APO2020 Virtual Workshop

Research activities for O_2/N_2 and Ar/N_2 in National Institute of Advanced Industrial Science and Technology (AIST)

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AIST research activities for O_2/N_2 and Ar/N_2

Observations (PI: Shigeyuki Ishidoya)

Gravimetric standard air (PI: Nobuyuki Aoki)

In this presentation, we introduce the observational programs quickly, and then discuss the round-robin experiments using the developed gravimetric standard air for O_2/N_2 (Aoki et el., in preparation)

Observations of O_2/N_2 and Ar/N_2

Surface stations:

background sites, urban area of Tokyo and Tsukuba, and a forest site

Collaborations with Meteorological Research Institute of Japan (MRI), Japan Meteorological Agency (JMA), National Institute for Environmental Studies (NIES), National Institute of Polar Research (NIPR), National Defense Academy of Japan (NDA), Tokai Univ. and Gifu Univ.

Aircrafts:

C130H and CRJ over Japan

Collaborations with MRI, JMA and Tohoku Univ. (TU)

Scientific Balloon:

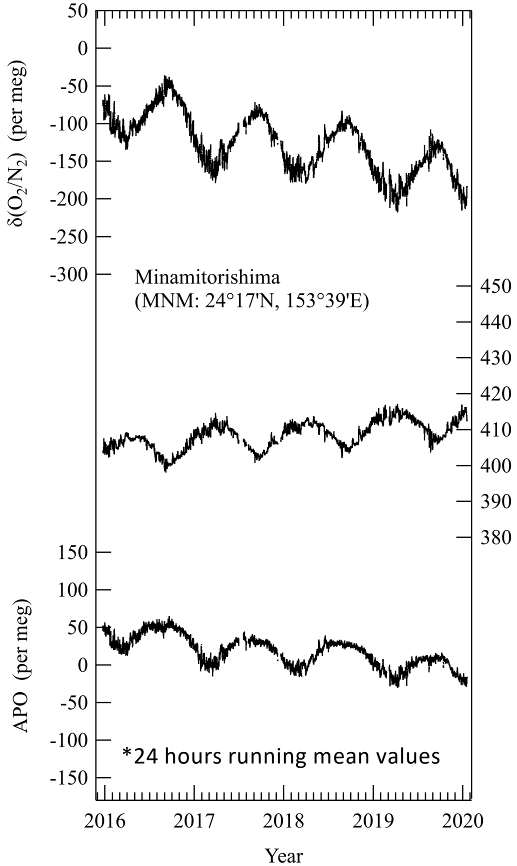
Stratosphere over Japan, Antarctica, Arctic and the equatorial region

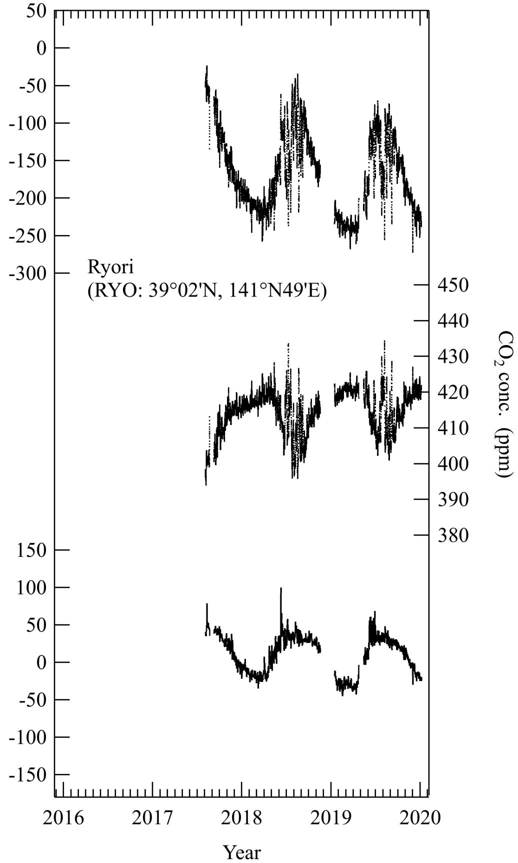
Collaborations with Miyagi Univ. of Edu. (MUE), TU, Tokyo Univ. of Tech. (Tokyo Tech), Hokkaido Univ. (HU) and JAXA

Surface background stations and aircrafts:

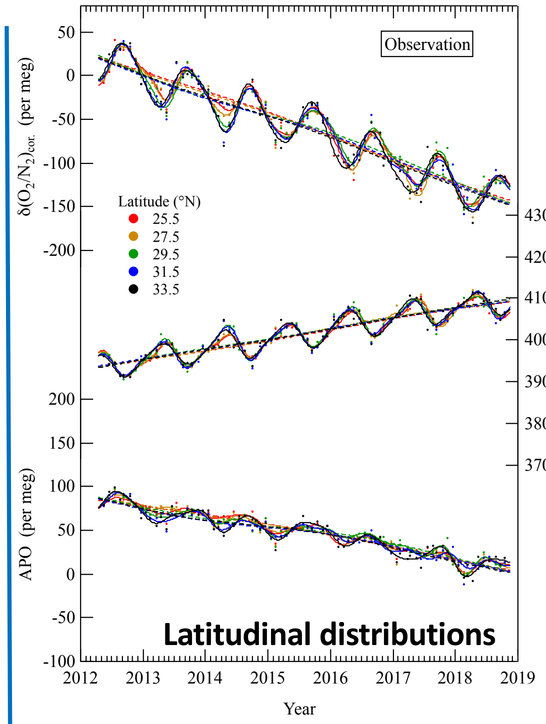
O_2/N_2

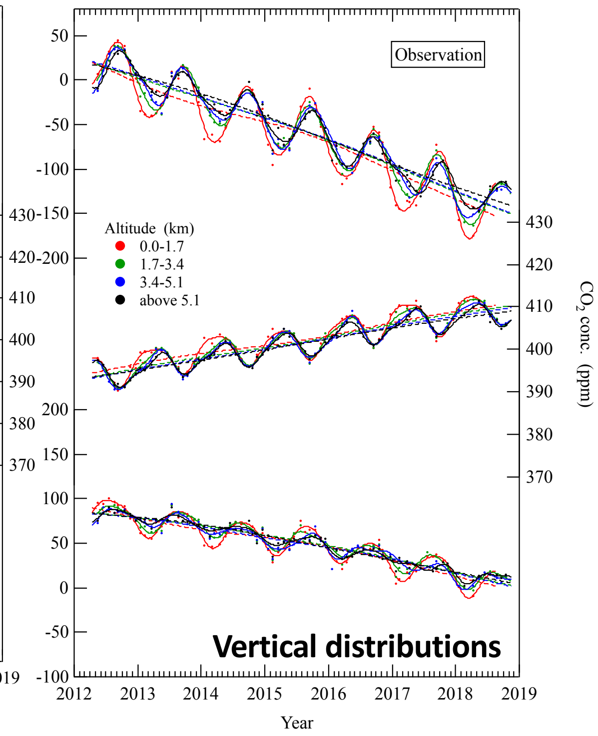
Continuous and flask observations of O_2/N_2, collaborations with MRI, JMA and TU

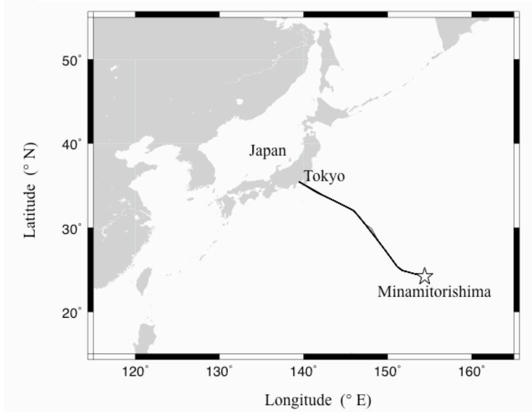




Updated from Ishidoya et al. (2017 SOLA), Ishidoya et al. (in preparation)







Artificial fractionations of O_2/N_2 have already been corrected by using Ar/N_2 for the air samples collected onboard C130H. We have also started to apply the corrections for the upper tropospheric air sample onboard CRJ since 2019 (not shown).

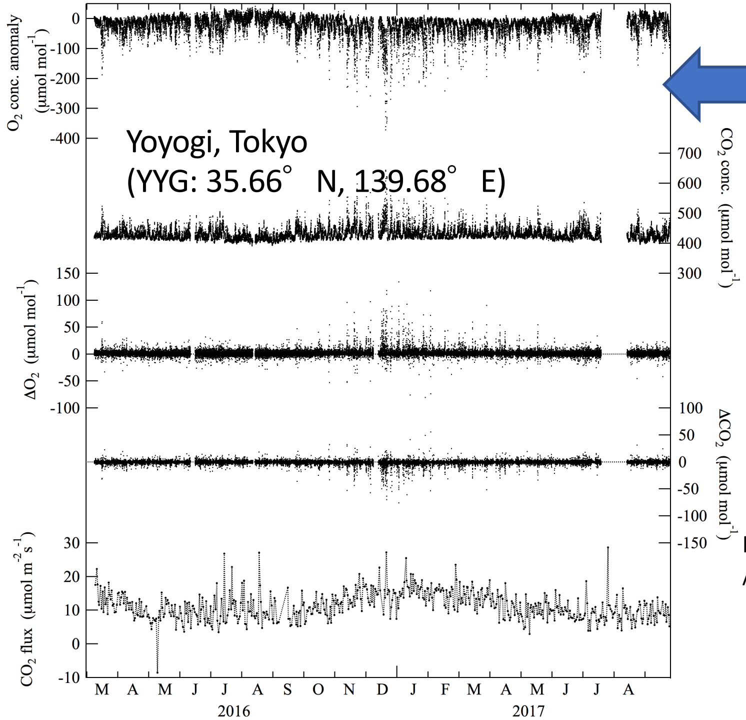
Updated from Ishidoya et al. (2014 SOLA), Ishiodya et al. (in preparation)

Objectives: Global CO_2 budget, air-sea O_2 flux and atmospheric transport processes

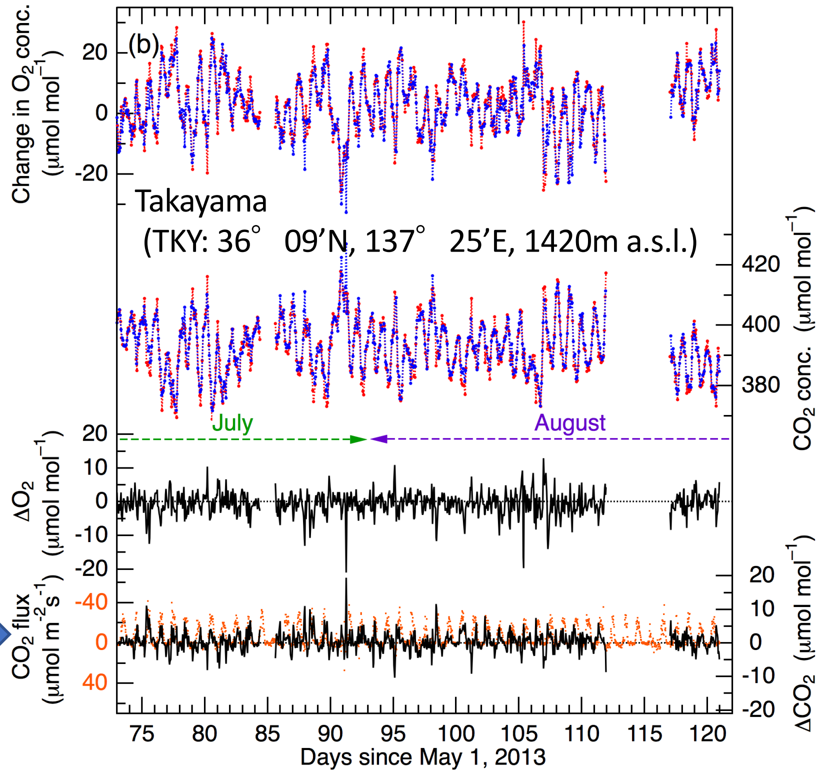
Surface urban stations and a forest station

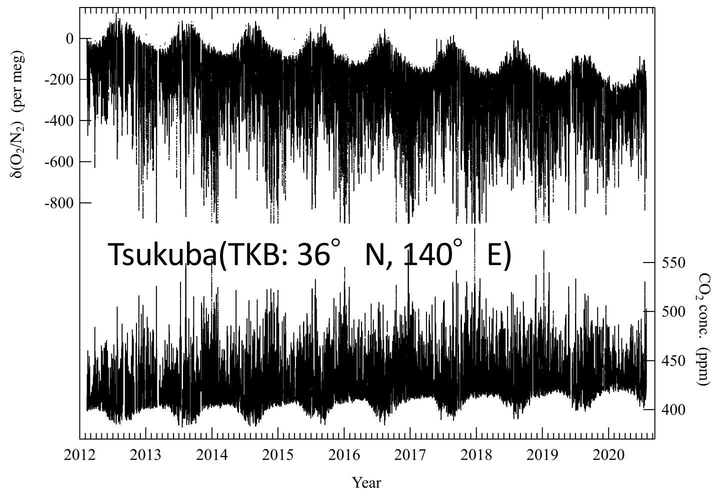
O_2/N_2

Continuous and flask observations of O_2/N_2, collaborations with NDA, Tokai Univ. and Gifu Univ.



https://www.aist.go.jp/aist_j/press_release/pr2020/pr20200515/pr20200515.html

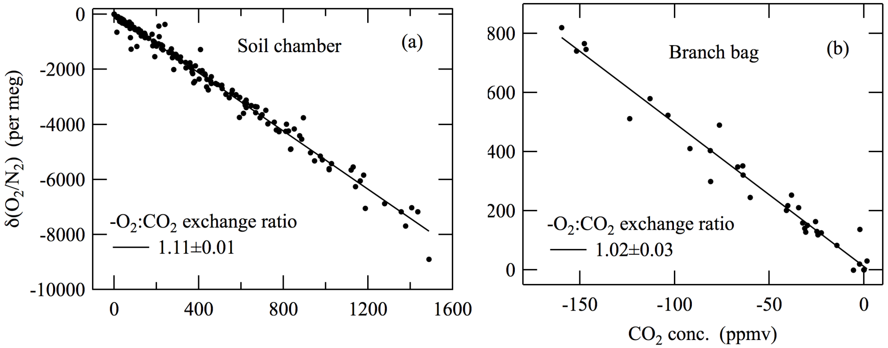




Ishidoya et al. (2020 ACP)

Updated from Ishidoya & Murayama (2014 Tellus B)

We will restart the continuous observation of O_2/N_2 at TKY this year.

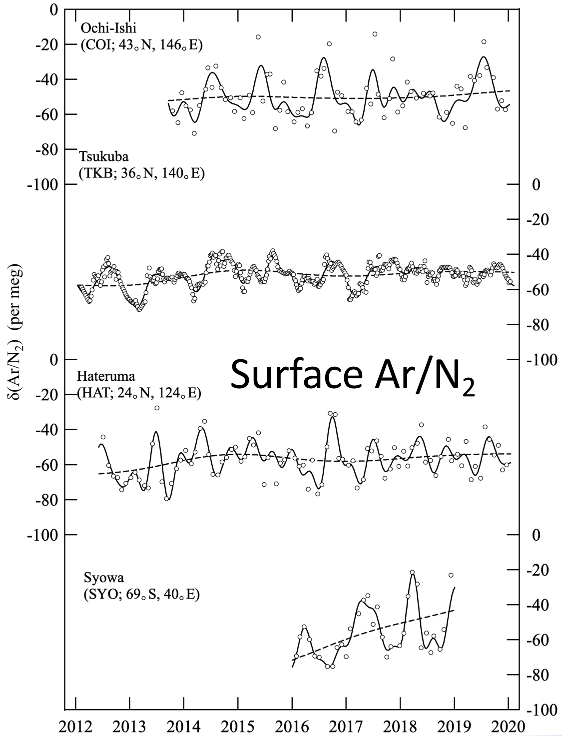


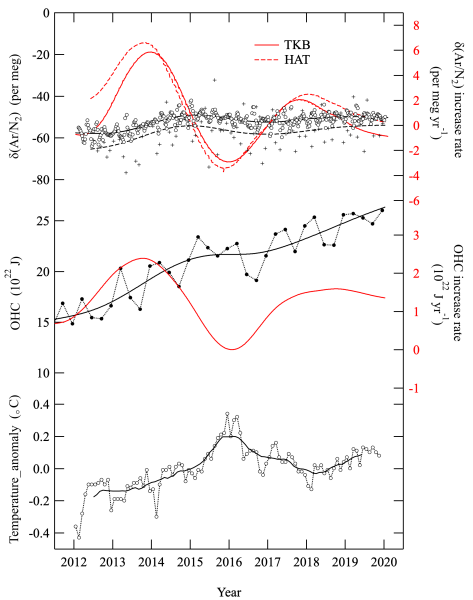
Ishidoya et al. (2013 Tellus B; 2015 Ecol. Res.)

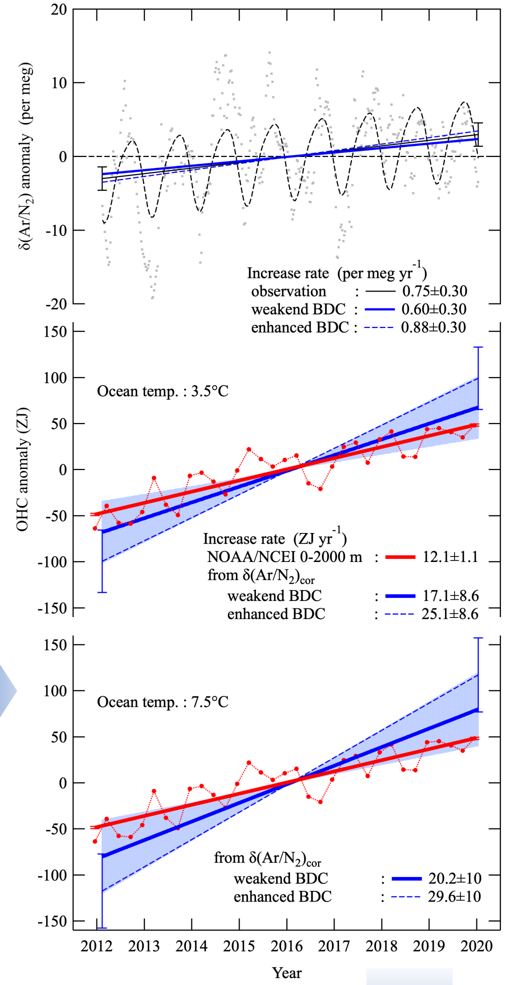
Objectives: Oxidative Ratio for the net turbulent flux, and CO_2 budget in a megacity and forest

Surface stations and scientific balloon : Ar/N_2

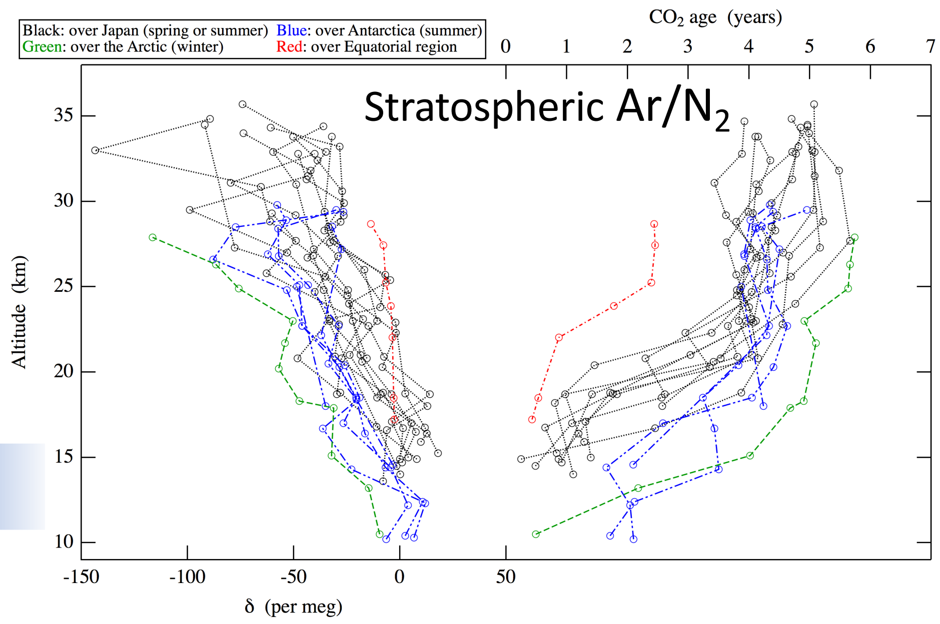
Flask observations of Ar/N_2, collaborations with MUE, NIES, TU, NIPR, MRI, Tokyo Tech, HU, and JAXA







Ishidoya et al. (ACPD, in review)



$*\delta = Ar/N_2 \times (1/12)$

Updated from Ishidoya et al. (2008 GRL; 2013 ACP) and Sugawara et al. (2018 ACP)

Surface Ar/N_2 trend = "Ocean Heat Content (OHC) change" + "Stratospheric change"

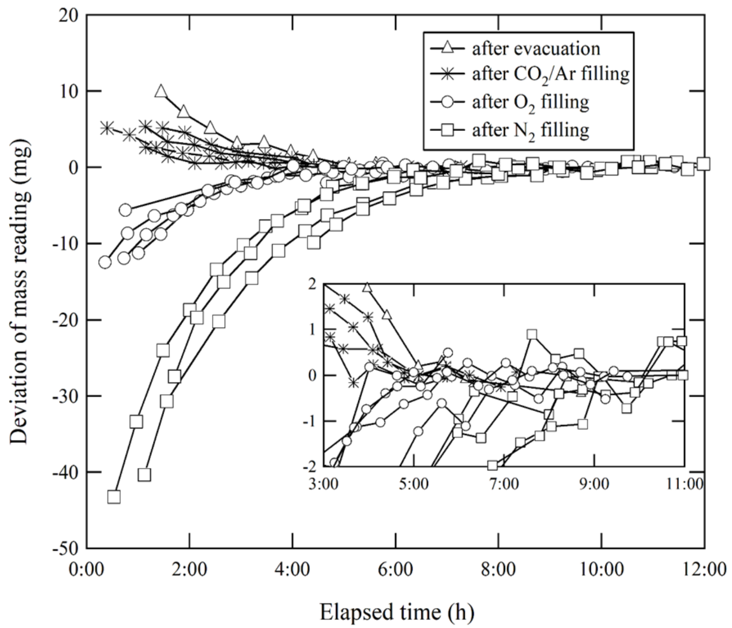
Objectives: OHC and Brewer-Dobson circulation (BDC) changes

To achieve the research objectives, it is vitally important to prepare precise and reproducible standard air for O_2/N_2 and Ar/N_2.

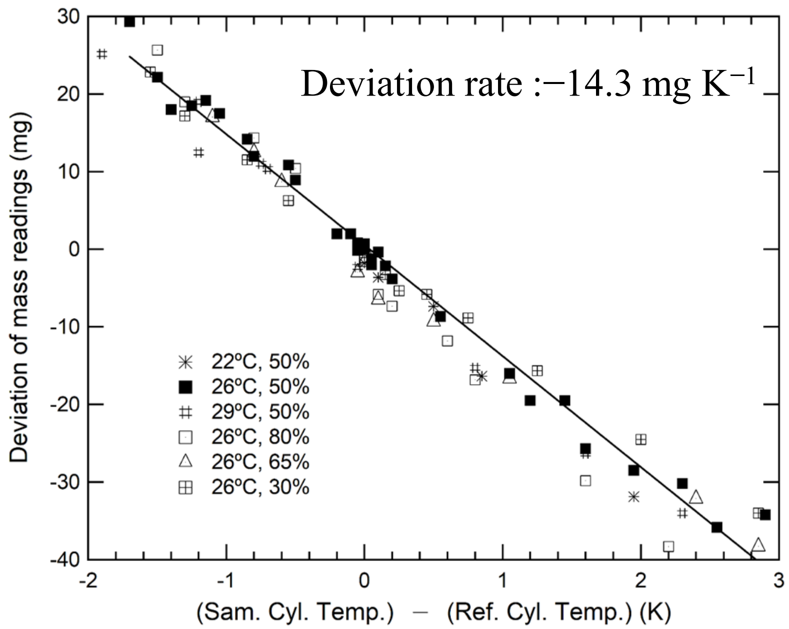
In the following, Nobuyuki Aoki-san will present results of the round-robin experiments using the gravimetric standard air for O_2/N_2 developed by Aoki et al. (2019). (Aoki et el., in preparation)

Development of gravimetric standard gases

We improved measurement precision of cylinder mass by measuring after eliminating difference in temperature between sample cylinder and reference cylinder.

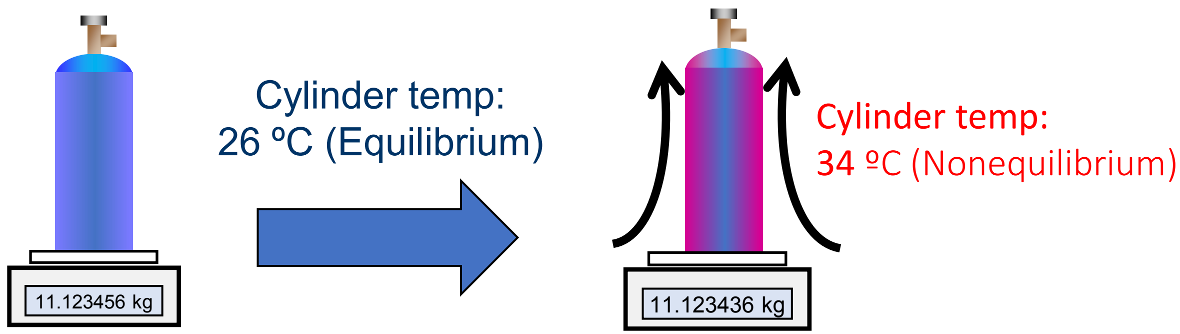


Changes in mass readings of sample cylinders after evacuation of the cylinder and filling of source gases (Aoki et al. 2019, AMT).



Changes in the mass readings observed for sample cylinders plotted against temperature differences (Aoki et al. 2019, AMT).

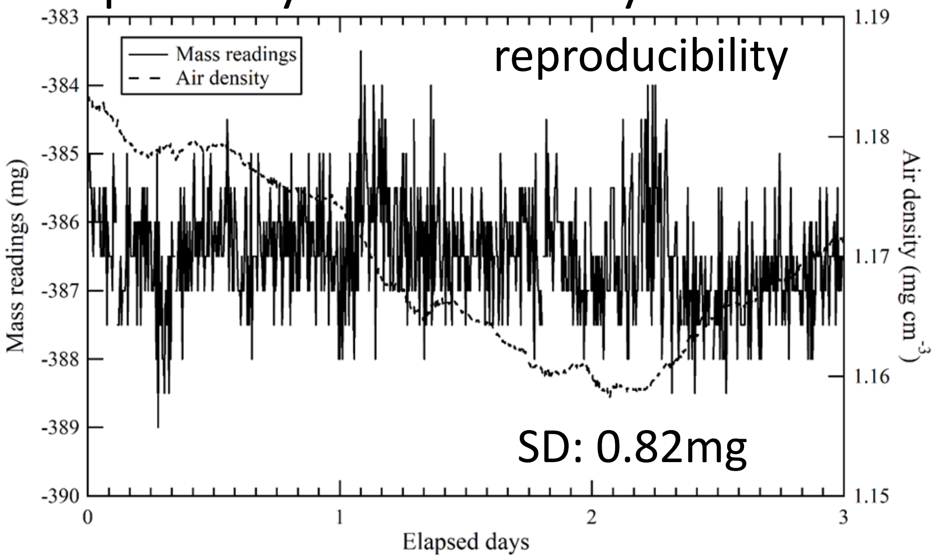
The change amount of weight difference between both cylinders depend on their temperature difference because only temperature of a sample cylinder changes in preparation process.



Cylinder weight change by up and down flow of air cooled or heated by the sample cylinder

Development of gravimetric standard gases

We were successful to develop high-precision oxygen standard gases with less than 5 per meg standard uncertainty by measuring isotopic composition of source gases and cylinder mass precisely and accurately.

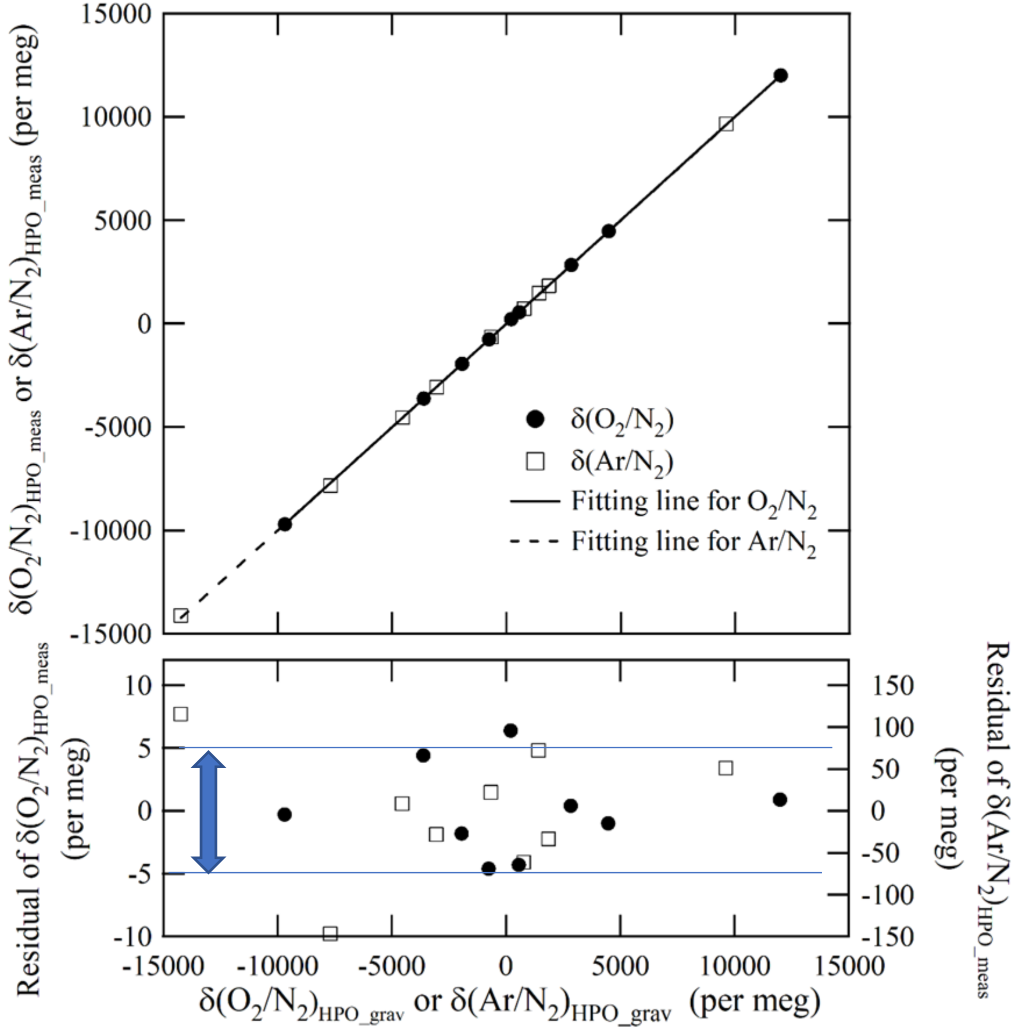


Repeatability of mass readings obtained for the sample (Aoki et al. 2019, AMT).

Isotopic composition and atomic masses of pure O_2 and N_2

Isotope	Atomic mass	Isotope abundance	
		Atmosphere	Source gas
^{14}N	14.0030740074(18)	0.996337(4)	0.996346(4)
^{15}N	15.000108973(12)	0.003663(4)	0.003654(4)
^{16}O	15.9949146223(25)	0.9975684(9)	0.9975887(9)
^{17}O	16.99913150(22)	0.0003836(8)	0.0003818(8)
^{18}O	17.9991604(9)	0.0020481(5)	0.0020295(5)

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



Relationship between δ(O_2/N_2)$_{HPO\_grav}$ and δ(Ar/N_2)$_{HPO\_meas}$ (upper). Fitting residuals are likewise shown (lower) (Aoki et al. 2019, AMT)

Outline of the round-robin experiment

Comparison of each O_2/N_2 scale was carried out between four laboratories: AIST, NIES, Tohoku University, SIO. Each laboratory analyzed the five gravimetric standard gases prepared by NMIJ/AIST and reported $\delta(O_2/N_2)$ values on own scales to NMIJ/AIST.

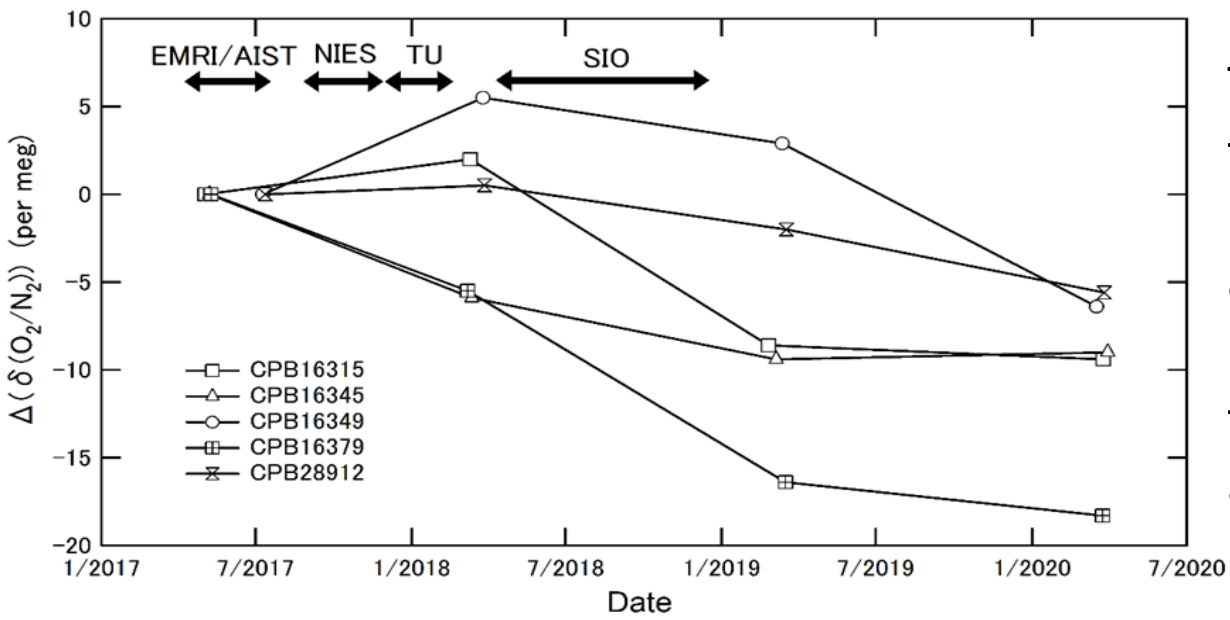
Constituent	EMRI/AIST	NIES	TU	SIO
Analysis period	**May–July, 2017**	**Sep.–Nov., 2017**	**Dec., 2017–Jan., 2018**	**May–Nov., 2018**
Measurement technique	**Mass spectrometry**	**Gas chromatography**	**Mass spectrometry**	**Interferometric method**
Measurement species	$^{14}N^{14}N$, $^{15}N^{14}N$, $^{16}O^{16}O$, $^{17}O^{16}O$, $^{18}O^{16}O$	O_2, N_2, Ar	$^{16}O^{16}O$, $^{14}N^{15}N$	O_2 (Interferometer) ^{40}Ar, $^{14}N^{14}N$ (mass spectrometer)
Reported values	$\delta(^{16}O^{16}O\,/^{14}N^{14}N)$	$\delta(O_2/N_2)$	$\delta(^{16}O^{16}O\,/^{15}N^{14}N)$[a]	$\delta(O_2/N_2)$

Composition: N_2, O_2, Ar, CO_2
Comparison range: -4000 per meg to 2000 per meg
Standard uncertainty : 3.3 per meg to 4.0 per meg

Gravimetric $\delta(O_2/N_2)$ values were calculated against the O_2/N_2 ratio in the atmosphere (0.20946/0.78084=0.26825) (Machta and Hughes, 1970).

Stability of $\delta(O_2/N_2)$ during the round-robin experiment

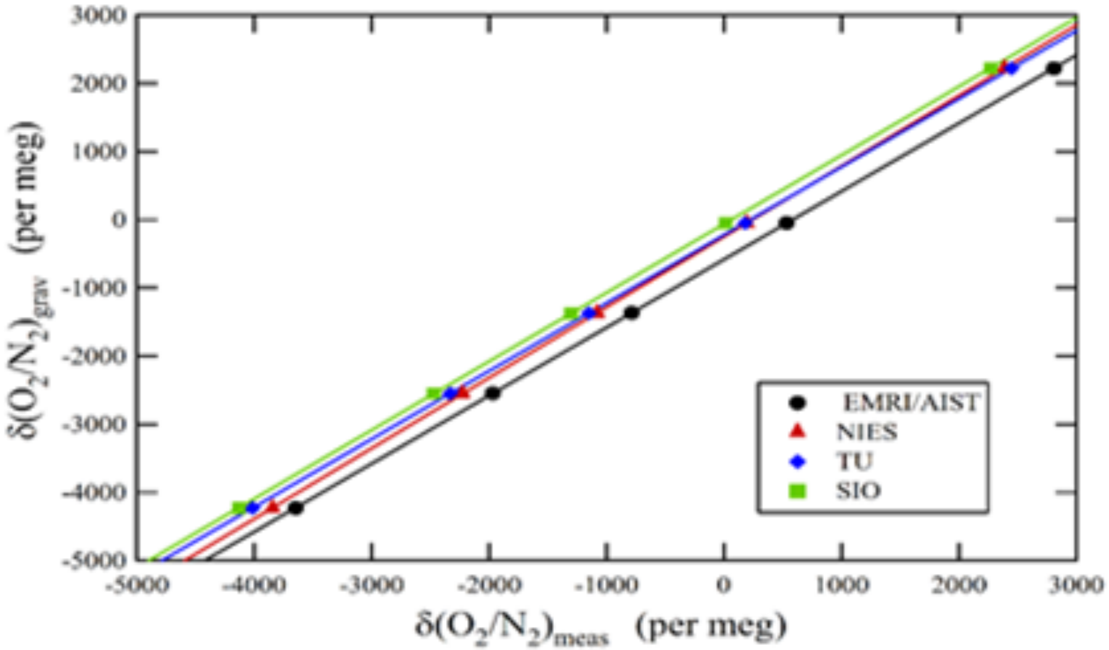
The $\delta(O_2/N_2)$ values decreased slightly with time in all cylinders, especially for the cylinder no. CPB16379.The average decreasing rate of the $\delta(O_2/N_2)$ values in the cylinders except the CPB16379 was -3.2 ± 1.1 per meg yr^{-1}, while that of the CPB16379 cylinder was -6.7 ± 2.1 per meg yr^{-1}.



To correct the temporal drifts during the round-robin experiment, we linearly interpolated the gravimetric $\delta(O_2/N_2)$ value of the date analyzed by individual laboratories using the temporal drift values before and after analysis of individual laboratories

Difference between each span sensitivity

A Deming least square fits was applied to the individual laboratory's values. The deviations from 1 for the slopes of the lines represent the differences from the span sensitivity of the NMIJ/AIST scale, which were in range from –0.17% to 3.3%.

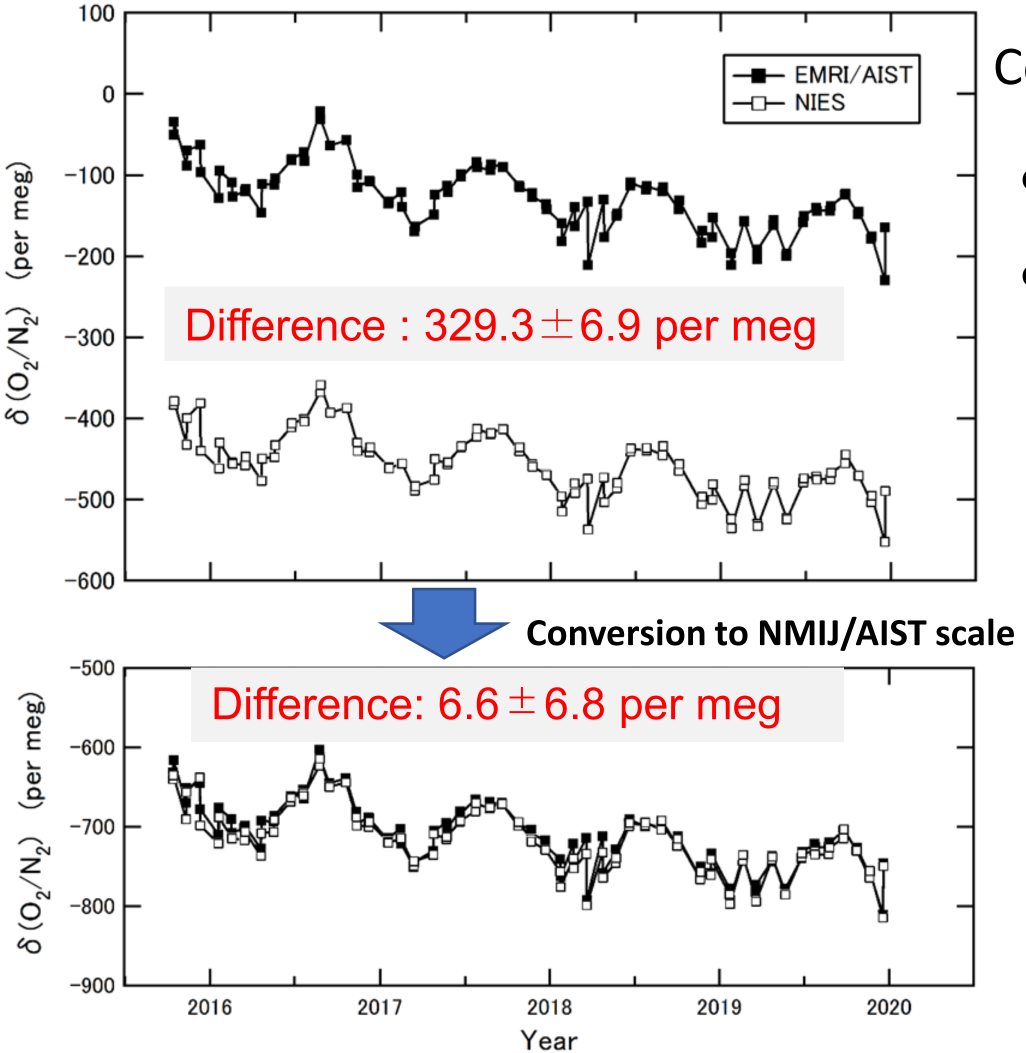


The differences of NIES and TU from SIO were consistent with those obtained from past inter-comparison experiments (the GOLLUM comparison, 2015)

Institutes	Slopes	Intercepts	Deviation from SIO scale	Deviation from SIO values in the GOLLUM 15
AIST	0.9983±0.0010	−581.0±2.2	−530.3 ± 3.3	–
TU	0.9983±0.0013	−221.4±3.1	−170.7 ± 3.9	−160±10.8
NIES	1.0329±0.0013	−243.0±3.0	−192.4 ± 3.9	−195±10
SIO	1.0087±0.0010	-50.7 ± 2.4	–	0

Compatibility of the atmospheric $\delta(O_2/N_2)$ data between AIST and NIES

We compared the O_2/N_2 ratios measured by AIST and NIES based on flask samples collected at HAT from October, 2015 to December, 2019 (Tohjima et al., 2008), to confirm compatibility of AIST and NIES data after conversion to the NMIJ/AIST scale. The values of NIES after March, 2018 are preliminary data.



Conversion equation to the NMIJ/AIST scale

$$\delta(O_2/N_2)_{\mathrm{NMIJ/AIST}} = \boxed{a_{AIST}} \cdot \delta(O_2/N_2)_{AIST} + \boxed{b_{AIST}}$$

$$\delta(O_2/N_2)_{\mathrm{NMIJ/AIST}} = \boxed{a_{NIES}} \cdot \delta(O_2/N_2)_{NIES} + \boxed{b_{NIES}}$$

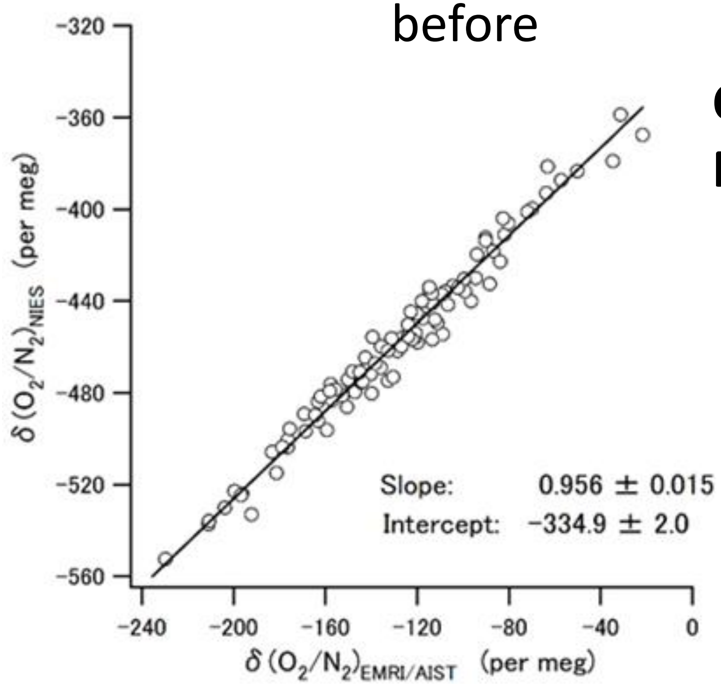
Slope Intercept

This scale conversion reduced the bias between $\delta(O_2/N_2)$ values of AIST and NIES to 6.6±6.8 per meg. The bias dropped within the uncertainty which represents standard deviation of the differences.

Comparison of Hateruma samples measured by AIST and NIES

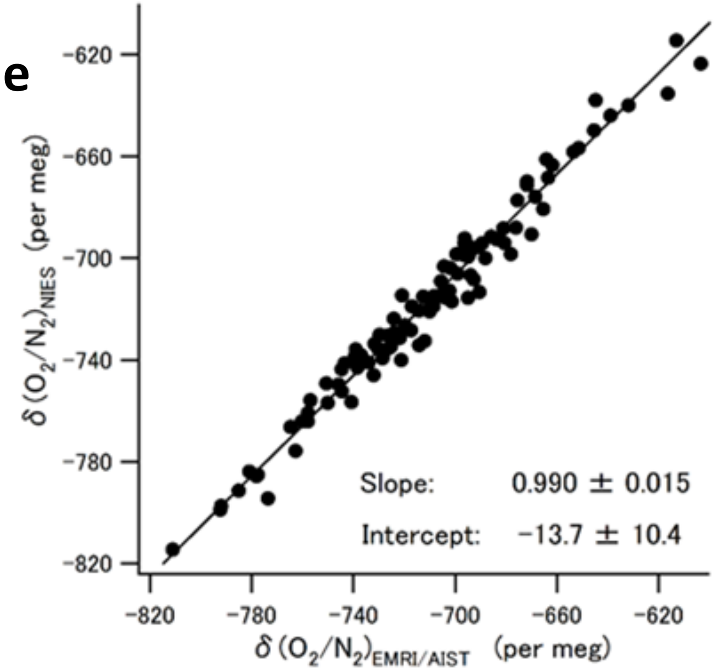
We confirm compatibility between span sensitivities on the AIST scale and the NIES scale using scatter plots. The lines represent a Deming least square fit applied to the scatter plots.

before



Conversion to the NMIJ/AIST scale

after



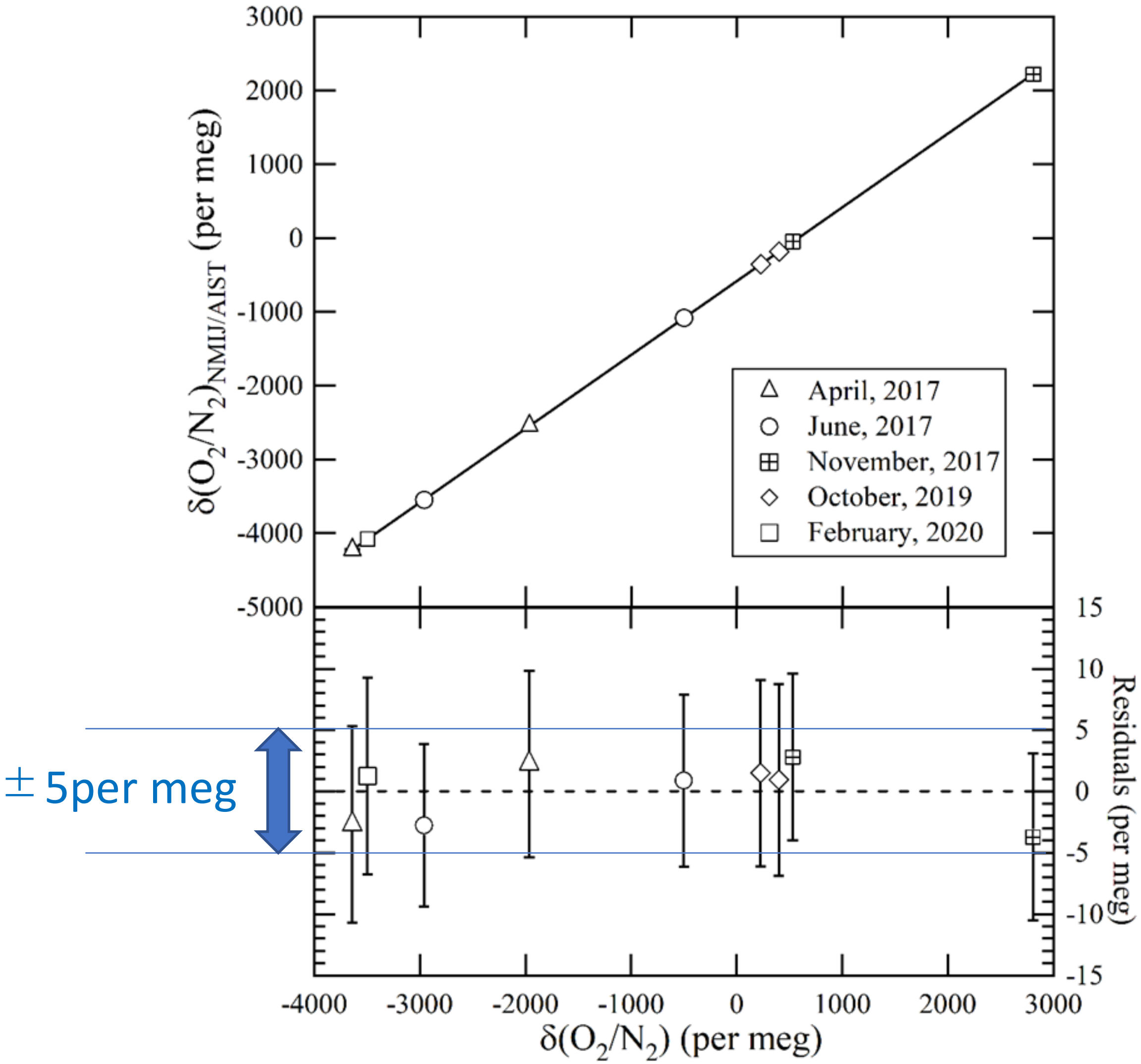
Slope: 0.956 ± 0.015

Slope: 0.990 ± 0.015

The slope of the line before scale conversion and its standard deviation is 0.956 ± 0.015, which consisted with the difference of the span sensitivity between both scales (0.9983/1.0329= 0.967) within uncertainty. The slope after the scale conversion and its standard deviation is 0.990 ± 0.015, identifying that the difference in span sensitivity between AIST and NIES scales was corrected by the scale conversion to the NMIJ/AIST scales.

Reproducibility of O_2/N_2 scale

Reproducibility of NMIJ/AIST scale was also evaluated using nine high-precision standard mixtures prepared in different period (from April, 2017 to February, 2020).



All residuals were within the expanded uncertainties, suggesting that NMIJ/AIST scale will be reproduced by preparing the high-precision oxygen standard mixtures.