Evaluation of an influence of the atmospheric minor components on the precise atmospheric oxygen measurements

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Outline

- Background
- Development of standard gas mixtures composed of N_2, O_2, Ar, and CO_2.
- Development of standard gas mixtures including minor components
- Influence of minor components on precise O_2/N_2 measurements

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Background

- In atmospheric O_2 observation, small variation of O_2 molar fraction has been observed with the precision of 1 μmol/mol or less. The molar fraction should be measured using standard gas mixtures with their standard uncertainties of less than 1 μmol/mol, to directly compare each laboratory's data. However, the preparation technique under the uncertainty of 1 μmol/mol was not established.
- Tohjima et al. (2005) tried to develop standard gas mixtures for O_2 observation by a gravimetric method. The reproducibility of O_2 molar fractions was 2.9 μmol/mol.
- Four years ago, we succeeded in developing gravimetric O_2 standard gas mixtures with the standard uncertainty of less than 1 μmol/mol (Aoki et al., 2019) and then conducted round robin excise among AIST, NIES, TU, and SIO (Aoki et al., 2021). The results of the intercomparison revealed the relationship in the O_2/N_2 scales among the respective laboratories.

Objective

The previous standard gas mixtures only consisted of N_2, O_2, Ar, and CO_2, including no the atmospheric minor components such as rare noble gases and so on.

As a result, influence of the minor components on the precise O_2/N_2 measurements is not clear yet.

Therefore, we developed the standard gas mixtures including the minor components of Ne, He, Kr, Xe, and CH_4, to understand the influence on the precise O_2/N_2 measurements.

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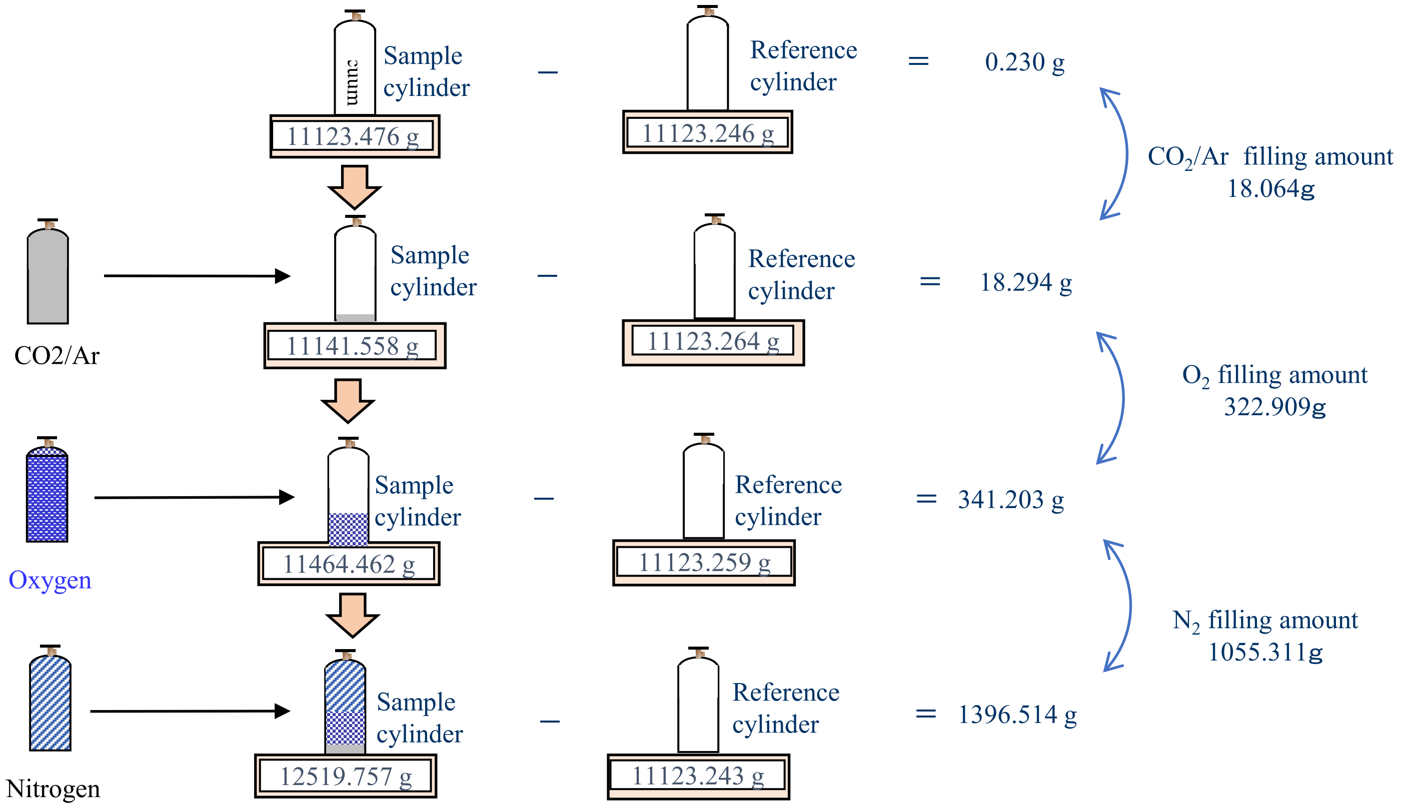
Preparation of O_2 standard gas mixtures



Calculation formula of components

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

Molar fractions of components were determined from the following values;

1. masses of source gases (N_2, O_2, CO_2/Ar)
2. molar masses of components in source gases
3. molar fractions of components in source gases

The mass of a sample cylinder was measured by compared to nearly identical reference cylinder.

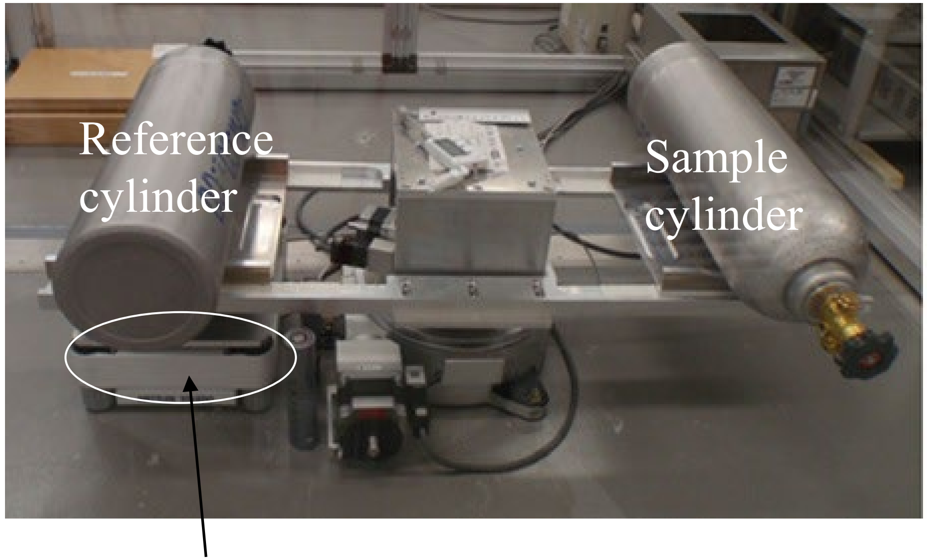
Uncertainty budget table of the gravimetric standard mixtures (a conventional method)

Component	Unit	Value	Standard uncertainty g	Sensitivity coefficient	Uncertainty contribution µmol/mol
Mass of O_2	g	245	0.0037	6.76.E-04	2.5
Molar mass of O_2	g	31.9988	0.00035	5.17.E-03	1.8
Mass of N_2	g	800	0.0037	2.04.E-04	0.75
Molar mass of N_2	g	28.0134	0.00023	5.83.E-03	1.3
Mass of Ar	g	14	0.0037	1.43.E-04	0.53
Molar mass of Ar	g	39.948	0.00058	5.02.E-05	0.029
Mass of CO_2	g	0.65	0.0037	1.30.E-04	0.48
Molar mass of CO_2	g	44.0095	0.00058	1.92.E-06	0.001
Molar fraction of O_2				209312 µmol/mol	
Standard uncertainty				3.5 µmol/mol	

Masses and molar masses of O_2, N_2, Ar, and CO_2, were determined based on the cylinder mass and IUPAC atomic masses, respectively.

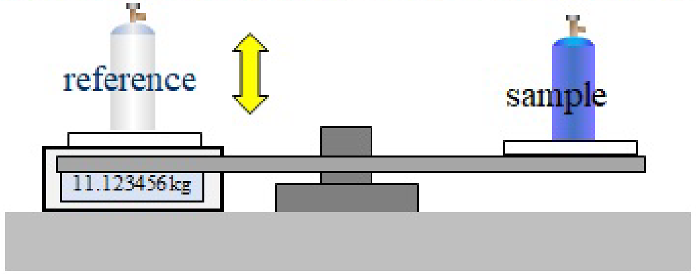
We improved the determination processes of the cylinder mass and atomic mass.

Weighing procedure of cylinder in NMIJ

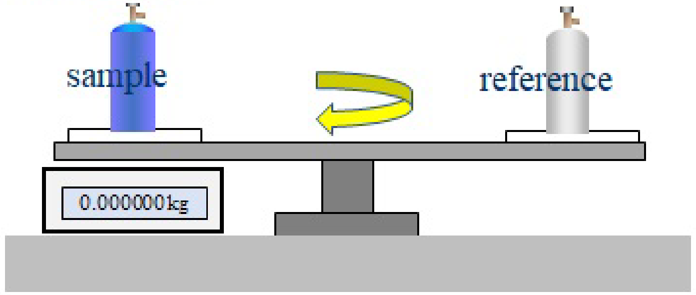


Specification of Mass comparator	
Mass comparator	Mettler Toledo XP26003L
Resolution	1 mg
Max	26 kg

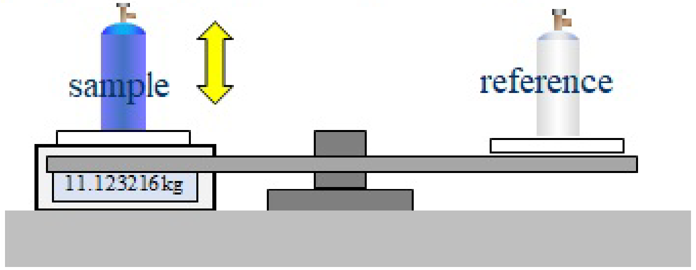
Weighing a reference cylinder by lowering an arm



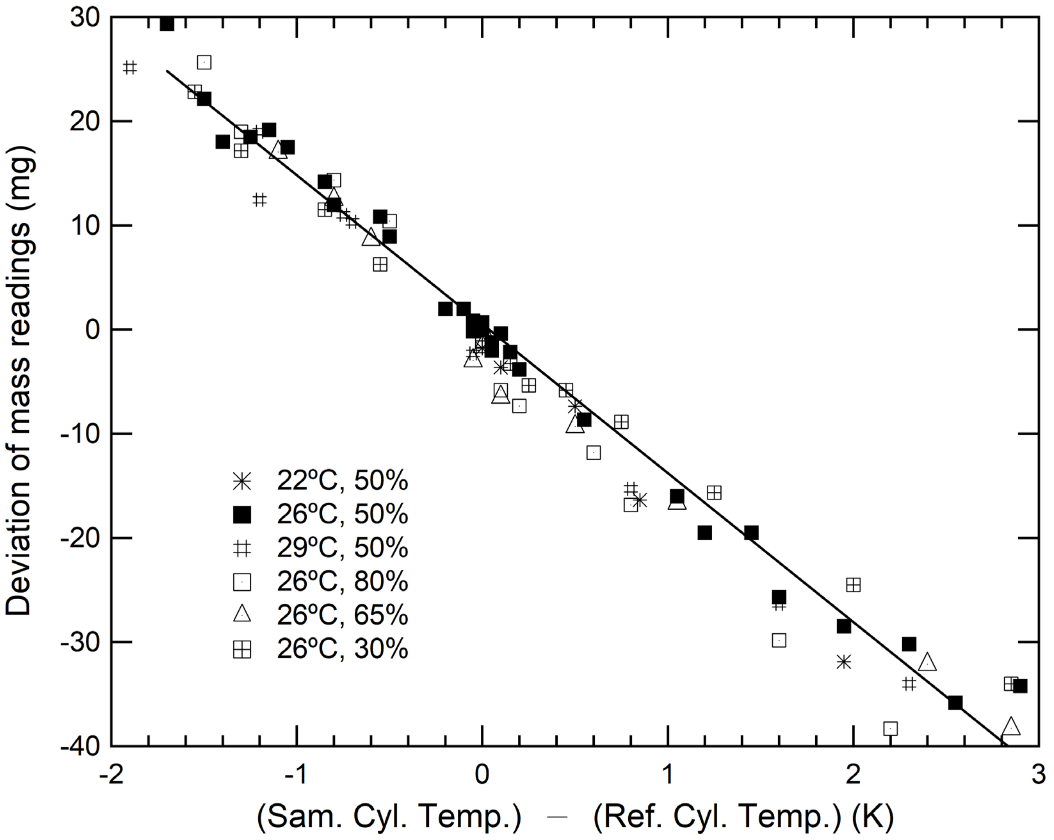
Exchange of a reference cylinder and a sample cylinder by turn



Weighing a sample cylinder by lowering the arm

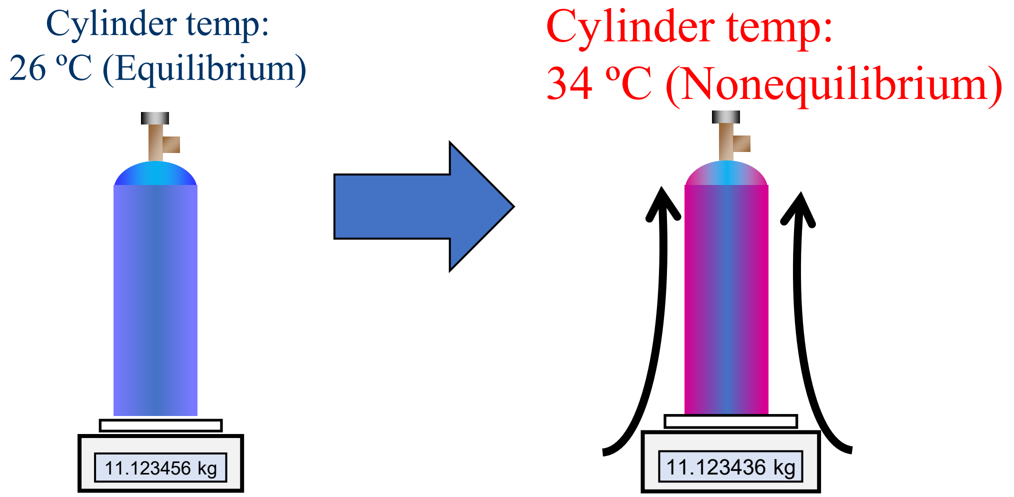


Improvement of cylinder weighing



Deviation amount of mass readings depends on temperature difference between sample and reference cylinders

The cylinder mass readings deviated in proportion to the temperature difference between the sample and reference cylinders rather than water amount adsorbed on the cylinder surface.



The deviation is caused by up and down flow of air cooled or heated by the sample cylinder.

We measured the cylinder mass after confirming that there was no temperature difference between both cylinders. The procedure have reduced standard uncertainty of the cylinder mass from 2.6 mg to 0.8 mg.

Atomic masses in pure N_2 and O_2 gases

Isotope	Atomic mass[a,b]	Isotope abundance		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)	$\delta^{15}N = (-2.397 \pm 0.001)$ ‰
^{16}O	15.9949146223(25)	0.9975684(9)[d]	0.9975887(9)	
^{17}O	16.99913150(22)	0.0003836(8)[d]	0.0003818(8)	$\delta^{17}O = (-4.66 \pm 0.05)$ ‰
^{18}O	17.9991604(9)	0.0020481(5)[d]	0.0020295(5)	$\delta^{18}O = (-9.075 \pm 0.003)$ ‰

Atomic masses of N and O were determined by measuring precisely the difference in isotope ratios from the corresponding atmospheric values using IRMS.

Sources	Atomic mass of nitrogen[a]	Atomic mass of oxygen[a]
IUPAC	14.00686 ± 0.00043	15.99940 ± 0.00037
Source gases	14.006717 ± 0.000004	15.999366 ± 0.000001

Uncertainties of the atomic masses were about 100 times lower than the previous uncertainties.

[a] Numbers in the parentheses represent the standard uncertainty in the last digits.
[b] Atomic mass and the standard uncertainty as determined by De Laeter et al. (2003).
[c] 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] 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 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] Isotopic ratio is defined as the difference in the corresponding atmospheric value (AIST reference air) measured using a mass spectrometer. Numbers following the symbol ± denote the standard uncertainty.

Uncertainty budget table of the improved procedure

Component	Unit	Value	Standard uncertainty	Sensitivity coefficient	Uncertainty contribution µmol/mol
Mass of O_2	g	245	0.0011	6.76.E-04	0.74
Molar mass of O_2	g	31.998732	0.000002	5.17.E-03	0.01
Mass of N_2	g	800	0.0011	2.04.E-04	0.22
Molar mass of N_2	g	28.013434	0.000002	5.83.E-03	0.01
Mass of Ar	g	14	0.0011	1.43.E-04	0.16
Molar mass of Ar	g	39.94789	0.0000070	5.02.E-05	0.0004
Mass of CO_2	g	0.65	0.0011	1.30.E-04	0.14
Molar mass of CO_2	g	44.0095	0.00058	1.92.E-06	0.001
	Molar fraction of O_2			209312	µmol/mol
	Standard uncertainty			0.8 µmol/mol	

- Uncertainties of these masses were reduced to less than 1 µmol/mol.
- Uncertainties of these molar masses were negligible.
- Uncertainty of O_2 molar fraction was less than 1 µmol/mol.

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Overview of influence evaluation of minor components

- The standard gas mixtures with minor components were prepared using almost the same technique for the previous gravimetric standard gas mixtures of pure N_2, O_2, Ar, and CO_2..

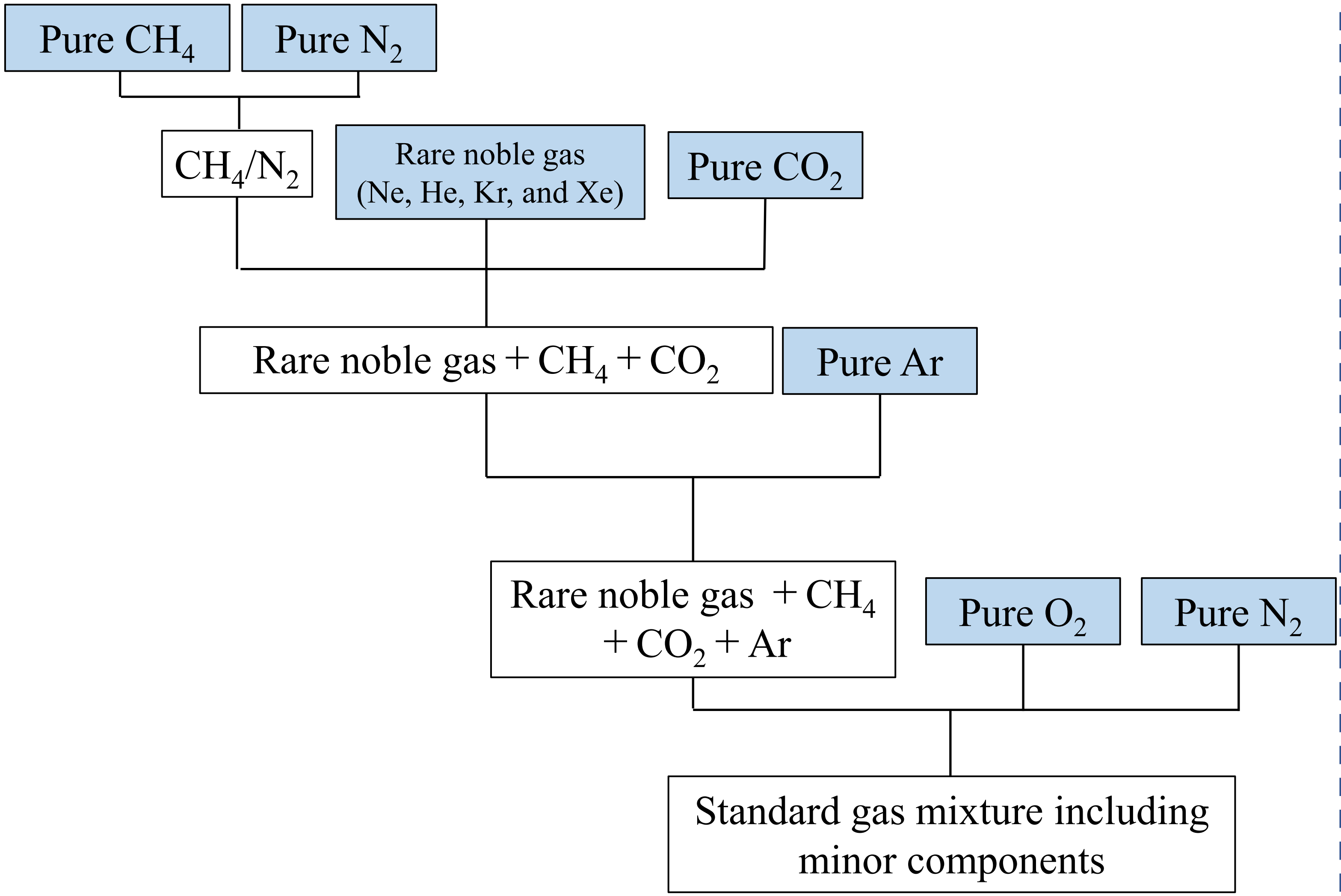
- Only the filling procedure was different from the preparation technique of the standard gas mixtures without minor components.

- Four standard gas mixtures, of which O_2 molar fractions ranged from 0.2091 mol/mol to 0.2097 mol/mol, were prepared.

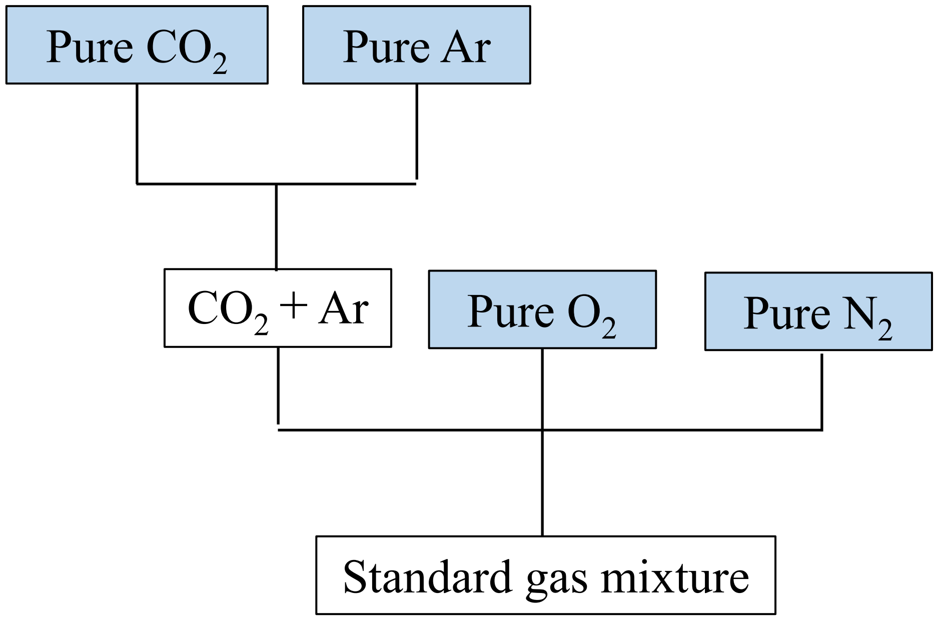
- The standard gas mixtures with and without minor components were measured using three types of analyzers.

Preparation procedure

Standard gas mixture including Ne,He,Kr,CH_4,and Xe



Standard gas mixture



The standard gas mixtures including minor components

Cylinder No	Date	Gravimetric values (μmol/mol)								
		N_2	O_2	Ar	CO_2	Ne	He	Kr	CH_4	Xe
CPB16345	2021.10.7	780481.6 ± 0.9	209686.8 ± 0.7	9364.7 ± 0.7	438.66 ± 0.04	19.27 ± 0.03	5.53 ± 0.03	1.20 ± 0.01	1.942 ± 0.002	0.091 ± 0.001
CPC00415	2021.9.30	780706.3 ± 0.9	209484.5 ± 0.8	9343.4 ± 0.7	437.66 ± 0.04	19.23 ± 0.03	5.52 ± 0.03	1.20 ± 0.01	1.938 ± 0.002	0.091 ± 0.001
CPB16315	2021.11.2	780991.2 ± 0.9	209210.2 ± 0.7	9333.4 ± 0.6	437.20 ± 0.04	19.21 ± 0.03	5.51 ± 0.03	1.20 ± 0.01	1.936 ± 0.002	0.091 ± 0.001
CPB16379	2021.10.12	781122.8 ± 0.9	209110.0 ± 0.7	9303.3 ± 0.7	435.79 ± 0.04	19.15 ± 0.03	5.50 ± 0.03	1.20 ± 0.01	1.930 ± 0.002	0.091 ± 0.001
Atmosphere		780882.9	209339.1	9334.4	417.06	18.18	5.24	1.14	1.911	0.09

Numbers following the symbols ± represents the standard uncertainty.

The standard uncertainties were almost same as those in the standard gas mixtures without the minor components.

The molar fractions of the minor components were slightly higher than atmospheric values.

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Paramagnetic oxygen analyzer

Outline of analytical method

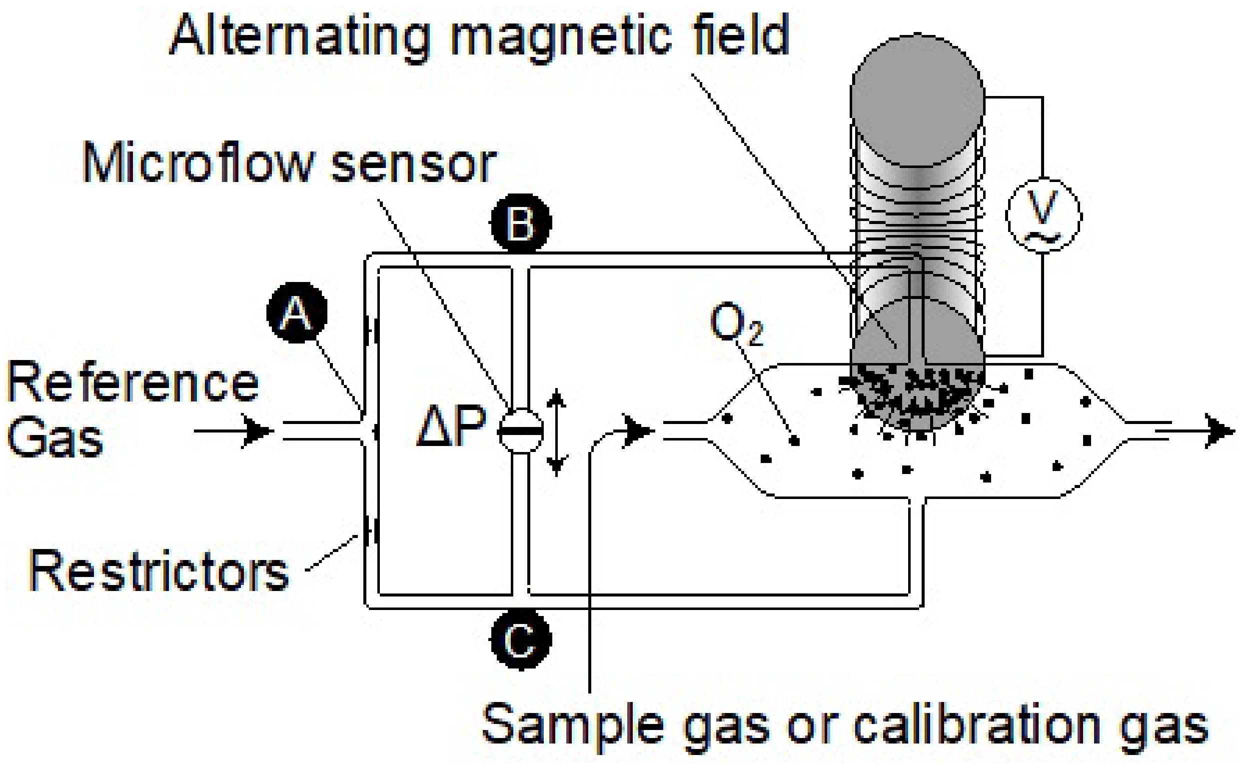
Instrument	Paramagnetic oxygen analyzer （Air liquid Japan POM-6E: this is similar to OXYMAT 6E (SIEMENS, Germany))
Measured species	O_2
Precision	0.7 µmol/mol (O_2 molar fraction)
Flow rate of sample	80 ml/min

Measurement value

Gravimetric value

$$\delta(O_2/N_2) = \delta\left\{\frac{(O_2/N_2)_{STD}}{(O_2/N_2)_{ref}} - 1\right\} \times 10^6$$

0.2680761=0.2093391/0.7808943 (Aoki et al., 2019)

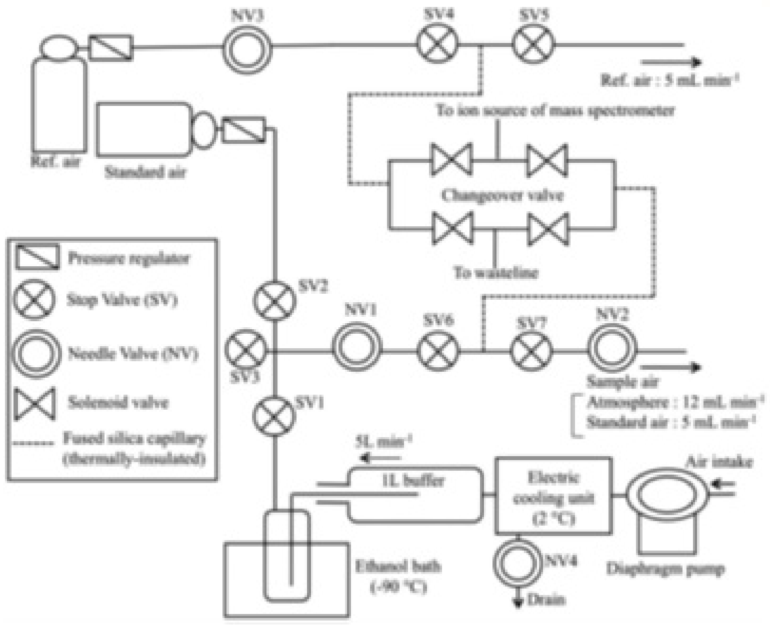


The paramagnetic analyzer for O_2 measurement (Aoki & Shimosaka, *Anal. Sci*, 2018)

Mass spectrometer

Outline of analytical method

Instrument	Mass spectrometer (Thermo Scientific Delta-V)
Measured species	$^{14}N^{14}N$, $^{15}N^{14}N$, $^{16}O^{16}O$, $^{17}O^{16}O$, $^{18}O^{16}O$, ^{36}Ar, ^{40}Ar, $^{12}C^{16}O^{16}O$
Precision	3.2 per meg ($\delta(^{16}O_2/^{14}N_2)$)
Flow rate of sample	3 ml/min



Mass spectrometer for O_2/N_2 measurement (Ishidoya & Murayama, *Tellus B,* 2014)

Calculation method of δ(O_2/N_2)

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

These values were calculated form $\delta(^{16}O^{16}O/^{14}N^{14}N)$,

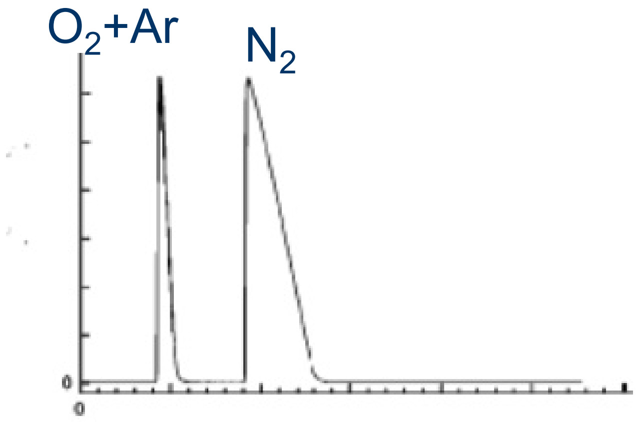
These values were calculated from the measurement values ($\delta(^{18}O^{16}O/^{16}O^{16}O)$, $\delta(^{17}O^{16}O/^{16}O^{16}O)$, $\delta(^{15}N^{14}N/^{14}N^{14}N)$)

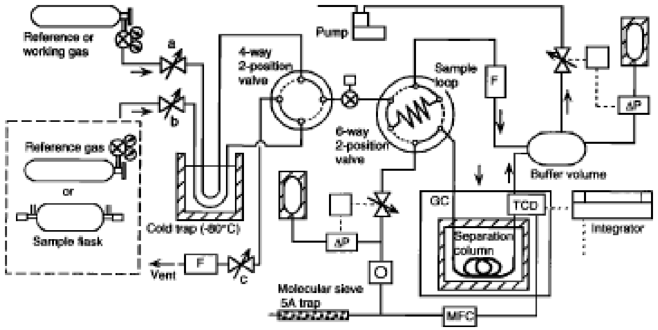
These values were calculated using isotope ratio of natural air (Junk & Svec, 1958, Barkan &Luz, 2005)

GC/TCD

Outline of analytical method

Instrument	GC/TCD (Hewlett-Packard HP5890)
Measured species	N_2, O_2 (including Ar)
Precision	5 per meg ($\delta(O_2/N_2)$)
Flow rate of sample	8 ml/min





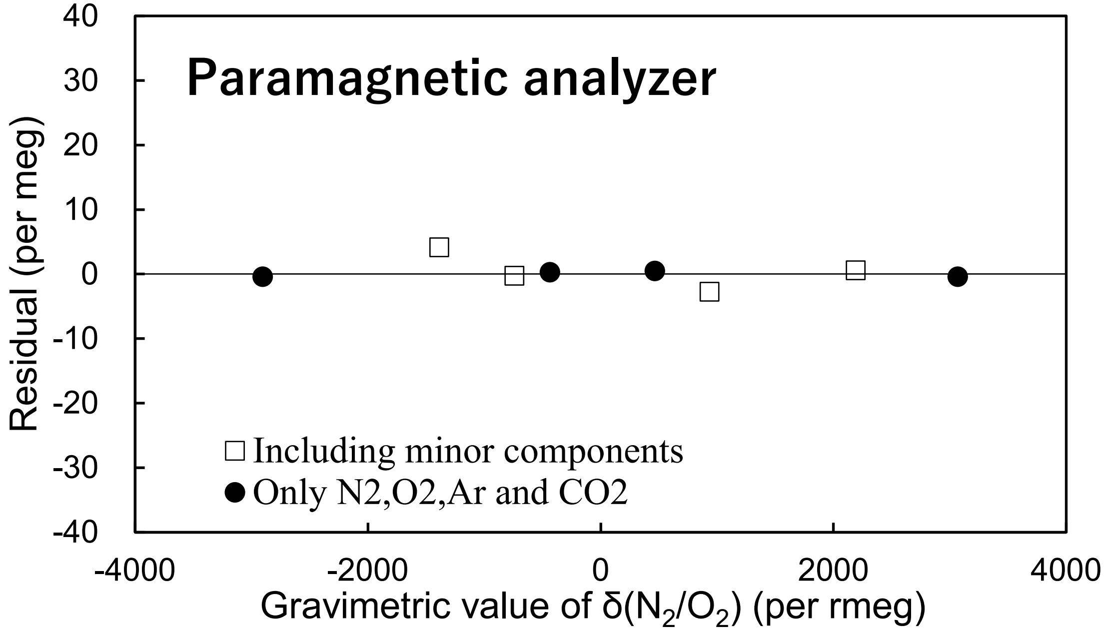
The GC-TCD for O_2/N_2 measurement
(Tohjima, *JGR*, 2000)

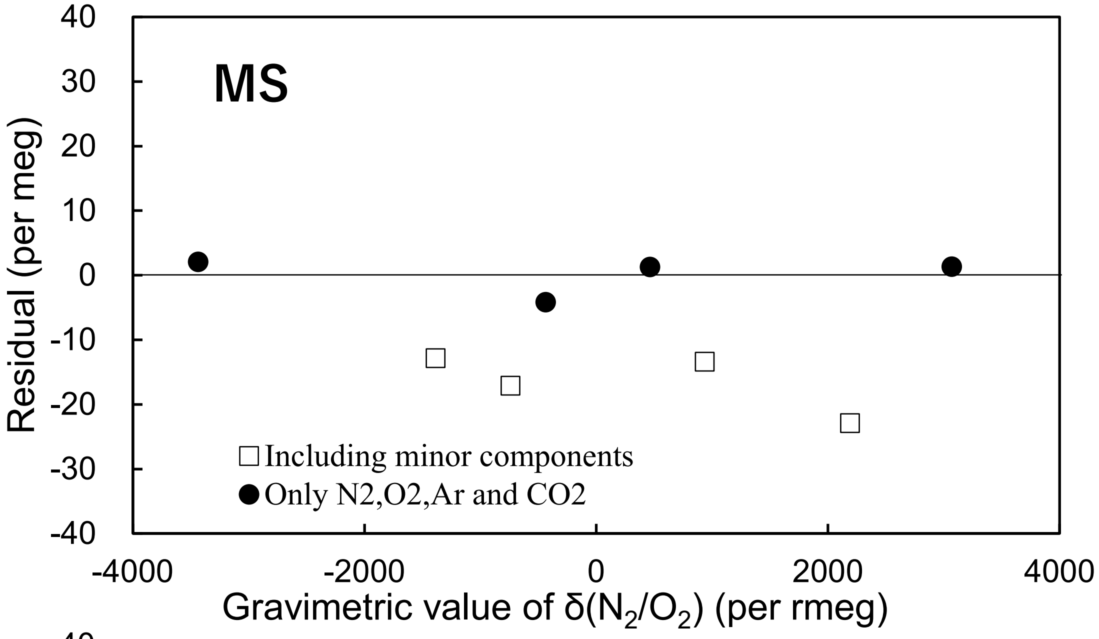
Calculation method of $\delta(O_2/N_2)$

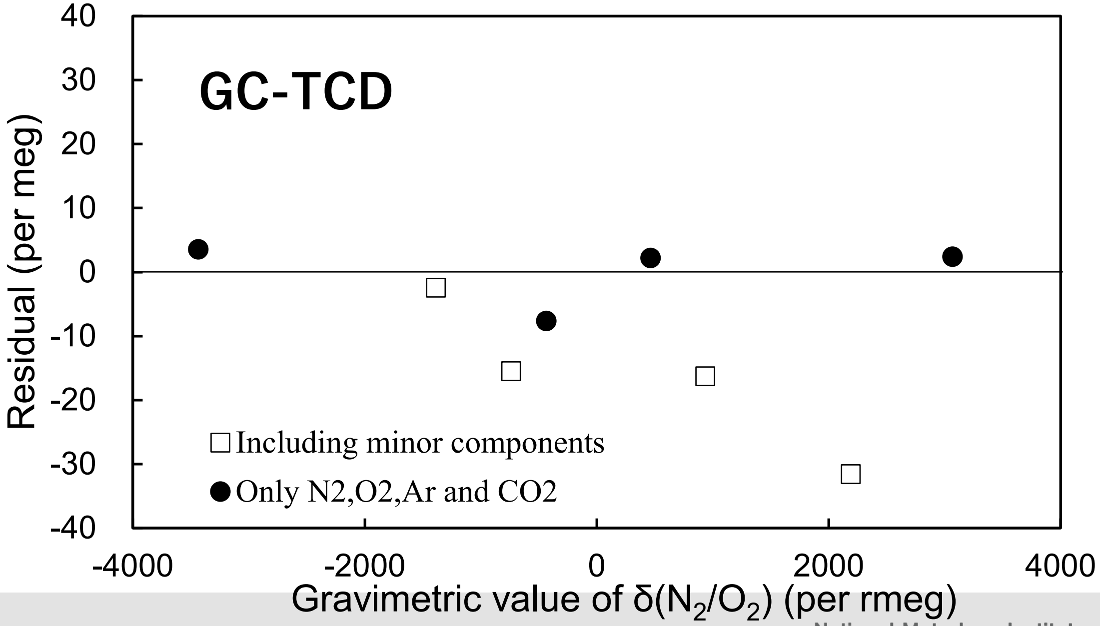
$$\delta(O_2/N_2) = \delta\{(O_2 + Ar/N_2)\} \times \{([O_2] + k[Ar])/[O_2]\}_{ref}$$

Difference in Ar molar fractions in the standard gas mixtures from atmospheric Ar molar fraction were corrected using the gravimetric values.

Results measured using three types of analyzers







There were significant differences in the O_2/N_2 ratios measured by the MS and GC/TCD between the standard gas mixtures with and without minor components, while there was not significant differences in those by the paramagnetic analyzer.

Conclusion remark

- We prepared the standard gas mixtures including minor components of Ne, He, CH_4, Kr and Xe with the standard uncertainty of less than 1 µmol/mol.
- The molar fractions of minor components in the standard gas mixtures had slightly higher than atmospheric values.
- The standard gas mixtures with or without minor components were measured using three types of analyzers, a paramagnetic analyzer, a MS, and a GC-TCD, to understand influence of minor components on precise O_2/N_2 measurements.
- Although there were significant differences in the O_2/N_2 ratios measured by the MS and GC/TCD between the standard gas mixtures with and without minor components in a MS and a GC-TCD, there was not significant differences in those by the paramagnetic analyzer.

Acknowledgements

This study was partly supported by the JSPS KAKENHI (grant nos. 22H05006 and 19H01975 and 19K05554) and the Global Environment Research Coordination System from the Ministry of the Environment, Japan (grant nos. METI1454, METI1953).