

# Development of a southern oceanic air standard reference material

George C. Rhoderick<sup>1</sup> · Michael E. Kelley<sup>1</sup> · Walter R. Miller<sup>1</sup> · Gordon Brailsford<sup>2</sup> · Antonio Possolo<sup>3</sup>

Received: 20 October 2015 / Revised: 19 November 2015 / Accepted: 24 November 2015 / Published online: 9 December 2015  
© Springer-Verlag Berlin Heidelberg (outside the USA) 2015

**Abstract** In 2009, the United States Congress charged the National Institute of Standards and Technology (NIST) with supporting climate change research. As part of this effort, the Gas Sensing Metrology Group at NIST began developing new gas standard mixtures for greenhouse gas mixtures relevant to atmospheric measurements. Suites of gravimetrically prepared primary standard mixtures (PSMs) were prepared at ambient concentration levels for carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), and nitrous oxide (N<sub>2</sub>O) in a dry-air balance. In parallel, 30 gas cylinders were filled, by the National Institute of Water and Atmospheric Research (NIWA) in Wellington, New Zealand, to high pressure from pristine southern oceanic air at Baring Head, New Zealand, and shipped to NIST. Using spectroscopic instrumentation, NIST analyzed the 30 cylinder samples for mole fractions of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O. Certified values were assigned to these mixtures by calibrating the instrumentation with the PSM suites that were recently developed at NIST. These mixtures became NIST Standard Reference Material (SRM) 1721 Southern Oceanic Air and

are certified for ambient mole fraction, the first of their kind for NIST. The relative expanded uncertainties corresponding to coverage intervals with 95 % probability are no larger than 0.06 % of the certified values, representing the smallest uncertainties to date ever assigned to an NIST gas SRM.

**Keywords** Long-lived greenhouse gases (LLGHG) · Gravimetric preparation · Primary standard mixture (PSM) · Standard Reference Material (SRM) · Southern oceanic air

## Introduction

Carbon dioxide (CO<sub>2</sub>), methane (CH<sub>4</sub>), and nitrous oxide (N<sub>2</sub>O) are all greenhouse gases (GHGs) that make important contributions to climate change. A recent analysis from the Global Atmosphere Watch (GAW) Observations Program of the World Meteorological Organization (WMO) shows that the globally averaged mole fractions of GHGs reached new highs in 2013. These maxima include (396.0 ± 0.1) μmol mol<sup>-1</sup> for CO<sub>2</sub>, (1824 ± 2) nmol mol<sup>-1</sup> for CH<sub>4</sub>, and (325.9 ± 0.1) nmol mol<sup>-1</sup> for N<sub>2</sub>O [1, 2]. Compared to pre-industrial levels (prior to 1750), these are relative changes in concentration of 140, 250, and 120 %, respectively. A recent update by the National Oceanic and Atmospheric Administration (NOAA) reports the preliminary global CO<sub>2</sub> level at 400.83 μmol mol<sup>-1</sup> as of March 2015 [3]. All three species are long-lived greenhouse gases (LLGHGs) which absorb electromagnetic radiation and affect the budget of tropospheric and stratospheric ozone (O<sub>3</sub>). Thus, these LLGHGs contribute significantly to atmospheric radiative forcing and have an important role in atmospheric chemistry. As the most important anthropogenic GHG in the atmosphere, CO<sub>2</sub> has contributed 65 % to radiative forcing by LLGHGs. Methane is the second most important contributor to radiative forcing

**Electronic supplementary material** The online version of this article (doi:10.1007/s00216-015-9218-9) contains supplementary material, which is available to authorized users.

✉ George C. Rhoderick  
george.rhoderick@nist.gov

<sup>1</sup> Gas Sensing Metrology Group, Chemical Sciences Division, Materials Measurement Laboratory, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899-8393, USA

<sup>2</sup> Tropospheric Chemistry, National Institute of Water and Atmospheric Research, Wellington 6021, New Zealand

<sup>3</sup> Statistical Engineering Division, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899-8980, USA

by LLGHGs, with a contribution of  $\approx 17\%$  followed by  $\text{N}_2\text{O}$  at  $\approx 6\%$  [1, 2].

In order to accurately establish trends in gas concentration, assess the role of LLHGLs in atmospheric chemistry, and relate measurement records from many laboratories and researchers, it is essential to have a stable, accurate, and internationally recognized source of calibration standards or scales. The longest available records of atmospheric  $\text{CO}_2$  measurements date back to those started in 1957 at the Scripps Institution of Oceanography (SIO), La Jolla, CA. These measurements were based on manometry [4]. NOAA began their  $\text{CO}_2$  measurement program in 1968 and eventually developed a manometric system for absolute calibrations of  $\text{CO}_2$  in dry-air mixture gas [5]. NOAA is the WMO Central Calibration Laboratory (CCL) for  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ , and some other key atmospheric species [6, 7]. Thus, NOAA maintains calibration standards and scales and disseminates that scale to WMO participants via tertiary calibration mixtures. They maintain their own measurement records for these LLGHGs which can be found at [www.esrl.noaa.gov/gmd](http://www.esrl.noaa.gov/gmd). Another organization that has a long history of measurements, beginning in 1978, is the Advanced Global Atmospheric Gases Experiment (AGAGE) at <http://agage.eas.gatech.edu/>. AGAGE does not focus on  $\text{CO}_2$  but does measure and track  $\text{CH}_4$ ,  $\text{N}_2\text{O}$ , and halocarbons.

The ever-increasing number of measurements outside of the current atmospheric measurement networks had increased demand for standards. In 2009, the United States Congress funded the National Institute of Standards and Technology (NIST) to support climate change research. As part of this effort, NIST's Gas Sensing Metrology Group (GSMG) began developing gas standards required for accurate measurements of GHGs for ground-based and ambient atmosphere applications. Initial efforts included the development of gas-cylinder-contained gravimetric primary standard mixture (PSM) suites of ambient atmospheric-level  $\text{CH}_4$  and  $\text{N}_2\text{O}$  in a dry-air balance as previously described [8, 9]. A PSM suite for ambient-level  $\text{CO}_2$  was also produced but has not yet been described in the literature, although key issues that had to be addressed in the preparation techniques have been documented [10].

A key component of the NIST primary standards program involves maintaining strong international links with other National Metrology Institutes (NMIs) through key comparisons proposed by the Gas Analysis Working Group (GAWG) of the Consultative Committee for Amount-of-Substance: Metrology in Chemistry and Biology (CCQM). The CCQM's mission is to establish global comparability of measurement results through promoting traceability to the SI [11]. CCQM key comparisons of ambient  $\text{CO}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{CH}_4$  have been conducted in 2006, 2008, and 2013, respectively [12–14]. The results of these comparisons show agreement within the reported measurement uncertainties between NIST, many other NMIs, and NOAA. We note that as a

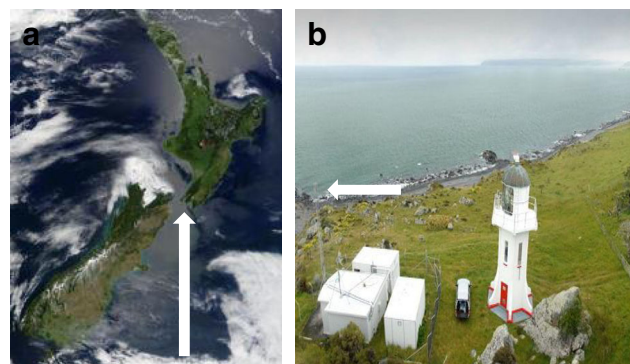
signatory of the Mutual Recognition Arrangement (MRA) of the Consultative Committee of Weights and Measures (CIPM), the WMO recommends the CCL for the species being compared as an official participant in a CCQM Key Comparison [6]. Thus, NOAA, as the WMO-CCL for  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2\text{O}$ , can participate in key comparisons for these three analytes.

The PSM suites developed at NIST are kept in-house and are used to certify other calibration mixtures such as reference materials (RMs) and certified reference materials (CRMs). CRMs certified by NIST are trademarked as Standard Reference Materials<sup>®</sup> (SRMs). After NIST developed and verified the PSM suites for  $\text{CO}_2$ ,  $\text{CH}_4$ , and  $\text{N}_2\text{O}$  through in-house processes, and bilateral and/or international key comparisons, these mixtures were subsequently used to certify SRM 1721 Southern Oceanic Air.

SRM 1721 is one of two new, first ever, natural air SRMs. It was developed to support those needing calibration standards: (a) state and local government agencies performing ground-level urban and remote measurements, (b) the automotive industry which measures  $\text{N}_2\text{O}$  fugitive emissions from autos needing a baseline calibration point, (c) mega-cities projects needing a low-end calibration point, (d) academia performing research and atmospheric measurements, and (e) scientists in general measuring these GHGs in many atmospheric environments. In the remainder of this article, we describe the development and eventual certification of this new SRM.

## Experimental procedure

**Preparation of mixtures** The SRM candidate mixtures were prepared from southern oceanic air by the National Institute of Water and Atmospheric Research (NIWA) at their research station at Baring Head, New Zealand, as shown in Fig. 1. The facility, contained in three small buildings, is located at the coast on a cliff 79 m above the ocean at latitude of  $41^\circ 25'$  S and longitude of  $174^\circ 52'$  E (the windiest area in New



**Fig. 1** **a** optimal wind direction from Antarctica shown with white arrow and **b** Position of sample line of tower of NIWA Baring Head station buildings

Zealand). The prime conditions for pristine oceanic air occur during the months of March and April (white arrow in Fig. 1a) when the prevailing winds originate from Antarctica and subsequently traverse the southern Pacific Ocean to New Zealand. The sampling tube/line is mounted on a tower outside the building at a height of about 4.6 m as indicated by the white arrow in Fig. 1b.

Thirty new aluminum compressed gas cylinders of 29.5 L internal volume, conditioned for ambient CO<sub>2</sub> gas mixture use by Scott-Marrin, Riverside, CA, were pumped with air to a pressure of approximately 14.5 MPa. The Rix SA6E compressor used to pressurize the cylinders was equipped with a 0.01- $\mu$ m pore-size filter (SMC, SFD200-N02) in order to remove salt and other particulates during the sampling process. Additionally, the sampled air was dried in three stages. The first two stages involved the use of two drying towers on the pump. In this process, air was spun inside each unit, with water being condensed and drained from below while the “dryer” air exited the top. These two stages were followed by a final high-pressure step which used magnesium perchlorate as a chemical desiccant. The high-pressure samples are collected with a factory-standard ring material, which imparts no significant change to the air composition.

NIWA used a Siemens Model 3A non-dispersive infrared (NDIR) spectrometer to measure CO<sub>2</sub> concentration at the start of the sampling process for each cylinder. The fill date, start time (NZST), wind direction, wind speed, and the CO<sub>2</sub> mole fraction at the start of sampling are given in Table 1. After pressurizing 30 cylinders, these samples were shipped to NIST in Gaithersburg, MD, USA, for commencement of the analysis and certification process.

**Analysis of SRM mixtures** One of the 30 cylinder samples, sample number 1721-AL-01 (cylinder # CC2598), was designated as the lot standard (LS). The LS was analyzed repeatedly and served as an analytical control to compensate for any instrument drift during a measurement sequence. One to three of the candidate SRM sample cylinders were analyzed between analyses of the LS. All analyses were accomplished using a computer-operated gas analysis system (COGAS) developed at NIST. COGAS consists of 12 ports+1 common stainless steel gas sampling stream selection valve where one cylinder sample is connected to a single port. While one port is being sampled, the other 11 are dead ended with the sample stream flow through the common port and controlled by a needle valve. A low dead-volume two-stage regulator (Model Y12-C144D, Airgas Specialty Gases, Riverton, NJ) is attached to each cylinder with a section of 0.16-mm stainless steel tubing from the regulator to the port in the gas sampling valve. Up to 11 samples can be connected to COGAS, one of which is designated as a control (the LS in this instance). The 12th port is reserved as a “rest port” which is connected to some source of air, either a cylinder mixture or

“house” air. After completion of all cycles, the COGAS stream selection valve is advanced to the rest port. The computer program allows the user to select the number of samples to run between two control samplings. A complete sequence represents each of the samples being analyzed, and up to ten sequences can be made in continuous operation

The COGAS was used to randomly sample from six to ten samples in a full cycle. Ten instrument response measurements were taken as each sample was analyzed, and an average was calculated. All measurement sets were equally separated in time. A ratio ( $r_i$ ) of the  $i$ th candidate sample ( $cs_i$ ) to that of the LS was determined by dividing the corresponding average instrument response  $\bar{S}_i$  by the interpolated value of the LS responses according to

$$r_i = \frac{\bar{S}_i}{\bar{S}_{LS,1} + \frac{i(\bar{S}_{LS,2} - \bar{S}_{LS,1})}{i_{cs} + 1}} \quad (1)$$

where  $\bar{S}_{LS,1}$  and  $\bar{S}_{LS,2}$  are the averaged LS responses that bracket the candidate sample(s) and  $i_{cs}$  is the number of candidate samples within a complete sequence. A typical analysis sequence would be LS,  $cs_1$ ,  $cs_2$ , and LS, for which  $i_{cs}=2$ , representing an “LS set.”<sup>1</sup> (In some cases,  $i_{cs}=1$ .) Analyses were repeated for enough cycles in order to obtain a minimum of ten ratios of each sample to the LS. The Picarro Models G1301-c and G2101-I cavity ring-down spectroscopy (CRDS) analyzers were used to measure the CH<sub>4</sub> and CO<sub>2</sub> concentrations, respectively, and a Los Gatos Research Model 23d off-axis Cavity-Enhanced Absorption Spectroscopy (CEAS) system was used for measurement of the N<sub>2</sub>O. All three instruments measured the same sample stream by sampling the main sample line via internal instrument pumps as illustrated in Fig. 2.

All ratios determined for CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O for each SRM candidate sample are listed in the Electronic Supplementary Material (ESM) Table S1. Each SRM candidate sample, which is assigned a “Sample Number,”<sup>2</sup> as listed in ESM Table S1, was analyzed and bracketed by analyses of the LS. Several SRM samples are analyzed between the LS analyses representing one “LSSet”<sup>1</sup>. Continuous analyses of the SRM samples, randomly chosen, representing several LSSet<sup>1</sup> without interruption represent a “Break Set.”<sup>3</sup> There can be several Break Sets<sup>3</sup> during a full “Day”<sup>4</sup> of analyses. The “Port Number” is the port on COGAS to which the

<sup>1</sup> LS set is all ratios measured between LS measurements and are assigned the same number.

<sup>2</sup> Sample number of the candidate SRM: i.e., sample number 6 is SRM sample ID 1721-A-06

<sup>3</sup> Break set includes all ratios measured without significant interruption.

<sup>4</sup> All measurements taken on the same 24-h calendar day

**Table 1** SRM Southern Oceanic Air sample data

Cylinder number	NIST SRM sample number	Suite	Fill date	Fill time (NZST)	Measurements at start of collection		
					Wind direction (°) <sup>a</sup>	Wind speed (m/s)	CO <sub>2</sub> (μmol mol <sup>-1</sup> )
CC2583	1721-A-22	A1	Jul 25, 2011	14:15	199	22	388.03
CC2589	1721-A-30	A2	Jul 26, 2011	14:15	199	22	388.03
CC2587	1721-A-16	A3	Jul 27, 2011	14:15	199	22	388.03
CC332560	1721-A-27	A4	Jul 28, 2011	14:15	199	22	388.03
CC332456	1721-A-20	B1	Sept 20, 2011	10:54	178	16	388.03
CC2578	1721-A-15	B2	Sept 20, 2011	10:54	178	16	388.43
CC2581	1721-A-18	B3	Sept 20, 2011	10:54	178	16	388.43
CC2594	1721-A-13	B4	Sept 20, 2011	10:54	178	16	388.43
CC2577	1721-A-14	C1	Sept 20, 2011	14:14	158	14	388.43
CC2576	1721-A-24	C2	Sept 20, 2011	14:14	158	14	389.42
CC2571	1721-A-03	C3	Sept 20, 2011	14:14	158	14	389.42
CC332561	1721-A-17	C4	Sept 20, 2011	14:14	158	14	389.42
CC332700	1721-A-02	D1	Dec 20, 2011	10:04	150	9	389.42
CC2572	1721-A-23	D2	Dec 20, 2011	10:04	150	9	388.01
CC332678	1721-A-04	D3	Dec 20, 2011	10:04	150	9	388.01
CC2573	1721-A-29	D4	Dec 20, 2011	10:04	150	9	388.01
CC332701	1721-A-25	E1	Dec 21, 2011	11:41	158	9	388.01
CC2580	1721-A-28	E2	Dec 21, 2011	11:41	158	9	388.58
CC339480	1721-A-06	E3	Dec 21, 2011	11:41	158	9	388.58
CC2597	1721-A-21	E4	Dec 21, 2011	11:41	158	9	388.58
CC332439	1721-A-08	F1	Dec 22, 2011	11:32	145	11	388.58
CC2595	1721-A-09	F2	Dec 22, 2011	11:32	145	11	386.67
CC332431	1721-A-10	F3	Dec 22, 2011	11:32	145	11	386.67
CC2598	1721-AL-01	F4	Dec 22, 2011	11:32	145	11	386.67
CC2599	1721-A-11	G1	Feb 27, 2012	16:17	147	10	386.67
CC2574	1721-A-12	G2	Feb 27, 2012	16:17	147	10	388.45
CC2596	1721-A-26	G3	Feb 27, 2012	16:17	147	10	388.45
CC332689	1721-A-07	G4	Feb 27, 2012	16:17	147	10	388.45
CC332571	1721-A-19	H1	Mar 8, 2012	10:30	163	18	388.45
CC332578	1721-A-05	H2	Mar 8, 2012	10:30	163	18	388.86

<sup>a</sup> Where “°” is north

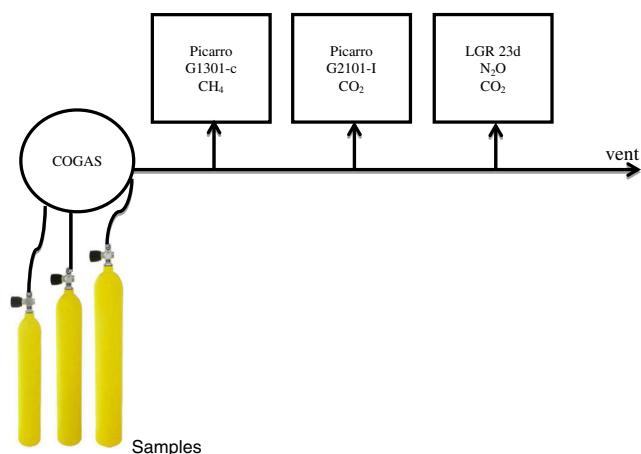
sample gas is connected. This configuration may or may not have been the same for all ratio determinations.

**Analysis of SRM LS to primary standards** The same instrumentation was used as above to analyze the LS against the suites of gravimetric primary standard mixtures (PSMs). Development of the CH<sub>4</sub> in dry, whole-air (natural) suite (NIST\_CH<sub>4</sub>\_2011) and N<sub>2</sub>O in synthetic air (O<sub>2</sub>/N<sub>2</sub>) suite (NIST\_N<sub>2</sub>O\_2012) has previously been discussed [8, 9]. Preliminary analysis of the N<sub>2</sub>O using the CEAS system indicated that argon needed to be present when measuring whole-air samples, a known phenomenon due to the impact of the matrix composition on the pressure broadening coefficient of the absorption line used by the analyzer to deduce the N<sub>2</sub>O mole fraction [15–18]. Therefore, a new suite of N<sub>2</sub>O PSMs

was developed in 2014 (NIST\_N<sub>2</sub>O\_2014) in a balance of synthetic air which included argon. A bias between assigned values to an air sample using the argon-free versus argon-included N<sub>2</sub>O PSM suites was confirmed and found to be ~.8 nmol mol<sup>-1</sup> when using CEAS. The development of these new N<sub>2</sub>O PSMs has not yet been published. NIST is currently comparing the NIST\_N<sub>2</sub>O\_2012 (matrix of ~20.9 % O<sub>2</sub>/79.1 % N<sub>2</sub>) and NIST\_N<sub>2</sub>O\_2014 (matrix of ~0.93 % Ar/20.9 % O<sub>2</sub>/78.2 % N<sub>2</sub>) suites with a gas chromatograph/electron capture detector (GC/ECD) to make sure the suites are in agreement. (Theoretically, there should be no matrix affect due to argon when using GC/ECD.)

When using these spectroscopic instruments for analyses of natural air samples, the isotopic composition may also come into play. In the case of CH<sub>4</sub>, measured with the Picarro Model





**Fig. 2** Diagram of instruments sampling of gas stream

G1301-c instrument, the PSMs were prepared from pure methane (99.9993 %±0.06 %), with an isotopic composition of −43‰ <sup>13</sup>δC (VPDB), in methane-free dry whole air. This then would mimic the whole-air SRMs, thus reducing both pressure broadening and isotopic composition concerns. However, a recent study suggests that this is not a significant issue for CH<sub>4</sub> [19]. In the case of CO<sub>2</sub>, the authors realize the spectroscopic issues related to the isotopic compositions and different isotopologues that are involved when measuring ambient samples. However, while the authors were able to measure the <sup>13</sup>C-CO<sub>2</sub> (described later) to the total CO<sub>2</sub>, it is only considered a rough determination with higher uncertainties than required. Therefore, we cannot properly address these issues at this time. Methods development for accurate <sup>13</sup>C and <sup>12</sup>C measurements as well as the development of isotopic standards is in its beginning phases at NIST and will be part of future work in GHG standards development.

The NIST CO<sub>2</sub> primary gravimetric standards were prepared from pure CO<sub>2</sub> obtained from Airgas Specialty Gases (Riverton, NJ) and dry CO<sub>2</sub> scrubbed whole air from Scott-Marrin (Riverside, CA). The same general procedures described for the preparation of CH<sub>4</sub> and N<sub>2</sub>O [8, 9] were used to prepare the CO<sub>2</sub> suite. The pure CO<sub>2</sub> was recovered from the flue at the AES Warrior Run power plant fired from bituminous coal mined in Maryland. NIST obtained a large sample of this CO<sub>2</sub> from Airgas who sourced it from the Linde Carbonic facility (Cumberland, MD). The GSMG at NIST analyzed the pure CO<sub>2</sub> for other components of air and determined it to be (99.9994 %±0.0002) % mol mol<sup>−1</sup> CO<sub>2</sub>. Further analyses to determine the relative amounts of <sup>12</sup>C and <sup>13</sup>C were made by Fourier transform infrared spectroscopy (FTIR) (Nicolet Nexus 670, Nicolet Instrument Corp., Madison, WI). A nominal 500 μmol mol<sup>−1</sup> PSM, prepared from this pure CO<sub>2</sub> and dry CO<sub>2</sub> scrubbed dilution air, was analyzed. Using the same approach as is common in the atmospheric community [20–22], the relative 13C content was determined by ratio of the responses to each other; C<sup>13</sup>/<sup>12</sup>C.

The resulting ratio was determined to be 0.01092±0.00022 (1.092±0.022)%, resulting in a δ<sup>13</sup>C-CO<sub>2</sub> isotopic delta value of about −28‰ (VPDB scale) in the PSMs compared to ≈−8‰ (VPDB) determined in two of the SRM candidate mixtures. (Only two of the 30 samples were measured for the δ<sup>13</sup>C-CO<sub>2</sub> as at this time NIST does not have PSMs for <sup>13</sup>C-CO<sub>2</sub> or the instrumental equipment necessary to make accurate measurements and suitable uncertainties).

The dilution air was analyzed for major components including O<sub>2</sub>, Ar, CH<sub>4</sub>, N<sub>2</sub>O, and CO, as well as trace CO<sub>2</sub> (typical levels 0.2 μmol mol<sup>−1</sup>). Nitrogen was determined by subtraction. Atomic masses taken from IUPAC data [23, 24] were used to calculate the molecular mass and the uncertainty of the dry whole-air diluent gas for each cylinder of natural air from the sum of the analyzed component fractions. The isotopic content of the <sup>12</sup>C and <sup>13</sup>C in the pure CO<sub>2</sub> was also taken into account in the calculation of the gravimetric CO<sub>2</sub> mole fraction. The development of the NIST CO<sub>2</sub> PSMs (NIST\_CO<sub>2</sub>\_2012) has not yet been published, although previous work describes issues that needed to be addressed such as absorption/desorption of CO<sub>2</sub> within the cylinders used to prepare the PSMs [10]. The cylinders used to prepare each of the CO<sub>2</sub> PSMs were tested for initial absorption, and the gravimetric mole fractions were adjusted accordingly.

The measurements of the LS to the CH<sub>4</sub>, CO<sub>2</sub>, and N<sub>2</sub>O PSM suites were carried out individually. COGAS was used to randomly sample all PSMs against the LS in a full cycle. The average of ten instrument response measurements, given by  $\bar{S}_{\text{PSM}}$ , was obtained for the analysis of each PSM. A ratio ( $r_{\text{PSM}}$ ) of each PSM to the LS was determined by dividing  $\bar{S}_{\text{PSM}}$  by the average instrument response to the LS given by  $\bar{S}_{\text{LS}}$ . This definition gives

$$r_{\text{PSM}} = \frac{\bar{S}_{\text{PSM}}}{\frac{1}{2}(\bar{S}_{\text{LS},1} + \bar{S}_{\text{LS},2})} \quad (2)$$

Only one PSM was randomly analyzed between LS analyses, within one Break Set for a full cycle and several cycles during a full “Day” of analyses. Analyses were repeated for enough cycles over several days in order to obtain a minimum of ten PSM-to-LS ratios for each PSM. The PSM cylinder numbers used in the calibrations for CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O are listed in Table 2 along with the gravimetric mole fraction, its associated combined standard uncertainty ( $u$ ) and expanded uncertainties ( $U$ ) representing an approximate 95 % confidence interval. The  $u$  values can be considered as “one standard deviation” estimates that include all known components of measurement uncertainty.

**Other analytes** All the cylinders were analyzed for moisture content using a Meeco Aquavolt (P<sub>2</sub>O<sub>5</sub>) moisture analyzer and carbon monoxide (CO) by Cavity-Enhanced Absorption

Spectroscopy (CEAS), Los Gatos Research. Molecular oxygen ( $O_2$ ) and argon (Ar) were determined in only two cylinders in order to conserve sample pressure in the SRM samples. The  $O_2$  analysis was accomplished using a Siemens Oxymat 6 paramagnetic analyzer calibrated with NIST SRM 2659a LS (71-DL-01) at  $20.7236 \pm 0.0005 \%$  (0.002 % relative). Argon was analyzed using an Agilent 6890 gas chromatograph equipped with a thermal conductivity detector (GC/TCD) calibrated with NIST SRM 1676 LS (19-BL-01) at  $0.980 \pm 0.001 \%$ .

## Results and discussion

The analysis functions used to assign values to the SRM and the evaluations of uncertainty for the assigned values were computed as described. These functions have been built using methods that extend the methods described in ISO 6143 [25] to take into account the case when statistical evaluations of uncertainty are based on small numbers of observations and when Monte Carlo methods are used to evaluate the uncertainty associated with the certified values [26, 27]. These procedures are routinely used by the NIST Gas Sensing

Metrology Group for value assignment and uncertainty evaluation of reference materials.

Final expanded uncertainties ( $U$ ) are expressed and calculated from

$$U_{95\%} = ku \quad (3)$$

with coverage factor  $k$  determined separately for each GHG species and described later. The true value for each analyte mole fraction,  $x_{\text{analyte}}$ , is asserted to lie in the interval  $[x_{\text{analyte}} \pm U_{95\%}(x_{\text{analyte}})]$  with a level of confidence of approximately 95 %. Data treatment discussions follow for each of the greenhouse gas species being certified in this SRM 1721.

**Function for carbon dioxide ( $CO_2$ ), methane ( $CH_4$ ), and nitrous oxide ( $N_2O$ )** Four  $CO_2$ , five  $CH_4$ , and six  $N_2O$  PSMs listed in Table 2 were analyzed against the SRM LS control, and instrument response ratios were calculated. The ratios, mole fractions,  $x_{\text{analyte}}$ , and associated uncertainties  $u(x_{\text{analyte}})$  for each PSM are listed in ESM Tables S2, S3, and S4, respectively. Figure 3a, b depicts the analysis function (first-order polynomial) selected

**Table 2** PSMs used to value assign mole fractions to SRM 1721 samples

Cylinder number	Mole fraction ( $\mu\text{mol mol}^{-1}$ )	Combined uncertainty <sup>a</sup>	Expanded uncertainty <sup>b</sup>
CO <sub>2</sub> PSMs (NIST_CO <sub>2</sub> _2012)			
APEX1005714	421.178	0.062	0.124
APEX1005721	398.854	0.063	0.126
APEX1005674	396.489	0.059	0.118
APEX1005690	379.444	0.060	0.120
CH <sub>4</sub> PSMs (NIST_CH <sub>4</sub> _2012)			
FF4249	1892.84	0.79	1.58
FF4288	1836.16	0.75	1.50
FF4283	1795.10	0.75	1.50
FF4264c	1756.75	0.72	1.44
FF4260	1687.15	0.78	1.56
N <sub>2</sub> O PSMs (NIST_N <sub>2</sub> O_2014)			
FF22146	344.378	0.060	0.120
FF22181	338.390	0.058	0.116
FF22145	331.135	0.057	0.114
CAL016773	326.325	0.057	0.114
FF22225	319.646	0.048	0.096
FF22270	314.952	0.047	0.094

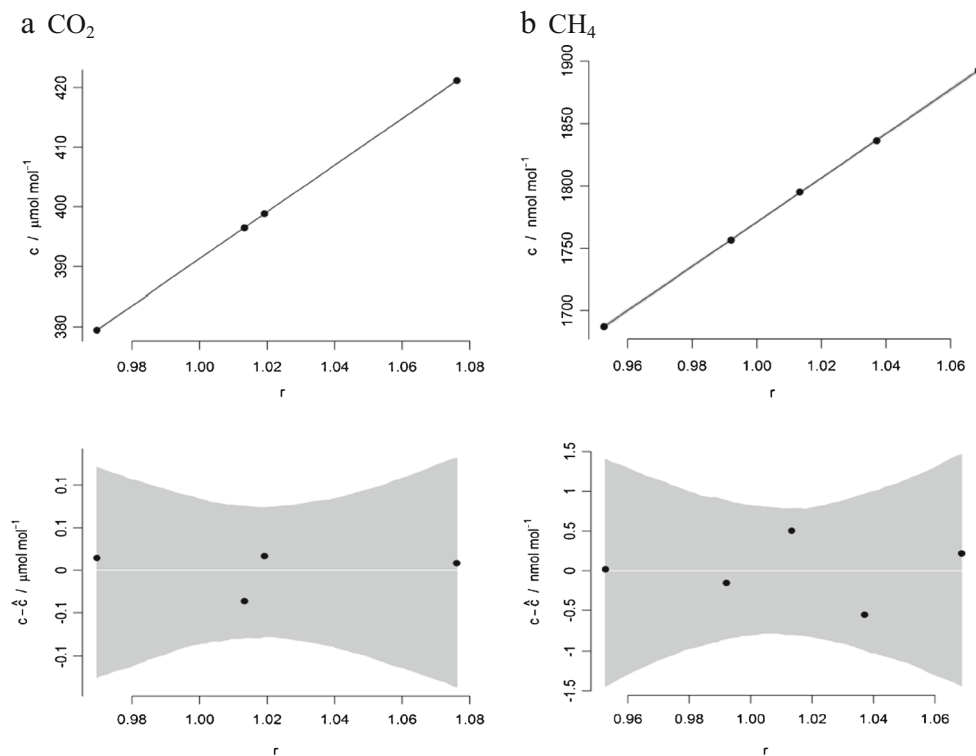
<sup>a</sup> Combined standard uncertainty ( $k=1$ ), micromoles per mole for  $CO_2$  and nanomoles per mole for  $CH_4$  and  $N_2O$ , expressing all recognized sources of uncertainty

<sup>b</sup> Expanded uncertainty ( $k=2$ ) at the 95 % confidence interval, micromoles per mole for  $CO_2$  and nanomoles per mole for  $CH_4$  and  $N_2O$ , expressing all recognized sources of uncertainty

<sup>c</sup> The original [6] PSM was expelled and the same cylinder used to prepare a new PSM in 2014

<sup>d</sup> PSMs are not those discussed in reference [9] but are the new suite (NIST\_N<sub>2</sub>O\_2014) made using the same technique and including argon

**Fig. 3** **a, b** Plots of first-order polynomial for CO<sub>2</sub> and CH<sub>4</sub> PSMs from ratiometric and gravimetric mole fraction data, and residuals between gravimetric and corresponding predicted values of the PSMs by the analysis function.  $c$  represents the mole fraction (concentration) in micromoles per mole for CO<sub>2</sub> and nanomoles per mole for CH<sub>4</sub>.  $\hat{c}$  represents the predicted mole fraction (concentration) in micromoles per mole for CO<sub>2</sub> and nanomoles per mole for CH<sub>4</sub>.  $r$  is the ratio of the peak areas of the PSM to the LS. The gray regions represent the 95 % coverage of the uncertainty in the values



\* $c$  represents the mole fraction (concentration) in  $\mu\text{mol mol}^{-1}$  for CO<sub>2</sub> and  $\text{nmol mol}^{-1}$  CH<sub>4</sub>.

\* $\hat{c}$  represents the predicted mole fraction (concentration) in  $\mu\text{mol mol}^{-1}$  for CO<sub>2</sub> and  $\text{nmol mol}^{-1}$  CH<sub>4</sub>.

\* $r$  is the ratio of the peak areas of the PSM to the LS.

\*The gray regions represent the 95 % coverage of the uncertainty in the values.

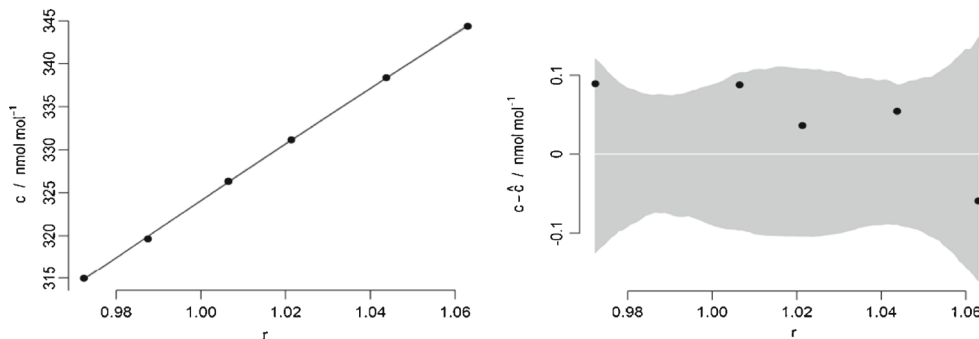
from among the first-, second-, and third-order polynomials for CO<sub>2</sub> and CH<sub>4</sub>. (Second- and third-order polynomials were tested to assure that the instruments were responding in a linear manner as would be expected.) This expression gives the mole fractions,  $c_j$  (ordinates) of the  $j$ th PSM (denoted by PSM <sub>$j$</sub> ), as a function of the measured response ratios (abscissae). The fitted first-

order polynomial analysis function gives the unknown SRM CO<sub>2</sub>, ( $c_{\text{CO}_2,j}$ ), or CH<sub>4</sub>, ( $c_{\text{CH}_4,j}$ ), mole fraction in terms of the response ratio as

$$c_{\text{CO}_2,j} = \bar{r}_{\text{SRM},j} b_1 + b_0 \quad (4)$$

where  $\bar{r}_{\text{SRM},j}$  is the average SRM sample response ratio for CO<sub>2</sub>, or CH<sub>4</sub>, corresponding to the  $j$ th SRM. A residual plot,

**Fig. 4** Plot of second-order polynomial for N<sub>2</sub>O PSMs from ratiometric and gravimetric mole fraction data, and residuals between gravimetric and corresponding predicted values of the PSMs by the analysis function.  $c$  represents the gravimetric mole fraction (concentration) in nanomoles per mole.  $\hat{c}$  represents the predicted mole fraction (concentration) in nanomoles per mole.  $r$  is the ratio of the peak areas of the PSM to the LS. The gray regions represent the 95 % coverage of the uncertainty in the values



\* $c$  represents the gravimetric mole fraction (concentration) in  $\text{nmol mol}^{-1}$ .

\* $\hat{c}$  represents the predicted mole fraction (concentration) in  $\text{nmol mol}^{-1}$ .

\* $r$  is the ratio of the peak areas of the PSM to the LS.

\*The gray regions represent the 95 % coverage of the uncertainty in the values.

**Table 3** Function coefficients for CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O

GHG species	Function coefficients		
	$b_0, \mu\text{mol mol}^{-1}$	$b_1, \text{nmol mol}^{-1}$	$b_2, \text{nmol mol}^{-1}$
CO <sub>2</sub>	-0.1500±0.8307	391.488±0.815	
CH <sub>4</sub>	0.245±0.009	1770.81±0.84	
N <sub>2</sub> O	-152.18±34.39	620.643±67.650	-144.36±33.24

the difference between the gravimetric mole fraction,  $c$ , and the predicted,  $\hat{c}$ , for each polynomial, is also shown below the analysis function plot including a 95 % coverage region for such differences.

Figure 4 depicts the N<sub>2</sub>O analysis function (second-order polynomial) selected from among first- through fifth-order polynomials. This expression gives the mole fractions,  $c_j$  (ordinates) of the  $j$ th PSM (denoted by PSM <sub>$j$</sub> ), as a function of the measured response ratios (abscissae). It should be noted that while the fifth-order polynomial, depicted in ESM Fig. S1, better captures a slight curvature at the low end, it has larger associated uncertainties (see gray uncertainty bounds). The second-order polynomial has more marked lack of fit but smaller associated uncertainties. Because the differences in the SRM sample  $x_{\text{N}_2\text{O}}$  are not significantly different (<0.03 nmol mol<sup>-1</sup> in most cases), as shown in ESM Table S5, we chose to use the second-order polynomial fit. The fitted analysis function gives the unknown SRM N<sub>2</sub>O mole fraction in terms of the response ratio as

$$c_{\text{N}_2\text{O}} = \bar{r}_{\text{SRM},j}^2 b_2 + \bar{r}_{\text{SRM},j} b_1 + b_0 \quad (5)$$

where  $\bar{r}_{\text{SRM},j}$  is the average SRM sample response ratio corresponding to the  $j$ th SRM. A residual plot, showing the difference between the gravimetric mole fraction,  $c$ , and the predicted,  $\hat{c}$ , for the N<sub>2</sub>O polynomial with the 95 % coverage region, is also shown beside the analysis function plot. That all but one residual are positive suggests systematic lack of fit for the second-order polynomial, possibly owing to a non-linear response of the instrument used for measurement. Since a third-order polynomial would improve the residual pattern without reducing the magnitude of the residuals overall, we adopted the simpler model.

Table 3 lists the coefficients  $b_0$  and  $b_1$  for the CO<sub>2</sub> and CH<sub>4</sub> functions. This linear response equation was used to assign CO<sub>2</sub> and CH<sub>4</sub> mole fraction values and their combined standard uncertainties to the LS, 1721-AL-01, (391.338 ± 0.034) μmol mol<sup>-1</sup> and (1771.06 ± 0.34) nmol mol<sup>-1</sup>, respectively. The  $x_{\text{analyte}}$  and  $u(x_{\text{analyte}})$  were also calculated for each SRM sample using the respective ratio data and Eq. 4. The post hoc value for the 95 % expansion factor of Eq. 3 was computed using Monte Carlo method results as  $k=U_{95\%}/u$ :  $k(\text{CO}_2)=1.78$  and  $k(\text{CH}_4)=1.97$ . The  $U_{95\%}(x_{\text{CO}_2})$  and  $U_{95\%}(x_{\text{CH}_4})$  for each SRM sample were calculated using Eq. 3. Table 3 also lists

the coefficients  $b_0$ ,  $b_1$ , and  $b_2$  for the N<sub>2</sub>O second-order function. This quadratic response equation was used to assign an N<sub>2</sub>O value to the LS of 324.101 nmol mol<sup>-1</sup> with a combined standard uncertainty ( $k=1$ ) of ±0.042 nmol mol<sup>-1</sup>. A value and combined standard uncertainty were also calculated for each SRM sample using their respective ratio data and Eq. 5. The post hoc value of the coverage factor was computed as the ratio between the 95 % expanded uncertainty and the combined standard uncertainty, both evaluated using the Monte Carlo method,  $k=1.72$ . The expanded uncertainty ( $U_{95\%}$ ) of  $x_{\text{N}_2\text{O}}$  for each SRM sample was calculated using Eq. 3. The individual  $x_{\text{analyte}}$ ,  $u(x_{\text{analyte}})$ , and  $U_{95\%}(x_{\text{analyte}})$  for all three analytes in each SRM sample are given in Table 4.

**Components of air** Water content ranged from (0.5 to 20.4) μmol mol<sup>-1</sup> while CO values were (36 to 56) nmol mol<sup>-1</sup>. Due to instability in the NIST PSMs, in the form of growth of CO observed over time, and possibly the SRM samples themselves, it is not possible to certify the CO at this time. Further research is needed to assess the CO instability problem and determine if a suitable cylinder/treatment process can be developed to solve this problem. The H<sub>2</sub>O and CO (at the time of its determination) are given in ESM Table S6 but are provided only as information of potential interest. Cylinders 1721-AL-01 and 1721-A-14 were analyzed for molecular oxygen (O<sub>2</sub>) and argon. The mole fraction values were the same for both samples at 20.93 and 0.93 % for oxygen and argon, respectively.

**Final certified values** The final certified mole fraction  $x_{\text{analyte}}$  and  $U_{95\%}(x_{\text{analyte}})$  for CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O corresponding to each of the 27 SRM samples are given in Table 5. The  $U_{95\%}(\text{CO}_2)$  range from (±0.07 to ±0.14) μmol mol<sup>-1</sup> or (0.018 to 0.035)% relative to the certified value. The  $U_{95\%}(\text{analyte})$  for the CH<sub>4</sub> and N<sub>2</sub>O were rounded up to ±1.0 nmol mol<sup>-1</sup> (0.06 % relative) and ±0.20 nmol mol<sup>-1</sup> (0.06 % relative), respectively. The uncertainties associated with the mole fractions of the analytes in the SRM samples are often smaller than those associated with the PSMs. This is a consequence of the averaging effect of the regression function used for value assignment, and of the assumption that none of the uncertainty components expressed in the uncertainty evaluations for the PSMs reflect persistent errors (biases). In future versions of the procedure currently in use at NIST, we will make provisions to accommodate the presence of persistent errors that will not average out as more and more sample values are combined into derivative quantities. The Monte Carlo method described in [26] is sufficiently flexible to allow such accommodation.

One of the goals in this SRM development was to provide standards with uncertainties that were equivalent or exceeded the WMO Data Quality Objectives (DQOs) [28]. The combined standard uncertainties,  $u$ , of the certified values as given in Table 2 are well within the WMO DQOs (which are one standard



**Table 4** NIST mole fraction values and uncertainties for SRM 1721 Southern Oceanic Air samples

SRM sample	Cylinder number	Certified value, $\mu\text{mol mol}^{-1}$	Carbon dioxide ( $\text{CO}_2$ ) combined uncertainty ( $u$ ), $\mu\text{mol mol}^{-1}$	Expanded uncertainty ( $U$ 95 %), $\mu\text{mol mol}^{-1}$	Certified value, $\text{mmol mol}^{-1}$	Methane ( $\text{CH}_4$ ) combined uncertainty ( $u$ ), $\text{mmol mol}^{-1}$	Expanded uncertainty ( $U$ 95%), $\text{mmol mol}^{-1}$	Certified value, $\text{mmol mol}^{-1}$	Nitrous oxide ( $\text{N}_2\text{O}$ ) combined uncertainty ( $u$ ), $\text{mmol mol}^{-1}$	Expanded uncertainty ( $U$ 95 %), $\text{mmol mol}^{-1}$
1721	CC2598	391.34	0.04	0.07	1771.05	0.34	0.68	324.10	0.04	0.07
1721	CC332700	387.97	0.07	0.13	1760.65	0.38	0.76	323.98	0.05	0.10
1721	CC2571	388.93	0.06	0.11	1779.42	0.38	0.74	323.66	0.09	0.16
1721	CC332678	387.98	0.06	0.11	1760.52	0.42	0.82	323.93	0.05	0.10
1721	CC332578	388.09	0.06	0.11	1745.75	0.41	0.80	323.91	0.06	0.12
1721	CC339480	388.45	0.06	0.12	1755.58	0.40	0.79	323.96	0.05	0.10
1721	CC332689	388.18	0.05	0.10	1745.01	0.47	0.92	324.12	0.05	0.10
1721	CC332439	391.36	0.07	0.13	1771.14	0.39	0.76	324.09	0.08	0.15
1721	CC2595	391.21	0.04	0.08	1771.08	0.35	0.70	324.06	0.06	0.12
1721	CC332431	391.36	0.05	0.10	1770.96	0.37	0.73	324.08	0.07	0.13
1721	CC2599	388.11	0.04	0.09	1744.99	0.43	0.84	324.09	0.05	0.11
1721	CC2574	388.05	0.05	0.10	1744.97	0.45	0.89	324.12	0.08	0.16
1721	CC2594	388.72	0.06	0.11	1777.43	0.46	0.89	323.57	0.07	0.14
1721	CC2577	388.93	0.06	0.12	1779.13	0.35	0.69	323.65	0.09	0.16
1721	CC2578	388.67	0.06	0.14	1777.37	0.36	0.71	323.56	0.07	0.14
1721	CC2587	388.12	0.05	0.10	1772.02	0.43	0.84	323.25	0.06	0.12
1721	CC332561	388.94	0.05	0.10	1779.37	0.38	0.74	323.65	0.09	0.16
1721	CC2581	388.72	0.05	0.10	1777.42	0.43	0.83	323.55	0.07	0.13
1721	CC332571	388.15	0.06	0.12	1745.57	0.42	0.82	323.92	0.08	0.14
1721	CC332456	388.77	0.06	0.11	1777.54	0.38	0.74	323.57	0.06	0.11
1721	CC2597	388.30	0.11	0.19	1755.46	0.42	0.82	323.93	0.05	0.11
1721	CC2583	388.13	0.06	0.11	1772.09	0.38	0.75	323.23	0.06	0.12
1721	CC2572	388.00	0.04	0.08	1760.53	0.38	0.74	323.93	0.07	0.13
1721	CC2576	388.91	0.06	0.11	1779.24	0.42	0.81	323.65	0.07	0.13
1721	CC332701	388.44	0.05	0.09	1755.61	0.48	0.96	323.95	0.07	0.13
1721	CC2596	388.16	0.06	0.11	1744.99	0.44	0.87	324.16	0.06	0.12
1721	CC332560	388.16	0.06	0.11	1772.17	0.43	0.83	323.25	0.06	0.12
1721	CC2580	388.37	0.06	0.12	1755.38	0.46	0.89	323.98	0.05	0.10
1721	CC2573	387.98	0.05	0.10	1760.40	0.38	0.75	323.99	0.06	0.12
1721	CC2589	388.10	0.08	0.15	1772.19	0.35	0.70	323.27	0.07	0.14

**Table 5** NIST-certified mole fraction values for SRM 1721 Southern Oceanic Air samples

Cylinder number	Sample number	CO <sub>2</sub> certified value <sup>a</sup> , μmol mol <sup>-1</sup>	CH <sub>4</sub> certified value <sup>a</sup> , nmol mol <sup>-1</sup>	N <sub>2</sub> O certified value <sup>a</sup> , nmol mol <sup>-1</sup>
CC332700	1721-A-02	387.97±0.13	1760.6±1.0	323.98±0.20
CC2571	1721-A-03	388.93±0.11	1779.4±1.0	323.66±0.20
CC332678	1721-A-04	387.98±0.11	1760.5±1.0	323.93±0.20
CC332578	1721-A-05	388.09±0.11	1745.7±1.0	323.91±0.20
CC339480	1721-A-06	388.45±0.12	1755.6±1.0	323.96±0.20
CC332689	1721-A-07	388.18±0.10	1745.0±1.0	324.12±0.20
CC332439	1721-A-08	391.36±0.13	1771.1±1.0	324.09±0.20
CC2595	1721-A-09	391.21±0.08	1771.1±1.0	324.06±0.20
CC332431	1721-A-10	391.36±0.10	1771.0±1.0	324.08±0.20
CC2599	1721-A-11	388.11±0.09	1745.0±1.0	324.09±0.20
CC2574	1721-A-12	388.05±0.10	1745.0±1.0	324.12±0.20
CC2594	1721-A-13	388.72±0.11	1777.4±1.0	323.57±0.20
CC2577	1721-A-14	388.93±0.12	1779.1±1.0	323.65±0.20
CC2578	1721-A-15	388.67±0.14	1777.4±1.0	323.56±0.20
CC2587	1721-A-16	388.12±0.10	1772.0±1.0	323.25±0.20
CC332561	1721-A-17	388.94±0.10	1779.4±1.0	323.65±0.20
CC2581	1721-A-18	388.72±0.10	1777.4±1.0	323.55±0.20
CC332571	1721-A-19	388.15±0.12	1745.6±1.0	323.92±0.20
CC332456	1721-A-20	388.77±0.11	1777.5±1.0	323.57±0.20
CC2597	1721-A-21	388.30±0.19	1755.5±1.0	323.93±0.20
CC2583	1721-A-22	388.13±0.11	1772.1±1.0	323.23±0.20
CC2572	1721-A-23	388.00±0.08	1760.5±1.0	323.93±0.20
CC2576	1721-A-24	388.91±0.11	1779.2±1.0	323.65±0.20
CC332701	1721-A-25	388.44±0.09	1755.6±1.0	323.95±0.20
CC2596	1721-A-26	388.16±0.11	1745.0±1.0	324.16±0.20
CC2580	1721-A-28	388.37±0.12	1755.4±1.0	323.98±0.20
CC2589	1721-A-30	388.10±0.15	1772.2±1.0	323.27±0.20

<sup>a</sup> Expanded uncertainty corresponding to a coverage interval with 95 % coverage probability

deviation specifications) for CH<sub>4</sub> and N<sub>2</sub>O, the DQO for CH<sub>4</sub>= 2 nmol mol<sup>-1</sup> and N<sub>2</sub>O=0.1 nmol mol<sup>-1</sup>. The standard deviation of CH<sub>4</sub> values of standards from their reference values was 1.7 nmol mol<sup>-1</sup> in the most recent international comparison [14] compared to the reported relative combined uncertainty,  $u$  ( $k=1$ ), of <0.5 nmol mol<sup>-1</sup> for this work. This smaller  $u$  is owed to the use of the NIST statistical program assessing the variability of the ratios as previously mentioned in the previous section.

**Final certified values** For 25 of the 27 SRM cylinders, the  $u(x_{\text{CO}_2})$  meets the southern hemisphere DQO of ±0.05 μmol mol<sup>-1</sup>. The NIST  $u$  includes both the uncertainty in the PSMs used for calibration and the measurement of the individual SRM sample.

## Conclusions

This SRM will assist those scientists, researchers, and state and government agencies that need or require certified,

traceable GHG concentration standards. It will allow the calibration of instrumentation used to provide GHG concentrations and to a wide variety of groups and monitoring communities. Additionally, this SRM provides the metrological basis required for researchers to accurately track the long-term growth rates of CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O in urban, rural, and atmospheric environments. For those laboratories that do not need to report to the WMO/GAW (which requires traceability to the CCL (NOAA)), this SRM will be of particular interest. For instance, NIST has received verbal inquiries from the Automobile Industry/Government Emissions (AIGER) group about obtaining SRM 1721 specifically for the measurement of N<sub>2</sub>O. The certified N<sub>2</sub>O concentration in SRM 1721 will complement the recently developed SRM 1718 which contains N<sub>2</sub>O, in a synthetic air blend of Ar/O<sub>2</sub>/N<sub>2</sub> mimicking whole-air mole fractions, at nominal mole fraction value of 1000 nmol mol<sup>-1</sup>, and a mixture specifically developed for AIGER members at ≈400 nmol mol<sup>-1</sup> in O<sub>2</sub>/N<sub>2</sub> synthetic air.

Future development of GHG primary standards at NIST will focus on well-characterized isotopic gas standards

beginning with the carbon isotopes of CO<sub>2</sub>. Pure <sup>12</sup>C-CO<sub>2</sub> and <sup>13</sup>C-CO<sub>2</sub> starting materials will be blended that will have final mole fractions with different isotopic delta values. Those standards can then be used to calibrate the optical and mass spectroscopic instruments used to measure samples or atmospheres for CO<sub>2</sub>. Eventually, the isotopes of O<sub>2</sub> will also be well characterized within those primary standards.

#### Compliance with ethical standard

**Conflict of interest** The authors declare that they have no competing interests.

**Disclaimer** Certain commercial equipment, instruments, and materials are identified in order to specify experimental procedures as completely as possible. In no case does such identification imply a recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that any of the materials, instruments, or equipment identified are necessarily the best available for the purpose.

#### References

- WMO Greenhouse Gas Bulletin, No. 10, 2014
- NOAA/ESRL/GMD website: [www.esrl.noaa.gov/gmd/](http://www.esrl.noaa.gov/gmd/)
- NOAA/ESRL/GMD website: <http://www.esrl.noaa.gov/gmd/ccgg/trends/global.html>
- Keeling CD, Piper SC, Whorf TP, Keeling RF (2011) Evolution of natural and anthropogenic fluxes of atmospheric CO<sub>2</sub> from 2003. *Tellus Series B-Chem Phys Metrol* 63:1
- Zhao CL, Tans PP, Thoning KW (1997) A high precision manometric system for absolute calibrations of CO<sub>2</sub> in dry air. *J Geophys Res* 102(D5):5885–5894
- (2013) 17th WMO/IAEA Meeting on Carbon Dioxide, Other Greenhouse Gases and Related Tracers Measurement Techniques (GGMT-2013), GAW Report No. 213
- NOAA website: <http://www.esrl.noaa.gov/gmd/ccl/refgas.html>
- Rhoderick GC, Carney J, Guenther FR (2012) NIST gravimetrically prepared atmospheric level methane in dry air standards suite. *Anal Chem* 84(8):3802–3810
- Kelley ME, Rhoderick GC, Guenther FR (2014) Development and verification of air balance gas primary standards for the measurement of nitrous oxide at atmospheric levels. *Anal Chem* 86(9):4544–4549
- Miller WR, Rhoderick GC, Guenther FR (2015) Investigating adsorption/desorption of carbon dioxide in aluminum compressed gas cylinders. *Anal Chem* 87(3):1957–1962
- CCQM website: <http://www.bipm.org/en/committees/cc/ccqm/>
- Wessel RM, van der Veen AMH, Ziel, Steele P, Langenfelds R, van der Schoot M, Smeulders D, Besley L, Smarçao da Cunha V, Zhou Z, Qiao H, Heine HJ, Martin B, Macé T, Gupta PK, Amico di Meane E, Sega M, Rolle F, Maruyama M, Kato K, Matsumoto N, Kim JS, Moon KM, Lee JB, Murillo FR, Nambo CR, Caballero VMS, Salas Mde JA, Castorena AP, Konopelko LA, Kustikov YA, Kolobova AV, Pankratov VV, Efremova OV, Musil S, Chromek F, Valkova M, Milton MJT, Vargha G, Guenther FR, Miller WR, Botha A, Tshilongo J, Mokgoro IS, Leshabane N (2008) International comparison CCQM-K52: carbon dioxide in synthetic air. *Metrologia* 45 Tech. Suppl.: 08011
- Lee J, Lee J, Moon D, Kim JS, Wessel R, Aoki N, Kato K, Guenther F, Rhoderick G, Konopelko LA, Han Q, Hall B (2011) CCQM-K86 final report international comparison CCQM K68 nitrous oxide in synthetic air. *Metrologia* 48, Tec Suppl
- Flores E, Viallon J, Choteau T, Moussay P, Wielgosz RI, Kang N, Kim BM, Zalewska E, van der Veen AMH, Konopelko L, Wu H, Han Q, Rhoderick GC, Guenther FR, Watanabe T, Shimosaka T, Kato K, Hall B, Brewer P (2015) International comparison CCQM-K82: methane in air at ambient level (1800 to 2200) nmol/mol. *Metrologia* 52 Tech Suppl 08001
- Chen H, Winderlich J, Gerbig C, Hoefler A, Rella CW, Crosson ER, Van Pelt AD, Steinbach J, Kolle O, Beck V, Daube BC, Gottlieb EW, Chow VY, Santon GW, Wofsy SC (2010) High-accuracy continuous airborne measurements of greenhouse gases (CO<sub>2</sub> and CH<sub>4</sub>) using the cavity ring-down spectroscopy (CRDS) technique. *Atmos Meas Tech* 3(2):375–386
- Winderlich J, Chen H, Gerbig C, Seifert T, Kolle O, Lavric JV, Kaiser C, Hofer A, Heimann M (2010) Continuous low-maintenance CO<sub>2</sub>/CH<sub>4</sub>/N<sub>2</sub>O measurements at the Zotino tall tower observatory (ZOTTO) in central Siberia. *Atmos Meas Tech* 3(4):1113–1128
- Nara H, Tanimoto H, Tohjima Y, Mukai H, Nojiri Y, Katsumata K, Rella CW (2012) Effect of air composition (N-2, O-2, Ar, and H2O) on CO<sub>2</sub> and CH<sub>4</sub> measurement by wavelength-scanned cavity ring-down spectroscopy: calibration and measurement strategy. *Atmos MeasTech* 5(11):2689–2701
- Long DA, Gameson L, Truong GW, Bielska K, Cygan A, Hodges JT, Whetstone JR, van Zee RD (2013) The effects of variations in buffer gas mixing ratios on commercial carbon dioxide cavity ring-down spectroscopy sensors. *J Atmos Ocean Tech* 30:2604–2609. doi:10.1175/JTECH-D-13-00039.1
- Flores E, Rhoderick GC, Viallon J, Moussay P, Choteau T, Gameson L, Guenther FR, Wielgosz RI (2015) Methane standards made in whole and synthetic air compared by cavity ring down spectroscopy and gas chromatography with flame ionization detection for atmospheric monitoring applications. *Anal Chem* 87(6):3272–3279. doi:10.1021/ac5043076
- Keeling CD (1961) The concentration and isotopic abundances of carbon dioxide in rural and marine air. *Geochim Cosmochimica Acta* 24(3–4):277–298
- Pataki DE, Bowlind DR, Ehleringer JR (2003) Seasonal cycle of carbon dioxide and its isotopic composition in an urban atmosphere: anthropogenic and biogenic effects. *J Geophys Res* 108(D23):735
- Santoni GW, Daube BC, Kort EA, Jiménez R, Park S, Pittman JV, Gottlieb E, Xiang B, Zahniser MS, Nelson DD, McManus JB, Peischl J, Ryerson TB, Holloway JS, Andrews AE, Sweeney C, Hall B, Hintsa EJ, Moore FL, Elkins JW, Hurst DF, Stephens BB, Bent J, Wofsy SC (2014) Evaluation of the airborne quantum cascade laser spectrometer (QCLS) measurements of the carbon and greenhouse gas suite – CO<sub>2</sub>, CH<sub>4</sub>, N<sub>2</sub>O, and CO – during the CalNex and HIPPO campaigns. *Atmos Meas Tech* 7:1509–1526
- Wieser ME, Holden N, Coplen TB, Böhlke JK, Berglund M, Brand WA, Bièvre PD, Gröning M, Loss RD, Meija J, Hirata T, Prohaska T, Schoenberg R, O'Connor G, Walczyk T, Yoneda S, Zhu X-K (2013) Atomic weights of the elements 2011 (IUPAC technical report). *Pure Appl Chem* 85(5):1047–1078
- Website: <http://www.ciaaw.org/atomic-weights.htm>
- International Organization for Standardization, “ISO 6143:2001 gas analysis—determination of composition of calibration gas mixtures—comparison methods”, 2nd edition
- Guenther FR, Possolo A (2011) Calibration and uncertainty assessment for certified reference gas mixtures. *Anal Bioanal Chem* 399:489–500
- BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP and OIML (2008) Evaluation of measurement data—supplement 1 to the “Guide to expressions of uncertainty in measurement: –Propagation of distributions using a Monte Carlo method. *JCGM* 101
- GAW Report No. 80* (1992)