



Hill-Pearce, R. E., Hillier, A., Mussell Webber, E., Charoenpornpukdee, K., O'Doherty, S., Mohn, J., Zellweger, C., Worton, D. R., & Brewer, P. J. (2021). Characterisation of gas reference materials for underpinning atmospheric measurements of stable isotopes of nitrous oxide. *Atmospheric Measurement Techniques*, 14(8), 5447-5458. <https://doi.org/10.5194/amt-14-5447-2021>

Publisher's PDF, also known as Version of record

License (if available):  
CC BY

Link to published version (if available):  
[10.5194/amt-14-5447-2021](https://doi.org/10.5194/amt-14-5447-2021)

[Link to publication record in Explore Bristol Research](#)  
PDF-document

This is the final published version of the article (version of record). It first appeared online via EGU at <https://doi.org/10.5194/amt-14-5447-2021>. Please refer to any applicable terms of use of the publisher.

## University of Bristol - Explore Bristol Research

### General rights

This document is made available in accordance with publisher policies. Please cite only the published version using the reference above. Full terms of use are available: <http://www.bristol.ac.uk/red/research-policy/pure/user-guides/ebr-terms/>



# Characterisation of gas reference materials for underpinning atmospheric measurements of stable isotopes of nitrous oxide

Ruth E. Hill-Pearce<sup>1</sup>, Aimee Hillier<sup>1</sup>, Eric Mussell Webber<sup>1</sup>, Kanokrat Charoenpornpukdee<sup>1,2</sup>, Simon O'Doherty<sup>2</sup>, Joachim Mohn<sup>3</sup>, Christoph Zellweger<sup>3</sup>, David R. Worton<sup>1</sup>, and Paul J. Brewer<sup>1</sup>

<sup>1</sup>National Physical Laboratory, Hampton Road, Teddington, TW11 0LW, United Kingdom

<sup>2</sup>Atmospheric Chemistry Research Group, University of Bristol, Bristol, United Kingdom

<sup>3</sup>Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Air Pollution/ Environmental Technology, Dübendorf, Switzerland

**Correspondence:** Ruth E. Hill-Pearce (ruth.pearce@npl.co.uk)

Received: 17 February 2021 – Discussion started: 25 February 2021

Revised: 21 May 2021 – Accepted: 1 June 2021 – Published: 9 August 2021

**Abstract.** The precise measurement of the amount fraction of atmospheric nitrous oxide (N<sub>2</sub>O) is required to understand global emission trends. Analysis of the site-specific stable isotopic composition of N<sub>2</sub>O provides a means to differentiate emission sources. The availability of accurate reference materials of known N<sub>2</sub>O amount fractions and isotopic composition is critical for achieving these goals. We present the development of nitrous oxide gas reference materials for underpinning measurements of atmospheric composition and isotope ratio. Uncertainties target the World Meteorological Organisation Global Atmosphere Watch (WMO-GAW) compatibility goal of 0.1 nmol mol<sup>-1</sup> and extended compatibility goal of 0.3 nmol mol<sup>-1</sup>, for atmospheric N<sub>2</sub>O measurements in an amount fraction range of 325–335 nmol mol<sup>-1</sup>. We also demonstrate the stability of amount fraction and isotope ratio of these reference materials and present a characterisation study of the cavity ring-down spectrometer used for analysis of the reference materials.

332 nmol mol<sup>-1</sup> have been published by the WMO (WMO, 2020). The growing field of N<sub>2</sub>O research is focused on improving understanding of the global N<sub>2</sub>O budget. A comprehensive identification of the N<sub>2</sub>O sources and sinks and the contribution of each to the global N<sub>2</sub>O budget is required for N<sub>2</sub>O mitigation studies (Lewicka-Szczebak et al., 2014).

Anthropogenic N<sub>2</sub>O is released into the atmosphere mainly via multiple reaction pathways from soil and marine sources as a result of fertiliser use and technical emissions from industrial and combustion processes (Snider et al., 2015; Kantnerová et al., 2019; Toyoda et al., 2017). These different sources emit N<sub>2</sub>O with distinct isotopic compositions, which can be used as an isotopic signature or fingerprint for identification (Denk et al., 2017). The most abundant N<sub>2</sub>O isotopocules are <sup>14</sup>N<sup>14</sup>N<sup>16</sup>O, <sup>14</sup>N<sup>14</sup>N<sup>18</sup>O, <sup>14</sup>N<sup>15</sup>N<sup>16</sup>O and <sup>15</sup>N<sup>14</sup>N<sup>16</sup>O. The site-specific isotopomers display <sup>15</sup>N substitution at the central, alpha (α, <sup>14</sup>N<sup>15</sup>N<sup>16</sup>O) and the terminal beta (β, <sup>15</sup>N<sup>14</sup>N<sup>16</sup>O) positions.

Isotopic abundances are given in the delta notation (δ) and expressed as the amount fraction ratio (*x*) of minor to major isotopic species in a sample (*R*<sub>sample</sub>), relative to a reference value (*R*<sub>reference</sub>). For δ<sup>15</sup>N, the isotope abundance scale is AIR-N<sub>2</sub>, and for δ<sup>18</sup>O it is VSMOW (Vienna Standard Mean Ocean Water) (Toyoda and Yoshida, 1999). As differences in isotopic composition between sample and reference are usually small, delta values are generally expressed in per mille (‰).

## 1 Introduction

Nitrous oxide (N<sub>2</sub>O) is a greenhouse gas with a global warming potential approximately 265 times that of carbon dioxide (CO<sub>2</sub>) (Myhre et al., 2013). Atmospheric amount fractions of N<sub>2</sub>O are increasing at a rate of ~0.36 % yr<sup>-1</sup> (WMO, 2019b). Recent measurements of N<sub>2</sub>O in the unpoluted troposphere are in an amount fraction range of 325–335 nmol mol<sup>-1</sup> (WMO, 2019a). Current amount fractions of

$$R = \frac{x(^{15}\text{N})}{x(^{14}\text{N})} \quad (1)$$

$$\delta^{15}\text{N}[\text{‰}] = \left( \frac{R_{\text{sample}}}{R_{\text{reference}}} - 1 \right) \quad (2)$$

Isotopologue quantification is well established for atmospheric  $\text{CO}_2$  (Flores et al., 2017). However, quantification of  $\text{N}_2\text{O}$  isotopocules proves a greater analytical challenge due to (i) substantially lower atmospheric amount fractions; (ii) analytical difficulties in the provision of position specificity of the standard technique, isotope ratio mass spectrometry (IRMS), due to difficulty in the application of correction factors to account for the re-arrangement of  $^{15}\text{N}$  and  $^{14}\text{N}$  within the ion source (Mohn et al., 2014); and (iii) the lack of internationally accepted  $\text{N}_2\text{O}$  isotope reference materials with stated uncertainty (Ostrom et al., 2018).

In summary, this results in a limited compatibility of laboratory analyses for  $\text{N}_2\text{O}$  isotope measurements (Mohn et al., 2014). In turn, an improvement in standardisation of the assignment of delta values, within and between laboratories, can only be achieved through calibration with accurate isotope ratio reference materials.

Atmospheric  $\text{N}_2\text{O}$  has a relative abundance of  $0.9903 \text{ mol mol}^{-1}$  for the major isotopocule  $^{14}\text{N}^{14}\text{N}^{16}\text{O}$ . The minor isotopocules  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$ ,  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$  and  $^{14}\text{N}^{14}\text{N}^{18}\text{O}$  display a relative abundance of  $3.64 \times 10^{-3}$ ,  $3.64 \times 10^{-3}$  and  $1.99 \times 10^{-3} \text{ mol mol}^{-1}$ , respectively (Kantnerová et al., 2019). This corresponds to less than  $1 \text{ nmol mol}^{-1}$  for  $^{14}\text{N}^{14}\text{N}^{18}\text{O}$  in ambient amount fraction  $\text{N}_2\text{O}$  reference materials. High-sensitivity instrumentation is required to precisely quantify the low amount fractions of the minor  $\text{N}_2\text{O}$  isotopocules (Griffith et al., 2012).

Recent advances in spectroscopic instrumentation have improved  $\text{N}_2\text{O}$  isotopocule quantification. Cavity ring-down spectroscopy (CRDS) has been applied to the real-time amount fraction and isotopic composition measurements of  $\text{N}_2\text{O}$  in ambient air. In the laboratory, this technique has demonstrated a precision (Allan deviation) of  $< 0.05 \text{ nmol mol}^{-1}$  for  $\text{N}_2\text{O}$  amount fraction and  $< 0.5 \text{ ‰}$  for  $\delta^{15}\text{N}^\alpha$ ,  $\delta^{15}\text{N}^\beta$  and  $\delta^{18}\text{O}-\text{N}_2\text{O}$  with 5 min averaging times (Harris et al., 2020; Erler et al., 2015). This precision is comparable with off-axis integrated cavity output spectroscopy (OA-ICOS) analysis (van der Schoot et al., 2015), which demonstrated in-field analytical precisions of  $< 0.07 \text{ nmol mol}^{-1}$ , and superior to the standard technique for  $\text{N}_2\text{O}$  amount fraction, gas chromatography with electron capture detector (GC-ECD) (Lopez et al., 2015). For  $\delta^{15}\text{N}^\alpha$  and  $\delta^{15}\text{N}^\beta$  the performance of CRDS is approaching IRMS (Ostrom et al., 2018).

Advances in instrumentation must be coupled with advances in high-precision isotope ratio reference materials, particularly for the calibration of the site-specific isotopic composition  $\delta^{15}\text{N}^\alpha$  and  $\delta^{15}\text{N}^\beta$ , to achieve accurate calibra-

tion of the small variations in isotopocule abundances observable in ambient  $\text{N}_2\text{O}$  (Ostrom and Ostrom, 2017). Isotope ratio reference materials are required which span the full range expected in ambient  $\text{N}_2\text{O}$  samples and covered by the World Metrological Organisation (WMO) scale ( $260\text{--}370 \text{ nmol mol}^{-1}$ ). The currently available pure  $\text{N}_2\text{O}$  secondary reference materials USG5S1 and USG5S2 (Reston Stable Isotope Laboratory) differ in their  $\delta^{15}\text{N}^\alpha$  and  $\delta^{15}\text{N}^\beta$  values but span a narrow range of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values ( $< 1 \text{ ‰}$ ), limiting applicability for use as calibration materials (Ostrom et al., 2018). The availability of  $\text{N}_2\text{O}$  isotope ratio reference materials has the potential to improve calibration of analytical instrumentation and increase interlaboratory agreement.

Crucial for the development of reference materials is the stability of the  $\text{N}_2\text{O}$  composition and isotope ratio. Ganesan et al. (2013) reported no significant drift in amount fraction for a  $325 \text{ nmol mol}^{-1}$   $\text{N}_2\text{O}$  in compressed air reference material in an aluminium cylinder (Scott Marrin, now Praxair) over a 3-year period. Similar findings were reported by Lushozi et al. (2019), but no study is available yet on the stability of the  $\text{N}_2\text{O}$  isotope ratio at ambient amount fractions. In addition, improvements in the preparation and availability of  $\text{N}_2\text{O}$  reference materials at ambient amount fraction is required to achieve the challenging WMO-GAW compatibility goals (Brewer et al., 2019b).

We present work on the development of  $\text{N}_2\text{O}$  reference materials for underpinning atmospheric composition and isotope ratio with uncertainties targeting the WMO-GAW compatibility goals. We describe the characterisation of precision, repeatability and drift of a CRDS laser spectrometer. We also present work on all elements of the preparation process such as gravimetry, purity analysis, validation, stability, passivation of storage media and matrix effects. These developments are extended to multi-component mixtures of  $\text{N}_2\text{O}$  with other greenhouse gases ( $\text{CO}_2$ ,  $\text{CH}_4$  and  $\text{CO}$ ) in a synthetic air matrix containing atmospheric amount fractions of argon, oxygen and nitrogen, as required for calibration of spectroscopic instruments for atmospheric measurements.

## 2 Experimental

### 2.1 Gravimetric preparation of primary reference materials (PRMs)

All primary reference materials (PRMs) were prepared by gravimetry, in accordance with ISO 6142-1:2015, in 10 L aluminium cylinders (Luxfer) with a range of outlet diaphragm valves (Ceodeux): BS341 no. 14, DIN 477 no. 1 and DIN 447 no. 8. The cylinders have SGS™ internal surface (Luxfer) or were treated internally with a range of proprietary passivation processes including SpectraSeal™ (BOC), Megalong™ and Aculife IV/III™ (Air Liquide). Cylinders were evacuated using an oil-free pump (Scrollvac SC15D,

Leybold Vacuum) and turbo molecular pump with magnetic bearing (Turbovac 340M, Leybold Vacuum) to a pressure of  $< 3 \times 10^{-7}$  mbar. Synthetic air was gravimetrically produced by blending argon (BIP+, Air Products), oxygen (N6.0, BOC) and nitrogen (BIP+, Air Products) to match atmospheric amount fractions (0.94, 20.96 and  $78.10 \text{ cmol mol}^{-1}$ , respectively) (Tohjima et al., 2009). The purity of the matrix gas was assessed for amount fraction of  $\text{N}_2\text{O}$  as detailed below.

The reference materials were produced gravimetrically by the addition of  $\text{N}_2\text{O}$  (5.0, Air Liquide) via a transfer vessel (capped 1/4 in. diameter tube, with a nominal volume of 45 mL, Swagelok, electro-polished stainless steel). The transfer vessel was weighed against a tare vessel matched for size and shape before and after  $\text{N}_2\text{O}$  addition into the evacuated cylinder (Mettler-Toledo XP2004S,  $\pm 0.3 \text{ mg}$  weighing uncertainty). The  $\text{N}_2\text{O}$  was introduced into the evacuated cylinder through expansion to vacuum. Filling via a transfer vessel was used to achieve low uncertainty on the addition of small masses. Nitrogen was added via direct addition to the cylinder, through purged 1/16 in. tubing (Swagelok, electro-polished stainless steel) to produce reference materials with nominal  $\text{N}_2\text{O}$  amount fractions of  $500 \mu\text{mol mol}^{-1}$ . The mass of nitrogen added was determined by weighing of the cylinder before and after addition against a tare cylinder on an automatic weighing facility, developed by the Korean Research Institute for Standards and Science (KRISS) (Mettler-Toledo XP26003L,  $\pm 3 \text{ mg}$  weighing uncertainty) (Lim et al., 2017).

Atmospheric amount fraction reference materials in the range 300–360  $\text{nmol mol}^{-1}$   $\text{N}_2\text{O}$  were prepared by the addition of  $500 \mu\text{mol mol}^{-1}$   $\text{N}_2\text{O}$  reference materials via a transfer vessel into an evacuated 10 L cylinder and dilution with synthetic air by the direct addition of argon, oxygen and nitrogen at atmospheric amount fractions (Tohjima et al., 2009). The cylinder was weighed before and after each matrix gas addition. Argon was added to the cylinder from a 30 % argon-in-nitrogen pre-mixture cylinder.

Gravimetric uncertainties associated with the preparation of  $\text{N}_2\text{O}$  reference materials were calculated according to the *Guide to the Expression of Uncertainty in Measurement* (BIPM et al., 2008). The gravimetric uncertainty associated with the  $\text{N}_2\text{O}$  amount fraction in the prepared mixtures is determined by the software package gravcalc2 (Brown, 2009), which combines the uncertainty in relative molar mass, the uncertainty in the mass of the parent mixture addition, and the uncertainty in the amount fraction of  $\text{N}_2\text{O}$  in the parent mixture according to ISO 6142 (ISO, 2015).

The total gravimetric uncertainty of the reference material combines gravimetric uncertainty from the uncertainty in mass added in each addition with uncertainty in the amount of  $\text{N}_2\text{O}$  in the matrix gases. For low amount fraction reference materials, the total uncertainty can be dominated by uncertainty in accurately quantifying trace amount fractions of the compound of interest within the matrix gases. As such, a careful analysis of the trace  $\text{N}_2\text{O}$  in the matrix gases is re-

quired. The amount fraction of  $\text{N}_2\text{O}$  in the matrix was determined by standard addition of a  $325 \text{ nmol mol}^{-1}$  reference material into a synthetic air prepared with the same argon-in-nitrogen premix and the same oxygen and nitrogen cylinders. This method, as described in Hill-Pearce et al. (2018), determined  $0.75 \pm 0.09 \text{ nmol mol}^{-1}$   $\text{N}_2\text{O}$  in the synthetic air matrix.<sup>1</sup> The zero offset of the analyser was determined by removal of trace  $\text{N}_2\text{O}$  in the matrix gas (SAES Getter/Entegris PS15 GC-50).

## 2.2 Preparation of reference materials for studying the influence of pressure on composition

Aluminium cylinders (0.85 L, Luxfer) were filled to 30–35 bar with a  $325 \text{ nmol mol}^{-1}$   $\text{N}_2\text{O}$  in synthetic air reference material. Within 1 week of filling, the cylinders were sampled at an excess flow rate of  $0.5 \text{ L min}^{-1}$  into the CRDS analyser (Picarro G5131-*i*), until the cylinders were at ambient pressure. The cylinder pressure was monitored during sampling with a pressure transducer (Omega PXM 319), and data were recorded via LabVIEW.

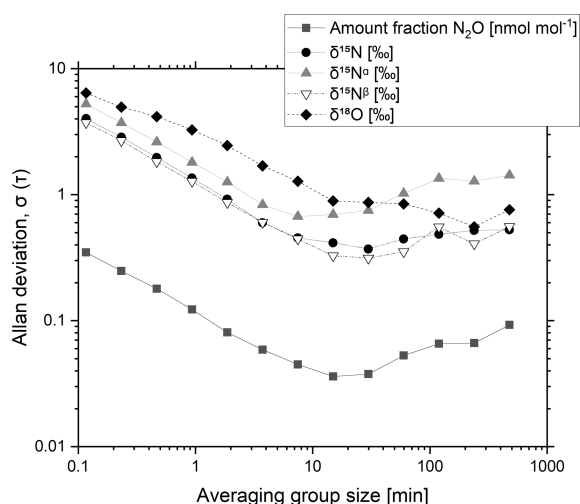
In a second approach,  $325 \text{ nmol mol}^{-1}$   $\text{N}_2\text{O}$  in synthetic air reference materials were prepared from the same  $500 \mu\text{mol mol}^{-1}$   $\text{N}_2\text{O}$  reference material in 10 L cylinders with three different commercially available internal passivation processes. The cylinders were sampled into the CRDS analyser following the same procedure as for the 0.85 L cylinders.

## 2.3 Analytical methods

A cavity ring-down spectrometer (Picarro G5131-*i*) was used for the analysis of the ambient amount fraction  $\text{N}_2\text{O}$  mixtures. The instrument allows simultaneous monitoring of  $\text{N}_2\text{O}$  amount fraction and isotopic composition through measurement of the bulk  $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}$ , and site-specific  $\delta^{15}\text{N}^\alpha$  and  $\delta^{15}\text{N}^\beta$ . Bulk  $\delta^{15}\text{N}$  is calculated as the average of the site-specific  $\delta^{15}\text{N}^\alpha$  and  $\delta^{15}\text{N}^\beta$ . The instrument comprises an internal pump and a critical orifice to reduce the gas flow into the cavity of the analyser. An excess flow was provided to the instrument ( $0.5 \text{ L min}^{-1}$ ), and the excess was vented to the atmosphere to ensure stable (atmospheric) inlet pressure and no contamination with ambient air.

Analysis of the amount fraction of argon in the 30 % argon-in-nitrogen pre-mixture cylinders was performed by gas chromatography with a thermal conductivity detector (GC-TCD; Agilent 6890) using a capillary column (Molsieve 5A,  $30 \text{ m} \times 0.53 \text{ mm} \times 0.50 \mu\text{m}$ ) operated isothermally at  $30 \pm 1^\circ\text{C}$ .

<sup>1</sup>There is ongoing research to improve the accuracy of the quantification of trace  $\text{N}_2\text{O}$  in the synthetic air matrix which may form the basis of a future publication.



**Figure 1.** Typical Allan deviation plot for a CRDS  $\text{N}_2\text{O}$  isotope analyser (G5131-*i*) as a function of averaging time for a  $325 \text{ nmol mol}^{-1}$   $\text{N}_2\text{O}$  reference material.

### 3 Characterisation of the CRDS

#### 3.1 Analytical uncertainty

##### Allan deviation

A  $325 \text{ nmol mol}^{-1}$   $\text{N}_2\text{O}$ -in-synthetic-air reference material was analysed continuously over 25 h, collecting temporal trends of  $\text{N}_2\text{O}$  amount fractions and isotope delta values. The Allan deviation was calculated to assess the optimum averaging time and the maximum precision (Fig. 1).

The Allan deviation initially decreases with an increase in the averaging time and reaches a minimum for  $\text{N}_2\text{O}$  amount fractions ( $0.036 \text{ nmol mol}^{-1}$ ) and delta values  $\delta^{15}\text{N}$  ( $0.37 \text{ ‰}$ ),  $\delta^{15}\text{N}^\alpha$  ( $0.67 \text{ ‰}$ ),  $\delta^{15}\text{N}^\beta$  ( $0.33 \text{ ‰}$ ) and  $\delta^{18}\text{O}$  ( $0.89 \text{ ‰}$ ) for averaging times of around 15 min. For longer averaging times, an increase in the Allan deviation is shown and likely to be a result of analyser drift. An averaging time of 10 min was adopted to ensure both minimal uncertainty for comparing the reference gas to a sample gas and efficient use of the reference material. Achieved precisions for  $\text{N}_2\text{O}$  amount fraction and isotope ratios are in agreement with the typical precisions reported by Picarro in the instrument specification of  $< 0.05 \text{ nmol mol}^{-1}$   $\text{N}_2\text{O}$  and  $< 0.7 \text{ ‰}$  for  $\delta^{15}\text{N}$ ,  $\delta^{15}\text{N}^\alpha$ ,  $\delta^{15}\text{N}^\beta$  and  $\delta^{18}\text{O}$  for a 10 min averaging period (Picarro, 2017).

#### 3.2 Characterisation of the CRDS for reported delta values with $\text{N}_2\text{O}$ amount fraction

The characterisation of the CRDS for reported delta values with  $\text{N}_2\text{O}$  amount fraction was assessed with both statically and dynamically generated reference materials. Dynamic reference materials were produced in the amount fraction range

$150\text{--}1100 \text{ nmol mol}^{-1}$  by dilution from a  $320 \text{ nmol mol}^{-1}$   $\text{N}_2\text{O}$ -in-synthetic-air reference material with synthetic air using a dynamic dilution device comprising one diluent and three standard critical flow orifices (Hill-Pearce et al., 2018). The static and dynamic reference materials were generated alternately for four iterations, with synthetic air measured between each set. Due to the large number of measurements recorded, a reduced sampling time of 5 min was adopted for each measurement interval, resulting in a slightly lower standard deviation of  $0.03 \text{ nmol mol}^{-1}$  for amount fractions.

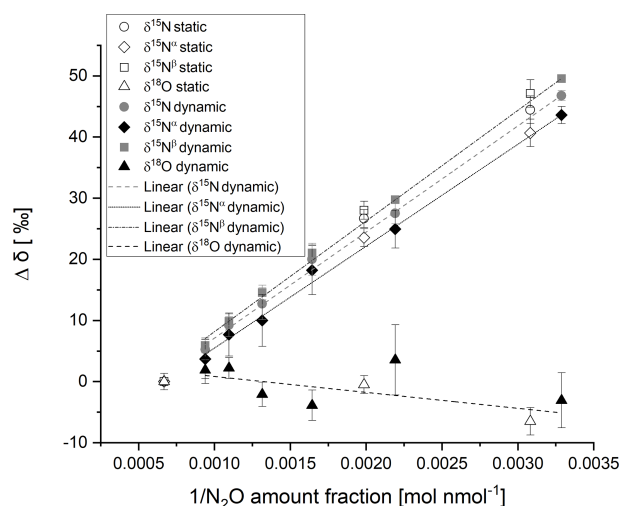
#### 3.3 Delta $^{15}\text{N}$

The  $\delta^{15}\text{N}$  values analysed by the G5131-*i* analyser were recorded for each static and dynamic reference material for four repetitions of 5 min. The mean value of the stable response was calculated. The change in reported delta value with amount fraction was assessed and found to vary with a linear function with respect to the reciprocal of  $\text{N}_2\text{O}$  amount fraction as reported by Harris et al. (2020) for the same CRDS model, with a different year of manufacture. Figure 2 shows the CRDS analyser response to  $\delta^{15}\text{N}$  for static and dynamic reference materials prepared from the same pure  $\text{N}_2\text{O}$  source in the amount fraction range of  $300\text{--}1500 \text{ nmol mol}^{-1}$ . Winther et al. (2018) reported the same trend for dependence of reported  $\delta^{15}\text{N}$  on  $\text{N}_2\text{O}$  amount fraction, attributing the amount fraction dependence to offsets in the measurement of  $^{14}\text{N}^{15}\text{N}^{16}\text{O}$  and  $^{15}\text{N}^{14}\text{N}^{16}\text{O}$ . The agreement between static and dynamic reference materials is discussed in the results section.

#### 3.4 Delta $^{18}\text{O}$

Similarly, the  $\delta^{18}\text{O}$  channel response was recorded for static and dynamic reference materials. No variation in reported  $\delta^{18}\text{O}$  was observed between the analyser response of the static and dynamic reference materials beyond the measurement uncertainty for  $\text{N}_2\text{O}$  amount fractions over the range of  $300\text{--}1500 \text{ nmol mol}^{-1}$  (Fig. 2). Harris et al. (2020) reported a linear increase in  $\delta^{18}\text{O}$  of  $\sim 4 \text{ ‰}$  with the reciprocal of  $\text{N}_2\text{O}$  amount fraction over a similar  $\text{N}_2\text{O}$  amount fraction range for the same model analyser (2015 model) but stated that the change in delta value with amount fraction might vary between different analysers of the same model.

The agreement in  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  between static and dynamic reference materials (shown in Fig. 2) indicates minimal fractionation of isotopocules on dilution through a critical flow orifice-based dynamic system or on production of the reference materials by filling through an intermediate vessel and dilution. No variation in reported delta values beyond the measurement uncertainty for  $\text{N}_2\text{O}$  amount fractions over the range of  $300\text{--}1500 \text{ nmol mol}^{-1}$  was observed between the analyser response of the static and dynamic reference materials (Fig. 2). However, the large uncertainty makes comparisons of the delta value between similar amount fractions



**Figure 2.** CRDS analyser response for  $\delta^{15}\text{N}$  (circles),  $\delta^{15}\text{N}^{\alpha}$  (diamonds),  $\delta^{15}\text{N}^{\beta}$  (squares) and  $\delta^{18}\text{O}$  (triangles) with the 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  $\text{nmol mol}^{-1}$ . Error bars represent the repeatability in per mille between the four repetitions of a 5 min average. The dotted and dashed lines represent the linear regression of dynamic reference materials for each isotopocule.

challenging. The uncertainty would be reduced by increasing the averaging time.

## 4 Results and discussion

### 4.1 Uncertainty in $\text{N}_2\text{O}$ amount fraction

Uncertainty in the amount fraction of  $\text{N}_2\text{O}$  in a reference material has several sources including uncertainty due to gravimetric preparation (weighing uncertainties), uncertainty in the purity of the gases used (e.g. amount fraction of  $\text{N}_2\text{O}$  in the matrix), cylinder effects such as adsorption of the gas molecules onto the walls of the cylinder and valve, uncertainties in amount fraction due to the stability of the gas reference material, and analytical precision of the measurement technique. Each uncertainty contribution is discussed below.

#### 4.1.1 Uncertainty and reproducibility in the amount fraction of reference materials due to gravimetric production

To assess the uncertainty in the amount fraction from production of  $\text{N}_2\text{O}$  reference materials, eight reference materials were produced by two separate operators from two separate 500  $\mu\text{mol mol}^{-1}$   $\text{N}_2\text{O}$ -in-nitrogen reference materials but the same matrix gases and pure  $\text{N}_2\text{O}$  source. Four of the reference materials were produced at 337  $\text{nmol mol}^{-1}$  and four were produced at 326  $\text{nmol mol}^{-1}$ .

The combined contribution to the uncertainty due to gravimetry and purity of the components for the ambient amount fraction  $\text{N}_2\text{O}$  in synthetic air reference materials produced, as detailed above, is 0.08 % ( $k = 2$ ) 0.28  $\text{nmol mol}^{-1}$ . This uncertainty is within the WMO-GAW extended compatibility goals of  $\pm 0.3 \text{ nmol mol}^{-1}$ .

The sources of uncertainty and their contribution to the combined gravimetric uncertainty ( $k = 2$ ) are detailed in Table 1. The uncertainty is dominated by the 0.3 mg uncertainty on the mass of  $\text{N}_2\text{O}$  added in the indirect transfer vessel additions to prepare the 500  $\mu\text{mol mol}^{-1}$   $\text{N}_2\text{O}$  intermediate and 325  $\text{nmol mol}^{-1}$  reference material.

#### 4.1.2 Uncertainty in the amount fraction of reference materials for validation measurements

The amount fraction of  $\text{N}_2\text{O}$  in a prepared mixture was validated through comparison to National Physical Laboratory (NPL) in-house PRMs. The PRMs used for validation were derived from different parent mixtures which are, where possible, produced by different operators in order to provide a greater degree of independence from errors in amount fraction of a parent mixture. In-house PRMs and unknown mixtures were measured alternately for 10 min periods. To determine the certified amount fraction of the unknown mixture ( $Y$ ), the gravimetric amount fraction of the in-house PRM ( $X_1$ ) is multiplied by the mean ratio in analyser response ( $X_2$ ), as shown in Eq. 3. Four repetitions provide four distinct measurements of this ratio.

$$Y = f(X_1 X_2) \quad (3)$$

Input quantities ( $X_1, X_2$ ) have associated uncertainties that are combined to give a combined standard uncertainty for the measurement of  $\text{N}_2\text{O}$  amount fraction derived from each validation. The standard uncertainty associated with the gravimetric amount fraction  $u(x_1)$  is provided by the software Gravcalc2 (Brown, 2009). The standard uncertainty in the ratio measurement  $u(x_2)$  is the standard deviation of the mean of the four ratios. Both input quantities were modelled with normal distributions, and sensitivity coefficients ( $c_1, c_2$ ) were taken as the partial derivatives with respect to each input quantity.

$$c_1 = \frac{\partial f}{\partial x_1} = x_2 \quad (4)$$

$$c_2 = \frac{\partial f}{\partial x_2} = x_1 \quad (5)$$

Standard uncertainties were multiplied by respective sensitivity coefficients and combined in quadrature to provide a combined standard uncertainty for each validation. To combine the standard uncertainty from each validation, a sensitivity coefficient ( $c = \frac{1}{3}$ ) was applied to each, providing equal weighting to the final analytical uncertainty.

**Table 1.** Sources of uncertainty and their relative contribution to the combined expanded uncertainty ( $k = 2$ ) for the preparation of a  $325 \text{ nmol mol}^{-1}$   $\text{N}_2\text{O}$ -in-synthetic-air reference material.

Source of uncertainty	Contribution to the gravimetric expanded uncertainty (%)
Mass of $\text{N}_2\text{O}$ : indirect transfer vessel additions	72
Mass of matrix gas (Ar, $\text{O}_2$ and $\text{N}_2$ ): direct additions	1
Relative molar masses	2
$\text{N}_2\text{O}$ impurity in pure Ar	Negligible
$\text{N}_2\text{O}$ impurity in pure $\text{O}_2$	5
$\text{N}_2\text{O}$ impurity in pure $\text{N}_2$	17
Matrix gas impurity	2

Expanded analytical uncertainties of 0.07 % ( $k = 2$ ) were demonstrated using this approach. The final combined expanded uncertainty contains the contributions from gravimetric 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  $0.36 \text{ nmol mol}^{-1}$ .

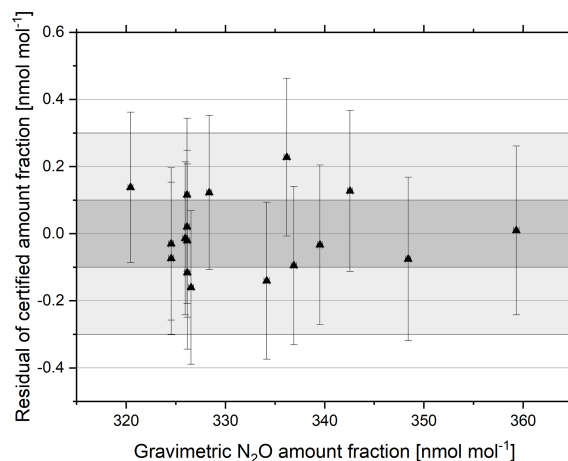
#### 4.1.3 Reproducibility of reference gas production

The WMO-GAW has published an amount fraction range of  $325\text{--}335 \text{ nmol mol}^{-1}$  representative of the unpolluted troposphere, while the range of  $\text{N}_2\text{O}$  amount fractions covered by the WMO scale is somewhat broader ( $260\text{--}370 \text{ nmol mol}^{-1}$ ). The linearity of the CRDS analyser response to changes in amount fraction and the influence of amount fraction on apparent isotope delta values were investigated in the amount fraction range  $320\text{--}360 \text{ nmol mol}^{-1}$  using a set of gravimetric prepared reference materials. The lower boundary for amount fraction was defined by the CRDS analyser (Picarro G5131-*i*)  $\text{N}_2\text{O}$  amount fraction range for measurement of delta values.

The gravimetrically prepared reference materials were validated against a reference material prepared at  $325 \text{ nmol mol}^{-1}$ . Figure 3 shows the residual of the linear regression of the certified amount fraction as a function of the gravimetric amount fraction for each reference material. The deviation from the linear regression does not show any obvious trend with gravimetric amount fraction and falls within the extended WMO-GAW compatibility goal for all reference materials of  $\pm 0.3 \text{ nmol mol}^{-1}$ , demonstrating the suitability and linearity of the CRDS analytical technique for certifying  $\text{N}_2\text{O}$  reference materials in this range and the reproducibility of the reference materials produced.

#### 4.2 Stability of $\text{N}_2\text{O}$ reference materials for amount fraction and isotopic composition

The demonstration of stability is important to achieve measurements of amount fraction and isotope ratio in the field with low uncertainty and also safeguards against drift in mea-

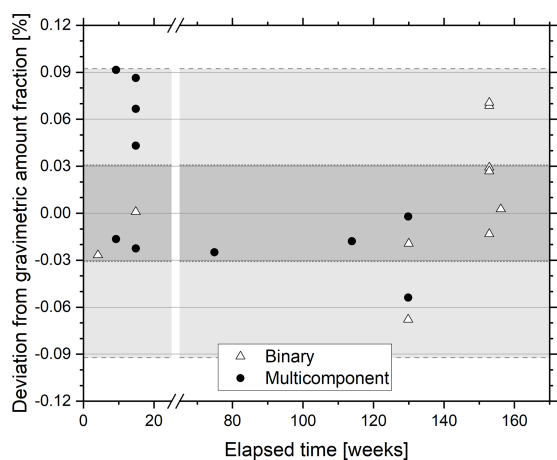


**Figure 3.** Residuals of the linear regression of the certified amount fraction as a function of the gravimetric amount fraction for  $\text{N}_2\text{O}$  reference materials in the amount fraction range  $320\text{--}360 \text{ nmol mol}^{-1}$  certified against a  $325 \text{ nmol mol}^{-1}$  reference material. The WMO-GAW Data Quality Objective (DQO) ( $\pm 0.1 \text{ nmol mol}^{-1}$ ) is indicated within the dark grey shading, and the extended DQO ( $\pm 0.3 \text{ nmol mol}^{-1}$ ) is indicated within the lighter grey shading. Error bars represent the combined ( $k = 2$ ) analytical ( $y$  axis) and gravimetric ( $x$  axis, not visible) uncertainty.

surements as a result of changes in the reference material. The effect of storage of reference materials of  $\text{N}_2\text{O}$  in synthetic air, with and without other greenhouse gas components in cylinders with different surface treatments, was investigated.

#### 4.2.1 Stability of reference materials for extended storage times

The stability of a  $325 \text{ nmol mol}^{-1}$   $\text{N}_2\text{O}$ -in-synthetic-air reference material was assessed over a 3-year period by comparison with freshly prepared binary reference materials comprising  $\text{N}_2\text{O}$  in synthetic air prepared in the amount fraction range  $300\text{--}360 \text{ nmol mol}^{-1}$  and reference materials containing  $\text{N}_2\text{O}$  in synthetic air and trace gases  $\text{CO}_2$  ( $290\text{--}$



**Figure 4.** Percentage difference between gravimetric and certified  $\text{N}_2\text{O}$  amount fraction of a  $325 \text{ nmol mol}^{-1}$  reference material as a function of storage time. The reference material was certified against freshly prepared  $\text{N}_2\text{O}$  reference materials in the amount fraction range  $320\text{--}360 \text{ nmol mol}^{-1}$ . The freshly prepared reference materials were either diluted in synthetic air (open triangle) or contained other greenhouse gases (filled circle). The WMO-GAW compatibility goal is indicated on the plot in dark grey shading, and the extended compatibility goal is indicated by lighter grey shading.

$800 \mu\text{mol mol}^{-1}$ ),  $\text{CH}_4$  ( $1.8\text{--}3.0 \mu\text{mol mol}^{-1}$ ) and  $\text{CO}$  ( $0.07\text{--}1.00 \mu\text{mol mol}^{-1}$ ) (Fig. 4). All validations within this period demonstrated agreement of amount fraction within the extended WMO compatibility goal of  $\pm 0.3 \text{ nmol mol}^{-1}$  and thus demonstrate the stability of the  $325 \text{ nmol mol}^{-1}$   $\text{N}_2\text{O}$  reference material. The linearity of response of the CRDS in this amount fraction range is detailed above. No clear distinction between agreement of validation of  $\text{N}_2\text{O}$  in synthetic air and  $\text{N}_2\text{O}$  within multi-component gas mixtures was observed, suggesting minimal interference of these gases on the CRDS analyser response to the total reported amount fraction of  $\text{N}_2\text{O}$ . The findings show agreement with those of Erler et al. (2015) and Harris et al. (2020) where no significant effect of  $\text{CH}_4$ ,  $\text{CO}$  or  $\text{CO}_2$  at atmospheric amount fraction was found on the reported  $\text{N}_2\text{O}$  amount fraction. In contrast, the authors reported a strong effect of  $\text{O}_2$  amount fractions on apparent  $\text{N}_2\text{O}$  amount fraction, which they attribute to changes in the pressure broadening. Similar effects on the  $\text{CO}_2$  and  $\text{CH}_4$  reported amount fractions with changing matrix composition when using CRDS have been observed earlier by Nara et al. (2012).

#### 4.2.2 Stability of reference materials with reducing cylinder pressure

Figure 5 shows 5 min averages for amount fraction,  $\delta^{15}\text{N}^\alpha$ ,  $\delta^{15}\text{N}^\beta$  and  $\delta^{18}\text{O}$  with reducing pressure. No statistically relevant trend for  $\text{N}_2\text{O}$  amount fraction or delta value was observed as the cylinder pressure decreases. The experiment was conducted over 1.5 h. During venting of the cylinder

through the analyser, a small excess flow rate of between  $0.3$  and  $0.5 \text{ L min}^{-1}$  was maintained to optimise the pressure through the analyser, reduce back diffusion into the analyser and ensure thermodynamic effects do not occur. A drift correction was conducted on the  $\text{N}_2\text{O}$  amount fraction and isotope delta values through subtraction of analyser response against a linear regression of the  $\text{N}_2\text{O}$  parent cylinder analysed immediately before and after each of the  $0.85 \text{ L}$  cylinders. There is good agreement within the standard deviation of the 5 min responses between the amount fraction and delta values of the four cylinders and the parent cylinder. The data indicate that adsorption onto cylinder walls causes negligible changes in amount fraction and delta value with pressure. The findings show agreement with Lushozi et al. (2019) and Brewer et al. (2019b) where no adsorption losses were identified in cylinder-to-cylinder transfer of a  $330 \text{ nmol mol}^{-1}$  reference material.

#### 4.2.3 Cylinder treatments for enhanced stability with pressure

Greenhouse gas reference materials are prepared at NPL in passivated cylinders to inhibit the adsorption of target components. While adsorption of  $\text{N}_2\text{O}$  is not expected to be as large as adsorption of  $\text{CO}_2$  (Brewer et al., 2019a), it is nevertheless of interest to investigate the effects of cylinder passivation.

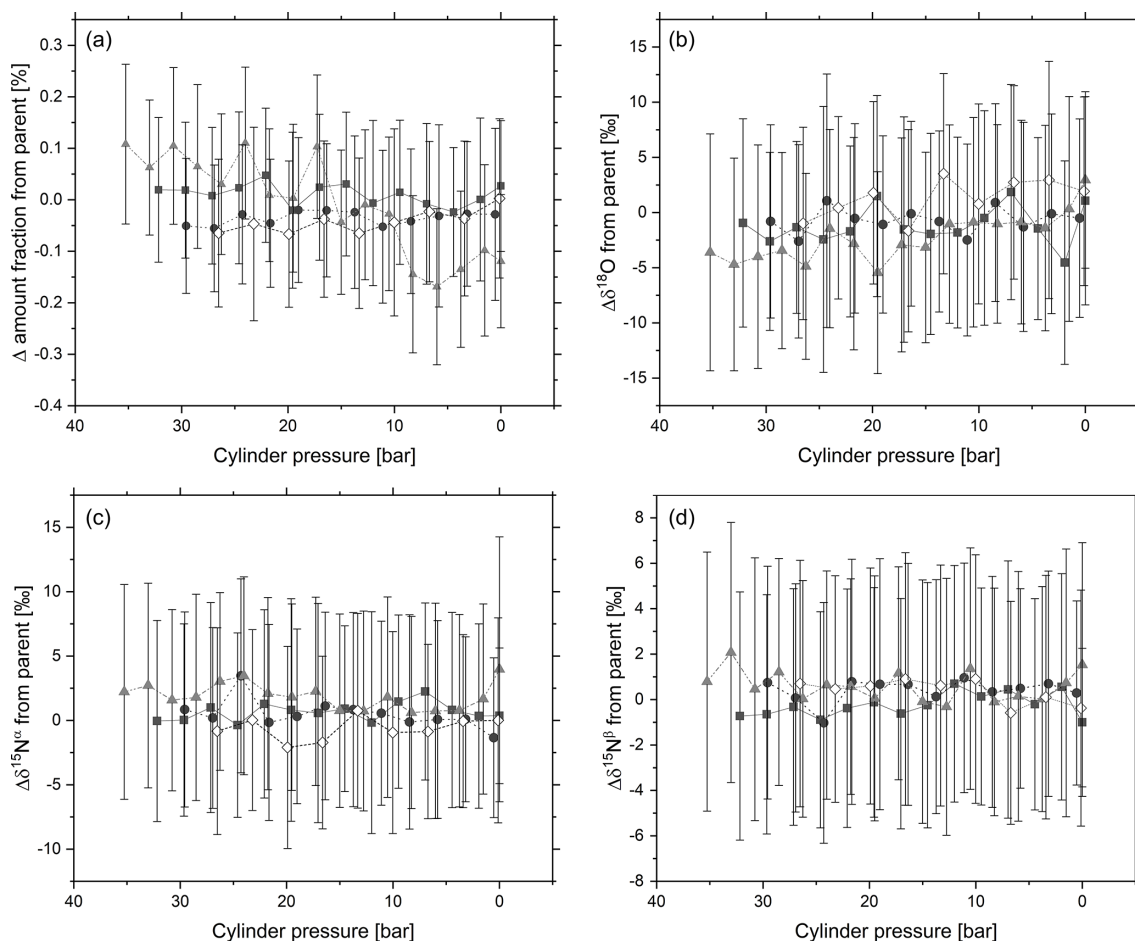
Figure 6 shows the 5 min average of the response of  $\text{N}_2\text{O}$  amount fraction with pressure relative to initial amount fraction for the three cylinders with different passivation processes. There is no difference in the reported  $\text{N}_2\text{O}$  amount fraction between the three passivation processes, with all stable to within  $0.05 \text{ nmol mol}^{-1}$ . The data demonstrate that the internal passivation process causes negligible changes to the  $\text{N}_2\text{O}$  analyser response for amount fraction with changes in cylinder pressure. The water vapour content of similar mixtures in synthetic air was measured to be around  $0.5 \mu\text{mol mol}^{-1}$  (Hill-Pearce et al., 2018).

#### 4.3 Absence of fractionation effects for static mixture production

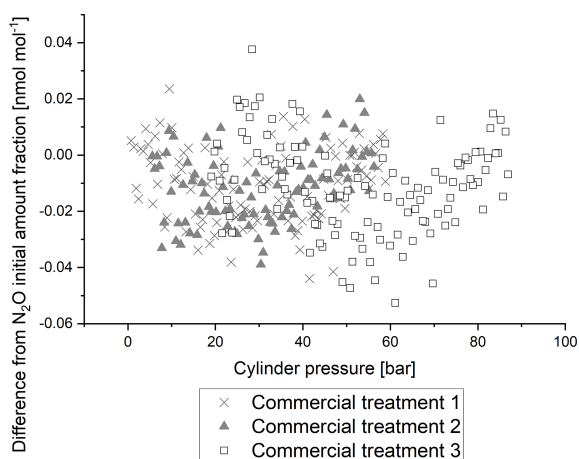
The effects of the production and storage of ambient amount fraction  $\text{N}_2\text{O}$  in synthetic air reference materials in cylinders on the reported amount fraction and delta value were compared to reported values for dynamic reference materials produced from the same pure  $\text{N}_2\text{O}$  source diluted with synthetic air (Fig. 7). Dynamic reference materials demonstrate reduced adsorption effects compared to static standards, particularly for low-amount-fraction reference materials (Platonov et al., 2018). Differences in reported delta value for static and dynamic standards of the same amount fraction would indicate fractionation events in either production method.

The generated dynamic reference materials were validated against static reference materials of a similar amount frac-





**Figure 5.** Temporal change in (a)  $\text{N}_2\text{O}$  amount fraction and delta values: (b)  $\delta^{18}\text{O}$ , (c)  $\delta^{15}\text{N}^\alpha$  and (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 5 min average of analyser response, and error bars represent 1 standard deviation across the 5 min average.



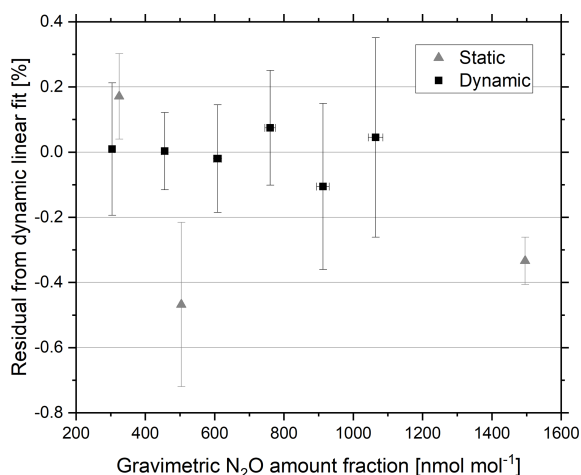
**Figure 6.** Difference from initial  $\text{N}_2\text{O}$  amount fraction with reducing cylinder pressure for three  $325 \text{ nmol mol}^{-1}$   $\text{N}_2\text{O}$ -in-synthetic-air reference materials produced in 10 L cylinders with three different commercially available cylinder passivation processes.

tion. The residuals of the static and dynamic linear regression of analyser response as a function of increasing gravimetric amount fraction of dynamic reference materials are shown in Fig. 7. Agreement within 0.05 % ( $0.16 \text{ nmol mol}^{-1}$ ) was achieved between the static and dynamic reference materials at  $325 \text{ nmol mol}^{-1}$ .

#### 4.4 Comparison with existing scales

Two comparisons of amount fraction were carried out between NPL and the WMO-GAW World Calibration Centre (WCC-Empa) on reference materials prepared at Empa and NPL.

In a first approach, five reference materials were prepared by Empa containing  $\text{N}_2\text{O}$  in the amount fraction range  $290\text{--}370 \text{ nmol mol}^{-1}$  and certified against reference materials on the WMO-X2006A calibration scale (Hall et al., 2007; NOAA/ESRL, 2011) via quantum cascade laser absorption spectroscopy (QCLAS, model: QC-TILDAS-CS,  $2200 \text{ cm}^{-1}$ , Aerodyne Inc., USA). The Empa reference mate-



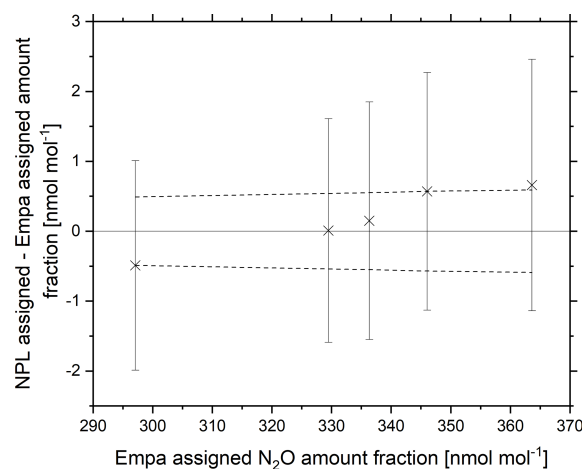
**Figure 7.** Residuals from the linear regression of analyser response with increasing gravimetric amount fraction of the dynamic reference materials. Static (triangles) and dynamic (squares) reference materials in the amount fraction range 300–1500 nmol mol<sup>-1</sup> N<sub>2</sub>O in synthetic air. Error bars represent the gravimetric uncertainty ( $k = 2$ ) ( $x$  axis) and the percent reproducibility between the four repetitions of a 5 min average ( $y$  axis).

rials contained greenhouse and reactive gas components CO<sub>2</sub> (360–800 μmol mol<sup>-1</sup>), CH<sub>4</sub> (1.7–3.2 μmol mol<sup>-1</sup>) and CO (120–560 nmol mol<sup>-1</sup>). The reference materials were validated over a period of 6 months prior to analysis at NPL and were re-validated afterwards at Empa with a linear interpolation applied to account for any drift in amount fraction.

The reference materials were certified at NPL via CRDS against NPL in-house PRMs static reference materials in the amount fraction range of 325–360 nmol mol<sup>-1</sup>. Each sample was averaged across four 10 min repetitions. Agreement within the WMO-GAW compatibility goal was achieved for amount fractions at 330 nmol mol<sup>-1</sup> (Fig. 8) and within the extended WMO-GAW compatibility goal at 337 nmol mol<sup>-1</sup>. Reference materials with amount fractions within the range 295–345 nmol mol<sup>-1</sup> were verified within the experimental extended combined standard uncertainty ( $k = 2$ ) for NPL certified amount fraction. A trend was observed with lower NPL amount fractions certifying lower and higher NPL amount fractions certifying higher.

In a second approach, a 325 nmol mol<sup>-1</sup> N<sub>2</sub>O-in-synthetic-air reference material containing 526 nmol mol<sup>-1</sup> CO was prepared at NPL using the method described above and analysed at the World Calibration Centre (WCC-Empa) against NOAA/GMD reference materials on the WMO-X2006A calibration scale. Validations were performed via quantum cascade laser absorption spectroscopy (QCLAS, model: QC-TILDAS-CS, 2200 cm<sup>-1</sup>, Aerodyne Inc., USA).

Agreement within the combined gravimetric uncertainty ( $k = 2$ ) was achieved for the 325 nmol mol<sup>-1</sup> reference material (Fig. 9). The uncertainty in the analytical amount fraction certified by Empa combines uncertainty contributions from



**Figure 8.** Certified NPL amount fraction minus the certified Empa amount fraction of five N<sub>2</sub>O reference materials in the range 290–370 nmol mol<sup>-1</sup> (crosses). Error bars represent the extended combined standard uncertainty ( $k = 2$ ) for NPL certified amount fraction. The Empa certified amount fraction is marked by a solid line at  $y = 0$ , and dashed lines represent the Empa measurement uncertainty.

traceability to the NOAA scale, scale propagation and repeatability of the analytical system from analyser drift and pressure changes. For the Aerodyne analyser used in the comparison to validate the 325 nmol mol<sup>-1</sup> N<sub>2</sub>O reference material, the sources of uncertainty were combined to the combined standard uncertainty ( $u_{\text{N}_2\text{O}}$ ) as shown in Eq. (6).

$$u_{\text{N}_2\text{O}} = \left[ \left( 0.06 \text{ nmol mol}^{-1} \right)^2 + \left( 8.13 \times 10^{-4} \times c \right)^2 \right]^{1/2}, \quad (6)$$

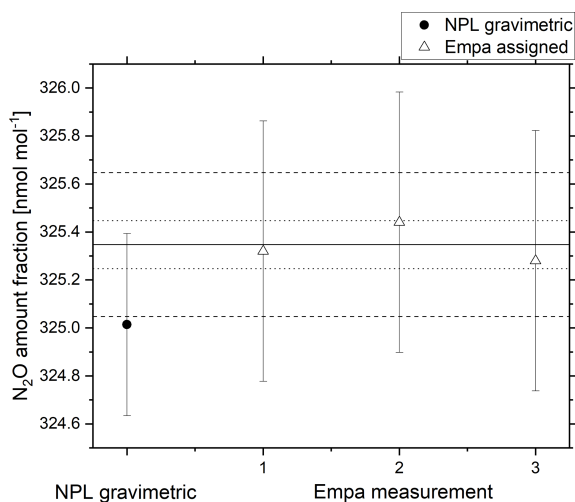
where  $c$  refers to the amount fraction of N<sub>2</sub>O in the reference material in nmol mol<sup>-1</sup>. The term  $8.13 \times 10^{-4}$  combines the uncertainty contributions from uncertainty in NOAA scale propagation and uncertainty due to pressure changes. The term  $0.06 \text{ nmol mol}^{-1}$  combines the concentration-independent uncertainty contributions from scale propagation and analyser drift.

The expanded uncertainty ( $U_{\text{N}_2\text{O}}$ ) ( $k = 2$ ) was determined from the standard uncertainty as shown in Eq. (7).

$$U_{\text{N}_2\text{O}} = 2 \times u_{\text{N}_2\text{O}} \quad (7)$$

## 5 Summary

N<sub>2</sub>O reference materials with low uncertainty in amount fraction and isotope ratio are required for atmospheric monitoring. The stability of these reference materials is crucial to achieve these low uncertainties. We have demonstrated the production of atmospheric amount fraction N<sub>2</sub>O reference materials with a gravimetric uncertainty within the WMO DQO for compatibility. Repeatability of the



**Figure 9.** Gravimetric amount fraction (filled circle) and amount fraction certified by Empa (open triangle) against the NOAA/GMD reference scale for a 325 nmol mol<sup>-1</sup> reference material. The solid black line represents the average value certified by Empa, the dotted lines represent the WMO-GAW DQO and the dashed lines represent the extended WMO-GAW DQO. Error bars represent the combined expanded uncertainty ( $k = 2$ ).

amount fraction of these reference materials was also within  $\pm 0.3$  nmol mol<sup>-1</sup>. Gravimetry is the largest source of uncertainty for these reference materials; reducing the uncertainty further would require the use of lower uncertainty balances for the indirect transfer of N<sub>2</sub>O. The effect of including other greenhouse gases at atmospheric amount fractions in the reference materials did not significantly affect the amount fraction recorded by CRDS. Agreement between static and dynamic reference materials of 0.05 % was achieved between reference materials at 325 nmol mol<sup>-1</sup>.

The amount fraction of a prepared N<sub>2</sub>O reference material in synthetic air with atmospheric amount fraction of CO was compared to internationally recognised scales (WMO-X2006A) and found to be in agreement within the gravimetric uncertainty. The amount fraction of reference materials produced at Empa was measured at NPL through comparison with NPL in-house PRMs. For a 330 nmol mol<sup>-1</sup>, the NPL- and Empa-assigned amount fraction values were in agreement within the WMO DQO for compatibility of  $\pm 0.1$  nmol mol<sup>-1</sup>, and the full range of PRMs (290–370 nmol mol<sup>-1</sup>) were in agreement within the measurement uncertainty of  $\pm 0.5$  nmol mol<sup>-1</sup>.

The change in amount fraction of the mixtures with decreasing cylinder pressure was shown to be smaller than measurement uncertainty regardless of cylinder passivation chemistry, and the stability of the mixtures over 3 years was within the expanded WMO-GAW DQO for compatibility. The isotopic composition of the reference mixtures was also demonstrated to be stable with reducing pressure, and agreement of delta values was achieved for static reference ma-

terials with dynamic dilutions within the analytical uncertainty. The next steps towards producing reference materials for source apportionment will be to produce reference materials with a range of isotopic values and to verify the assignment of their delta values.

*Data availability.* The data underlying the figures in this paper are available upon request to the corresponding author.

*Author contributions.* The standard preparation and analysis work was undertaken by REHP, AH, EMW and KC, with JM and CZ comparing reference materials to existing scales. All authors (REHP, AH, EMW, KC, SO'D, JM, CZ, DRW, PJB) contributed to discussions and writing of the paper.

*Competing interests.* The authors declare that they have no conflict of interest.

*Disclaimer.* Publisher's note: Copernicus Publications remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

*Financial support.* This research has been supported by the European Metrology Programme for Innovation and Research (EMPIR) programme co-financed by the participating states and the European Union's Horizon 2020 research and innovation programme.

*Review statement.* This paper was edited by Frank Keppler and reviewed by Stefan Persijn and one anonymous referee.

## References

- BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP, and OIML: Evaluation of measurement data – guide to the expression of uncertainty in measurement, International Bureau of Weights and Measures/Bureau International des Poids et Mesures, Working group 1 of the Joint Committee for Guides in Metrology (JCGM 100: 2008, GUM 1995 with minor corrections), available at: <http://www.bipm.org/utis/common/documents/jcgm/JCGM1002008E.pdf> (last access: 20 January 2021), 2008.
- Brewer, P. J., Brown, R. J., Mussell Webber, E. B., van Aswegen, S., Ward, M. K., Hill-Pearce, R. E., and Worton, D. R.: Breakthrough in Negating the Impact of Adsorption in Gas Reference Materials, *Anal. Chem.*, 91, 5310–5315, <https://doi.org/10.1021/acs.analchem.9b00175>, 2019a.
- Brewer, P. J., Kim, J. S., Lee, S., Tarasova, O. A., Viallon, J., Flores, E., Wielgosz, R. I., Shimosaka, T., Assonov, S., and Allison, C. E.: Advances in reference materials and measurement techniques for greenhouse gas atmospheric observations, *Metrologia*, 56, 034006, <https://doi.org/10.1088/1681-7575/ab1506>, 2019b.

- Brown, A.: GravCalc2 (version 2.3.0) User Guide, National Physical Laboratory (NPL), Teddington, UK, 2009.
- Denk, T. R., Mohn, J., Decock, C., Lewicka-Szczebak, D., Harris, E., Butterbach-Bahl, K., Kiese, R., and Wolf, B.: The nitrogen cycle: A review of isotope effects and isotope modeling approaches, *Soil Biol. Biochem.*, 105, 121–137, <https://doi.org/10.1016/j.soilbio.2016.11.015>, 2017.
- Erler, D. V., Duncan, T., Murray, R., Maher, D. T., Santos, I. R., Gatland, J., Mangion, P., and Eyre, B. D.: Applying cavity ring-down spectroscopy for the measurement of dissolved nitrous oxide concentrations and bulk nitrogen isotopic composition in aquatic systems: Correcting for interferences and field application, *Limnol. Oceanogr.-Meth.*, 13, 391–401, <https://doi.org/10.1002/lom3.10032>, 2015.
- Flores, E., Viallon, J., Moussay, P., Griffith, D. W., and Wielgosz, R. I.: Calibration strategies for FT-IR and other isotope ratio infrared spectrometer instruments for accurate  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  measurements of  $\text{CO}_2$  in air, *Anal. Chem.*, 89, 3648–3655, <https://doi.org/10.1021/acs.analchem.6b05063>, 2017.
- Ganesan, A. L., Chatterjee, A., Prinn, R. G., Harth, C. M., Salameh, P. K., Manning, A. J., Hall, B. D., Mühle, J., Meredith, L. K., Weiss, R. F., O'Doherty, S., and Young, D.: The variability of methane, nitrous oxide and sulfur hexafluoride in Northeast India, *Atmos. Chem. Phys.*, 13, 10633–10644, <https://doi.org/10.5194/acp-13-10633-2013>, 2013.
- Griffith, D. W. T., Deutscher, N. M., Caldow, C., Kettlewell, G., Riggensbach, M., and Hammer, S.: A Fourier transform infrared trace gas and isotope analyser for atmospheric applications, *Atmos. Meas. Tech.*, 5, 2481–2498, <https://doi.org/10.5194/amt-5-2481-2012>, 2012.
- Hall, B., Dutton, G., and Elkins, J.: The NOAA nitrous oxide standard scale for atmospheric observations, *J. Geophys. Res.-Atmos.*, 112, D09305, <https://doi.org/10.1029/2006JD007954>, 2007.
- Harris, S. J., Liisberg, J., Xia, L., Wei, J., Zeyer, K., Yu, L., Barthel, M., Wolf, B., Kelly, B. F. J., Cendón, D. I., Blunier, T., Six, J., and Mohn, J.:  $\text{N}_2\text{O}$  isotopocule measurements using laser spectroscopy: analyzer characterization and intercomparison, *Atmos. Meas. Tech.*, 13, 2797–2831, <https://doi.org/10.5194/amt-13-2797-2020>, 2020.
- Hill-Pearce, R. E., Resner, K. V., Worton, D. R., and Brewer, P. J.: Synthetic Zero Air Reference Material for High Accuracy Greenhouse Gas Measurements, *Anal. Chem.*, 91, 1974–1979, <https://doi.org/10.1021/acs.analchem.8b04297>, 2018.
- ISO: 6142-1: Gas analysis-Preparation of calibration gas mixtures – Part 1: Gravimetric method for Class I mixtures, Geneva, Switzerland, 2015.
- Kantnerová, K., Tuzson, B., Emmenegger, L., Bernasconi, S. M., and Mohn, J.: Quantifying isotopic signatures of  $\text{N}_2\text{O}$  using quantum cascade laser absorption spectroscopy, *CHIMIA*, 73, 232–238, <https://doi.org/10.2533/chimia.2019.232>, 2019.
- Lewicka-Szczebak, D., Well, R., Köster, J. R., Fuß, R., Senbayram, M., Dittert, K., and Flessa, H.: Experimental determinations of isotopic fractionation factors associated with  $\text{N}_2\text{O}$  production and reduction during denitrification in soils, *Geochim. Cosmochim. Ac.*, 134, 55–73, <https://doi.org/10.1016/j.gca.2014.03.010>, 2014.
- Lim, J. S., Lee, J., Moon, D., Kim, J. S., Lee, J., and Hall, B. D.: Gravimetric standard gas mixtures for global monitoring of atmospheric  $\text{SF}_6$ , *Anal. Chem.*, 89, 12068–12075, <https://doi.org/10.1021/acs.analchem.7b02545>, 2017.
- Lopez, M., Schmidt, M., Ramonet, M., Bonne, J.-L., Colomb, A., Kazan, V., Laj, P., and Pichon, J.-M.: Three years of semi-continuous greenhouse gas measurements at the Puy de Dôme station (central France), *Atmos. Meas. Tech.*, 8, 3941–3958, <https://doi.org/10.5194/amt-8-3941-2015>, 2015.
- Lushozi, S., Tshilongo, J., and Chimuka, L.: Verification of nitrous oxide primary standard gas mixtures by gas chromatography and cavity ring-down spectroscopy for ambient measurements in South Africa, *Accredit. Qual. Assur.*, 24, 203–214, <https://doi.org/10.1007/s00769-019-01375-x>, 2019.
- Mohn, J., Wolf, B., Toyoda, S., Lin, C. T., Liang, M. C., Brüggemann, N., Wissel, H., Steiker, A. E., Dyckmans, J., and Szewc, L.: Interlaboratory assessment of nitrous oxide isotopomer analysis by isotope ratio mass spectrometry and laser spectroscopy: current status and perspectives, *Rapid Commun. Mass Sp.*, 28, 1995–2007, <https://doi.org/10.1002/rcm.6982>, 2014.
- Myhre, G., Shindell, D., Bréon, F., Collins, W., Fuglestedt, J., Huang, J., Koch, D., Lamarque, J., Lee, D., and Mendoza, B.: Anthropogenic and Natural Radiative Forcing, *Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change*, edited by: Stocker, T. F., Qin, D., Plattner, G.-K., Tignor, M., Allen, S. K., Boschung, J., Nauels, A., Xia, Y., Bex, V., and Midgley, P. M., Cambridge University Press, Cambridge, UK and New York, NY, USA, 659–740, <https://doi.org/10.1017/CBO9781107415324.018>, 2013.
- Nara, H., Tanimoto, H., Tohjima, Y., Mukai, H., Nojiri, Y., Katsumata, K., and Rella, C. W.: Effect of air composition ( $\text{N}_2$ ,  $\text{O}_2$ , Ar, and  $\text{H}_2\text{O}$ ) on  $\text{CO}_2$  and  $\text{CH}_4$  measurement by wavelength-scanned cavity ring-down spectroscopy: calibration and measurement strategy, *Atmos. Meas. Tech.*, 5, 2689–2701, <https://doi.org/10.5194/amt-5-2689-2012>, 2012.
- NOAA/ESRL: Nitrous oxide ( $\text{N}_2\text{O}$ ) WMO scale: [https://www.esrl.noaa.gov/gmd/ccl/n2o\\_scale.html](https://www.esrl.noaa.gov/gmd/ccl/n2o_scale.html) (last access: 21 December 2020), 2011.
- Ostrom, N. E. and Ostrom, P. H.: Mining the isotopic complexity of nitrous oxide: a review of challenges and opportunities, *Biogeochemistry*, 132, 359–372, <https://doi.org/10.1007/s10533-017-0301-5>, 2017.
- Ostrom, N. E., Gandhi, H., Coplen, T. B., Toyoda, S., Böhlke, J. K., Brand, W. A., Casciotti, K. L., Dyckmans, J., Giesemann, A., and Mohn, J.: Preliminary assessment of stable nitrogen and oxygen isotopic composition of USGS51 and USGS52 nitrous oxide reference gases and perspectives on calibration needs, *Rapid Commun. Mass Sp.*, 32, 1207–1214, <https://doi.org/10.1002/rcm.8157>, 2018.
- Picarro:  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  Isotopic and Nitrous Oxide Gas Concentration Analyzer, available at: [https://www.picarro.com/support/library/documents/g513li\\_analyzer\\_datasheet](https://www.picarro.com/support/library/documents/g513li_analyzer_datasheet) (last access: 20 January 2021), 2017.
- Platonov, I., Rodinkov, O., Gorbacheva, A., Moskvina, L., and Kolesnichenko, I.: Methods and devices for the preparation of standard gas mixtures, *J. Anal. Chem.*, 73, 109–127, <https://doi.org/10.1134/S1061934818020090>, 2018.
- Snider, D. M., Venkiteswaran, J. J., Schiff, S. L., and Spoelstra, J.: From the ground up: Global nitrous oxide sources are

- constrained by stable isotope values, *PLoS one*, 10, e0118954, <https://doi.org/10.1371/journal.pone.0118954>, 2015.
- Tohjima, Y., Katsumata, K., Morino, I., Mukai, H., Machida, T., Akama, I., Amari, T., and Tsunogai, U.: Theoretical and experimental evaluation of the isotope effect of NDIR analyzer on atmospheric CO<sub>2</sub> measurement, *J. Geophys. Res.-Atmos.*, 114, D13302, <https://doi.org/10.1029/2009JD011734>, 2009.
- Toyoda, S. and Yoshida, N.: Determination of nitrogen isotopomers of nitrous oxide on a modified isotope ratio mass spectrometer, *Anal. Chem.*, 71, 4711–4718, <https://doi.org/10.1021/ac9904563>, 1999.
- Toyoda, S., Yoshida, N., and Koba, K.: Isotopocule analysis of biologically produced nitrous oxide in various environments, *Mass Spectrom. Rev.*, 36, 135–160, <https://doi.org/10.1002/mas.21459>, 2017.
- van der Schoot, M., Langenfelds, R., Fraser, P., Krummel, P., Ward, J., and Somerville, N.: The WMO/GAW Cape Grim Baseline Air Pollution Station Air Archive, Asia-Pacific GAW on Greenhouse Gases, Korea Metrological Administration (KMA), vol. 6. 13–20, 2015.
- Winther, M., Balslev-Harder, D., Christensen, S., Priemé, A., Elberling, B., Crosson, E., and Blunier, T.: Continuous measurements of nitrous oxide isotopomers during incubation experiments, *Biogeosciences*, 15, 767–780, <https://doi.org/10.5194/bg-15-767-2018>, 2018.
- WMO: 20th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2019), World Meteorological Organization, Geneva, Switzerland, 2019a.
- WMO: Greenhouse Gas Bulletin (GHG Bulletin) – No. 15: The State of Greenhouse Gases in the Atmosphere Based on Global Observations through 2018, World Meteorological Organization, Geneva, Switzerland, available at: <https://public.wmo.int/en/resources/library/wmo-greenhouse-gas-bulletin-no-15> (last access: 13 January 2021), 2019b.
- WMO: Carbon dioxide levels continue at record levels, despite COVID-19 lockdown, available at: <https://public.wmo.int/en/media/press-release/carbon-dioxide-levels-continue-record-levels-despite-covid-19-lockdown> (last access: 13 January 2021), 2020.