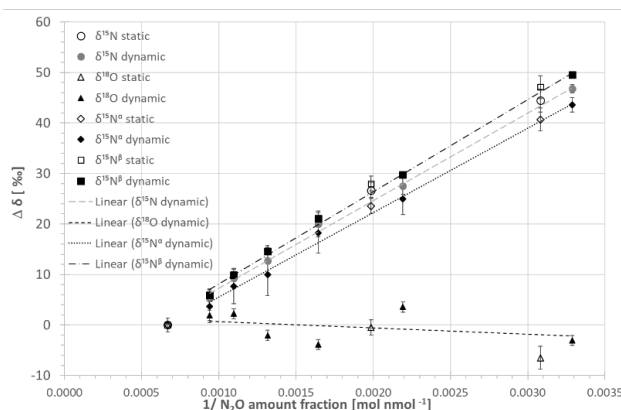
Static and dynamic reference materials were developed by dilution of the pure  $\text{N}_2\text{O}$  reference materials at NPL to produce amount fractions in the ambient range of  $300 \text{ nmol mol}^{-1}$  –  $1000 \text{ nmol mol}^{-1}$  in an air matrix for use in instrument calibration. The uncertainty in assigned amount fraction of the  $\text{N}_2\text{O}$  reference materials combined contributions from gravimetric preparation and analytical uncertainty. The combined expanded uncertainty of ambient amount fraction  $\text{N}_2\text{O}$  reference materials is calculated to be 0.11 % ( $k=2$ ) or  $0.36 \text{ nmol mol}^{-1}$  which is within the uncertainty of 5% aimed for in the project.

The effect of passivation chemistry of cylinders and influence on  $\text{N}_2\text{O}$  amount fractions and isotope deltas was studied alongside fractionation effects during dilution and storage in cylinders and the effect of different matrix gases on the measured isotope ratio of the ambient amount fraction  $\text{N}_2\text{O}$  reference materials. No effect in amount fraction or delta value was found on decant with the effect on the amount fraction and delta value assessed on the depletion of the reference materials produced via decanting a parent mixture into four smaller cylinders (Figure 3).



**Figure 3: Temporal change in (a)  $\text{N}_2\text{O}$  amount fraction and delta values: (b)  $\delta^{18}\text{O}$ , (c)  $\delta^{15}\text{N}^{\alpha}$ , (d)  $\delta^{15}\text{N}^{\beta}$  in response to changes in cylinder pressure of four 0.85 L aluminium cylinders. Each data point represents a five minute average of analyser response, error bars represent one standard deviation across the five minute average.**

Dynamic dilution systems allowing for dilution to 1 in 2000 were developed and used to assess the agreement between statically and dynamically produced reference materials in the amount fraction range  $300\text{-}1000 \text{ nmol mol}^{-1}$  (figure 4).



**Figure 1:** CRDS analyser response for  $\delta^{15}\text{N}$  (circles),  $\delta^{15}\text{N}^{\text{a}}$  (diamonds),  $\delta^{15}\text{N}^{\text{b}}$  (squares) and  $\delta^{18}\text{O}$  (triangles) with reciprocal of  $\text{N}_2\text{O}$  amount fraction for static (open data labels) and dynamic (filled data labels) reference materials in the amount fraction range of 300-1500 nmol mol<sup>-1</sup>. Error bars represent the repeatability in ‰ between the four repetitions of a five-minute average. The dotted and dashed lines represent the linear regression of dynamic reference materials for each isotopocule.

A number of high-accuracy gravimetric  $\text{N}_2\text{O}$  in  $\text{N}_2$  gas mixtures were produced by NPL and provided to Empa for  $\text{N}_2\text{O}$  isotopic analyses. Standards were made using an intermediate mixture (12 cmol mol<sup>-1</sup>  $\text{N}_2\text{O}$  in  $\text{N}_2$ ). Most standards were produced from one intermediate volume (2620) in the following order: CG5 – (CG4, CG3, same day but order unclear) – CG2 – CG1. Thereafter the intermediate volume was refilled (2620R) and CG6 and CG7 were filled the same day with unclear order.

The  $\text{N}_2\text{O}$  amount fractions of the CGs were validated by an additional gravimetric dilution to 325 nmol mol<sup>-1</sup> in synthetic air and subsequent analysis against NPL in-house standards by cavity ring-down spectroscopy (G5131-I, Picarro Inc., Santa Clara, CA, USA). Possible fractionation effects during production of the CGs were characterised by analysis of CG1–CG7 using QCLAS against reference gases anchored to the international scales. Prior to analysis, all gases were diluted to 100  $\mu\text{mol mol}^{-1}$   $\text{N}_2\text{O}$  in synthetic air (20.5%  $\text{O}_2$  in  $\text{N}_2$ ; Messer Schweiz AG).

The analytical results obtained using QCLAS for the mother tanks, agree with the  $\delta$  values of CG1–CG7 within their expanded uncertainty limits. Nonetheless, a systematic effect was observed with higher delta values for cylinders filled first and a decreasing trend towards cylinders filled later. This could point towards fractionation effects.

**Table 1:** Characteristics of the gravimetric calibration gases provided by NPL.  $\text{N}_2\text{O}$  amount fractions ( $x_{\text{N}_2\text{O}}$ ), related uncertainty,  $\delta$  values for the  $\text{N}_2\text{O}$  calibration gases (CG1 – CG7) and the  $\text{N}_2\text{O}$  validation gas (VG1) with standard deviations (rel. to Air- $\text{N}_2$  and VSMOW, analysed by QCLAS). The uncertainty of the  $\text{N}_2\text{O}$  amount fraction is given as a standard uncertainty multiplied by a coverage factor ( $k=2$ ), while for  $\delta$  values the standard deviation for repeated measurements is reported, which does not include the uncertainties of the calibration chain.

mixture	$x_{\text{N}_2\text{O}} / \text{mmol mol}^{-1}$	uncertainty / mmol mol <sup>-1</sup>	$\delta^{15}\text{N}^{\text{a}} / \text{‰}$	$\delta^{15}\text{N}^{\text{b}} / \text{‰}$	$\delta^{18}\text{O} / \text{‰}$
CG1	15.0079	0.0030	-0.29±0.06	0.70±0.06	38.42±0.23
CG2	15.2040	0.0030	-0.31±0.10	0.81±0.17	38.41±0.26
CG3	15.2961	0.0031	-0.16±0.09	0.92±0.08	38.77±0.23
CG4	15.4035	0.0031	0.21±0.16	1.03±0.01	38.64±0.08
CG5	15.5976	0.0031	0.28±0.03	1.07±0.08	38.76±0.12
CG6	17.0044	0.0034	-0.10±0.06	0.68±0.06	38.64±0.16
CG7	18.5054	0.0037	-0.27±0.05	0.64±0.05	38.17±0.12
mother tank CG	pure	-	-0.11±0.20	0.95±0.21	38.57±0.25
VG1	15.3048	0.0031	16.07±0.13	16.62±0.14	54.05±0.12
mother tank VG1	pure	-	15.69±0.25	16.89±0.30	53.87±0.25

The isotopic standards used by QCLAS for the analysis of the CGs and their original pure  $\text{N}_2\text{O}$  gas were: (1)  $\delta^{15}\text{N}^{\text{a}} = (2.06 \pm 0.05) \text{‰}$ ;  $\delta^{15}\text{N}^{\text{b}} = (1.98 \pm 0.20) \text{‰}$ ;  $\delta^{18}\text{O} = (36.12 \pm 0.32) \text{‰}$ ; and (2)  $\delta^{15}\text{N}^{\text{a}} = (-48.59 \pm 0.25) \text{‰}$ ;  $\delta^{15}\text{N}^{\text{b}} = (-46.11 \pm 0.43) \text{‰}$ ;  $\delta^{18}\text{O} = (27.37 \pm 0.11) \text{‰}$ . The standards used for the analysis of the VG1 and its original pure  $\text{N}_2\text{O}$  gas were: (1)  $\delta^{15}\text{N}^{\text{a}} = (25.73 \pm 0.24) \text{‰}$ ;  $\delta^{15}\text{N}^{\text{b}} = (25.44 \pm 0.36) \text{‰}$ ;  $\delta^{18}\text{O} = (35.86 \pm 0.22) \text{‰}$ ; and (2)  $\delta^{15}\text{N}^{\text{a}} = (-48.59 \pm 0.25) \text{‰}$ ;  $\delta^{15}\text{N}^{\text{b}} = (-46.11 \pm 0.43) \text{‰}$ ;  $\delta^{18}\text{O} = (27.37 \pm 0.11) \text{‰}$ . The uncertainty is expressed as expanded standard uncertainty at the 95% confidence interval.

The pure and ambient  $\text{N}_2\text{O}$  isotope reference materials produced will enable future users to implement a recommended two-point calibration approach for their analysers. The availability of  $\delta^{17}\text{O}$  data for  $\text{N}_2\text{O}$  RMs is expected to improve data quality / correction algorithms with respect to SP analysis by mass spectrometry.  $\text{N}_2\text{O}$  isotope RMs will improve data quality within and compatibility between laboratories and accelerate the progress in this emerging field of research.

Objective 3 was fully achieved with respect to the established pure and diluted  $\text{N}_2\text{O}$  isotope reference material and their uncertainties and the provided reference materials are expected to be taken up by the scientific community.

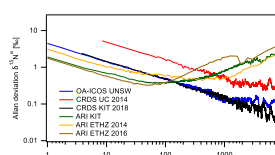
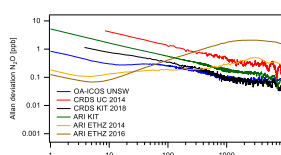
**Objective 4: Advancing optical isotope ratio spectroscopy for  $\text{CO}_2$  and  $\text{N}_2\text{O}$**  - Develop spectroscopic methods for isotope ratio measurements of  $\text{CO}_2$  with an uncertainty target of 0.1 ‰ for  $\delta^{13}\text{C}\text{-CO}_2$  and 0.5 ‰ for  $\delta^{18}\text{O}\text{-CO}_2$ , and of  $\text{N}_2\text{O}$ , including site specific delta values in real time with a target precision of 0.1 ‰ for  $\delta^{15}\text{N}^\alpha$ ,  $\delta^{15}\text{N}^\beta$  and  $\delta^{18}\text{O}\text{-N}_2\text{O}$ . The methods will be suitable for use in the field and include spectral line data measurements to improve isotope-specific line parameters.

PTB, VTT and Empa prepared a protocol which outlines the metrological characterization of spectroscopic isotope analysers; PTB and RUG characterized two commercial spectroscopic analysers (Thermo Scientific Delta Ray and Aerodyne dual laser spectrometer). VTT has finished the development of a field deployable carbon dioxide analyser, INRIM has developed a FTIR based method for  $\delta^{13}\text{C}\text{-CO}_2$  determination in carbon dioxide/air mixtures. Uncertainty budgets have been estimated for OIRS by PTB and RUG. Both OIRS measurements methods meet the uncertainty target of 0.1 ‰ for  $\delta^{13}\text{C}\text{-CO}_2$  and 0.5 ‰ for  $\delta^{18}\text{O}\text{-CO}_2$ . Meeting the uncertainty targets of the project.

PTB's field-deployable system was investigated as a candidate optical isotope ratio standard. Based on this research and the underlying spectroscopy of  $\text{CO}_2$  isotope lines, PTB demonstrated that the known matrix and concentration dependency artefacts could mostly been eliminated. Data, processed results and conclusions are due to be published as J. Braden-Behrens et al. "Eliminating the effect of air composition in optical isotope ratio spectroscopy", AMDT, in preparation 2021, and shall not be disclosed here prior to original publication.

Empa and VTT reviewed suitable spectral regions for  $\text{N}_2\text{O}$  isotope analysis; Empa reported and implemented factors to enhance performance of a QCLAS analyser to target precision of 0.1 ‰ for  $\delta^{15}\text{N}^\alpha$ ,  $\delta^{15}\text{N}^\beta$  and  $\delta^{18}\text{O}$ .

Empa metrologically characterised  $\text{N}_2\text{O}$  isotope laser spectrometers from Aerodyne Research Inc. (QCLAS, 4 x CW-QC-TILDAS-200), Los Gatos Research Inc. (LGR 914-0027) and Picarro Inc. (2 x G5131-I) and a research – grade instrument from Empa (TRES-QCLAS) for spectral interferences ( $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{CO}$ ), gas matrix effects ( $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{Ar}$ ), non-linearities and temperature effects (Figure xx). Empa compiled an uncertainty budget for the tested laser spectrometers and finalized the validation report with input from partners.





**Figure 5: Exemplary Allan deviation (square root of Allan variance) plots for the OA-ICOS I (blue), CRDS I (red), CRDS II (black), QCLAS I (green), QCLAS II (yellow) and QCLAS III (brown) at 1000 ppb N<sub>2</sub>O. The Allan deviations of all analyzers tested were reproducible on three separate occasions prior to the test results presented here.**

Objective 4 was fully achieved.

## 5 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<sup>th</sup>/20<sup>th</sup> 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 CO<sub>2</sub> - 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<sub>2</sub> and N<sub>2</sub>O will support future Key Comparisons organised by the working group, for example (N<sub>2</sub>O: 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<sub>2</sub> 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<sub>2</sub>O 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<sub>2</sub> in Natural Air, Natural Air without CO<sub>2</sub>) 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<sub>2</sub>.

#### *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<sub>2</sub> reference materials and target methane to address the requirements for global atmospheric observations.

## 6 List of publications

- N<sub>2</sub>O 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 N<sub>2</sub>O 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](https://www.euramet.org/repository/research-publications-repository-link/?no_cache=1#c1384)

## 7 Contact details

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