We wish to express our appreciation for your significant and useful comments. We have revised the manuscript, considering your comments and suggestions.

Referee #1 Received and published: 24 July 2018
This paper presents an improved method for preparing gravitational mixtures of O2, N2, Ar, and CO2 in air, with potential importance for a range of atmospheric measurements, particularly for detection of long-term trends in O2/N2 ratio. I sense the basic gravitational work was done with great care. But the presentation itself is not polished, and I had difficulty following some of the methods and discussions, such as the comparisons with natural air. The presentation is sufficiently unclear that it will be of limited value in documenting the method and results. There is also at least one outstanding analytical issue that may need to be addressed with further lab work. I recommend resubmission after major revision, although with the large number of substantive issues, this would be equivalent to withdrawing and resubmitting.

General concerns:
I can't follow the method by which the absolute mole ratios in the reference (natural) air cylinder CR00045 were assessed based on comparison the standards. This is not well explained, and seems possibly problematic. I specifically missed clarification that the mass spectrometer used to measured (O2/N2) and d(Ar/N2) in fact measures the dominant isotopologue ratio 16O2/14N2 and Ar/14N2. Thus it should be sufficient to know the absolute 16O2/14N2 and Ar/14N2 ratios in the gravimetric standards to assess the absolute 16O2/14N2 and Ar/14N2 of CR00045 through the delta measurements. From the absolute 16O2/14N2 and Ar/14N2 ratios in CR00045, one could determine the absolute O2/N2 and Ar/N2 ratios including all isotopologues in CR00045 simply by knowing the isotopic abundances in natural air. Eqs (3) and (4), which I assume are being used in this comparison, look incorrect because they include irrelevant information on the isotopic abundances of the standard mixture. Could the authors perhaps have made the incorrect assumption that the mass spectrometer actually measures the delta based on the sum of all isotopologues?

Response: The absolute values which were precisely determined by the gravimetric method were the (O2/N2) and (Ar/N2) ratios not the (16O2/14N2) and (40Ar/14N2) ratios. Additionally, if the absolute (O2/N2) is calculated based on the (16O2/14N2), its uncertainty is larger than the gravimetrically calculated uncertainty. Therefore, we discussed the d(O2/N2) and d(Ar/N2) ratios based on the absolute (O2/N2) and (Ar/N2) ratios not isotopologue ratios 16O2/14N2 and 40Ar/14N2. We revised the sentence to be easy to be understood.(section 2.4.1, 5.1)

The paper overlooks the possibility that the concentrations delivered from the tanks for analysis might differ from gravimetric ratios by either homogeneous or inhomogeneous fractionation. Numerous previous studies (e.g. Leuenberger et al., AMT 2015; Langenfelds et al, 2005, JGR -Atmospheres 110(D13); Keeling et al, JGR 1998; Keeling et al Tellus B 2004) have drawn attention to these issues, which often dominate errors and therefore cannot be ignored. As shown by both the Keeling and Leuenberger studies, a pertinent measurement is to assess the change in composition of the tank as it is depleted. This effectively is a constraint on both types of fractionation. Surface adsorption/fractionation at lower pressure ranges could be assessed by filling an evacuated tank up to modest pressure (e.g. 3 atmospheres) and looking at composition anomalies in the residual gas caused by the filling. Tests of this sort could be done with similar tanks filled with natural air, sparing the gravimetric tanks. Perhaps the authors have other ideas. In any case, some additional lab work is needed to assess these effects, which cannot realistically be assessed theoretically. Another omission is a discussion of the interferences from gases other than O2/N2, Ar, and CO2 on the mass spectrometer measurement. Ne, He, Kr, CH4, H2, and N2O all have abundances over 0.1 ppm in air, but presumably not in the gravimetric tanks. The effects may be small but need evaluation or discussion.
Response: we used the same type of the cylinders which Tohjima et al. had used. Since they had already verified the change of the concentrations delivered from the tanks for analysis, we didn't perform this verification. However, because we didn't discuss the verification in this paper, we add the sentences about their verification (P13, L14–L18). We carried out an additional experiment for the interferences from Ne and added the result in the paper (P12, L17–L22), since the molar fraction of Ne is highest in the minor components.

It's unclear what was learned from the paramagnetic measurements that compare gravimetric standards to a tank of synthetic air. Also, the discussion of the paramagnetic measurements lacks a discussion of interferences. I suggest that this content be cut, as it doesn't appear to address anything important.
Response: We removed this content according to your comment

The study lacks a direct comparison with the previous gravimetric work of Tohjima et al (2005). Section 6.1 is entitled "Comparison between O2/N2 ratios on the AIST and NIES scales", but in stead of reporting such a comparison,e.g. by exchanging cylinders with NIES, this section does something else entirely: They use their measurements to report a trend in O2/N2 by combining the previous absolute estimate of O2 mole fraction at Hateruma station in Tohjima et al, with a new absolute determination at Hateruma done by the authors 15 years later. The inferred trend in O2/N2 at Hateruma is shown to be significantly smaller than the trend measured at La Jolla over the same period by the Scripps group. But before they make this very speculative comparison, they first need to carry out a direct comparison of standards. Also, I believe that the NIES group has made measurements over the full time frame at Hateruma. Surely, the NIES data should be examined before comparing with La Jolla. Other points: Page 2, line 21. The context of the 500 per meg figure is unclear. I assume it may reflect the decrease over some time period of measurement, but this isn't clear nor is the reason for this statement.

Response: We revised to the comparison between the O2/N2 ratios at Hateruma in 2015 determined by AIST and by NIES. Now, a direct comparison between NIES scale and AIST scale using gravimetric standard gases is being performed. In other paper, we will present detail of the results (section 6.1).

Page 2, lines 21-31. This paragraph is intended to provide motivation, but I found it hard to follow. It also misses important content. I suggest this prose be replaced with a summary of current practice of calibrating O2/N2 measurements and explaining why the development of absolute standards would satisfy an important need by overcoming the reliance on the long-term stability of O2/N2 ratios in high pressure aluminum gas cylinders. Here might also be a good place to mention the relevance of homogenous and heterogeneous fractionation mechanisms and the relevance of good practice in withdrawing air from tanks.

Response: We revised to explaining why the development of absolute standards would satisfy an important need by overcoming the reliance on the long-term stability of O2/N2 ratios in high pressure aluminum gas cylinders in accordance with your comments (P2, L20–P3, L9)

Page 3, line 30. Punctuation problem. "as such" is start of new sentence.

Response: We revised the sentence (P4, L25).

Page 3, line 31. Meaning of "calibration lines" is unclear to me.

Response: We revised the sentence from "calibration lines" to "the relation between the outputs of mass comparators and the masses of artifacts".

Section 2.3.2. This section lacks adequate motivation. Why is it relevant to measure the O2/N2 and Ar/N2 ratios of the gravimetric mixtures when their ratios are known from the gravimetric preparation? I think the context here is a comparison with natural air. Another title for this section and few sentences of explanation are needed.
Response: We add the motivation in section 2.4.1 (p5, L26-L27)

Page 5, line 11. I can't follow, as the distinction between sample and standard is unclear here. Is CRC0045 the sample or the standard? Note that the delta value for CRC00045 will be zero by definition. This is true whether the delta value is based on the dominant isotopes or not. This content therefore makes no sense to me.
Response: CRC0045 is used as the reference air not sample air. The section 2.3 were revised overall (moving from the section 2.3 to the section 2.4).

Page 5, line 14 and Eq. (3) and (4). In the context of this section, it is unclear what is meant by δ(O2/N2)and δ(Ar/N2) without isotopic label. Does this refer to a ratioformed based on the sum of all isotopologues?
Page 5, Eq. (3) and (4). Why do 18O17O, 18O18O, 15N15N not appear in these equations?
Page 5, line 25. It would be good here to repeat that the label "standard" refers to CRC00045.
Response: The section 2.3 were revised overall (moving from the section 2.3 to the section 2.4).

Section 2.3.3. Similar to the last section, the section title seems wrong and motivation is lacking. It's especially confusing that a comparison to synthetic air is being done.
How was the value of 20.650% determined? Since the uncertainty on 20.650% is much greater than the uncertainty on the gravimetric mixtures, it's hard to see the point of this comparison. As discussed above, I suggest cutting this section.
Response: We removed this section.

Page 6, lines 25 and 26. Meaning of "work" unclear. Is this meant in a thermodynamic sense? Work versus heat? Generally, this paragraph is hard to follow.
Response: We revised the sentences (P7, L14 –L23).

Page 6, lines 32, 33 and 36. Meaning of "equilibrium" is unclear, and is perhaps the wrong word choice. It seems it is defined operationally by the stability of the readings overtime. I miss a statement about temperature measurements. How was temperature measured?

Response: The “equilibrium” mean thermal and water adsorption equilibrium for the surface of the sample cylinder (P7, L25). We add the statement about temperature measurements according to your comments (P4, L34 –L36)

Page7,line16-17. “The mass difference decreases...”Unclear that this is a statement about the sign, as it reads more as a statement about magnitude, e.g. would the difference be smallest with a very large temperature difference? Would be clearer if stated as “warmer cylinders appear lighter (or heavier?)”. Even on multiple readings I can’t figure out which direction is implied.

Response: We add the sentence according to your comments (P8, L2 –L3)

Page 7, lines 21-28. The information in this paragraph should be condensed and merged with the previous paragraph. It would be easier to follow the earlier paragraph if the temperature measurements were discussed BEFORE discussing the impact on weighings.

Response: We merged this paragraph and the previous paragraph and discuss the temperature measurements before discussing the impact on weighing (P7, L31–P8, L3)

Page 6-7, I urge that Sections 3.1 and 3.2 be merged into one section to improve readability. I note that there is no discussion of how the surface temperature of the cylinders was measured. Okay, reading further, I see it is eventually discussed. Maybe this should be mentioned above in Materials and Methods, where more detail could be given, e.g. how was thermocouple attached? Was it left in place during weighings?

Response: Section 3 was revised overall. The method to measure the cylinder’s temperature was mentioned in Materials and Methods.

Page 8, line 25. “humidity and temperature factors”. If the point is that the effect is due to temperature alone, why does this sentence mention temperature factors.

Response: We mistakes the sentence. Thermal effect is due to temperature difference alone. The sentence were revised (P9, L2 –L3)

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Page11. The leak-uprate of 0.013mg/day is more than two orders of magnitude faster than the upper bound reported in Keeling et al Tellus B, 59, 2007 for a presumably similar valve at cylinder pressure. The rate is admittedly small in the context of their application, but perhaps not in other applications, so their findings may raise concerns. They should at least cite Keeling et al and mention that the rate appears high compared to other work.

Response: The leak rate we measured was calculated from monitoring mass of leakage gas. The value reported by Keeling et al. is the change rate of O2/N2 ratio. Both value cannot be compared.

Page 8, line 28. Section 4. The header needs rewording. Suggest "Gravimetric Error Propagation"

Response: The header replaced from "preparation of the O2 standard mixtures" to "Evaluation of uncertainty factors for the O2 standard mixtures".

Page 12, line 3 "Table 5 shows..." Aside from the major question I raised above about the overall logic of this calculation, I miss how the value of (16O2/14N2) standard and (40Ar/14N2) standard are assigned.

Response: We explained above about this.

Page 12, line 37 "The d(O2/N2) values obtained were 0.16%..." I can't follow this sentence.

Response: We revised the sentence to easily understand it (P13, L5-L7).

Page 13, lines 4-10. This looks like important information, but I can't follow. I guess this reflects my difficulty understanding the overall logic of their approach.

Page 13, line 17-18, "Using these samples...". I can't follow. The sentence appears to assume that the atmospheric O2/N2 ratio is constant. What time of year? Are these annual mean values?

Response: We revised the sentence overall to easily understand the overall logic (P13, L7–L13).

Page 13, line 25. This paragraph is hard to follow. The need for Ar corrections is not explained. Wouldn't it be possible to work directly from O2/N2 measurements reported by the NIES group, who have taken care of this detail themselves? As mentioned previously, it's strange here not to directly compare gravimetric standards, so this section as a whole is problematic.

Response: The section 6.1 was revised overall. Our value was compared with annual average in 2015 reported by the NIES group.

Page 14, line 1-5. As mentioned in Keeling et al (JGR, 1998), the Scripps scale factor has in fact been compared to gravimetric standards.
Response: We removed the Scripps data.

Section6.2. I can't follow why this information is being presented and how it differs from material in the previous section. For example, between this and the previous section, two inconsistent values (0.2680761 and 0.2680701) for the O2/N2 ratio at Hateruma are reported for 2015. Confusing.
Response: We cannot completely verify the absolute values in the highly precise O2 standard mixtures (HPO), because there is no standard mixture with uncertainty to be able to verify the HPOs. A method unlike the method performed in the section 5 is considered to be necessary. Additionally, we think that the validation of absolute values is scientifically important to enable the comparison with a previous study, for example, O2 molar fraction (0.20946) determined by Machta and Hughes(1970), etc. We revised in consistent values according to your comments.

Page14, line25. "From 2000 to 2015, it was noted..."The basis for this estimate is not clear. Also, to report O2 changes in ppm risks causing confusion unless some context is given. Does this mole fraction basis include CO2? How does this estimate compare to one based on combining information on the change in O2/N2 with known changes in CO2 abundance?
Response: We removed the sentence.

Page 15, line 15. See early comment about this reported rate. Needs context to avoid misunderstanding.
Response: We removed the sentence.

Figure 1. It's unclear why these curves converge to zero. If the data shown is the change relative to the last point, this should be explained in the caption.
Response: We explained the point in the caption.

Figure 4. Unclear which curve goes with which axis.

Response: We revised Figure 4.

Figure 5a. The x axis is labeled O2/N2, but could it actually be showing both O2/N2 and Ar/N2?
Response: We revised Figure 5.

Table 2. This table is garbled. Some cells and some column headers appear to have in appropriate line breaks. The rows don’t line upproperly and the +/- symbols are often not located properly.
Response: We revised Table 2.

Reviewer #2:

This paper describes an improved method for preparing synthetic gas mixtures of oxygen in artificial air by gravimetry (weighing). The use of a new mass comparator in the automatic weighing system and a thorough uncertainty evaluation allows for a suite of mixtures that have exceptionally low uncertainties. These have been verified with high level analytical methods that show a very good consistency within the suite and with other/previous high level standard mixtures. Nevertheless there are some principal comments and specific issues that need to be revised. I therefore recommend resubmission after major revisions.

General comments

The metrics and terminology lack to some extent concordance with international recommendations, standards and good practice. Even if some quantity and unit 'habits' are well established in atmospheric science, they are not to be taken as a role model because they are very often source of misunderstanding and misconception. Some xamples are given in the following points:

1. The use of 'mole fraction' as a quantity denomination is depreciated and should be replaced by 'amount (of substance) fraction' or 'molar fraction'. Derived quantities should be defined by quantities and not by units (mole is a unit). Angles can be defined as 'length ratios' and not as 'meter ratios'. A mass fraction is not called gram fraction either. 'Mixing ratio' or 'atomic weight' are established use of quantity denominations but misleading because they mean 'molar fraction' and 'atomic mass'. Further literature is ISO 80000-9, IUPAC gold book, T. Cvitas, metrologia 2003.

Response: We revised from mole fraction to molar fraction in accordance with your comments

2. The use of the unit ppm for µmol/mol is also depreciated because it is not obvious if it is a relative or absolute unit. Please keep µmol/mol, it is not that long.

Response: We kept µmol/mol in this paper in accordance with your comments

3. The definition of δ (O_2/N_2) in 'per meg' is misleading because it contains the factor 10^6 (equations 1 to 4). All indications in 'per meg' are redundant but need a mention of the standard. We would prefer to omit this notation or

use it correctly. See also Coplen (DOI: 10.1002/rcm.5129) Note 7 page 2541 and Milton et al. (DOI: 10.1002/rcm.836)

Response:. We revised the equation 1 to 4 in accordance with your comments

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The aspects of pressure dependent adsorption and desorption of analytes inside the pressurised cylinders is not discussed but may be relevant for interpreting results of certain gases (carbon dioxide).

Response:. We added the sentences for aspects of pressure dependent adsorption and desorption in this paper (P13, L14L18).

The issue of analytical interference when comparing standards to real air samples is not discussed but may also be relevant (water-issue).

Response:. We added the sentences of the interferences in this paper (P12, L17-22)

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Specific comments:

Page 1, line 3: Replace mole fraction by molar fraction (throughout the text)

Response:. We replace mole fraction by molar fraction.

Page 1, line 4: Correct name Matsumoto

Response:. We revised the name.

Page 1, line 10: Omit per meg information in the abstract without introduction and replace ppm by µmol/mol

Response:. We omited per meg in the abstract without introduction and replaced ppm by µmol/mol according to your comment.

Page 2 line 2: omit (per meg) and '$\times 10^6$' and in equations 2 to 4)

Response:. We revised equation 2 to 4 according to your comment.

Page 2 line 24: use linear calibration function instead of calibration line (all instances)

Page 2 line 31: word order: … have not yet been …

Response:. This sentence was removed.

Page 2 line 33: Replace weight measurement by mass measurement (you indicate mg which is the unit of mass and not N which would be the unit of weight (gravitational force))

Response:. We replace weight measurement by mass measurement in accordance with your comment (P3, L13

Page 3 line 2: … were validated …

Response:. We revised the word according to your comment.(P3, L17)

Page 3 line 26: the expression of 'gravimetric cylinder' is misleading (further instances). In fact it is the cylinder containing the gravimetrically prepared mixture. Be clear in describing the procedure.

Response:. We revised the sentences of 'gravimetric cylinder' to 'sample cylinder' through this paper.

Page 3 line 36: … were traced to the International …

Response:. We revised the sentence according to your comment (P4 L31)

Page 4 line 14: these may not be ratios of CO2 to Ar but molar fractions?

Response:. We replaced ratios of CO2 to Ar by molar ratios of CO2 to Ar (P4,L1-L2)

Page 6 line 8: … factors of uncertainty…

Response:. We revised the sentence according to your comment (P6, L32).

Page 6 line 24: Sentence difficult to understand. Please rephrase

Response:. We revised the sentences according to your comment (P7, L14-L16)

Page 12 line 6: Why are the ratios absolute? Is there a convention to reference to AIST

Response:. We revised the caption of section 5.1.

Table 1 last column: the isotope ratios should be expressed as …= (x.xxx ± y.yyy) ‰

Response:. We expressed the isotope ratios as …= (x.xxx ± y.yyy) ‰

Table 2 is hardly readable. Please rearrange for better reading.

Response:. We rearranged the table 2

Table 5 title: The indicated numbers represent ratios not fractions

Response:. We revised from fractions to ratios

Figure 5 a: The x-axis concerns also Ar/N2.

Response:. We revised the x-axis according to your comment

Preparation of primary standard mixtures for atmospheric oxygen measurements with less than 1 µmol mol^{-1} uncertainty ~~less than 1 ppm~~ for oxygen ~~mole~~molar fractions

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Abstract. ~~Primary~~Precise monitoring of changes in atmospheric O_2 levels was implemented by preparing primary standard mixtures with less than 1 ~~ppm or 5 per meg~~µmol mol^{-1} standard uncertainty for O_2 ~~mole~~molar fractions~~ or for O_2/N_2 ratios were prepared to monitor changes, which occurred in atmospheric oxygen. These~~. In this study, these mixtures were crafted in 10 L high-pressure ~~aluminum~~aluminium alloy cylinders using a gravimetric method in which unknown uncertainty factors were ~~identified~~ theoretically determined and subsequently reduced. ~~The mole~~Molar fractions of the constituents~~,~~ (CO_2, Ar, O_2, and N_2~~,~~) in the primary standard mixtures were mainly ~~determined~~resolved using ~~the~~ masses of the respective source gases (CO_2, Ar, O_2, and N_2) that had been filled into the cylinders. To precisely determine the masses of the source gases~~ used in each case~~, the ~~differences~~difference in ~~the masses~~mass of the ~~cylinders~~cylinder before and after filling ~~were~~the respective source gas was calculated ~~and~~by compared ~~to nearly~~with an almost identical reference ~~cylinders~~cylinder. Although the ~~mass~~masses of the ~~cylinder~~cylinders filled with source gas with respect to the reference cylinder tended to ~~vary~~deviate in relation to temperature differences between ~~both cylinders~~the source gas filled cylinder and surrounding air, the degree of ~~change~~the deviation could be efficiently reduced by measuring ~~both~~the two cylinders at the exact same temperature. The standard uncertainty for the cylinder mass obtained in our weighing system was determined to be 0.82 mg. The standard uncertainties for the O_2 ~~mole~~molar fractions ~~and O_2/N_2 ratios~~ in the primary standard mixtures ranged from 0.7 ~~ppm~~µmol mol^{-1} to 0.8 ~~ppm and from 3.3 per meg to 4.0 per meg, respectively.~~ µmol mol^{-1}. Based on the primary standard mixtures, the ~~mole~~annual average molar fractions of atmospheric O_2 and Ar ~~on~~in 2015 at Hateruma Island, Japan~~. In 2015, the O_2 and Ar mole fractions,~~ were found to be 209339.1 ± 1.1 ~~ppm~~µmol mol^{-1} and 9334.4 ± 0.7 ~~ppm~~µmol mol^{-1}, respectively. The molar fraction for atmospheric Ar was in agreement with previous reports.

1 Introduction

Observation of atmospheric O_2 ~~mole~~molar fractions provides important information about the global carbon cycle (Keeling and Shertz, 1992; Bender et al., 1996; Keeling et al., 1996, 1998a; Stephens et al., 1998; Battle et al., 2000; Manning and Keeling, 2006). For example, long-term observation allows the estimation of land biotics and oceanic CO_2 uptake (Manning and Keeling, 2006; Tohjima et al., 2008; Ishidoya et al., 2012a, 2012b). Various measurement techniques have been developed for this purpose, including the utilization of interferometry (Keeling et al., 1998b), mass spectrometry (Bender et al., 1994; Ishidoya et al., 2003; Ishidoya and Murayama, 2014), a paramagnetic technique (Manning et al., 1999; Aoki et al., ~~2017~~2018;

Ishidoya et al., 2017), a vacuum-ultraviolet absorption technique (Stephens et al., 2003), gas chromatography (Tohjima, 2000), and a method ~~that uses~~utilizing fuel cells (Stephens et al., 2007; Goto et al., 2013). In all ~~of~~ these cases~~, the~~ calibration using standard mixtures is required to precisely determine the relationship between the ~~analyzers' outputs~~analysis output and O_2 ~~mole fraction values~~molar fractions obtained.

~~The mole fraction~~ Molar fractions of ~~atmospheric~~ O_2 ~~is~~and Ar are commonly expressed as ~~a function~~functions of the O_2/N_2 ~~ratio~~ and Ar/N_2 ratios relative to an arbitrary reference (Keeling and Shertz, 1992~~), according~~; Keeling et al., 2004) in per meg (one per meg is equal to ~~Eq. (~~1 × 10^{-6}).

$$\delta(\mathrm{O_2/N_2}\cancel{)(\text{per meg})}\ \cancel{=\left[\frac{(\mathrm{O_2/N_2})_{\text{sample}}}{(\mathrm{O_2/N_2})_{\text{standard}}}\right)} = \frac{[n(\mathrm{O_2})/n(\mathrm{N_2})]_{\text{sam}}}{[n(\mathrm{O_2})/n(\mathrm{N_2})]_{\text{ref}}} - 1\cancel{]\times 10^{6}} \qquad (1)$$

$$\delta(\mathrm{Ar/N_2}) = \frac{[n(\mathrm{Ar})/n(\mathrm{N_2})]_{\text{sam}}}{[n(\mathrm{Ar})/n(\mathrm{N_2})]_{\text{ref}}} - 1 \qquad (2)$$

In ~~this equation,~~ these equations, *n* depicts the amount of each substance, and the subscripts "~~sample~~sam" and "~~standard~~ref" refer to ~~a~~ sample air and ~~a standard~~reference air, respectively. As the O_2 ~~mole fraction of~~ and Ar molar fractions in air ~~is~~are 20.946~~ %, a~~% and 0.943%, respectively, a respective change of 4.8 per meg and 107 per meg in $\delta(O_2/N_2)$ and $\delta(Ar/N_2)$ corresponds to a change of 1 μmol mol^{-1} in ~~the~~ molar fractions of O_2 and Ar.

Reported peak-to-peak amplitudes of seasonal cycles and trends in atmospheric $\delta(O_2/N_2)$ were within the range of 50 – 150 per meg (10 – 30 μmol mol^{-1} for O_2 molar fractions) and −20 per meg yr^{-1} (−4 μmol mol^{-1} yr^{-1} for O_2 molar fractions) (Keeling et al., 1993; Battle et al., 2000; Van der Laan–Luijkx et al., 2013). ~~mole fraction.~~To monitor these slight variations, the development of primary standard mixtures with standard uncertainty of less than 5 per meg for O_2/N_2 ratios (1 μmol mol^{-1} for O_2 molar fractions) or less (Keeling et al., 1993; WMO, 2016) is required. In this study, the ~~unit~~primary O_2 standard mixture with the recommended uncertainty of ~~"~~5 per meg (1 μmol mol^{-1}~~"~~) or less is ~~abbreviated~~hereafter referred to as ~~"ppm."~~a "highly precise O_2 standard mixture (HPO)".

~~There are approved primary~~In general, standard mixtures ~~for use~~need to be prepared in ~~these types~~which molar fractions of ~~experiments for~~the greenhouse gas species, such as CO_2, CH_4, and N_2O, ~~which are prepared using either~~ are stable enough during the observation period to enable monitoring of long-term changes in atmospheric molar fractions of their species. For this purpose, it is indispensable to establish methods for determining absolute molar fractions of greenhouse gases in the standard mixtures with required precision. Approved primary standard mixtures exist for CO_2, CH_4, and N_2O, prepared by manometry (Zhao et al., 1997) or gravimetry (Tanaka et al., 1983; Matsueda et al., 2004; Dlugokencky et al., 2005; Hall et al., 2007). However, preparing an HPO is challenging since it is necessary to prepare it with the relative uncertainty of less than one-fifth of that for the CO_2 molar fraction in the CO_2 standard mixture. Since there is no common scale for atmospheric O_2 observation, such as the ratio of O_2/N_2 determined using HPOs, each laboratory has employed reference air determined using its own reference scale instead of a universal scale. This reference scale is determined based on O_2/N_2 ratios in primary standard mixtures filled in high-pressure cylinders and is considered to be sufficiently stable during the observation period (e.g. Keeling et al., 1998b; Tohjima et al~~.~~., 2008; Ishidoya et al., 2012b). However, there are many deterioration risks of the O_2/N_2 ratio in aluminium cylinders used for reference air and the primary standard mixtures. these include fractionations of O_2 and N_2 induced by pressure, temperature and water vapor gradients (Keeling et al., 1998b), adsorption/desorption of the constituents on the inner surface (Leuenberger et al., 2015), and permeation/leakage of the constituents from/through the valve (Sturm et al., 2004; Keeling et al., 2007). In order to avoid these risks, the cylinders are handled in accordance to certain best practices, including orienting cylinders horizontally to minimize thermal and gravitational fractionation (Keeling, et al. 2007, Leuenberger, et al., 2015).

Although causes behind the fractionation should be sufficiently described by now, the effects of permeation and adsorption/desorption have not been completely understood in the long-term scale. To enable comparison of O_2/N_2 values reported based on reference air with the difference scale directly, an independent development of primary standard mixtures with standard uncertainty of 5 per meg (1 μmol mol^{-1}) or less is needed. In a pioneering study, Tohjima et al. (2005) first prepared primary standard mixtures for ~~observation of~~the atmospheric O_2 ~~using~~measurement based on a gravimetric method ~~in which the~~. The standard uncertainties ~~were~~ for the O_2/N_2 ratio (the O_2 molar fraction) were noted at 15.5 per meg ~~for the O_2/N_2 ratio and 2.9 ppm for the O_2 mole fraction.~~(2.9 μmol mol^{-1}), which was larger than the required standard uncertainty of 5 per meg (1 μmol mol^{-1}) or less. Since the 2.9 ~~ppm~~μmol mol^{-1} standard uncertainty recorded by Tohjima et al. (2005) was ~~much~~significantly larger than the gravimetrically expected value of 1.6 ~~ppm~~μmol mol^{-1}, it was suggested that there are unknown factors exerting influence on the mass ~~readings~~results of~~ the~~ cylinders.

~~Reported peak-to-peak amplitudes of seasonal cycles and trends for atmospheric $\delta(O_2/N_2)$ were within the range of 50 per meg to 150 per meg (from 10 ppm to 30 ppm for O_2 mole fractions) and −20 per meg yr^{-1} (−4 ppm yr^{-1} for O_2 mole fractions), respectively (Keeling et al., 1993; Battle et al., 2000; Van der Laan-Luijkx et al., 2013). To monitor these slight variations, it was recommended~~Taking these facts into consideration, in this study we set out to develop ~~primary standard mixtures with O_2/N_2 ratios that had standard uncertainty of less than 5 per meg or O_2 mole fractions that had standard uncertainty of less than 1 ppm (Keeling et al., 1993; WMO, 2016). In this study, primary O_2 standard mixtures with the recommended uncertainty of less than 5 per meg or 1 ppm is hereafter expressed as "a highly precise O_2 standard mixture."~~

~~Since the variations in atmospheric O_2 were less than 500 per meg (100 ppm) (Bender et al., 1994; Tohjima, 2000; Stephens et al., 2007; Goto et al., 2013), the highly precise O_2 standard mixtures used to monitor atmospheric O_2 required the use of a range of 500 per meg (100 ppm) upwards. The resultant standard uncertainty would be higher than the recommended uncertainty, which could interfere with its corresponding slope of calibration line in an analyzer used for the monitoring. For example, when two standard gases that had uncertainty values of 3 ppm (15 per meg) and the difference in both O_2 mole fractions of 100 ppm (500 per meg) were used for calibration of an analyzer, the slope of the calibration line calculated for the analyzer would reflect a 6 % deviation from the actual value if one~~ a new gravimetric method to prepare an HPO by scientifically understanding the unknown uncertainty factors in the cylinder ~~would have O_2 mole fraction which would be 3 ppm higher than the true level while the other cylinder would have a deviation that was 3 ppm lower than the true level. Given this, it is important to verify not only the scale but also its corresponding slope for each laboratory's standard gas mixtures using highly precise O_2 standard mixtures. Because the highly precise O_2 standard mixtures have not been yet developed, there has been a need for their development.~~

mass measurement. Our laboratory has built upon ~~a~~the weighing system proposed by Matsumoto et al. (2004~~)~~), in which gravimetry was used to prepare standard mixtures. ~~This ~~Although this system allows accurate ~~weight~~mass measurements ~~in which the~~with a standard uncertainty ~~is~~of 2.6 mg~~. The integration of a new ~~, this proves insufficient to prepare an HPO. A new mass comparator with better repeatability ~~have been made~~was recently introduced to the weighing system. In ~~this~~the present study, we ~~developed a~~theoretically identified the unknown factors and presented an improved means of ~~identifying and ~~minimizing ~~unknown uncertainty factors that contributed to deviations in the mass readings of the cylinders during preparation of the highly precise O_2 standard mixtures with the weighing system.~~them. The standard uncertainties for ~~the mole~~molar fractions of ~~various~~all constituents in ~~the highly precise O_2 standard mixtures, which have been~~HPOs, prepared using ~~this~~these improved~~ weighing~~ means, are discussed. ~~Additionally~~Moreover, the molar fractions of all constituents in the ~~standard mixtures was~~HPOs were validated by ~~measuring~~comparing the ~~mole fractions~~gravimetric value with the measured values of CO_2 ~~and O_2, as well as both~~mole fraction, Ar/N_2 ratio, and O_2/N_2 ~~ratios. To~~ratio. In order to validate the scale of O_2/N_2 ratio at the National Institute of Advanced Industrial Science and Technology (AIST) determined using the ~~highly precise O_2 standard mixtures~~HPOs prepared in this study, the annual average of O_2/N_2 ratios ~~for air samples collected~~in 2015 at Hateruma Island (24°03′N, 123°49′E, Japan) obtained from our measurements of air samples were ~~preliminary~~preliminarily compared with the annual average of O_2/N_2 ratios in 2015 at Hateruma Island on the ~~scale of National Institute for Environmental Studies (~~NIES~~)~~ scale determined by Tohjima et al~~. (2005). Also~~.(NIES). Additionally, the ~~mole~~molar fractions for atmospheric Ar and O_2 in air samples ~~at Hateruma Island ~~were determined using the HPOs and compared with previously reported values.

2 Materials and Methods

2.1 ~~Weighing procedure for a high-pressure cylinder~~

~~The~~Preparation of the highly precise O_2 standard mixtures

Eleven HPOs were prepared in 10 L ~~aluminum~~aluminium alloy cylinders (Luxfer Gas Cylinders, UK), ~~which had~~with a diaphragm valve (G-55, Hamai Industries Limited, Japan) with poly(chlorotrifluoroethylene) (PCTFE) as sealant~~.~~ in accordance with ISO 6142-1:2015. Pure CO_2 (>99.998 %, Nippon Ekitan Corporation, Japan), pure Ar (G1-Grade, 99.9999 %, Japan Fine Products, Japan), pure O_2 (G1-Grade, 99.99995 %, Japan Fine Products, Japan), and pure N_2 (G1-Grade, 99.99995 %, Japan Fine Products, Japan) were used as source gases to prepare the HPOs. The value of $\delta^{13}C$ in pure CO_2 (which was adjusted to the atmospheric level) was −8.92‰ relative to Vienna Pee Dee Belemnite (VPDB). Impurities in the source gases were identified and quantified using gas chromatography with a thermal conductivity detector for N_2, O_2, CH_4 and H_2 in pure CO_2, and gas chromatography with a mass spectrometer for O_2 and Ar in pure N_2 and N_2 in pure O_2. A Fourier transform infrared spectrometer was used for detection of CO_2, CH_4 and CO in pure N_2, O_2, and Ar. A galvanic cell-type O_2 analyser was employed to quantify O_2 in pure Ar. A capacitance-type moisture meter measured H_2O in pure CO_2, and a cavity ring-down-type moisture meter measured H_2O in pure N_2, O_2 and Ar.

Primarily, standard mixtures of CO_2 in Ar were prepared by combining pure CO_2 and pure Ar using a gravimetric method. The molar ratios of CO_2 to Ar were close to the atmospheric molar ratio of CO_2 (400 μmol mol^{-1} or 420 μmol mol^{-1}) to Ar (9340 μmol mol^{-1}). The 10 L aluminium cylinder was used to prepare the HPO after evacuation by a turbomolecular pump. The source gases were filled ~~with highly precise O_2 ~~in the order of the mixtures of CO_2 in Ar, pure O_2 and pure N_2 in a filling room where the temperature was controlled at 23 ± 1 ºC and humidity was not regulated. The mass of the CO_2 in Ar standard mixture ~~was hereafter referred to as “gravimetric~~ filled was determined by the difference in the mass of the cylinder~~.”~~ before and after filling with the mixture. The masses of the filled pure O_2 and N_2 were treated in the same manner. The final pressure in the cylinder was 12 MPa, and masses of the individual gases were approximately 8 g of CO_2 in Ar standard mixture, 300 g of pure O_2, and 1000 g of pure N_2.

2.2 Weighing procedure for a cylinder

The masses obtained for the ~~gravimetric~~ cylinders were determined using ~~a~~the same weighing system ~~which is the same~~ as ~~that~~ reported by Matsumoto et al. (2004~~)~~), except ~~a~~for the mass comparator. ~~-~~The mass comparator used in the ~~research~~study of Matsumoto et al. was replaced with a new mass comparator (XP26003L, Mettler Toledo, Switzerland), which had a maximum capacity of 26.1 kg, a ~~readability~~sensitivity of 1 mg, and a linearity of 20 mg. ~~The~~In this study, a cylinder whose mass ~~measurements~~was measured is hereafter referred to as a “sample cylinder”. Mass measurement for ~~the gravimetric~~sample cylinders ~~were~~was performed in a weighing room ~~in which~~where temperature and humidity were controlled at 26 ± 0.5 ºC and 48 ± 1 %, respectively. The temperature, humidity, and atmospheric pressure surrounding ~~the~~our weighing system were measured using a USB connectable logger (TR-73, T ~~&~~and D Corporation, Japan).

~~The mass measurement~~Mass measurements of ~~each gravimetric~~the sample cylinder ~~was~~were conducted with respect to ~~a nearly~~an almost identical reference cylinder aiming to reduce any influence exerted by zero-point drifts, sensitivity ~~issue~~issues associated with the mass comparator, changes in buoyancy acting on the cylinder, and/or adsorption effects on the cylinder~~’~~s surface ~~as a result of~~due to the presence of water vapor (Alink et al., 2000; Milton et al., 2011). ~~Each weighing cycle for both the gravimetric and reference cylinders consisted of~~This is carried out according to several consecutive weighing operations in the ABBA order sequence, where “A” and “B” denote the reference cylinder and ~~gravimetric~~the sample cylinder, respectively. The process of loading and unloading of the cylinders was automated. One complete cycle of the ABBA sequence required five minutes. The “mass reading” recorded ~~from the~~by our weighing system was given ~~by~~as the ~~mass~~ difference between both cylinders mass readings, which was ~~computed~~obtained by subtracting the reference cylinder reading from the ~~gravimetric~~sample cylinder reading.

~~Generally,~~Because the ~~outputs~~output of mass comparators ~~are~~is generally known to be nonlinear, ~~as such,~~ there is a tendency to ~~underestimate~~under- or ~~to overestimate~~ over-estimate mass readings for the ~~differences~~ sample cylinders in ~~the mass values obtained after each reading.~~our weighing system. This is because the ~~calibration lines~~relation between the output of mass comparators and the ~~comparator~~mass of artefacts tend to be different ~~for~~among various scale ranges. To reduce the influence of this nonlinearity, ~~the~~sample cylinders were weighed only when the ~~weight~~ difference in readings between the ~~gravimetric~~sample and reference cylinders was less than 500 mg. This was achieved by placing standard weights ~~in the~~on a weighing pan alongside ~~each~~the sample or reference cylinder. Any mass differences obtained ~~for~~in our weighing system took into account the masses and ~~the~~ buoyancies of the standard weights. The masses of the standard weights were ~~traced~~traceable to the International System of Units. The standard uncertainties of the masses were 0.25 mg, 0.045 mg, 0.028 mg, 0.022 mg, 0.018 mg, 0.014 mg, 0.011 mg, and 0.0090 mg for the 500 g, 100 g, 50 g, 20 g, 10 g, 5 g, 2 g, and 1 g weights, respectively.

~~2.2 Preparation of the highly precise O_2 standard mixtures~~

~~Eleven highly precise O_2 standard mixtures were prepared in accordance with ISO 6142-1:2015. Pure CO_2 (>99.998 %, Nippon Ekitan Corporation, Japan), pure Ar (G1-Grade, 99.9999 %, Japan Fine Products, Japan), pure O_2 (G1-Grade, 99.9999 %, Japan Fine Products, Japan), and pure N_2 (G1-Grade, 99.9999 %, Japan Fine Products, Japan) were used as soruce gases. The value of $\delta^{13}C$ in pure CO_2 (which was adjusted to the atmospheric level) was −8.92 ‰ relative to Vienna Pee Dee Belemnite (VPDB). Impurities in the source gases were identified and quantified using a gas chromatograph with a thermal conductivity detector for N_2, O_2, CH_4 and H_2 in pure CO_2, a gas chromatograph with a mass spectrometer for O_2 and Ar in pure N_2 and N_2 in pure O_2, a Fourier transform infrared spectrometer for CO_2, CH_4 and CO in pure N_2, O_2, and Ar, a galvanic cell-type O_2 analyzer for O_2 in pure Ar, a capacitance-type moisture meter for H_2O in pure CO_2, and a cavity ring-down-type moisture meter for H_2O in pure N_2, O_2 and Ar.~~

~~First, standard mixtures of CO_2 in Ar were prepared from pure CO_2 and pure Ar using the gravimetric method. The molar ratios of CO_2 to Ar were close to the atmospheric ratio of Ar (9340 ppm) to CO_2 (400 ppm or 420 ppm). Next, the gravimetric cylinders were filled as follows with the mixtures of CO_2 in Ar, pure O_2 and pure N_2 in a filling room in which the temperature was controlled at 23 ± 1 °C and humidity was not controlled. The gravimetric cylinder was evacuated using a turbomolecular pump before being weighed using the ABBA technique. Afterward, the evacuated cylinder was filled with the CO_2 in Ar standard mixture and weighed again. The mass of the filled CO_2 in Ar standard mixture was determined by the difference in mass before and after filling. The masses of filled pure O_2 and N_2 were also treated in the same manner. The final pressure in the cylinder was 12 MPa, and the masses of the individual gases were approximately 8 g of the CO_2 in Ar standard mixture, 300 g of pure O_2, and 1000 g of pure N_2.~~

~~2.3 Analytical methods~~

~~To validate the constituents in the highly precise O_2 standard mixtures, the constituents were measured using a cavity ring-down spectrometer for measuring the mole fraction of CO_2, a mass spectrometer for measuring the Ar/N_2 and O_2/N_2 ratios, and a paramagnetic O_2 analyzer for measuring the mole fraction of O_2.~~

~~2.3.1 Measurement of CO_2 mole fraction~~

~~The mole fractions of CO_2 were measured using a cavity ring-down spectrometer (G2301, Picarro, USA), which was~~Temperatures of the sample and reference cylinders were alternately measured by a thermocouple-type thermometer with a resolution of 0.1 K (TX1001 digital thermometer, probe-90030, Yokogawa Test and Measurement Corporation, Tokyo, Japan) before and after weighing of the cylinders.

2.3 Determination procedure of isotopic abundances for O and N

Each HPO was prepared using pure O_2 from two 48 L cylinders and pure N_2 from three or four 48 L cylinders as source gases. The isotopic abundances (^{16}O, ^{17}O, ^{18}O, ^{14}N, and ^{15}N) for pure O_2 and N_2 may be different between cylinders, resulting in abundance differences among each HPO. The averaged values of isotopic abundances in pure O_2 (two cylinders) and pure N_2 (three or four cylinders) used for the respective HPOs were calculated based on the ratios of $^{18}O/^{16}O$, $^{17}O/^{16}O$, and $^{15}N/^{14}N$ in the HPOs. These were calculated using the equations, $^{18}O/^{16}O = [\delta(^{18}O/^{16}O) + 1] \times (^{18}O/^{16}O)_{ref}$, $^{17}O/^{16}O = [\delta(^{17}O/^{16}O) + 1] \times$

$(^{17}O/^{16}O)_{ref}$, and $^{15}N/^{14}N = [\delta(^{15}N/^{14}N) + 1] \times (^{15}N/^{14}N)_{ref}$. The terms $\delta(^{17}O/^{16}O)$, $\delta(^{18}O/^{16}O)$, and $\delta(^{15}N/^{14}N)$ which were determined by a mass spectrometer (Delta-V, Thermo Fisher Scientific Inc., USA) represent the deviation from the corresponding atmospheric value (Ishidoya and Murayama, 2014). The isotopic ratios of $\delta(^{17}O/^{16}O)$, $\delta(^{18}O/^{16}O)$, and $\delta(^{15}N/^{14}N)$ were approximately equal to those of $\delta(^{17}O^{16}O/^{16}O^{16}O)$, $\delta(^{18}O^{16}O/^{16}O^{16}O)$, and $\delta(^{15}N^{14}N/^{14}N^{14}N)$, since $^{17}O^{17}O/^{16}O^{16}O$, $^{18}O^{18}O/^{16}O^{16}O$ and $^{15}N^{15}N/^{14}N^{14}N$ tended to be much less than $^{17}O^{16}O/^{16}O^{16}O$, $^{18}O^{16}O/^{16}O^{16}O$ and $^{15}N^{14}N/^{14}N^{14}N$. Values of $(^{18}O/^{16}O)_{ref}$, $(^{17}O/^{16}O)_{ref}$, and $(^{15}N/^{14}N)_{ref}$ refer to ratios of $^{18}O/^{16}O$, $^{17}O/^{16}O$, and $^{15}N/^{14}N$ in reference air. In the present study, natural air in a 48 L aluminium cylinder (Cylinder No. CRC00045), equipped with a diaphragm valve (G-55, Hamai Industries Limited, Japan) was used as reference air in the AIST scale (hereafter referred to AIST reference air) (Ishidoya and Murayama, 2014). The corresponding atmospheric values shown in Table 1 were used as the ratios of $(^{17}O/^{16}O)_{ref}$, $(^{18}O/^{16}O)_{ref}$, and $(^{15}N/^{14}N)_{ref}$, as isotopic abundances in the troposphere are considered to be constant (Junk and Svec, 1958; Baertschi, 1976; Li et al., 1988; Barkan and Luz, 2005). Because differences between isotopic ratios of N_2, O_2, Ar in the AIST reference air and air samples at Hateruma were sufficiently small to be negligible, their fractionations due to preparation of the AIST reference air are ignored.

2.4 Analytical methods

In this study, a mass spectrometer was used to determine O_2/N_2 and Ar/N_2 ratios in the HPOs. A cavity ring-down spectrometer was used to examine consistency among molar fractions of CO_2 in the HPOs. In this section, we describe the analytical methods and relationships between the absolute O_2/N_2 (Ar/N_2) ratios and the mass-spectrometry based isotopic ratios.

2.4.1 Evaluations of O_2/N_2 and Ar/N_2 ratios in highly precise O_2 standard mixtures and natural air

Ratios of O_2/N_2 and Ar/N_2 in the HPOs were validated by comparison of gravimetrically calculated values with the measured values obtained by the mass spectrometer (Delta-V, Thermo Fisher Scientific Inc., USA). The mass spectrometer was adjusted to measure ion beam currents for masses 28 ($^{14}N^{14}N$), 29 ($^{15}N^{14}N$), 32 ($^{16}O^{16}O$), 33 ($^{17}O^{16}O$), 34 ($^{18}O^{16}O$), 36 (^{36}Ar), 40 (^{40}Ar), and 44 ($^{12}C^{16}O^{16}O$) simultaneously. Isotopic ratios of $\delta(^{15}N^{14}N/^{14}N^{14}N)$, $\delta(^{17}O^{16}O/^{16}O^{16}O)$, $\delta(^{18}O^{16}O/^{16}O^{16}O)$, $\delta(^{16}O^{16}O/^{14}N^{14}N)$, $\delta(^{36}Ar/^{40}Ar)$, and $\delta(^{40}Ar/^{14}N^{14}N)$ were determined against the AIST reference air using the mass spectrometer. In our prepared HPOs, the ratios of $\delta(O_2/N_2)_{HPO\_grav}$ and $\delta(Ar/N_2)_{HPO\_grav}$, comprised of all isotopes of O_2, N_2 and Ar and gravimetrically calculated, are not equal to the isotopic ratios of $\delta(^{16}O^{16}O/^{14}N^{14}N)_{HPO\_meas}$ and $\delta(^{40}Ar/^{14}N^{14}N)_{HPO\_meas}$ measured by the mass spectrometer. This is because the isotopic ratios in source gases are different from the corresponding atmospheric values. The subscripts "HPO_grav" and "HPO_meas" hereafter refer to the gravimetric value and the measured value in the HPO. Thus, mass-spectrometry based isotopic ratios need to be converted to values equivalent to the $\delta(O_2/N_2)_{HPO\_grav}$ ratio and the $\delta(Ar/N_2)_{HPO\_grav}$ ratio. The values of $\delta(O_2/N_2)_{HPO\_meas}$ and $\delta(Ar/N_2)_{HPO\_meas}$ were calculated using mass-spectrometry based on isotopic ratios $^{15}N^{14}N/^{14}N^{14}N$, $^{17}O^{16}O/^{16}O^{16}O$, $^{18}O^{16}O/^{16}O^{16}O$, $^{36}Ar/^{40}Ar$, and $^{38}Ar/^{40}Ar$ as depicted in equations (3) and (4). Isotopic species of $^{17}O^{17}O$, $^{18}O^{17}O$, $^{18}O^{18}O$, $^{15}N^{15}N$, were negligible because the abundance of these species was very small.

$$\delta(O_2/N_2)_{HPO\_meas} = \left[\delta({}^{16}O^{16}O/\,{}^{14}N\,{}^{14}N)_{HPO\_meas} + 1\right] \times \left[\frac{1+{}^{17}O^{16}O/{}^{16}O^{16}O+{}^{18}O^{16}O/{}^{16}O^{16}O}{1+{}^{15}N\,{}^{14}N/{}^{14}N^{14}N}\right]_{HPO} \Big/ \left[\frac{1+{}^{17}O^{16}O/{}^{16}O^{16}O+{}^{18}O^{16}O/{}^{16}O^{16}O}{1+{}^{15}N\,{}^{14}N/{}^{14}N\,{}^{14}N}\right]_{ref} - 1 \quad (3)$$

$$\delta(Ar/N_2)_{HPO\_meas} = \left[\delta({}^{40}Ar/\,{}^{14}N^{14}N)_{HPO\_meas} + 1\right] \times \left[\frac{1+{}^{36}Ar/{}^{40}Ar+{}^{38}Ar/{}^{40}Ar}{1+{}^{15}N\,{}^{14}N/{}^{14}N^{14}N}\right]_{HPO} \Big/ \left[\frac{1+{}^{36}Ar/{}^{40}Ar+{}^{38}Ar/{}^{40}Ar}{1+{}^{15}N\,{}^{14}N/{}^{14}N^{14}N}\right]_{ref} - 1 \quad (4)$$

The values of ${}^{15}N^{14}N/{}^{14}N^{14}N$, ${}^{17}O^{16}O/{}^{16}O^{16}O$, and ${}^{18}O^{16}O/{}^{16}O^{16}O$ in the HPOs and the AIST reference air were calculated using isotope abundances of O and N determined by the procedure described in section 2.3 (Table 1). The ${}^{36}Ar/{}^{40}Ar$ ratio of pure Ar filled in the HPOs was calculated using equation ${}^{36}Ar/{}^{40}Ar = [\delta({}^{36}Ar/{}^{40}Ar)_{HPO\_meas} + 1] \times ({}^{36}Ar/{}^{40}Ar)_{ref}$. The $\delta({}^{36}Ar/{}^{40}Ar)_{HPO\_meas}$ value was determined by mass spectrometry of the HPOs. The $({}^{36}Ar/{}^{40}Ar)_{ref}$ value obtained was the atmospheric value (${}^{36}Ar/{}^{40}Ar = 0.003349 \pm 0.000004$), because isotopic abundances of Ar in the AIST reference air were equal to that of the atmospheric value. The value of ${}^{38}Ar/{}^{40}Ar$ in the HPOs and the AIST reference air, which could not be measured, was assumed to be ${}^{38}Ar/{}^{40}Ar = 0.000631 \pm 0.000004$ taken from previous reports as the atmospheric values. Deviations of respective abundances of ${}^{38}Ar$ from the atmospheric value were considered to be less than the uncertainty of the atmospheric value for ${}^{38}Ar$. The atmospheric values of isotopic abundances for Ar were reported in an IUPAC technical report (Böhlk, 2014).

On the other hand, the absolute O_2/N_2 ratio in the AIST reference air was calculated by substituting the $(O_2/N_2)_{HPO\_grav}$ in the HPOs and the $\delta(O_2/N_2)_{HPO\_meas}$ for $(O_2/N_2)_{sam}$ and for $\delta(O_2/N_2)$ in equation (1). The absolute Ar/N_2 ratio in the AIST reference air was calculated in same manner (see the section 5.3).

2.4.2 Measurements of CO_2 in highly precise O_2 standard mixtures

Molar fractions of CO_2 in HPOs were verified using a cavity ring-down spectrometer (G2301, Picarro Inc., USA) equipped with a multi-port valve (Valco Instruments Co. Inc., USA) for gas introduction and a mass flow controller (SEC-N112, 100SCCM, Horiba STEC, CO., Ltd, Japan). ~~Mole~~Molar fractions were determined using three primary standard gases (364.50 ± 0.14 ~~ppm~~µmol mol^{-1}, 494.04 ± 0.14 ~~ppm~~µmol mol^{-1}, and 500.32 ± 0.14 ~~ppm~~µmol mol^{-1}) that had been prepared from pure CO_2 and purified Air (G1 grade, Japan Fine Products, Japan) in accordance with ISO 6142-1:2015~~, respectively~~. The ~~value of $\delta^{13}C$ in~~ pure CO_2 ~~(which~~ was ~~adjusted to~~ the ~~atmosphere level) was −8.92 ‰ relative to VPDB~~same as the source gas used for preparation of the HPOs.

~~2.3.2 Measurement of O_2/N_2 and Ar/N_2 ratios~~

~~The O_2/N_2 and Ar/N_2 ratios were measured using a mass spectrometer (Thermo Scientific Delta-V) (Ishidoya and Murayama, 2014). The O_2/N_2 ratio is expressed as $\delta(O_2/N_2)$ according to Eq. (1). The Ar/N_2 ratio, which is also expressed as $\delta(Ar/N_2)$, is defined by~~

~~$\delta(Ar/N_2)(\text{per meg}) = [\frac{(Ar/N_2)_{sample}}{(Ar/N_2)_{standard}} - 1] \times 10^6$ (2)~~

~~where the subscripts "sample" and "standard" refer to the sample air and standard air in the same way as $\delta(O_2/N_2)$, respectively. In this study, natural air in 48 L aluminum cylinder (Cylinder No. CRC00045), equipped with a diaphragm valve (G-55, Hamai Industries Limited, Japan) was used as the standard air to determine the $\delta(O_2/N_2)$ and $\delta(Ar/N_2)$ values on the AIST scale (Ishidoya and Murayama, 2014). The mass spectrometer was adapted to simultaneously measure ion beam currents for masses 28 ($^{14}N^{14}N$), 29 ($^{15}N^{14}N$), 32 ($^{16}O^{16}O$), 33 ($^{17}O^{16}O$), 34 ($^{18}O^{16}O$), 36 (^{36}Ar), 40 (^{40}Ar), and 44 ($^{12}C^{16}O^{16}O$). These masses were also noted as deviations in $\delta(^{15}N^{14}N/^{14}N^{14}N)$, $\delta(^{17}O^{16}O/^{16}O^{16}O)$, $\delta(^{18}O^{16}O/^{16}O^{16}O)$, $\delta(^{16}O^{16}O\ /^{14}N^{14}N)$, $\delta(^{36}Ar/^{40}Ar)$, $\delta(^{40}Ar/^{14}N_2)$, and $\delta(^{12}C\ ^{16}O^{16}O/^{14}N^{14}N)$ from the corresponding atmospheric values that had been recorded for the standard air.~~

~~In the case of sample air, it was assumed that both the $\delta(O_2/N_2)$ and $\delta(Ar/N_2)$ values were equal to those of $\delta(^{16}O^{16}O\ /^{14}N^{14}N)$ and $\delta(^{40}Ar/^{14}N^{14}N)$, since the ratios of Ar, O, and N isotopes present in the atmosphere tended to be spatiotemporally constant. On the other hand, the isotopic ratios of pure Ar, O_2, and N_2 used in this study were different from the atmospheric values listed in Table 1. Consequently, both the $\delta(O_2/N_2)$ and $\delta(Ar/N_2)$ values in the highly precise O_2 standard mixtures were computed using the measurements obtained for $^{15}N^{14}N/^{14}N^{14}N$, $^{17}O^{16}O/^{16}O^{16}O$, $^{18}O^{16}O/^{16}O^{16}O$, $^{36}Ar/^{40}Ar$, and $^{38}Ar/^{40}Ar$, as depicted in the equations below.~~

$$\delta(O_2/N_2) = \left\{\frac{(^{16}O^{16}O/\,^{14}N_2)_{STD}}{(^{16}O_2/\,^{14}N_2)_{standard}} \times \left[\frac{1+{}^{17}O^{16}O/^{16}O^{16}O+{}^{18}O^{16}O/^{16}O^{16}O}{1+{}^{15}N^{14}N/^{14}N^{14}N}\right]_{STD} \Big/ \left[\frac{1+{}^{17}O^{16}O/^{16}O^{16}O+{}^{18}O^{16}O/^{16}O^{16}O}{1+{}^{15}N^{14}N/^{14}N^{14}N}\right]_{standard} - 1\right\} \times 10^6 \qquad (3)$$

$$\delta(Ar/N_2) = \left\{\frac{(^{40}Ar/\,^{14}N^{14}N\,)_{STD}}{(^{40}Ar/\,^{14}N^{14}N\,)_{standard}} \times \left[\frac{1+{}^{36}Ar/^{40}Ar+{}^{38}Ar/^{40}Ar}{1+{}^{15}N^{14}N/^{14}N^{14}N}\right]_{STD} \Big/ \left[\frac{1+{}^{36}Ar/^{40}Ar+{}^{38}Ar/^{40}Ar}{1+{}^{15}N^{14}N/^{14}N^{14}N}\right]_{standard} - 1\right\} \times 10^6 \qquad (4)$$

~~The subscripts "STD" refer to the highly precise O_2 standard mixtures that were prepared in this study. The values of $^{15}N^{14}N/^{14}N^{14}N$, $^{17}O^{16}O/^{16}O^{16}O$, and $^{18}O^{16}O/^{16}O^{16}O$ in both the O_2 standard mixtures and standard air were calculated using the isotope abundances of O and N listed in Table 1. The $^{36}Ar/^{40}Ar$ ratio for the highly precise O_2 standard mixtures was calculated from $\delta(^{36}Ar/^{40}Ar)$ and $(^{36}Ar/^{40}Ar)_{standard}$. The value of $\delta(^{36}Ar/^{40}Ar)$ were determined using the mass spectrometer. The $(^{36}Ar/^{40}Ar)_{standard}$ was determined using the atmospheric value ($^{36}Ar/^{40}Ar = 0.003349 \pm 0.000004$), because the ratio of Ar isotopes in standard air was equal to that of the atmospheric value. On the other hand, the value of $^{38}Ar/^{40}Ar$ in the highly precise O_2 standard mixtures was $^{38}Ar/^{40}Ar = 0.000631 \pm 0.000004$ which was atmospheric values. The atmospheric values of abundance for Ar isotopes were reported in an IUPAC technical report (Böhlk, 2014).~~

~~2.3.3 Measurement of O_2 mole fractions~~

~~A paramagnetic oxygen analyzer (POM-6E, Air Liquide Japan) was used to measure the mole fractions of O_2 in the highly precise O_2 standard mixtures. Details regarding the analyzer used have been reported by Aoki and Shimosaka (2017). Briefly, the analyzer was equipped with inlets for sample and reference gases (Kocache, 1986). Synthetic air with O_2 mole fraction of 20.650 % was used as the reference gas, and the pressures of the reference gas and the sample gas were set at 300 kPa, and 180 kPa, respectively.~~

3 Identifying and minimizing unknown factors of uncertainty

As previously mentioned~~ before,~~, there ~~were~~are several unknown factors that ~~influenced the differences in~~influence mass readings obtained for ~~the gravimetric and reference~~sample cylinders. ~~These~~Identifying and minimizing these unknown factors ~~in uncertainty and the weighing procedure used to minimize them are~~ is discussed in this section.

3.1 Factors to cause deviations of mass readings

Generally, ~~the~~ mass ~~reading~~readings of a sample cylinder obtained from a mass comparator ~~tends~~tend to vary ~~as a result of~~ due to numerous factors~~. Buoyancy~~ such as buoyancy, adsorption/desorption and thermal effects~~ can be~~. The buoyancy effect is caused by changes in the density of the surrounding air due to ~~the~~ variations in ambient temperature, humidity, and pressure~~, whereas adsorption effects~~. Adsorption effect can greatly influence mass readings of ~~the~~a sample cylinder by ~~the~~ adsorption and desorption of water vapor ~~in~~from surrounding ambient air on the external surface of ~~the~~a sample cylinder (Alink et al., 2000; Mizushima, 2004, 2007; Milton et al., 2011). ~~Thermal effects are~~The thermal effect is related to ~~the~~ temperature gradients between ~~the~~a sample cylinder and the surrounding ambient air (Gläser, 1990, 1999; Mana et al., 2002; Gläser and Borys, 2009; Schreiber et al., 2015~~). They~~), which is able to change ~~a~~the weight force of the sample cylinder through ~~friction~~frictional forces exerted on the vertical surface of ~~the~~a sample cylinder and pressure forces on the horizontal surface. Both the friction and pressure forces are caused by the upward or downward flow of air~~, which was cooled or heated by the cylinder. Mass differences between the gravimetric and reference cylinders tend to deviate from true value when these effects are exerted independently and to varying degrees on the gravimetric and reference cylinders~~ that is heated or cooled, respectively, by the sample cylinder.

When the ABBA technique is ~~used to perform~~ employed for mass measurements under identical experimental conditions, the deviations of the mass readings due to the factors described above become negligible because they are equally exerted on both the ~~gravimetric~~sample and the reference ~~cylinders under identical experimental conditions. Actually, any~~cylinder. In fact, the buoyancy ~~effects~~effect could be ~~canceled~~cancelled by adopting the ABBA technique in our mass measurements (see Section 4.3.1). ~~However,~~ On the other hand, the identical experimental conditions tend to be disturbed by the temperature change on the ~~gravimetric~~sample cylinder~~'s~~ surface ~~could change~~ by adiabatic compression of the source gases and ~~the work (evacuating and filling) in the filling room where is different from the weighing room in temperature, whereas adsorption~~ by the temperature difference between the filling room and the weighing room. Mass readings of the sample cylinder deviate from true values when thermal effects due to a change in the sample cylinder surface temperature are exerted independently and at varying degrees on the sample and reference cylinders. Moreover, the amount of water ~~amounts~~adsorbed on the ~~gravimetric~~sample cylinder~~'s~~ surface ~~could change~~can also be influenced by humidity if the ~~work~~level in the filling room ~~where~~ is different from that in the weighing room~~ in humidity~~. This non-uniformity ~~was~~of temperatures and the water amount between the sample cylinder surface and the surrounding ambient air is assumed to be the main contributor of uncertainties in ~~the~~ obtained mass ~~values~~ readings of the sample cylinder (Matsumoto et al., 2008). ~~Therefore, we~~ In order to identify and minimize the contribution to the non-uniformity, we examined ~~achievement of~~ the equilibrium ~~in~~of both humidity and temperature for the ~~gravimetric cylinder's~~ surface~~, as well as~~ of the ~~surrounding ambient air,~~sample cylinder used in this study before carrying out any measurement~~ for identifying~~.

3.2 Identifying and minimizing ~~the contribution of the non-uniformity.~~ unknown uncertainty factors

~~3.1 The~~ Equilibrium in the temperature and the water amount between the sample cylinder surface and its surrounding ambient air is considered to be achieved by placing the sample cylinder on our weighing system for an appropriate duration of time ~~required for equilibration with ambient air~~

~~Achieving temperature and humidity~~before the mass reading. Here, the equilibrium between the reference cylinder~~'s~~ surface and its surrounding ambient air ~~could be done by placing the cylinder on the weighing system for an appropriate time interval before mass readings. Here the equilibrium at the reference cylinders' surface~~ is always ~~maintained because~~achieved as the reference cylinder ~~had been~~is permanently left on the weighing system~~, whereas the~~. The equilibrium for the sample cylinder is easily disturbed by the processes of its evacuation and filling of the source gases. To quantify the appropriate time interval needed to restore equilibrium~~ of the gravimetric cylinder's surface had often been disturbed by processes of the cylinder evacuation and the gas filling. To quantify the time needed for equilibration after the disturbing, the mass differences between the gravimetric and reference cylinders~~, the mass readings of the sample cylinder were recorded after the evacuation ~~of the gravimetric cylinder~~ and ~~subsequent~~after the filling~~ of the source gases were monitored. The~~. These values were plotted against the time ~~needed to achieve equilibrium~~ elapsed after evacuation and filling (Figure 1). ~~The equilibrium was~~The surface temperature of the sample cylinder recorded after the evacuation was 2 K lower, while the temperatures recorded after the filling for CO_2 in Ar standard mixture, pure O_2, and pure N_2 were −0.7 K, 1 K, and 6 K higher than that of the reference cylinder, respectively. In this experiment, the equilibria were considered to be achieved when the standard deviation of the ~~values~~ mass readings remained constant for two or more hours ~~and were less than~~ with the repeatability value of $<$ 0.82 mg (see in Section 4.3.1.). ~~Interesting~~Interestingly, the mass ~~differences~~readings recorded after ~~evacuating~~the evacuation and filling ~~with the~~for CO_2 in Ar mixture tended to decrease as time elapsed, while those after filling with pure O_2 and ~~the~~ N_2 gases tended to increase. Deviations in mass readings had some connection with the temperature difference between the reference and sample cylinders. The results imply that warmer cylinders appear lighter.

~~The~~Appropriate time ~~needed for equilibration is~~intervals were defined as the time elapsed from ~~cylinder~~the evacuation or the filling time to the point of re-achieving equilibrium. ~~The equilibrium~~This time interval was noted as 5 h after complete ~~cylinder~~ evacuation. ~~The times needed to achieve the equilibrium~~Time intervals required after ~~the cylinders were filled~~filling with ~~the~~ relevant ~~gas~~gases were different ~~between~~depending on the filled gas species to some extent. For the CO_2 in Ar mixture, ~~the equilibrium was~~ equilibria were achieved in 3 h to 5 h, while 4 h to 5 h were required for O_2 equilibration and 7 h to 9 h for N_2. ~~It~~These intervals indicate that preparation of a single HPO requires several days. To determine the mass of the sample cylinder in as short time as possible, a clear indicator for carrying out mass measurement is needed.

As described above, the deviations in mass readings are considered ~~that each equilibrium time~~ to have some ~~connection~~relation with the temperature ~~of the gravimetric cylinder just after the evacuation and the gas filling, since the mass readings of the gravimetric cylinder decreases depending on increase in its surface temperature as for either thermal effect or adsorption effect. This is because the temperature~~ differences ~~between~~in the ~~gravimetric~~sample and reference cylinders~~ was the main factor contributing to the friction and pressure forces of thermal effect at room temperature. The mass difference decreases as~~. Therefore, we proceeded to examine this relationship to understand whether the temperature ~~of the gravimetric cylinder becomes higher than that of the reference cylinder. On the other hand, amount of adsorbed water on gravimetric cylinder's~~

~~surface also decreases with increase of its temperature. The mass~~ difference ~~decrease as the temperature of the gravimetric cylinder becomes higher than that of the reference cylinder.~~

~~Actually, the deviations in the mass difference values shown in Figure 1 had some connection with the temperature of the gravimetric and reference cylinders, because the gravimetric cylinder's temperature recorded after the evacuation was 2 K lower while the temperatures recorded after filling with the standard CO_2 in Ar mixture, pure O_2, and pure N_2 were −0.7 K, 1 K, and 6 K higher, respectively, than that of the reference cylinder. On the other hand, the temperature of the gravimetric cylinder after the evacuation and the filling depends on amounts of the source gases and the conditions of the weighing room. Considering this, a reference parameter to clearly identify when equilibrium had been achieved was needed to determine more accurately the mass differences between the cylinders and to minimize associated factors of uncertainty~~

~~3.2 Deviation of the mass difference by thermal effect~~

~~The relationship between the deviation values obtained in the recorded mass differences and the temperature differences on the surface of the gravimetric and reference cylinders was investigated. The results of the~~can be the indicator. The closed squares shown in Figure 2 indicate that the deviation of mass readings was proportional to ~~the~~ temperature differences ~~and slope of the fitting line, which had been obtained by applying linear least square methods to the data~~. This deviation rate was determined to be −14.3 mg K^{-1}. Although the results indicate that a temperature difference of 0.1 K ~~caused~~causes a deviation of 1.4 mg, the deviation in the recorded mass ~~differences~~readings ensures the repeatability value of 0.82 mg that is achieved by reducing the temperature difference to below 0.06 K. By conducting measurements of the cylinder ~~temperatures~~temperature using ~~a~~the thermocouple-type thermometer ~~with the resolution of 0.1 K (TX1001 digital thermometer, probe 90030, Yokogawa Test & Measurement Corporation, Tokyo, Japan)~~ and ensuring that the mass readings were taken when the temperature of both cylinders ~~indicated~~were the same ~~values~~, we were able to reduce the deviation contributing to the mass ~~difference~~readings.

To validate the proposed weighing procedure, the reproducibility of ~~the~~ mass ~~difference values~~readings obtained after disturbing the equilibrium ~~had to be evaluated.~~was measured. Hence, the mass reading sequence after a cooling or heating cycle of the cylinders was examined. Figure 3 illustrates the results in which four heating cycles (number 1 to 4) and four cooling cycles (number 5 to 8) were conducted. In this experiment, ~~the~~ temperatures of the cooled or heated cylinder were 1 K to 3 K lower or 10 K to 20 K higher ~~, respectively,~~ than that of the reference cylinder~~.~~, respectively. When ~~the masses~~mass readings were recorded after ~~the~~ensuring equal temperatures of both the ~~gravimetric~~sample and reference cylinders ~~were equivalent~~, no difference in ~~the values~~mass readings recorded after the cooling and heating cycles was ~~noticed~~detected. The reproducibility of ~~the~~ mass ~~difference values~~readings was estimated to be 0.44 mg with regards to the standard deviation of the mass ~~difference values~~readings shown in Figure 3. The fact that ~~the standard deviation~~reproducibility was lower than the repeatability ~~values confirmed the validity of~~value validated the weighing procedure ~~and indicated that the changes in the mass differences attributable to~~. The contributions to mass readings by non-equilibrium conditions were negligible ~~. It was confirmed that~~ using the ~~proposed~~established weighing procedure ~~had a repeatability of 0.82 mg~~.

It is difficult to ~~state~~determine whether ~~changes~~deviations in ~~the~~ mass ~~differences~~readings recorded for ~~the~~sample cylinders ~~was~~were caused by thermal or adsorption effects simply by ~~analyzing~~analysing these results. This is because both effects are related to temperature fluctuations. However, ~~an important indication that the changes were caused by one factor or the other~~

~~is related to the fact that~~ the thermal ~~effects~~effect influenced the slope of the calibration ~~line~~function solely through temperature ~~fluctuations~~differences, whereas the adsorption~~ effects~~/desorption effect influenced the slope of the calibration ~~line~~function via a combination of both ambient temperature and humidity. This is ~~due to the fact that~~because the adsorbed or desorbed amounts of water on the surface of both cylinders ~~is~~are highly dependent on the ~~cylinders'~~cylinder temperature~~,~~ and humidity of the surrounding ambient air~~, and condition of the cylinder's surface.~~. To determine which of these effects contributed the most to the ~~changes in the mass readings~~deviations, the relationship between the deviations and temperature differences was investigated under various conditions in the weighing room. Humidity was ~~strictly~~stringently controlled at 30%, 50%, 65%, and 80%, whereas ~~the~~ temperature levels were maintained at 22 ºC, 26 ºC, and 29 ºC. As shown in Figure 2, the ~~results indicated that the deviation values~~slope did not depend on the humidity ~~and~~nor temperature~~ factors~~. These results ~~indicated~~indicate that the dominant factor of ~~changes in the mass~~deviations in mass readings was rather an effect of thermal gradients than adsorption, because the deviations depended on the temperature difference ~~values was temperature-related and not an effect of adsorption.~~only. Therefore, we focused on minimizing the impact of any thermal ~~effects during the~~ gradient in further experiments.

4 ~~Preparation of~~Evaluation of uncertainty factors for the O_2 Standard Mixtures

In this section, we discuss any uncertainty factors associated with ~~the mole~~molar fractions of ~~the~~ constituents in the ~~highly precise O_2 standard mixtures.~~HPOs. The gravimetric ~~mole~~molar fraction (y_k) of the constituent k (CO_2, Ar, O_2, and N_2) was calculated using the molar mass (M_i) and ~~a mole~~the molar fraction ($x_{i,j}$) of the constituent i (CO_2, Ar, O_2, N_2 and impurities) in the filled source gas j (CO_2 in Ar standard mixture, pure O_2, and pure N_2). Additionally, ~~the~~ mass (m_j) of the source gases filled ~~with~~into the sample cylinder were incorporated into ~~the Eq.~~equation (5) in accordance with ISO 6142-1:2015.

$$y_k = \frac{\sum_{j=1}^{r}\left(\frac{x_{k,j}\times m_j}{\sum_{i=1}^{q} x_{i,j}\times M_i}\right)}{\sum_{j=1}^{r}\left(\frac{m_j}{\sum_{i=1}^{q} x_{i,j}\times M_i}\right)} \qquad (5)$$

In this equation, r and q represent the number of source gases j and constituents i, respectively, while $x_{k,j}$ is the ~~mole~~molar fraction of the constituent k in the source gas j. Uncertainties ($u(y_k)$) associated with the gravimetric ~~mole~~molar fraction were calculated according to the law of propagation.

$$u^2(y_k) = \sum_{j=1}^{r}\sum_{i=1}^{q}\left(\frac{\partial y_k}{\partial x_{i,j}}\right)^2 \times u^2(x_{i,j}) + \sum_{i=1}^{q}\left(\frac{\partial y_k}{\partial M_i}\right)^2 \times u^2(M_i) + \sum_{j=1}^{r}\left(\frac{\partial y_k}{\partial m_j}\right)^2 \times u^2(m_j) \qquad (6)$$

In this equation, $u(A)$ ~~was~~depicts the standard uncertainty for A. Gravimetric ~~mole~~molar fractions of the ~~constituents~~constituent k and ~~their~~its associated ~~uncertainties~~ uncertainty in the ~~mole~~molar fractions for the ~~highly precise O_2 standard mixtures~~HPOs prepared in this study were calculated using ~~Eq.~~equation (5) and ~~Eq.~~equation (6~~)~~), and they are listed in Table 2. ~~As noted, the~~The standard uncertainties for the constituents N_2, O_2, Ar, and CO_2 were 0.8 ~~ppm to~~– 1.0 ~~ppm~~µmol mol^{-1}, 0.7 ~~ppm to~~– 0.8 ~~ppm~~µmol mol^{-1}, 0.6 ~~ppm to~~– 0.7 ~~ppm~~µmol mol^{-1}, and 0.03 ~~ppm~~µmol mol^{-1}, respectively. Table 3 lists the contribution of ~~each uncertainty factor to~~ the purity of the source gases, molar masses of the constituents, and masses of the source gases~~.~~ to the gravimetric molar fraction. These correspond to the square ~~roots~~root of the first, second, and third terms found in ~~Eq.~~equation (6), respectively. Uncertainty factors in the gravimetric ~~mole~~molar fractions in the HPOs were mainly those of the ~~masses obtained~~mass for the source gases~~.~~ filled into the sample cylinder. Contributions from other sources of uncertainty were negligible. ~~The purity~~Purity of the source gases and molar masses of the constituents *i*, as well as the masses of the source gases and their associated standard uncertainties, are described in Sections 4.1, 4.2, and 4.3.

4.1 Purity of source gas

Pure O_2, N_2, Ar, and CO_2 were used as source gases to prepare the ~~standard O_2 mixtures. The mole~~HPOs. Molar fractions of ~~the~~ impurities present in ~~the~~ source gases and their associated standard uncertainties were determined based on the primary standard gases prepared in accordance with ISO 6142-1:2015. When the ~~mole~~molar fraction of impurity *h* was under detection limit (L_h), the ~~mole~~molar fractions (x_h) and standard uncertainty ($u(x_{h,j})$) in the source gas *j* were calculated using the equations $x_{h,j} = L_{h,j}/2$ and $(x_{h,j}) = L_{h,j}/2\sqrt{3}$. The calculated values for the impurities and purities of the source gases are listed in Table 4.

4.2 Molar masses of constituents

~~The molar~~Molar masses (M_i) of the ~~source gases~~constituents were calculated using ~~the~~ most recent atomic masses and isotopic abundances reported by the IUPAC. However, IUPAC values for ~~the~~ atomic masses of O and N have large standard uncertainties because they reflect ~~the~~ variability present in ~~the~~ individual isotopic abundances of natural terrestrial matter. Using IUPAC values, ~~the~~ standard uncertainties for ~~the~~ N_2 and O_2 ~~mole~~molar fractions in the HPOs were calculated to be 4 ~~ppm~~μmol mol^{-1}. In addition, ~~the~~ atmospheric values of their isotopic abundances could not be used for calculating ~~the~~ molar masses of the source gases even though pure O_2 and N_2 were produced from air. This ~~was~~is because isotopically abundant O and N in ~~the source gases tended~~pure O_2 and N_2 tends to deviate from the corresponding atmospheric value during the production process. Therefore, the isotopic abundances of O and N in HPOs were precisely determined using mass spectrometry.

~~To prepare one highly precise O_2 standard mixture, pure O_2 of two 48 L cylinders were used, whereas pure N_2 of three or four 48 L cylinders were used. The abundances of the respective isotopes of O and N were determined based on the ratios of $^{15}N/^{14}N$, $^{18}O/^{16}O$, and $^{17}O/^{16}O$ in each the highly precise O_2 standard mixture. The ratios of $^{15}N/^{14}N$, $^{18}O/^{16}O$, and $^{17}O/^{16}O$ were calculated using the corresponding atmospheric values (Junk and Svec, 1958; Baertschi, 1976; Li et al., 1988; Barkan and Luz, 2005) and the ratios of the measured isotopes $\delta(^{15}N/^{14}N)$, $\delta(^{18}O/^{16}O)$, and $\delta(^{17}O/^{16}O)$ which were the deviation from the corresponding atmospheric value in each cylinder.The ratios of isotopes $\delta(^{15}N/^{14}N)$, $\delta(^{18}O/^{16}O)$, and $\delta(^{17}O/^{16}O)$ were equal to the values obtained for isotopes $\delta(^{15}N^{14}N/^{14}N^{14}N)$, $\delta(^{18}O^{16}O/^{16}O^{16}O)$, and $\delta(^{17}O^{16}O/^{16}O^{16}O)$, since $\delta(^{18}O^{18}O/^{16}O^{16}O)$ and $\delta(^{17}O^{17}O/^{16}O^{16}O)$ tended to be much less than $\delta(^{18}O^{16}O/^{16}O^{16}O)$ and $\delta(^{17}O^{16}O/^{16}O^{16}O)$. Examples of the isotopes' abundances and their~~ Their isotopic abundance and associated standards of uncertainty are shown in Table 1. The difference of isotopic abundances of O and N between respective HPOs were negligible.

~~The~~ Based on the isotopic abundances obtained in this study and the atomic masses of ~~N~~O and ~~O~~N in the filled source gases, ~~the~~ pure O_2 and N_2 were determined with ~~the~~ relative standard uncertainties of 0.000029 % and 0.000006 %, respectively. It was shown that the uncertainty in ~~the~~ molar masses is negligible (Table 3). Although the grade and supplier of the pure O_2 and N_2 used in this study were the same as those of the source gases used by Tohjima et al. (2005), the atomic masses (15.999366 (1) for O and 14.006717 (4) for N) obtained for ~~each element~~the two elements were different from Tohjima~~'s~~ et al. reported values (15.999481 (8) for O and 14.006677 (4) for N). These differences resulted in a deviation of 0.4 ~~ppm~~µmol mol^{-1} and 1.2 ~~ppm~~µmol mol^{-1} for O_2 and N_2, respectively. Since ~~this~~these results ~~inferred~~infer that the ratios of O and N isotopes ~~changed due to~~change with production time, the isotopic abundances of O and N in the source gases have to be precisely determined whenever ~~the highly precise O_2 standard mixtures is~~HPOs are prepared~~.~~ using different pure O_2 and N_2. On the other hand,~~ the~~ standard uncertainties in the atomic mass presented in an IUPAC technical report by De Laeter et al. (2003) were sufficient for further use in the case of Ar and CO_2 as source gases.

4.3 Determining the masses of the filled gases

~~The mass~~Masses of ~~each gas~~ individual gases that ~~was~~were filled into the ~~gravimetric~~sample cylinders ~~was~~were calculated using the mass ~~differences~~difference before and after the filling. The standard uncertainty of the ~~resultant~~obtained mass was calculated by combining ~~the~~ standard uncertainties ~~in the mass differences obtained for each gas~~of mass readings of the sample cylinder before and after filling each gas. To determine ~~the~~ uncertainty in ~~the~~ mass ~~difference~~reading of the sample cylinder, three factors were evaluated i.e., the repeatability~~,~~ $u(m_{rep})$ of the mass ~~difference values~~readings, permeation~~,~~ $u(m_{gas\ permeate})$ of the source gases during weighing, and buoyancy ~~changes,~~change $u(m_{buoyancy})$ due to the expansion of the ~~gravimetric~~ cylinder. The standard uncertainties ($u(m_{cyl})$) were defined according to equation (7).

$$u^2(m_{cyl}) = u^2(m_{rep}) + u^2(m_{gas\ permeate}) + u^2(m_{buoyancy}). \qquad (7)$$

These factors are discussed in detail in ~~Sections~~sections 4.3.1, 4.3.2, and 4.3.3.

4.3.1 Repeatability of ~~the~~ mass ~~difference measurements~~readings

The repeatability of ~~the weighing system~~mass readings was evaluated by ~~continuously measuring the mass difference between the gravimetric and reference~~ continuous mass measurement of sample cylinders using the ABBA technique over three days. This is because ~~the~~ preparation of ~~one highly precise O_2 standard mixture takes~~a single HPO requires three days. ~~The mass~~Mass readings were ~~taken~~recorded after the ~~gravimetric~~sample cylinder ~~had been~~was left on the weighing system for at least a week. ~~Using our weighing system, we also obtained~~Air density ~~values for the surrounding ambient air~~was likewise measured for three days by carefully monitoring temperature, humidity, and pressure changes in ~~the surrounding~~ ambient air (Figure 4). Our findings ~~indicated~~indicate that the ~~obtained~~ mass ~~difference values remained~~readings remain stable during the three-day experiment. The standard deviation of ~~the~~ mass ~~difference values~~readings (0.82 mg) ~~are~~is represented as repeatability~~,~~ $u(m_{rep})$. The fact that the mass ~~difference values~~readings were not affected by changes in the air density also ~~indicated~~indicates that buoyancy issues ~~infl~~influencing the sample cylinder were cancelled out by changes simultaneously affecting the reference cylinder.

4.3.2 Permeation of source gases during weighing

~~The gravimetric and reference~~All of the cylinders used in this study have diaphragm valves, which were joined to the cylinders via pipe fittings and sealed with Teflon tape. The seal of diaphragm valves was made from PCTFE, through which gases ~~tended~~tend to permeate quite slowly (Sturm, 2004). Since ~~the~~ permeation of the source gases during weighing the sample cylinders resulted in ~~the~~ evaluation error of the masses for the source gases, we examined the permeability of purified air by monitoring ~~the mass difference using the gravimetric~~mass of the sample cylinder filled with purified air at a pressure of 8 MPa. The changes in ~~the~~ mass ~~difference values~~readings were measured for over four months. From these results, it was determined that the permeability was 0.013 mg day^{-1}. This effect was considered to be negligible because it is much lower than the repeatability. ~~As such~~Therefore, the contribution of permeability ($u(m_{gas\ permeate})$) to the standard uncertainty calculations ($u(m_{cyl})$) was ignored. On the other hand, the ~~permeation~~ amount of ~~the~~ air permeating from the sample cylinder ~~over~~ during the course of a year was calculated to be about 4.7 mg. This quantity may cause changes in the composition of the ~~highly precise O_2 standard mixture~~HPO if the mixture is kept for ~~longtime~~extended periods of time, since the gas permeability depends on the gas species (Sturm, 2004).

4.3.3 Buoyancy effect of cylinder expansion

Oh et al. (2013) reported that ~~the~~ volume in the 10 L ~~aluminum~~aluminium cylinders linearly increases with ~~changes~~increase in ~~the~~ internal pressure, and ~~the~~ volume expansion was determined to be 24 ± 2 ml when the pressure difference in the ~~cylinder~~sample cylinders was 12 MPa. Tohjima et al. (2005) likewise reported a volume expansion of 22 ± 4 ml when the pressure difference was 10 MPa. In this study, we adopted ~~that the~~a volume expansion of the sample cylinders ~~was~~as 55 ± 5 ml~~, which was~~ measured by a cylinder supplier, when the pressure difference was 25 MPa. Compared to the expansion ~~rates~~rate with respect to pressure variations reported by Oh (2.0 ± 0.2 ml MPa^{-1}) (2013) and Tohjima (2.2 ± 0.4 ml MPa^{-1}) (2005), ~~the~~expansion rate of the sample cylinders used in this study was determined to be 2.2 ± 0.2 ml MPa^{-1} ~~because the factors contributing to uncertainty within these rates tended to remain constant.~~. The pressure ~~differences~~difference recorded before and after filling ~~were~~with source gases was 0.12 MPa, 2.5 MPa, and 9.4 MPa for CO_2 in Ar standard mixture, pure O_2, and pure N_2, respectively. These pressure differences were subsequently used to calculate buoyancy effects, which were reported as 0.3 mg, 6.4 mg, and 23.9 mg for CO_2 in Ar standard mixture, pure O_2, and pure N_2, respectively. In turn, these buoyancy effects caused changes in the gravimetric ~~mole~~molar fraction of +0.5 ~~ppm~~μmol mol^{-1} and −0.5 ~~ppm~~μmol mol^{-1} for O_2 and N_2, respectively. The final mass ~~difference values~~readings were corrected to take these changes into account. The standard uncertainties $u(m_{buoyancy})$ in linear expansion were considered to be negligible.

5 Validation of the ~~Constituents~~constituents in the ~~Highly Precise~~highly precise O_2 ~~Standard Mixtures~~standard mixtures

The O_2 ~~mole fraction~~ molar fractions in the ~~highly precise standard mixture would~~HPOs deviate from ~~the~~ gravimetric ~~value if~~values with deviation of the ~~mole~~molar fractions of other constituents ~~have the deviations from the gravimetric values.~~. In this section, the molar fractions of all constituents were validated. The gravimetric and measured values for the CO_2 ~~mole fractions, δ(Ar/N$_2$), δ(O$_2$/N$_2$), and O_2 mole~~molar fractions were compared ~~to validate the mole fractions of the constituents in the O_2 mole fractions in the highly precise O_2 standard mixtures. The~~ , along with the values of δ(Ar/N$_2$)$_{\text{HPO grav}}$,

$\delta(\mathrm{Ar/N_2})_{\mathrm{HPO\_meas}}$, $\delta(\mathrm{O_2/N_2})_{\mathrm{HPO\_grav}}$ and δ(~~Ar~~$\mathrm{O_2/N_2}$)~~ were~~$_{\mathrm{HPO\_meas}}$ to validate the ~~deviation from the corresponding values~~molar fractions of Ar, O_2 and N_2 in the ~~standard air on the AIST scale~~HPOs. Table 5 shows the ~~measured~~ $\delta(\mathrm{O_2/N_2})_{\mathrm{HPO\_meas}}$ and $\delta(\mathrm{Ar/N_2})_{\mathrm{HPO\_meas}}$ values calculated using ~~Eq.~~equation (3) and ~~Eq.~~ (4), as well as the values for $\delta(^{15}\mathrm{N}^{14}\mathrm{N}/^{14}\mathrm{N}^{14}\mathrm{N}$~~),~~$)_{\mathrm{HPO\_meas}}$, $\delta(^{17}\mathrm{O}^{16}\mathrm{O}/^{16}\mathrm{O}^{16}\mathrm{O}$~~),~~$)_{\mathrm{HPO\_meas}}$, $\delta(^{18}\mathrm{O}^{16}\mathrm{O}/^{16}\mathrm{O}^{16}\mathrm{O}$ ~~),~~$)_{\mathrm{HPO\_meas}}$, $\delta(^{16}\mathrm{O}^{16}\mathrm{O}$ $/^{14}\mathrm{N}^{14}\mathrm{N}$~~),~~$)_{\mathrm{HPO\_meas}}$, $\delta(^{36}\mathrm{Ar}/^{40}\mathrm{Ar}$~~),~~$)_{\mathrm{HPO\_meas}}$, and $\delta(^{38}\mathrm{Ar}/^{40}\mathrm{Ar}$~~).~~$)_{\mathrm{HPO\_meas}}$.

5.1 Determining the absolute (O_2/N_2) and (Ar/N_2) ratios ~~using the~~in AIST ~~scale~~reference air

The absolute ($\mathrm{O_2/N_2}$~~ and Ar/N₂ ratios (($\mathrm{O_2/N_2}$)$_{\mathrm{standard}}$~~)$_{\mathrm{HPO\_grav}}$ and ($\mathrm{Ar/N_2}$)~~$_{\mathrm{standard}}$)in the standard air on the AIST scale were calculated by substituting the gravimetric values of the O₂/N₂ and~~$_{\mathrm{HPO\_grav}}$ ratios, as well as the $\delta(\mathrm{O_2/N_2})_{\mathrm{HPO\_meas}}$ and δ($\mathrm{Ar/N_2}$ ~~ratios (($\mathrm{O_2/N_2}$)$_{\mathrm{STD}}$ and ($\mathrm{Ar/N_2}$)$_{\mathrm{STD}}$) as~~)$_{\mathrm{HPO\_meas}}$ values of the HPOs are listed in Table 2 ~~into the ($\mathrm{O_2/N_2}$)$_{\mathrm{sample}}$ and the ($\mathrm{Ar/N_2}$)$_{\mathrm{sample}}$ of the Eq. (1) and Eq. (2). The values for δ($\mathrm{O_2/N_2}$) and δ($\mathrm{Ar/N_2}$) were shown in~~ and Table 5.

~~The~~ Using these values~~ of (~~, the absolute ratios for $\mathrm{O_2/N_2}$~~)$_{\mathrm{standard}}$~~ and ~~(~~$\mathrm{Ar/N_2}$~~)$_{\mathrm{standard}}$~~ in AIST reference air were 0.~~2680869~~2680929 ± 0.0000016 and 0.~~0119544~~0119542 ± 0.~~0000013~~0000009, respectively. On the AIST scale, these values corresponded to $\delta(\mathrm{O_2/N_2}) = 0$ and $\delta(\mathrm{Ar/N_2}) = 0$. Associated standard uncertainties were determined with regards to the law of propagation of uncertainty.

The HPOs prepared in this study did not include minor components of Ne, He, Kr, CH_4, H_2 and N_2O which are present in air samples. Therefore, the variation of the $\delta(^{15}\mathrm{N}^{14}\mathrm{N}/^{14}\mathrm{N}^{14}\mathrm{N})$, $\delta(^{17}\mathrm{O}^{16}\mathrm{O}/^{16}\mathrm{O}^{16}\mathrm{O})$, $\delta(^{18}\mathrm{O}^{16}\mathrm{O}/^{16}\mathrm{O}^{16}\mathrm{O})$, $\delta(^{16}\mathrm{O}^{16}\mathrm{O}/^{14}\mathrm{N}^{14}\mathrm{N})$, $\delta(^{36}\mathrm{Ar}/^{40}\mathrm{Ar})$, and $\delta(^{40}\mathrm{Ar}/^{14}\mathrm{N}^{14}\mathrm{N})$ values obtained by the measurement of mass spectrometry was examined when molar fractions of Ne change from 0 μmol mol^{-1} to 500 μmol mol^{-1}. Consequently, the isotopic ratios did not change significantly depending on Ne. Since abundance of Ne is highest in minor components, the changes of the molar fractions of other minor components also might fail to affect the isotopic ratios measured in this study.

5.2 CO_2 ~~mole~~molar fractions and Ar/N_2 ratio

Three primary standard gases were used to measure ~~the~~ CO_2 ~~mole~~molar fractions in ~~the highly precise O_2 standard mixtures~~HPOs. Table 2 ~~shows~~illustrates the gravimetric and measured values and associated standard uncertainties. The CO_2 ~~mole~~molar fractions in the cylinder ~~labeled~~labelled CPB28679, which had been prepared on 29 March 2017, were not measured. Differences between the gravimetric and measured values (obtained by subtracting the measured value from ~~the~~ gravimetric value) were found to range from −0.17 ~~ppm~~μmol mol^{-1} to 0.03 ~~ppm~~μmol mol^{-1}. The gravimetric values were in line with the measured values, both~~ of which~~ being within the accepted levels of uncertainty.

From these results, ~~the~~ mass of the CO_2 in Ar standard mixture ~~was~~which we evaluated were considered ~~to be valid, since it was based on the mole fraction for the CO_2 utilized in this calculation.~~validated. Figure ~~5a~~5 shows the plot of the ~~measured~~ $\delta(\mathrm{Ar/N_2})_{\mathrm{HPO\_meas}}$ values ~~versus~~relative to the ~~gravimetric~~ $\delta(\mathrm{Ar/N_2})_{\mathrm{HPO\_grav}}$ values, as well as the residuals of the ~~measured~~ $\delta(\mathrm{Ar/N_2})_{\mathrm{HPO\_meas}}$ values that had been estimated using the best fitted line ~~of best fit obtained using~~by the least squares method. The standard deviation of the residuals was 78 per meg. This standard deviation represents a scatter in the ~~gravimetric~~ ($\mathrm{Ar/N_2}$ ~~ratio mole fractions~~)$_{\mathrm{HPO\_grav}}$ values, since the ~~measurement~~standard uncertainty for $\delta(\mathrm{Ar/N_2})_{\mathrm{HPO\_meas}}$ was much smaller than the obtained standard deviation (Ishidoya and Murayama, 2014). The standard uncertainties for ~~gravimetric~~ $\delta(\mathrm{Ar/N_2})_{\mathrm{HPO\_grav}}$ values ranged from ~~74~~65 per meg to 77 per meg. ~~The standard~~Standard uncertainties were comparable to the standard

~~deviation values~~deviations obtained for the residuals, ~~thus~~ supporting ~~that~~ the validity of uncertainty calculations for the constituents, Ar and N_2 ~~were valid~~.

5.3 O_2 ~~mole fraction and O_2~~/N_2 ratio

Figure ~~5b illustrates a plot of the measured O_2 mole fractions versus their gravimetric O_2 counterparts in the highly precise O_2 standard mixtures (Table 2), as well as the residual values, which had been determined from the fitting line obtained using least squares method. The standard deviation of the residuals shown in Figure 5b was determined to be 0.4 ppm, which was less than the standard uncertainties for the gravimetric O_2 mole fractions (0.7 ppm to 0.8 ppm).~~ ~~Figure 5a~~5 shows a plot of the ~~measured~~ $\delta(O_2/N_2)_{\text{HPO\_meas}}$ values listed in Table 5 against the ~~gravimetric~~ $\delta(O_2/N_2)_{\text{HPO\_grav}}$ values listed in Table 2, as well as ~~the~~ residuals from the ~~fitting~~fitted line ~~obtained using~~ by the least squares method. The slope of the ~~fitting~~fitted line was determined to be 1.00162 ± 0.00029~~. The~~, which indicated that the discrepancy between change rates of the $\delta(O_2/N_2)_{\text{HPO\_meas}}$ values ~~obtained were 0.16 % higher than those of gravimetric~~and the $\delta(O_2/N_2$~~), whereas the~~$)_{\text{HPO\_grav}}$ values was within 0.16%. The standard deviation of the residuals was 3.6 per meg~~. Since the standard uncertainties for gravimetric $\delta(O_2/N_2)$ ranged from 3.2 per meg to 4.0 per meg, the standard deviation~~, which proved to be in line with the standard uncertainties for the corresponding gravimetric values~~. Additionally, the results for O_2 mole fraction~~ since the standard uncertainties for the values of $\delta(O_2/N_2)_{\text{HPO\_grav}}$ ranged from 3.2 per meg to 4.0 per meg. The agreement with the gravimetric and ~~$\delta(O_2/N_2)$~~measured values reinforced the idea that the method for calculating the uncertainties of the constituents, O_2 and N_2, was proper and accurate. On the other hand, the ~~measured~~ $\delta(O_2/N_2)_{\text{HPO\_meas}}$ values were lower than their $\delta(^{16}O^{16}O/^{14}N^{14}N)_{\text{HPO\_meas}}$ counterparts by 18.2 per meg to 27.1 per meg (Table 5~~). The~~) and differences ~~between the $\delta(O_2/N_2)$ and $\delta(^{16}O^{16}O/^{14}N^{14}N)$ values~~ were larger than the standard uncertainties obtained for both values. This means that the ~~deviation of isotopic ratios for O and N in the highly precise O_2 standard mixtures from the corresponding atmospheric values contributed to the $\delta(O_2/N_2)$ values obtained, even though $\delta(O_2/N_2)$ can~~$\delta(O_2/N_2)$ values in the HPOs should be expressed ~~as~~by $\delta(O_2/N_2)_{\text{HPO\_meas}}$ rather than $\delta(^{16}O^{16}O/^{14}N^{14}N$~~), especially in case of air sample measurements.~~$)_{\text{HPO\_meas}}$.

The O_2/N_2 ratio of gases delivered from the cylinders may differ from the gravimetric O_2/N_2 ratio by either homogeneous or inhomogeneous fractionation (Leuenberger et al., 2015 Langenfelds et al., 2005 Keeling et al., 2004). In this study, we used the same type of valves and cylinders as in the study of Tohjima et al. (2005). Tohjima et al. examined changes in the O_2/N_2 ratio of the HPOs by releasing the inner air into a room at a flow rate of 8 mL min^{-1} and found that the fractionation of O_2 and N_2 during air release was negligible. Therefore, we chose not to evaluate fractionation in this study.

6 Comparison with Previous Values

To confirm the consistency of the results obtained using the ~~highly precise O_2 standard mixtures~~HPOs, we preliminarily compared O_2/N_2 ratios on both the AIST and NIES scale using annual average of $\delta(O_2/N_2)$ values in the air sample from Hateruma Island collected from January to December in 2015. Additionally, the ~~mole~~molar fraction of atmospheric O_2 and Ar were determined based on the ~~highly precise O_2 standard mixtures~~HPOs and then compared ~~to~~with previously reported values to confirm consistency of the results.

6.1 Comparison between O_2/N_2 ratios on the AIST and NIES scales

~~In 2015,~~ We observed the atmospheric $\delta(O_2/N_2)$ ~~values in the~~ by analysing air samples ~~from Hateruma Island were~~ collected at Hateruma Island from January to December in 2015. For the air samples, we confirmed that the isotopic ratios of N_2 and O_2 did not differ significantly from the atmospheric values, such that we regard the $\delta(^{16}O^{16}O/^{14}N^{14}N)$ value measured~~.~~ by the mass spectrometer is equivalent to $\delta(O_2/N_2)$ in equation (1). Twice a month, the air samples were collected in ~~a~~two Pyrex ~~glass.~~glasses arranged in series (one for AIST and the other for NIES). Using these air samples, ~~it was~~we determined that the annual average of $\delta(O_2/N_2)$ ~~value~~in 2015 on the AIST scale was −~~62.8~~63 ± 3~~.2~~ per meg. The number following the symbol ± denotes the standard uncertainty ~~was determined based on the standard deviation of the~~ ~~$\delta(O_2/N_2)$ values in air samples.~~of the measurement. Using ~~Eq.~~equation (1), the $\delta(O_2/N_2)$ value on the AIST scale was then converted to the absolute O_2/N_2 ratio by utilizing the absolute ~~(~~ratio of O_2/N_2~~$)_{\mathrm{standard}}$ value on the~~ in AIST ~~scale~~reference air determined in section 5.1. In 2015, the absolute O_2/N_2 ratio on Hateruma Island was 0.2680761 ± 0.0000018. This ~~absolute O_2/N_2~~ value ~~was~~can be converted to the corresponding $\delta(O_2/N_2)$ value on the NIES scale using ~~the Eq.~~equation (1), since the absolute ~~(~~O_2/N_2~~$)_{\mathrm{standard}}$ value on the~~ ratio in NIES ~~scale~~reference air was reported to be 0.2681708 ~~± 0.0000036, which corresponded to the results reported~~ by Tohjima ~~($\delta(O_2/N_2) = 0$) (Tohjima~~ et al.~~,~~ . (2005). The converted $\delta(O_2/N_2)$ value, which is expressed as $\delta(O_2/N_2)_{\mathrm{NIES\ on\ AIST}}$ in the following descriptions, was found to be −353 ± 6 per meg on the NIES scale. The uncertainty expresses the 95% confidence interval.

~~Next, we used the equation ($\delta(O_2/N_2) = \delta\{(O_2 + Ar)/N_2\} \times (O_2 + kAr/O_2)_{ref}$) provided by~~ On the other hand, the annual average of $\delta(O_2/N_2)$ in Hateruma island in 2015 measured by NIES on the NIES scale was -395 ± 5 per meg (Tohjima, Y., personal communications). The number following the symbol ± denotes the standard uncertainty of the measurement (Tohjima et al~~. (2005) to estimate the average~~ ., 2008). The $\delta(O_2/N_2)$ value ~~in 2000. Here *k* represents the sensitivity ratio Ar relative to O_2. They evaluated *k* to be 1.13. From the equation, we found that the~~is expressed as $\delta(O_2/N_2)$ ~~value in 2000 is −77 per meg on the NIES scale. The~~ $_{\mathrm{NIES\ on\ NIES}}$. There was a difference of 41 per meg between both values of δ~~{~~(O_2 ~~+ Ar)/N_2} value was reported to be −73 per meg for Hateruma Island in 2000 (Tohjima et al., 2005). The $\{(O_2 + kAr)/O_2\}_{ref}$ value was also estimated to be a ratio (0.2816768/0.2681708 = 1.05036) of the $\{(O_2 + kAr)/$~~/N_2~~}~~ ~~value reported by Tohjima et al. (2005) to the absolute $(O_2/N_2)_{\mathrm{standard}}$ value~~)$_{\mathrm{NIES}}$ $_{\mathrm{on}}$ ~~the NIES scale. The drop in the~~ $_{\mathrm{AIST}}$ and $\delta(O_2/N_2)$ ~~values from 2000 to 2015 was −277 ± 32 per meg. In this case, the uncertainty represents a 95 % confidence interval. The average decrease in rate over this period was 19.0 ± 2.2 per meg yr^{-1}, which was slightly lower than previously reported values (21.2 ± 0.8 per meg yr^{-1} and 22.0 ± 0.8 per meg yr^{-1}) (Ishidoya, 2012a).~~

~~Differences between the $\delta(O_2/N_2)$ values recorded at Hateruma Island in 2000 and 2015 were compared to the corresponding values recorded at La Jolla in 2000 and 2015. It was determined that the $\delta(O_2/N_2)$ value at La Jolla (Keeling and Manning, 2014) was −327 per meg.~~ $_{\mathrm{NIES\ on\ NIES}}$. This ~~value~~difference falls outside of the 95~~-~~% confidence interval~~-~~. The disagreement between $\delta(O_2/N_2)_{\mathrm{NIES\ on\ AIST}}$ and $\delta(O_2/N_2)_{\mathrm{NIES\ on\ NIES}}$ suggests that there are some inconsistencies between the gravimetric methods developed by Tohjima et al. (2005) and ~~may indicate the variations existing on the NIES and AIST scales. They may also imply that the slope of Scripps Institution of Oceanography (SIO) scale was higher than the actual value, since accurate verification of slope was not performed without highly precise O_2 standard mixtures.~~this study. Additionally, other sources of error ~~can~~may exist~~. For this study, we were unable to directly compare~~ (e.g. difference between instruments, sampling method, introduction method). Therefore, a direct comparison of the O_2/N_2 ratio or the O_2 ~~mole~~molar fraction between the AIST and

NIES scales~~. If the direct comparison was possible, then the difference between both scales would become clear, and the slope~~, by a round-robin experiment of the HPOs developed in this study, is required some time in the near future to quantify the differences in absolute values and span of each ~~scale could be verified by using the highly precise O_2 standard mixtures developed by our group~~gravimetric scale.

6.2 Determination of atmospheric O_2 and Ar ~~mole~~molar fractions and comparison with previous data

The ~~mole~~molar fractions for atmospheric O_2 and Ar were determined based on~~ the~~ $\delta(O_2/N_2)$ and $\delta(Ar/N_2)$ values for air samples taken at Hateruma Island in 2015. The $\delta(O_2/N_2)$ and $\delta(Ar/N_2)$ values were −62.8 per meg and −62.8 per meg, respectively. ~~Regarding~~Using the (O_2/N_2)~~$_{\mathrm{standard}}$~~$_{\mathrm{ref}}$ and (Ar/N_2)~~$_{\mathrm{standard}}$~~$_{\mathrm{ref}}$ ratios for ~~the ~~AIST ~~scale, these~~reference air, the $\delta(O_2/N_2)$ and $\delta(Ar/N_2)$ values were used to calculate the O_2/N_2 and Ar/N_2 ratios using ~~Eq.~~equation (1) and ~~Eq. ~~(2). In 2015, the calculated O_2/N_2 and Ar/N_2 ratios for samples from Hateruma Island were 0.~~26807012~~2680761 ± 0.~~00000130~~0000018 and 0.~~0119536650~~119534 ± 0.~~00000100~~000009, respectively. The ~~mole~~molar fractions of O_2 and Ar (~~x_{O_2}~~$x_{\mathrm{O_2}}$ and ~~x_{Ar}~~x_{Ar}) were calculated using the aforementioned O_2/N_2 and Ar/N_2 ratios by using the equations below.

~~x_{O_2}~~
$$x_{\mathrm{O_2}} = K \times \frac{\mathrm{O_2/N_2}}{(1+\mathrm{O_2/N_2}+\mathrm{Ar/N_2})} \qquad (8)$$

~~x_{Ar}~~
$$x_{\mathrm{Ar}} = K \times \frac{\mathrm{Ar/N_2}}{(1+\mathrm{O_2/N_2}+\mathrm{Ar/N_2})} \qquad (9)$$

In these two equations, K is the sum of N_2, O_2, and Ar ~~mole~~molar fractions in the air samples and was estimated to be 999567.8 ± 0.1 ~~ppm~~µmol mol^{-1}. To ~~calculate~~obtain this value, the ~~mole~~molar fractions of Ne (18.18 ~~ppm~~µmol mol^{-1}), He (5.24 ~~ppm~~µmol mol^{-1}), CH_4 (1.82 ~~ppm~~µmol mol^{-1}), Kr (1.14 ~~ppm~~µmol mol^{-1}), H_2 (0.52 ~~ppm~~µmol mol^{-1}), N_2O (0.32 ~~ppm~~µmol mol^{-1}), CO (0.15 ~~ppm~~µmol mol^{-1}) and Xe (0.09 ~~ppm~~µmol mol^{-1}) reported by Tohjima et al. (2005) and CO_2 (404.7 ~~ppm~~µmol mol^{-1}) in 2015 were used. The CO_2 ~~mole~~molar fraction was the average CO_2 ~~mole~~molar fraction ~~which was ~~measured using a mass spectrometer. The calculated O_2 and Ar ~~mole~~molar fractions were 209339.1 ± 1.1 ~~ppm~~µmol mol^{-1} and 9334.4 ± 0.7 ~~ppm~~µmol mol^{-1}, respectively. ~~The standard~~Standard uncertainties were estimated in accordance with the law of propagation of uncertainties. ~~From 2000 to 2015, it was noted that the O_2 mole fraction in the air samples taken at Hateruma decreased by 52.9 ppm with a rate of 3.5 ppm yr^{-1}.~~In 2000, Tohjima et al. (2005) reported ~~an~~the atmospheric Ar ~~mole~~molar fraction of 9333.2 ± 2.1 ~~ppm~~µmol mol^{-1} (2005), whereas the value reported for air samples collected on Korea's Anmyeon Island in 2002 and at Niwot Ridge in 2001 was 9332 ± 3 ~~ppm~~µmol mol^{-1} (Park et al., 2004). Hence, our values for atmospheric Ar were in line ~~with previously reported ones~~previous reports.

7 Conclusion

In this study, we demonstrated that the deviation of ~~difference in ~~mass ~~between~~readings of the ~~gravimetric and reference~~sample cylinders is susceptible to temperature differences between ~~these two~~the sample and reference cylinders. The contribution degree of the temperature difference was −14.3 mg K^{-1}. ~~We~~Our results also ~~indicated~~indicate that ~~the ~~variations ~~of the~~in mass ~~difference values~~readings due to ~~the ~~temperature difference ~~was able to~~could be reduced to negligible levels by ~~weighing both cylinders when the~~obtaining mass readings at thermal equilibrium~~ was reached.~~. A long time is required to reach thermal equilibrium. Since the variations mainly ~~depended~~depend on temperature differences rather than factors ~~relating~~related to the adsorption phenomena (e.g., the temperature of the ~~gravimetric~~ cylinder and/or the humidity of ~~the~~ ambient air), it was thus~~,~~ concluded that the ~~changes~~variations in ~~the~~ mass ~~differences~~readings were influenced solely by thermal effects.

We~~ have~~ developed a preparation technique for the production of ~~highly precise O_2 standard mixtures~~HPOs with atmospheric levels of CO_2, Ar, O_2, and N_2. To determine the O_2 ~~mole~~molar fractions with standard uncertainties of less than 1 ~~ppm~~µmol mol^{-1}, repeatability in measuring the mass ~~difference between the gravimetric and reference~~readings of the sample cylinders was determined~~.~~ to be 0.82 mg. The impact of leakage or permeation of the source gases through the ~~cylinders'~~cylinder valve, as well as change ~~of~~in buoyancy such as the expansion of the ~~gravimetric~~ cylinder as a factor of the cylinder~~'s~~ inner pressure ~~were~~was evaluated. Additionally, the molar masses of the ~~O_2 and N_2~~ source gases, pure O_2 and pure N_2, were determined based on the abundance of their isotopes. The~~ standard uncertainties~~ gravimetrically calculated standard uncertainties were in good agreement with the standard deviation for the corresponding measured values. This indicates that the uncertainty calculations of the gravimetric values for ~~the~~ constituents performed in this study were accurate and valid.

~~On~~Based on the ~~basis of the highly precise O_2 standard mixtures~~HPOs prepared in this study, we determined ~~the mole~~molar fractions of atmospheric Ar and O_2 at Hateruma Island in 2015. These values were 9334.4 ± 0.7 µmol mol^{-1} and 209339.1 ± 1.1 ~~ppm~~µmol mol^{-1}, for Ar and O_2, respectively. The atmospheric Ar ~~mole~~molar fraction was in line with the values reported by Park (9332 ± 3 ~~ppm~~µmol mol^{-1}) and Tohjima (9333.2 ± 2.1 ~~ppm~~µmol mol^{-1}) (Park et al., 2004; Tohjima et al., 2005).~~ Our research indicated that the atmospheric O_2 mole fraction decreased by 52.9 ppm between 2000 and 2015 with a rate of 3.5 ppm yr^{-1}.~~

Acknowledgments

This study was partly supported by funding from the Global Environment Research Coordination System from the Ministry of the Environment, Japan. We express our gratitude to Noritsugu Tsuda, Nobukazu Oda, Fujio Shimano of Global Environmental Forum, and Yasunori Tohjima of National Institute for Environmental Studies for their cooperation in collecting air samples at Hateruma Island.

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Table 1. Isotopic composition and atomic masses of pure oxygen and pure nitrogen used to prepare ~~a~~ highly precise O_2 standard ~~mixture for the cylinder labeled CPB28912.~~mixtures (HPOs).

Isotope	*Atomic mass*[a,b]	*Isotope abundance*		~~Isotope~~Isotopic *ratio of source gas*[e]
		Atmosphere[a]	Source gas[a]	
^{14}N	14.0030740074(18)	0.996337(4)[c]	0.996346(4)	
^{15}N	15.000108973(12)	0.003663(4)[c]	0.003654(4)	δ^{15}N = ~~−~~(−2.397 ± 0.001) ‰
^{16}O	15.9949146223(25)	0.9975684(9)[d]	0.9975887(9)	
^{17}O	16.99913150(22)	0.0003836(8)[d]	0.0003818(8)	δ^{17}O = ~~−~~(−4.66 ± 0.05) ‰
^{18}O	17.9991604(9)	0.0020481(5)[d]	0.0020295(5)	δ^{18}O = ~~−~~(−9.075 ± 0.003) ‰

Sources	Atomic mass of nitrogen[a]	Atomic mass of oxygen[a]
Atmosphere	14.006726(4)	15.999405(1)
Source gases	14.006717(4)	15.999366(1)

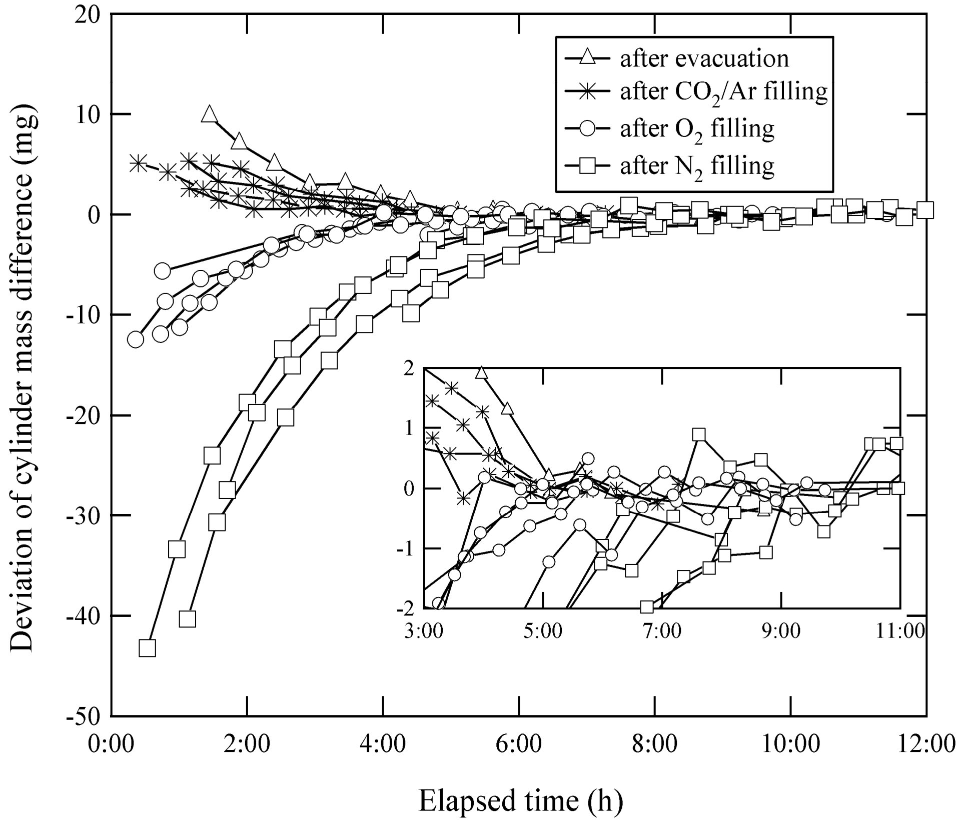
[a] ~~The numbers~~Numbers in the parentheses represent the standard uncertainty in the last digits.

[b] ~~The atomic~~Atomic mass and the standard uncertainty as determined by De Laeter et al. (2003).

[c] ~~The abundance~~Abundance of the isotope and the standard uncertainty as determined using calculations for the absolute ^{15}N/^{14}N ratio obtained by Junk and Svec (1958).

[d] ~~The abundance~~Abundance of the isotope and the standard uncertainty were calculated using ^{17}O/^{16}O = 12.08 ‰ and ^{18}O/^{16}O = 23.88 ‰ vs. the VSMOW as determined by Barkan and Luz (2005). The absolute ~~isotope~~isotopic ratio for VSMOW and the standard uncertainty were determined by Li et al. (1988) for ^{17}O/^{16}O and Baertschi (1976) for ^{18}O/^{16}O.

[e] ~~The isotope~~Isotopic ratio is defined as the difference in the corresponding atmospheric value (~~CRC00045~~AIST reference air) measured using a mass spectrometer. ~~The numbers~~Numbers following the symbol ± denote the standard uncertainty.



Deviation of cylinder mass difference (mg)
20
10
0
-10
-20
-30
-40
-50
0:00
2:00
4:00
6:00
8:00
10:00
12:00
Elapsed time (h)
after evacuation
after CO_2/Ar filling
after O_2 filling
after N_2 filling
2
1
0
-1
-2
3:00
5:00
7:00
9:00
11:00

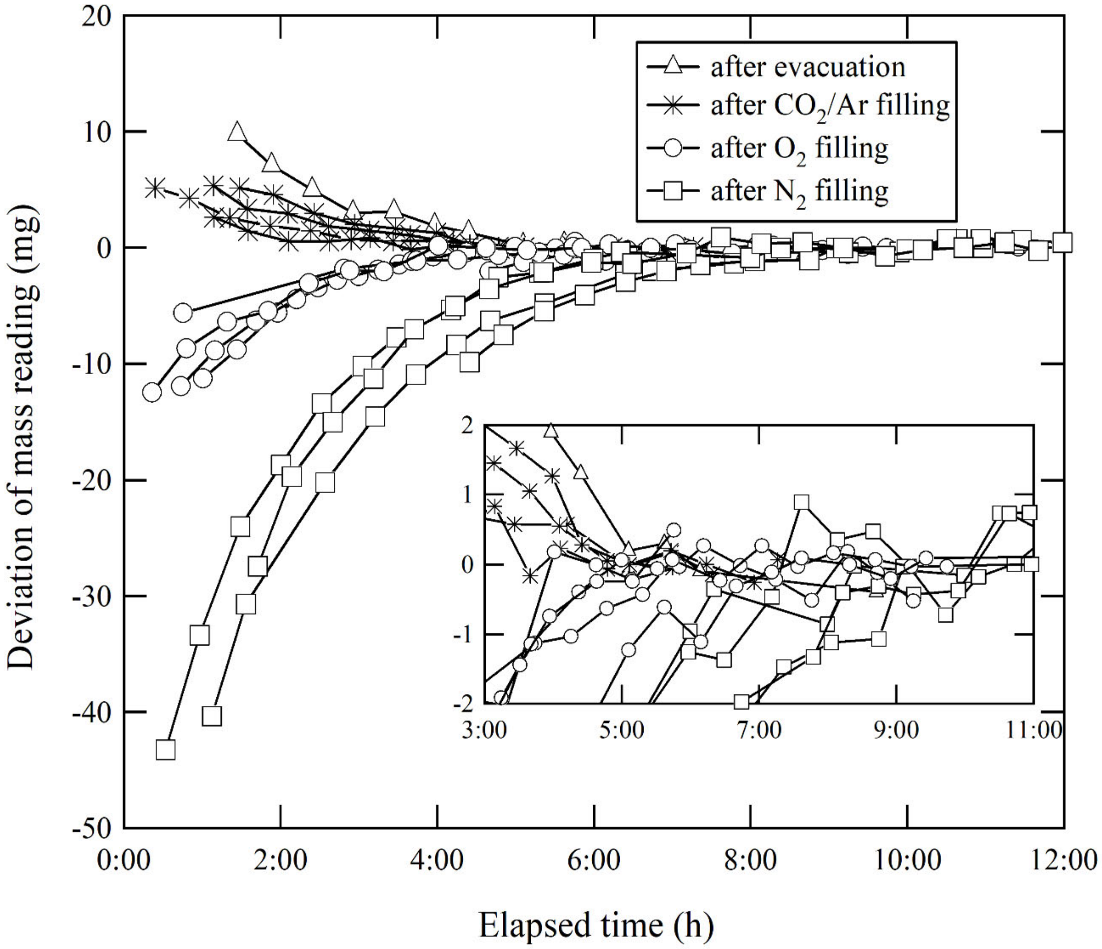
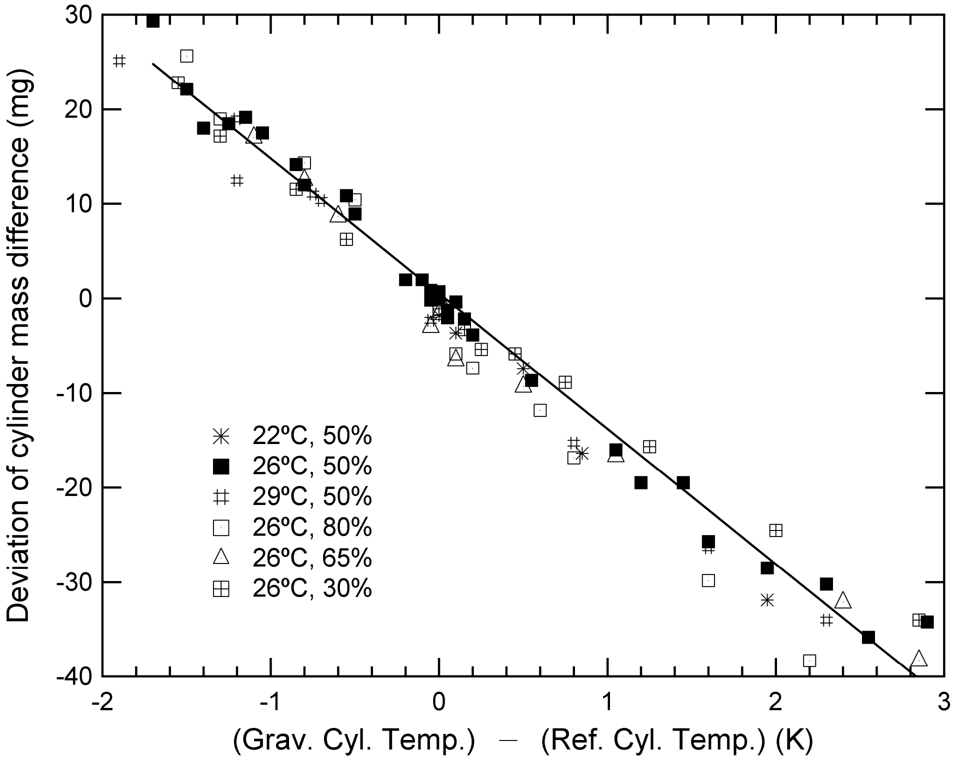


Figure 1 Changes in ~~the~~ mass ~~differences observed for the gravimetric and reference~~ readings of sample cylinders plotted against the time elapsed after evacuation of the ~~gravimetric~~ cylinder and filling of source gases. ~~Masses~~The mass readings were ~~measured~~obtained using the weighing system. Deviation of the mass reading is expressed as the change in amount from the equilibrium value, which was defined as the mass reading when the standard deviation of the values remained constant for two or more hours.


Deviation of cylinder mass difference (mg)
30
20
10
0
-10
-20
-30
-40
-2
-1
0
1
2
3
(Grav. Cyl. Temp.) – (Ref. Cyl. Temp.) (K)
✳ 22ºC, 50%
■ 26ºC, 50%
♯ 29ºC, 50%
□ 26ºC, 80%
△ 26ºC, 65%
⊞ 26ºC, 30%

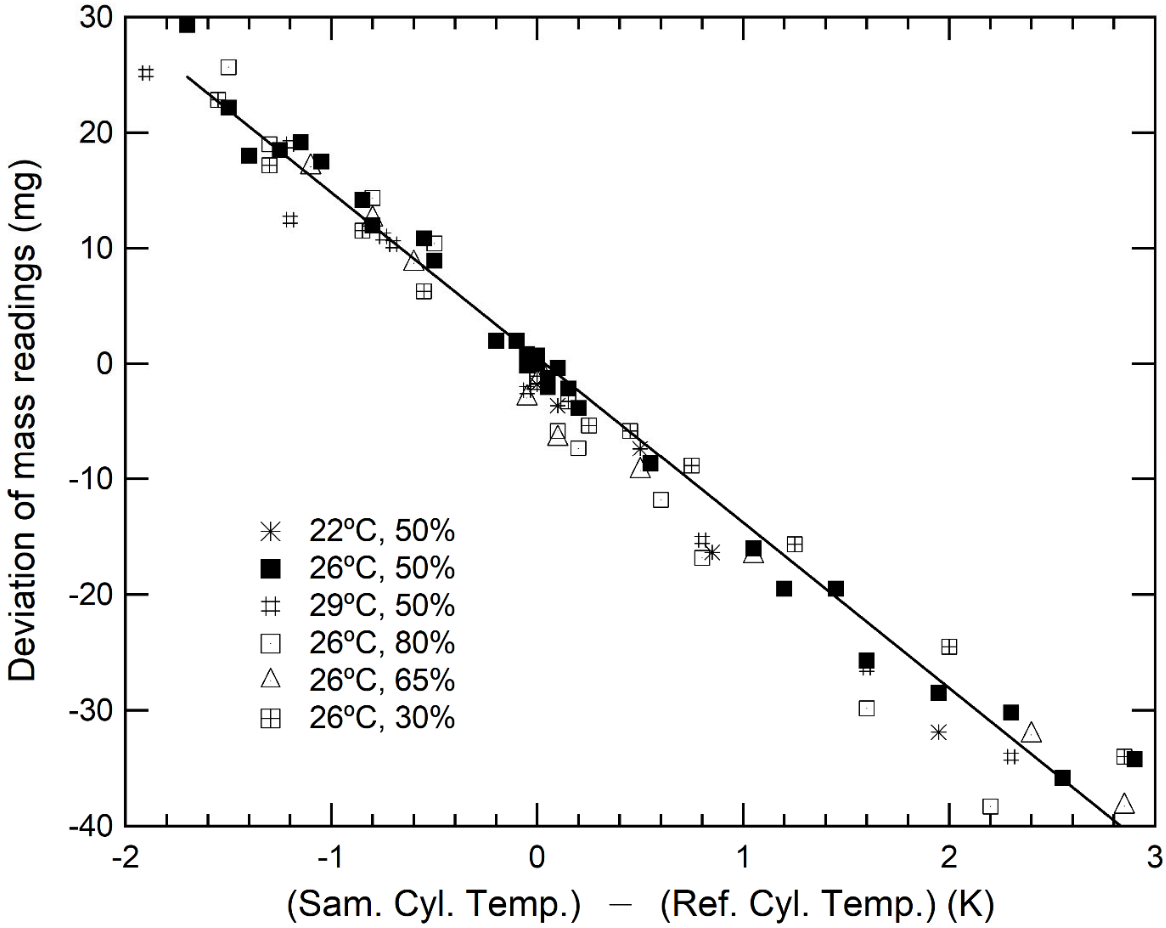


Figure 2 Changes in the mass ~~differences~~readings observed for ~~the gravimetric and reference~~sample cylinders plotted against temperature differences obtained under various conditions (a temperature range from 22 ºC to 29 ºC, a humidity range from 30~~ ~~% to 80~~ %.~~%.)

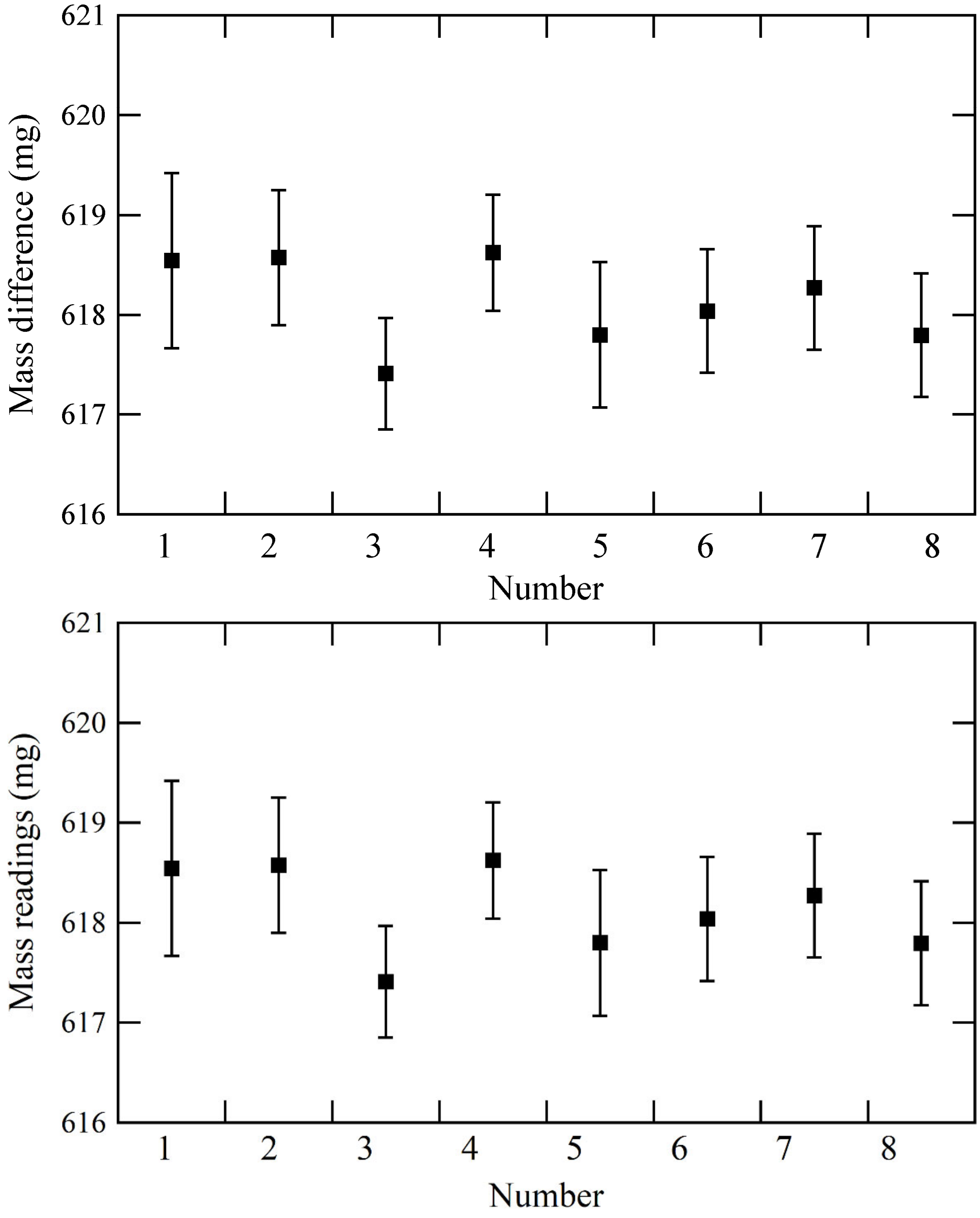


Figure 3 ~~Changes in the~~Reproducibility of mass ~~differences~~readings obtained for the ~~gravimetric and reference cylinders~~sample cylinder after cylinders had been heated at 40 ºC (~~Number~~numbers 1 to 4) or cooled at 23 ºC (~~Number~~numbers 5 to 8). The error bars represent the standard uncertainty.

Table 2. Gravimetric values of N_2, O_2, and CO_2 ~~mole~~molar fractions alongside (O_2/N_2 ~~ratios~~)$_{\mathrm{HPO\_grav}}$, (Ar/N_2)$_{\mathrm{HPO\_grav}}$, δ(O_2/N_2~~),~~)$_{\mathrm{HPO\_grav}}$, and δ(Ar/N_2~~),~~)$_{\mathrm{HPO\_grav}}$, as well as the measured values ~~obtained for~~of CO_2 ~~mole~~molar fractions ~~from precise measurements of O_2 standard gases~~in HPOs.

Cylinder number	*Preparation date*	Gravimetric values[a], µmol mol^{-1}								~~Gravimetric values[a], ppm~~	*Measured values,* ~~*ppm*~~µmol mol^{-1}
		N_2	O_2	Ar	CO_2	(O_2/N_2)~~STD~~$_{\mathrm{HPO\_grav}}$	(Ar/N_2)~~STD~~$_{\mathrm{HPO\_grav}}$	δ(O_2/N_2)$_{\mathrm{HPO\_grav}}$[b]	δ(Ar/N_2)$_{\mathrm{HPO\_grav}}$[b]		CO_2

CPC00556	15 March 2017	780094.1 ± 1.0	210068.3 ± 0.8	9415.2 ± 0.7	422.30 ± 0.03	0.2692858 ± 0.0000011	0.0120693 ± 0.0000009	4471.8 ± 4.0	9619 ± 77	422.37 ± 0.14
CPB28679	29 March 2017	782593.9 ± 0.8	207770.2 ± 0.7	9222.1 ± 0.6	413.64 ± 0.03	0.2654892 ± 0.0000009	0.0117841 ± 0.0000008	−9689.9 ± 3.4	−14244 ± 67	~~-~~ -
CPB16178	5 April 2017	779014.8 ± 1.0	211348.4 ± 0.8	9241.0 ± 0.7	395.78 ± 0.03	0.2713021 ± 0.0000010	0.0118624 ± 0.0000009	11993.0 ± 4.0	−7694 ± 77	395.96 ± 0.14
CPB16345	7 April 2017	781499.3 ± 1.0	208750.7 ± 0.8	9349.6 ± 0.7	400.43 ± 0.03	0.2671156 ± 0.0000011	0.0119636 ± 0.0000009	−3623.2 ± 4.0	777 ± 75	400.40 ± 0.14
CPB16315	12 April 2017	781264.1 ± 0.9	209040.6 ± 0.7	9297.0 ± 0.7	398.18 ± 0.03	0.2675671 ± 0.0000010	0.0118999 ± 0.0000009	−2595.1 ± 3.6	−5191 ± 79	398.21 ± 0.14
CPB16379	17 April 2017	781059.5 ± 0.8	209233.2 ± 0.7	9308.6 ± 0.6	398.68 ± 0.03	0.2678838 ± 0.0000009	0.0119179 ± 0.0000008	−757.9 ± 3.3	−3050 ± 65	398.68 ± 0.14
CPB16349	13 June 2017	780424.7 ± 0.8	209813.5 ± 0.7	9342.7 ± 0.6	419.06 ± 0.03	0.2688452 ± 0.0000009	0.0119713 ± 0.0000008	2828.5 ± 3.4	1419 ± 66	419.22 ± 0.14
CPB28912	15 June 2017	780792.3 ± 0.8	209437.0 ± 0.7	9351.1 ± 0.6	419.44 ± 0.03	0.2682366 ± 0.0000009	0.0119765 ± 0.0000008	558.1 ± 3.4	1851 ± 66	419.54 ± 0.14
CPB28679	22 June 2017	780869.0 ± 0.8	209383.9 ± 0.7	9328.6 ± 0.6	418.44 ± 0.03	0.2681421 ± 0.0000009	0.0119464 ± 0.0000008	205.8 ± 3.4	−664 ± 65	418.54 ± 0.14

[a] ~~The numbers~~Numbers following the symbol ± denote the standard uncertainty.

[b] ~~The values~~Values were calculated using the absolute O_2/N_2 and Ar/N_2 in ~~standard~~AIST reference air as ~~determined~~described in ~~Section~~section 5.1.

Table 3. Typical contribution of each source of uncertainty (including the mass of the source gas, molar mass, and purity) to the standard uncertainties obtained for the ~~mole~~molar fractions of N_2, O_2, Ar, and CO_2 in ~~a highly precise O_2 standard mixture~~the HPO.

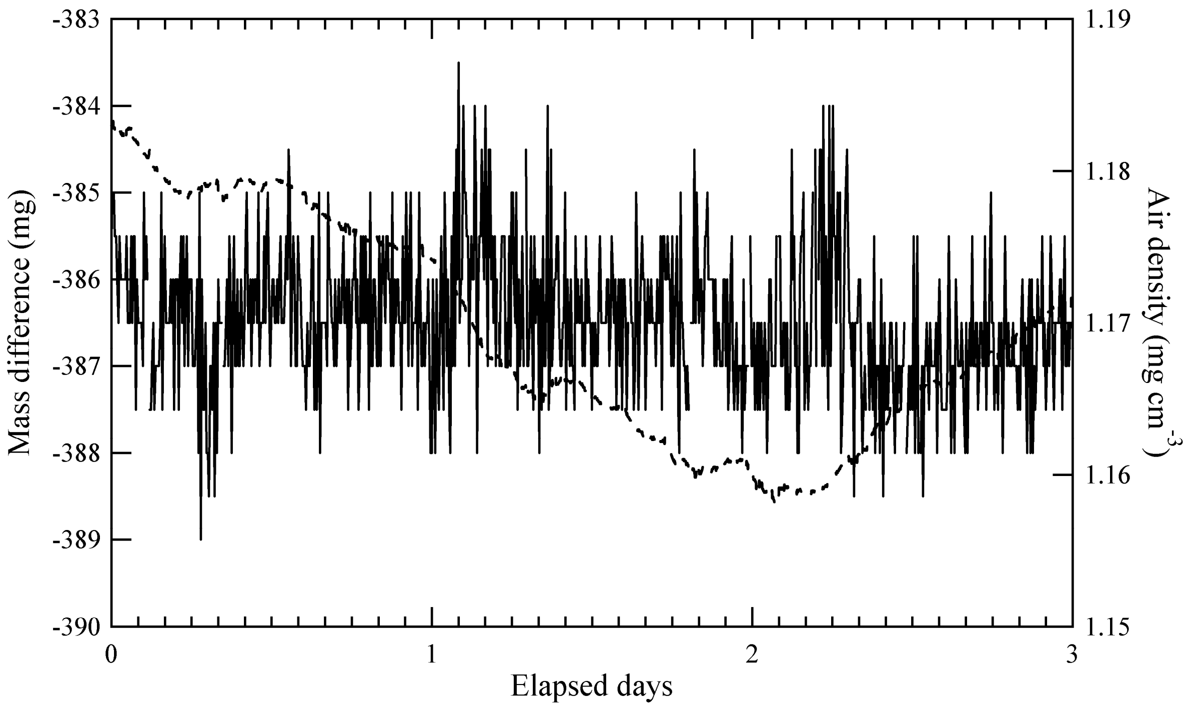
	Uncertainty source, ~~ppm~~µmol mol^{-1}			*Combined standard uncertainty, ~~ppm~~ µmol mol^{-1}*
Constituent	Mass of source gas	Molar mass	Purity	
N_2	0.77	0.11	0.05	0.77
O_2	0.63	0.03	0.03	0.63
Ar	0.56	0.13	0.02	0.58
CO_2	0.025	0.006	0.011	0.028

Table 4. Impurities in ~~the~~ source gases ~~to prepare highly precise O_2 standard mixtures~~for preparation of HPOs

Impurity	*Source gases,* ~~ppm~~μmol mol^{-1}			
	CO_2	Ar	O_2	N_2
N_2	0.9 ± 0.5	0.12 ± 0.07	0.12 ± 0.07	-
O_2	0.3 ± 0.1	0.5 ± 0.3	-	0.05 ± 0.03
Ar	-	-	0.089 ± 0.052	0.05 ± 0.03 0.28 ± 0.01 0.32 ± 0.03
CO_2	-	0.002 ± 0.001	0.124 ± 0.004	0.002 ± 0.001
H_2O	4.8 ± 2.7	0.05 ± 0.03	0.05 ± 0.03	0.05 ± 0.03
CH_4	0.6 ± 0.3	0.005 ± 0.003	0.005 ± 0.003	0.005 ± 0.003
CO	-	0.04 ± 0.02	0.04 ± 0.02	0.04 ± 0.02
H_2	2.2 ± 1.3	-	-	-
Purity %	99.99913	99.99993	99.999957	99.999980 99.999957 99.999954

~~The numbers~~Numbers following the symbol ± denote the standard uncertainty.

“-” represents the constituents which were not measured.


-383
-384
-385
-386
-387
-388
-389
-390
Mass difference (mg)
0
1
2
3
Elapsed days
1.19
1.18
1.17
1.16
1.15
Air density (mg cm^{-3})

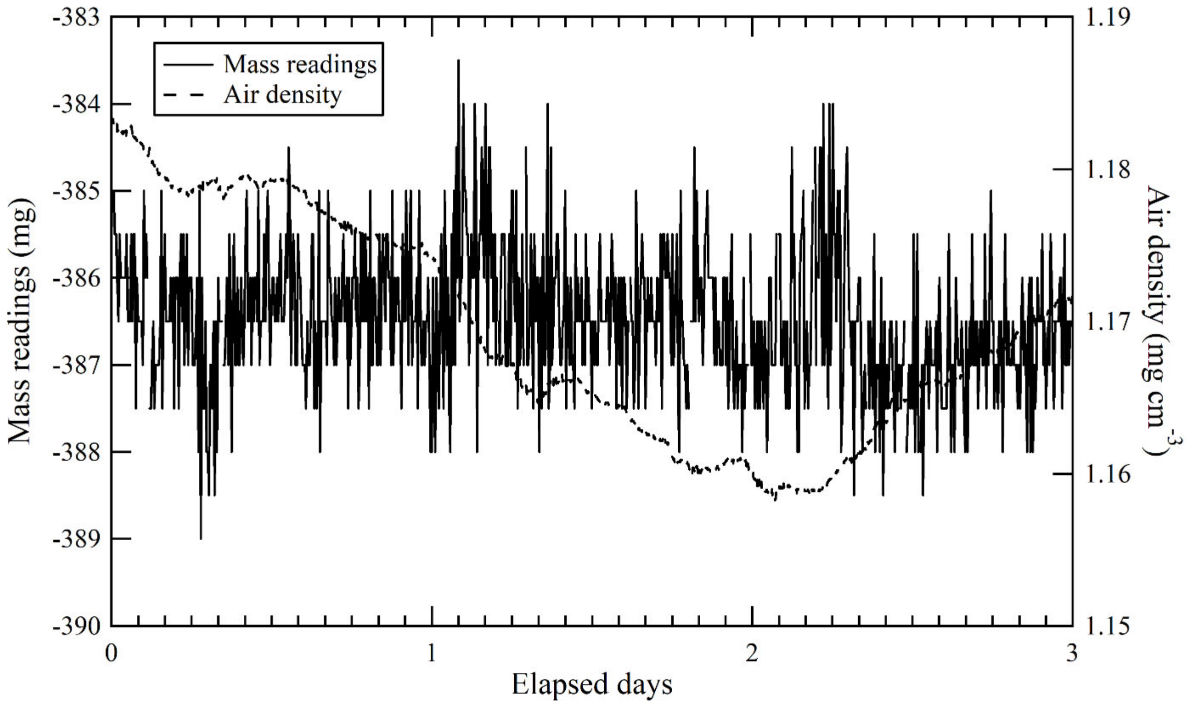

Mass readings
Air density
-383
-384
-385
-386
-387
-388
-389
-390
Mass readings (mg)
0
1
2
3
Elapsed days
1.19
1.18
1.17
1.16
1.15
Air density (mg cm^{-3})

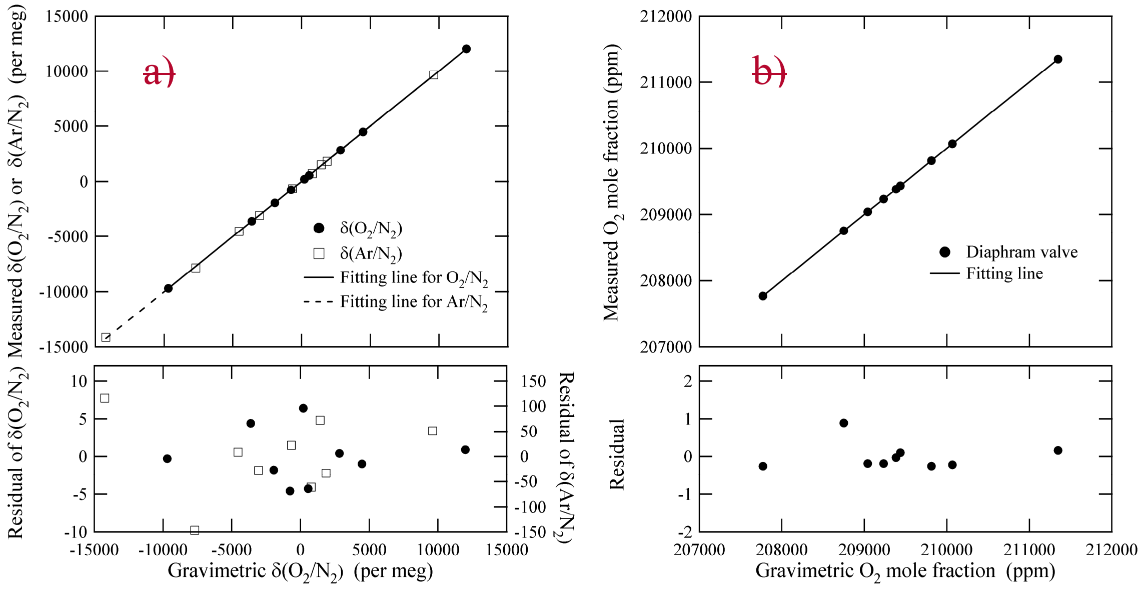
Figure 4 ~~Changes in the~~Repeatability of mass ~~differences~~readings obtained for the ~~gravimetric and reference~~sample cylinders and ambient air density for three days. ~~The solid~~Solid and dashed lines represent ~~the~~ mass ~~differences~~readings and ambient air density, respectively~~.~~

Table 5. ~~Mole fractions and standard uncertainties as determined in highly precise O_2 standard mixtures for~~ δ($^{15}N^{14}N/^{14}N^{14}N$~~),~~)$_{HPO\_meas}$, δ($^{17}O^{16}O/^{16}O^{16}O$~~),~~)$_{HPO\_meas}$, δ($^{18}O^{16}O/^{16}O^{16}O$~~),~~)$_{HPO\_meas}$, δ($^{16}O^{16}O/^{14}N^{14}N$~~), δ($O_2/N_2$),~~)$_{HPO\_meas}$, δ($^{36}Ar/^{40}Ar$~~), ~~)$_{HPO\_meas}$ and δ($^{40}Ar/^{14}N^{14}N$~~),~~)$_{HPO\_meas}$ measured by the mass spectrometer. δ(O_2/N_2)$_{HPO\_meas}$ and δ(Ar/ N_2~~).~~)$_{HPO\_meas}$ calculated using equations (3) and (4), and differences between δ(O_2/N_2)$_{HPO\_meas}$ and δ($^{16}O^{16}O/^{14}N^{14}N$)$_{HPO\_meas}$ are also shown.

Cylinder number	δ($^{15}N^{14}N/^{14}N^{14}N$~~)~~)$_{HPO\_meas}$	δ($^{17}O^{16}O/^{16}O^{16}O$~~)~~)$_{HPO\_meas}$	δ($^{18}O^{16}O/^{16}O^{16}O$~~)~~)$_{HPO\_meas}$	δ($^{16}O^{16}O/^{14}N^{14}N$)$_{HPO\_meas}$	δ(O_2/N_2)$_{HPO\_meas}$	δ(O_2/N_2~~)=~~)$_{HPO\_meas}$ −δ($^{16}O^{16}O/^{14}N^{14}N$)	δ($^{36}Ar/^{40}Ar$)$_{HPO\_meas}$	δ($^{40}Ar/^{14}N_2$)$_{HPO\_meas}$	δ(Ar/N_2)$_{HPO\_meas}$
CPC00556	−2365.0 ± 1.2	−4032 ± 50	−7907.8 ± 2.6	4477.5 ± 3.2	4459.2 ± 3.2	−18.2	−2465 ± 50	9649.0 ± 6.5	9658.1 ± 6.5
CPB28679	−2343.5 ± 1.2	−4032 ± 50	−8298.0 ± 2.6	−9704.7 ± 3.2	−9724.4 ± 3.2	−19.7	−1969 ± 50	−14102.6 ± 6.5	−14092.2 ± 6.5
CPB16178	−2372.5 ± 1.2	−4219 ± 50	−8279.7 ± 2.6	12011.7 ± 3.2	11991.7 ± 3.2	−20.0	−2197 ± 50	−7828.0 ± 6.5	−7818.1 ± 6.5
CPB16345	−2351.5 ± 1.2	−4676 ± 50	−9087.6 ± 2.6	−3624.2 ± 3.2	−3647.7 ± 3.2	−23.5	−2311 ± 50	712.0 ± 6.5	721.5 ± 6.5
CPB16315	−2356.2 ± 1.2	−4665 ± 50	−9069.6 ± 2.6	−1946.8 ± 3.2	−1970.2 ± 3.2	−23.4	−2228 ± 50	−4538.2 ± 6.5	−4528.5 ± 6.5
CPB16379	−2416.8 ± 1.2	−4655 ± 50	−9062.8 ± 2.6	−763.6 ± 3.2	−786.6 ± 3.2	−22.9	−2261 ± 50	−3074.4 ± 6.5	−3064.3 ± 6.5
CPB16349	−2407.9 ± 1.2	−4630 ± 50	−9036.0 ± 2.6	2833.1 ± 3.2	2810.2 ± 3.2	−23.0	−2360 ± 50	1485.7 ± 6.5	1495.4 ± 6.5
CPB28912	−2397.2 ± 1.2	−4656 ± 50	−9075.3 ± 2.6	554.6 ± 3.2	531.5 ± 3.2	−23.2	−2348 ± 50	1812.2 ± 6.5	1821.9 ± 6.5
CPB28679	−2390.8 ± 1.2	−5109 ± 50	−9941.2 ± 2.6	212.5 ± 3.2	185.4 ± 3.2	−27.1	−2338 ± 50	−642.8 ± 6.5	−633.2 ± 6.5

These values ~~were calculated using~~are on the AIST scale, i.e., determined against AIST reference air and ~~were~~are given in per meg.

~~The numbers~~Numbers following the symbol ± denote the standard uncertainty.


~~a)~~
Measured $\delta(O_2/N_2)$ or $\delta(Ar/N_2)$ (per meg)
15000
10000
5000
0
-5000
-10000
-15000
$\delta(O_2/N_2)$
$\delta(Ar/N_2)$
Fitting line for O_2/N_2
Fitting line for Ar/N_2
Residual of $\delta(O_2/N_2)$
10
5
0
-5
-10
Residual of $\delta(Ar/N_2)$
150
100
50
0
-50
-100
-150
-15000
-10000
-5000
0
5000
10000
15000
Gravimetric $\delta(O_2/N_2)$ (per meg)
~~b)~~
Measured O_2 mole fraction (ppm)
212000
211000
210000
209000
208000
207000
Diaphram valve
Fitting line
Residual
2
1
0
-1
-2
207000
208000
209000
210000
211000
212000
Gravimetric O_2 mole fraction (ppm)

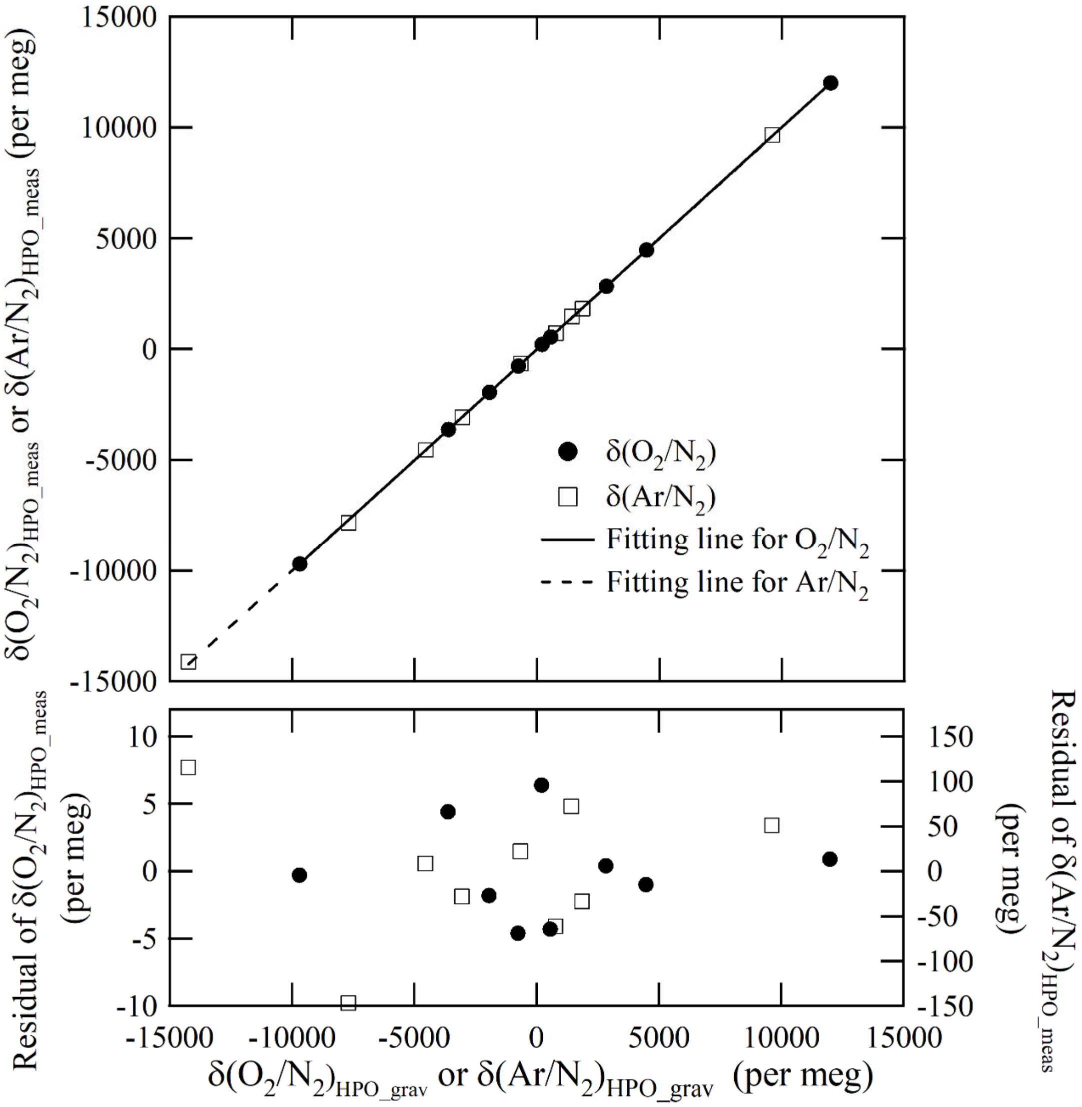


Figure 5 ~~a) The relationship~~Relationship between ~~the measured and gravimetric values for~~ $\delta(O_2/N_2)_{HPO\_grav}$ and $\delta(Ar/N_2)$ ~~as determined using~~$_{HPO\_meas}$ on the AIST scale (upper). ~~The~~Fitting residuals ~~of the values for~~ $\delta(O_2/N_2)_{HPO\_meas}$ and $\delta(Ar/N_2)$ ~~from the fitting line~~$_{HPO\_meas}$ are likewise shown (lower). ~~b) The relationship between the measured and gravimetric values for O_2 mole fractions as measured in highly precise O_2 standard mixtures (upper). The residuals of the measured O_2 mole fraction from the fitting line (lower).~~