Influence of fractionation of CO_2 and air during preparation of a standard mixture

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Background

- Recently, several studies have shown that CO_2 adsorbed on internal surface of a high-pressure cylinder and desorbed from the surface, as internal pressure in the cylinder decreases (Langenfelds et al., 2005, Leuenberger et al., 2015, Brewer et al., 2018, Schibig et al., 2018, Hall et al., 2019). The adsorbed CO_2 causes a small bias in the gravimetrically assigned CO_2 molar fraction in standard gas mixtures.
- From a series of “mother−daughter” experiments in which they transferred half of a CO_2/air mixture from a “mother” cylinder into an evacuated “daughter” cylinder, Miller et al. (2015) and Hall et al. (2019) reported that CO_2 in mother and daughter cylinders increased and decreased , respectively, due to fractionation caused by the transfer of the mixtures. Their reported CO_2 change amounts were 5 to 10 times larger than the adsorbed amount estimated from their decanting experiments.
- Results of the decanting and mother-daughter experiments have shown that CO_2 mole fractions in standard gas mixtures should deviate from the gravimetrically assigned values due not only to selective adsorption of CO_2 to the inner wall of a cylinder but also to fractionation during the multiple transfer.

Objective

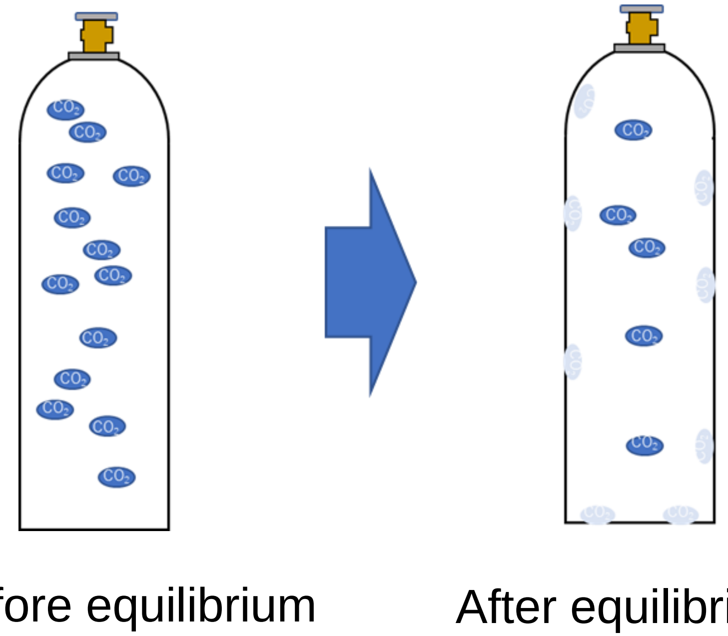
In first step, we developed a technique to prepare standard gas mixtures for atmospheric CO_2 level by a 1-step dilution method not to cause the fractionation.

In next step, we evaluated

- change of CO_2 molar fraction caused by the adsorption on inner surface when CO_2 standard gases are prepared into a 9.5-L Aluminum cylinder.
- change of CO_2 molar fraction caused by fractionation between CO_2 and air when source gasses (CO_2/Air mixtures) are transferred into a receiving daughter cylinder.
- deviation of CO_2 molar fraction in a standard gas from gravimetric value when the standard gase are prepared by a gravimetric method

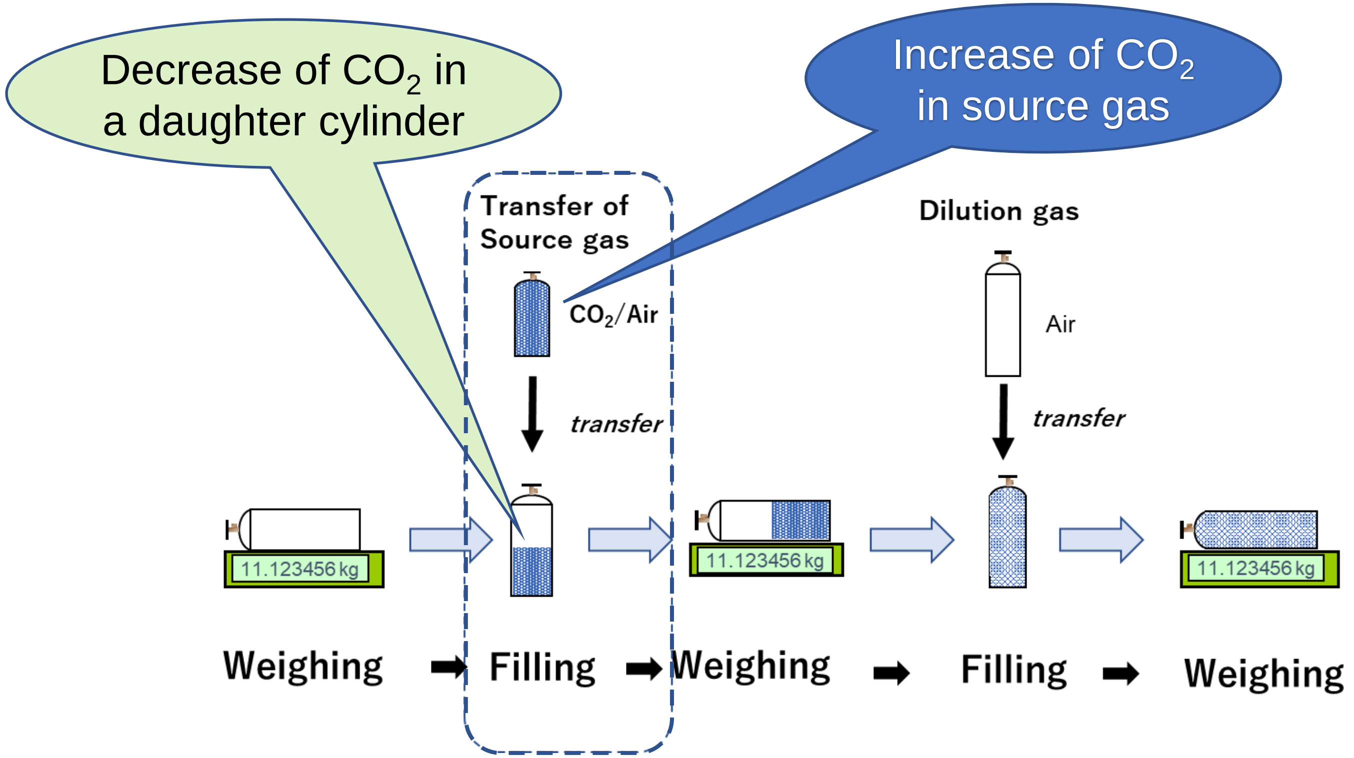
Influence of adsorption and fractionation effects

① Adsorption effect



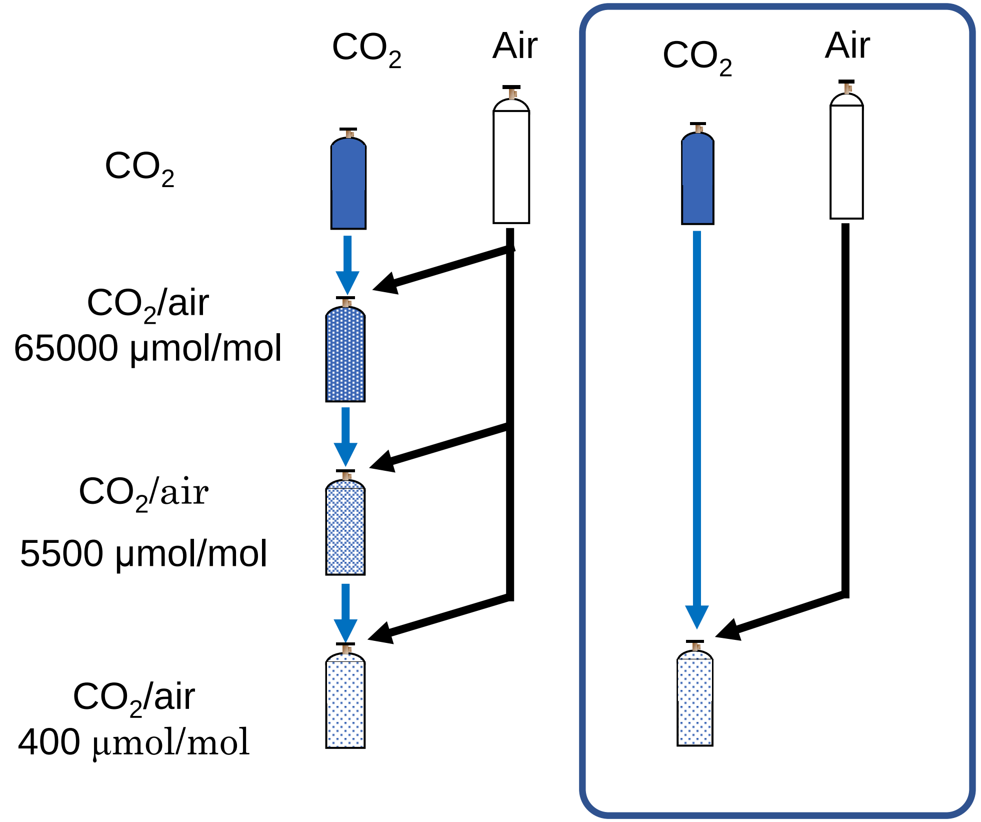
CO_2 molar fraction in the prepared standard gas mixture decreases.

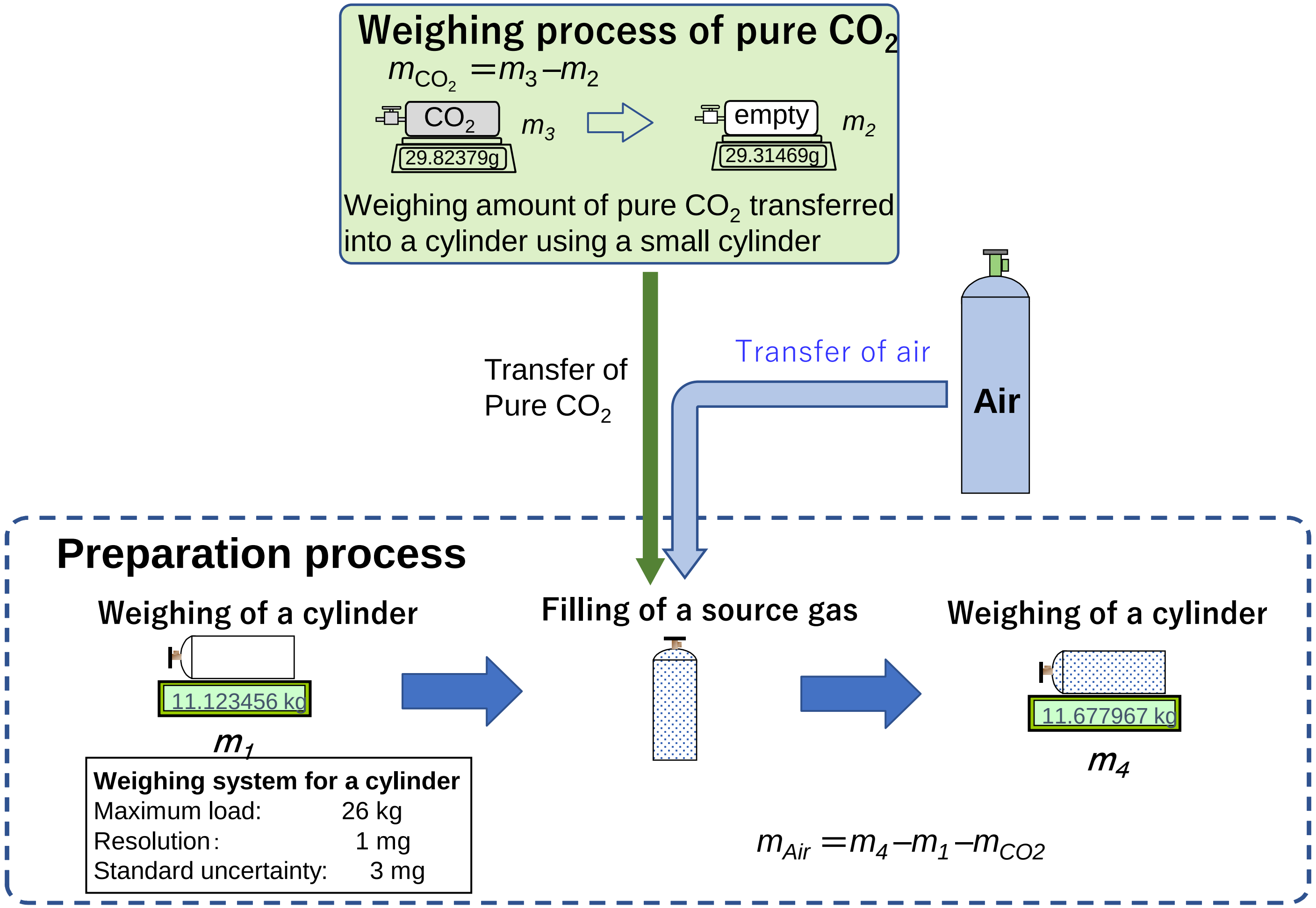
② Fractionation effect



CO_2 molar fractions in the transferred source gas decreases, while that in the remained source gas increases.

Preparation of CO_2 standard mixture without fractionation



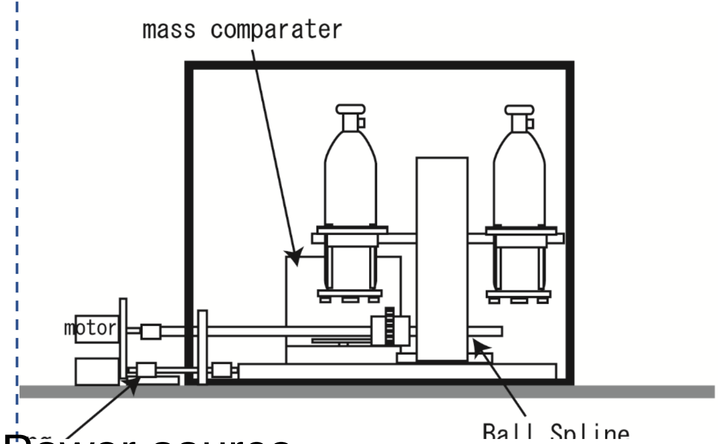


fractionation is not caused, because pure CO2 and air are directly mixed.

A preparation process of a CO_2 standard gas mixture for atmospheric observation by 1-step dilution method.

Performance of the developed weighing system

The developed weighing system

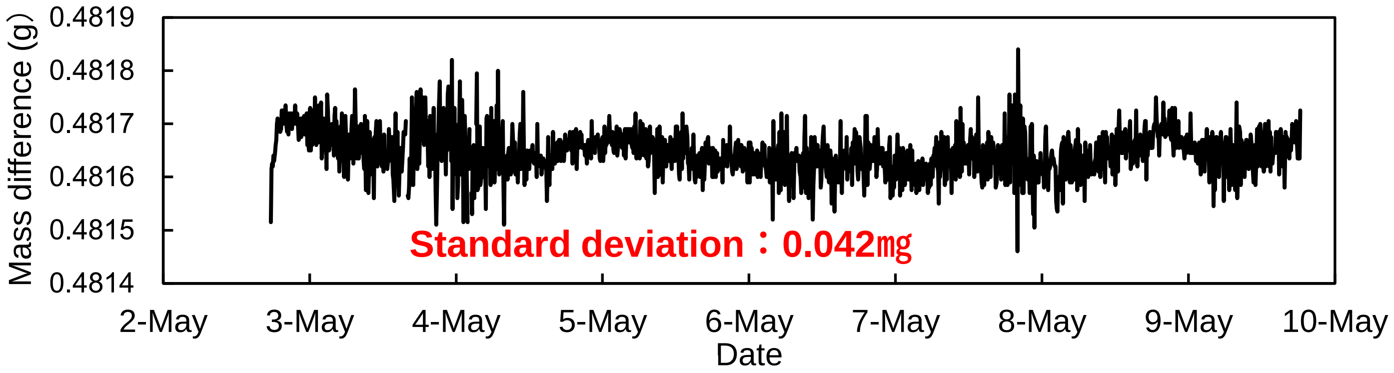


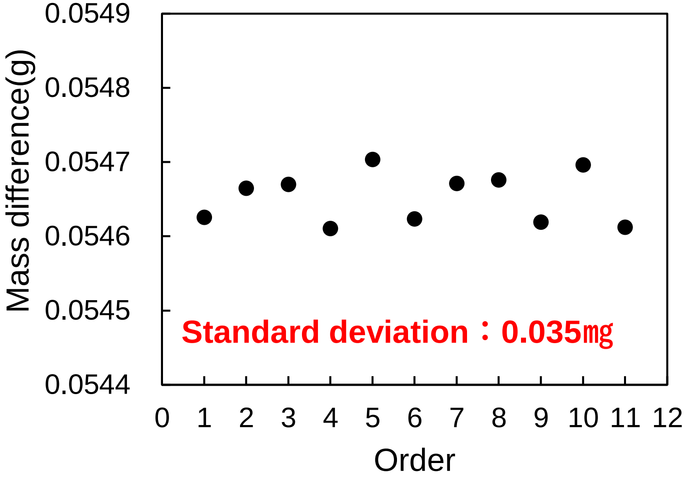
Power source

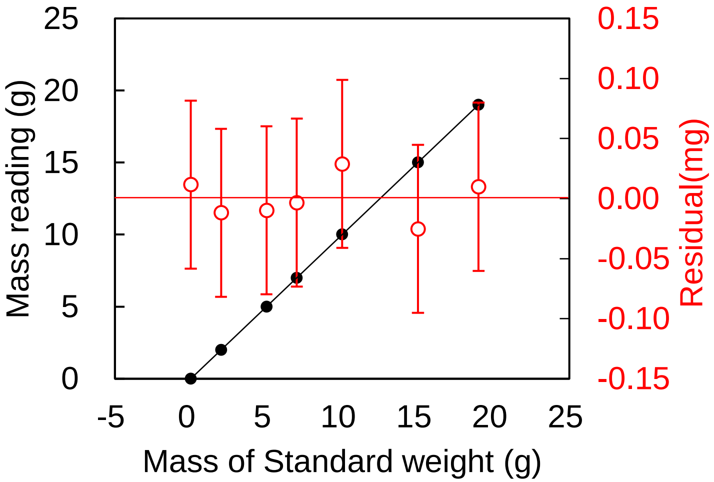
Balance for small cylinder
Maximum load: 2 kg
Resolution: 0.01 mg
Standard uncertainty0.08 mg

Validation

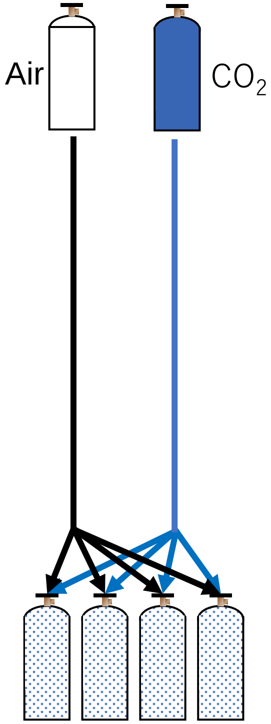
Stability of mass values when monitoring mass of a small cylinder for seven days

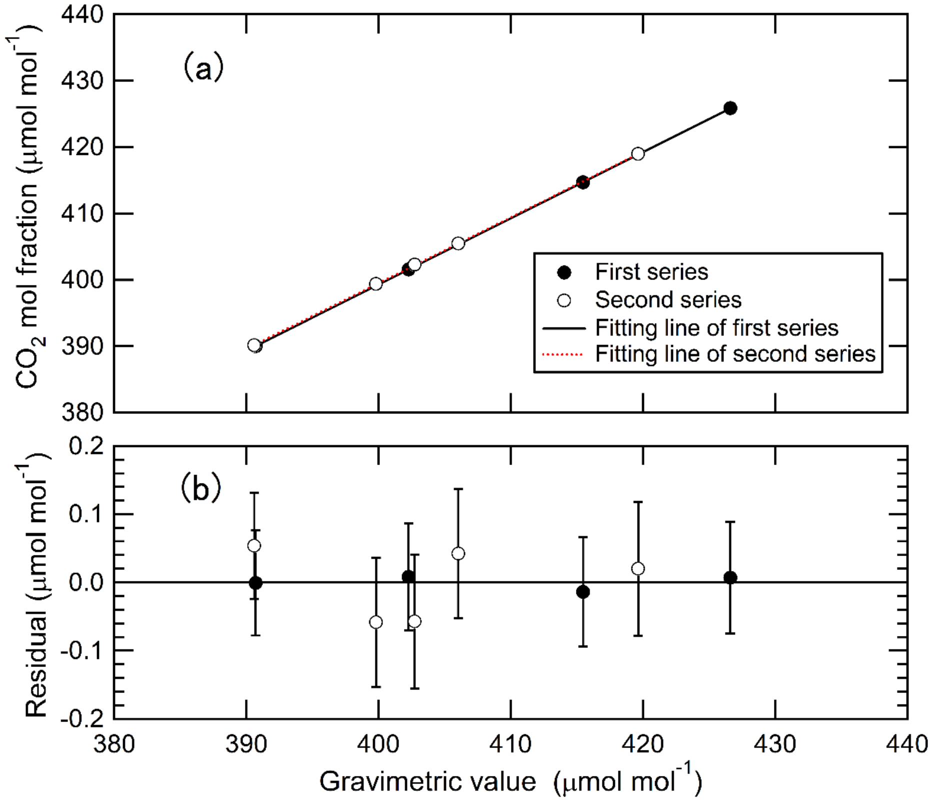






Performance of standard gas mixtures prepared by 1 step dilution

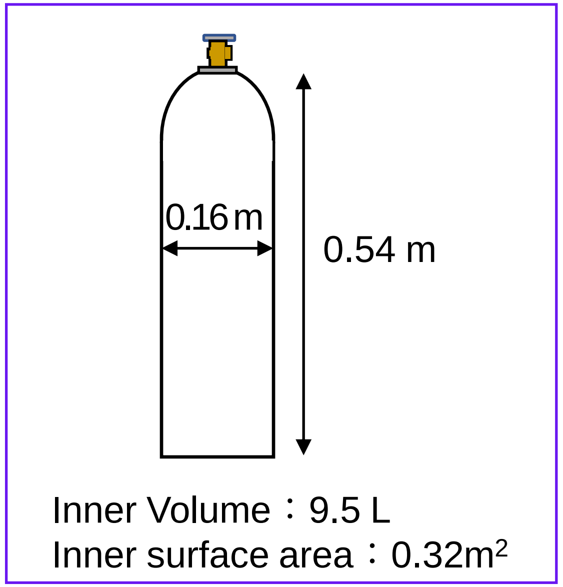


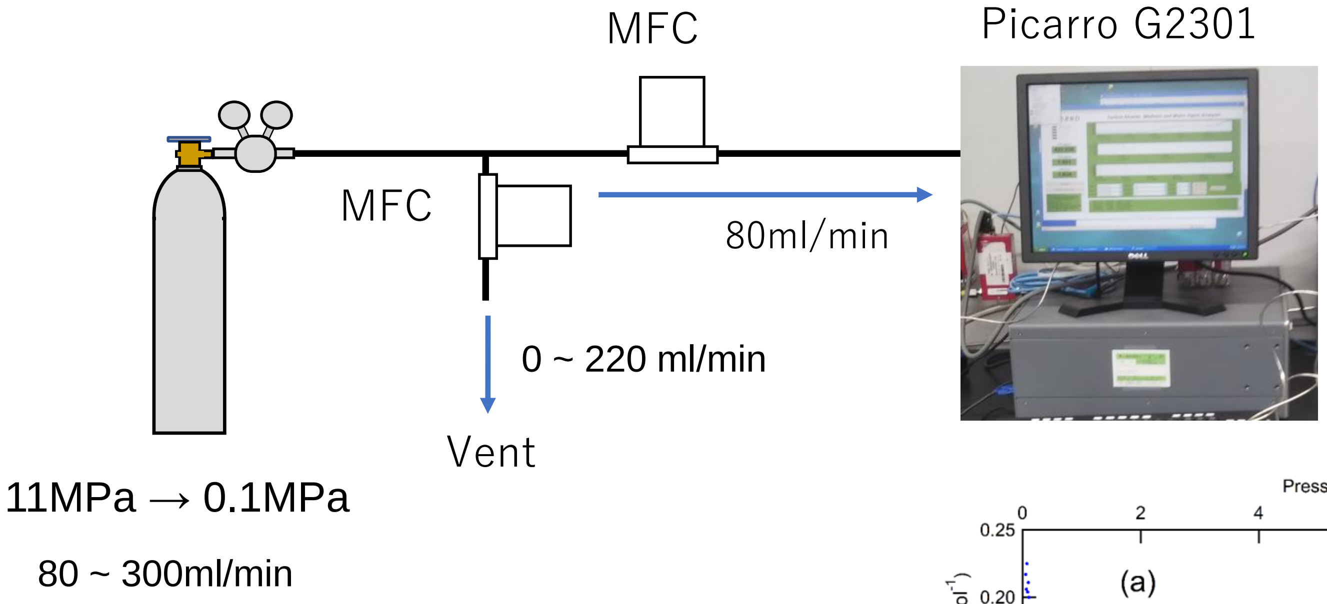


Two series of standard gas mixtures for atmospheric observation were prepared. Deming least square fit was applied to measurement results of each series.

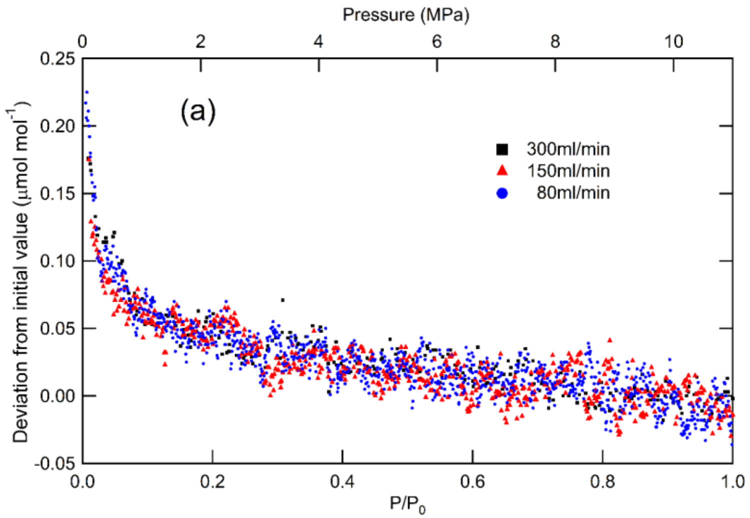
Residuals from the calibration lines were under the uncertainties of 0.07 μmol/mol.

Decanting experiment



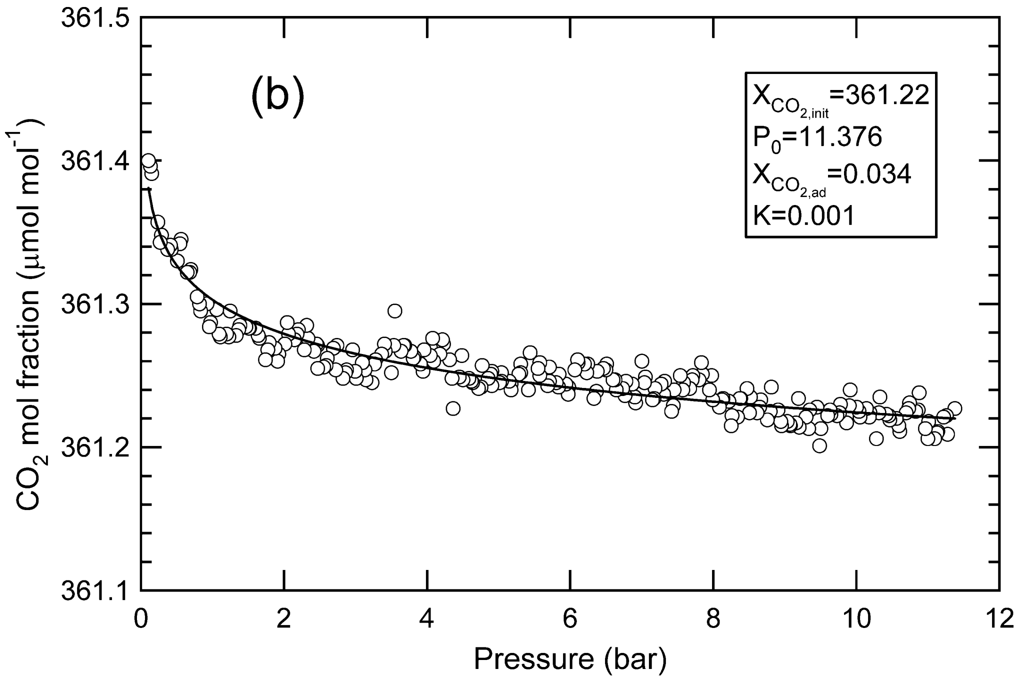


Results of flow dependence suggests that Increase of CO_2 molar fraction with depletion of pressure is caused by adsorption and desorption on inner surface



Flow dependence of CO_2 change on decanting experiment

Estimation of adsorbed CO_2 amount



Langmuir model equation

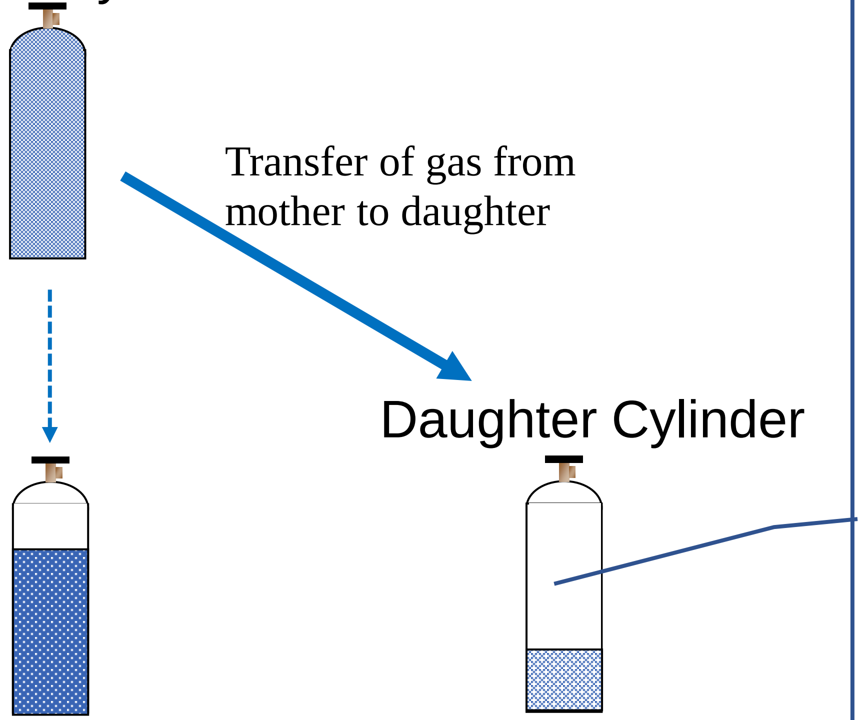
$$CO_{2,meas} = CO_{2,ad} \times \left(\frac{K\times(P-P_0)}{1+K\times P} + (1 + K \times P_0) \times ln\left(\frac{P_0\times(1+K\times P)}{P\times(1+K\times P_0)}\right)\right) + CO_{2,initial}$$

$X_{CO_2,meas}$: measured mole fraction, P : pressure in cylinder,
P_0 : initial pressure in cylinder, $X_{CO_2,initial}$: initial CO2 value at P_0,
$X_{CO_2,ad}$: the CO_2 molar fraction multiplied by the occupied adsorption sites at P_0
K : ratio of adsorption and desorption rate constants

Estimated adsorbed CO_2 amount was 0.027±0.004 μmol/mol at 10MPa and 350 − 450 μmol/mol.

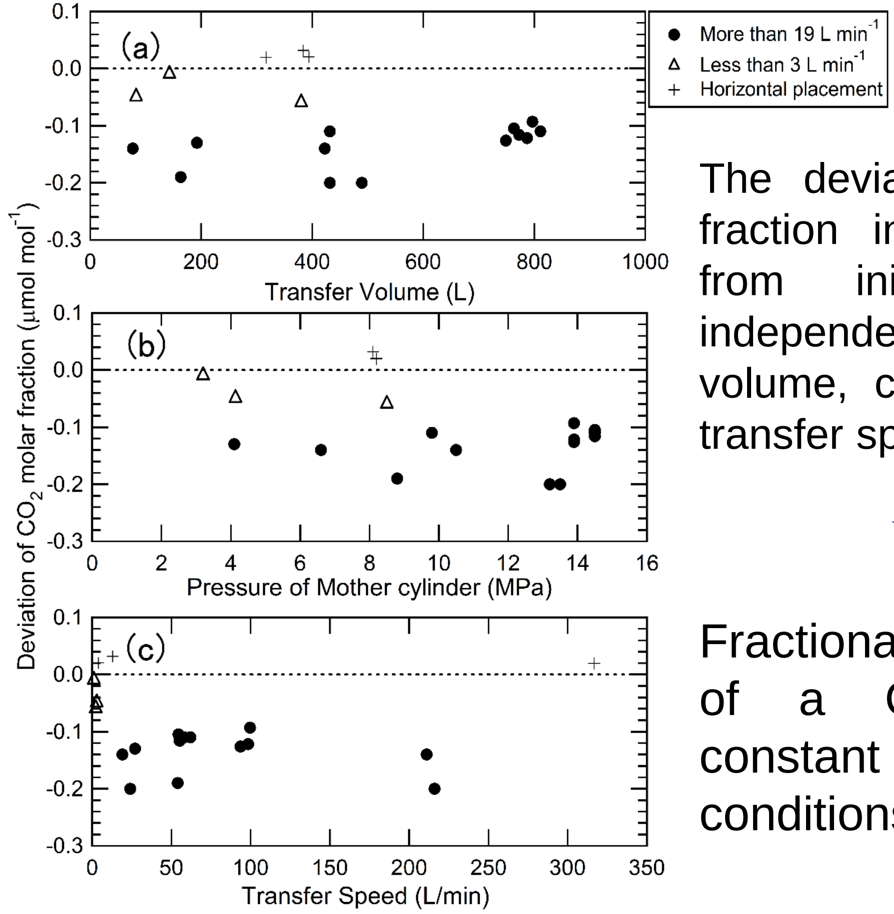
Mother-daughter transfer experiment

Mother Cylinder



CO_2 amount

Increase = decrease

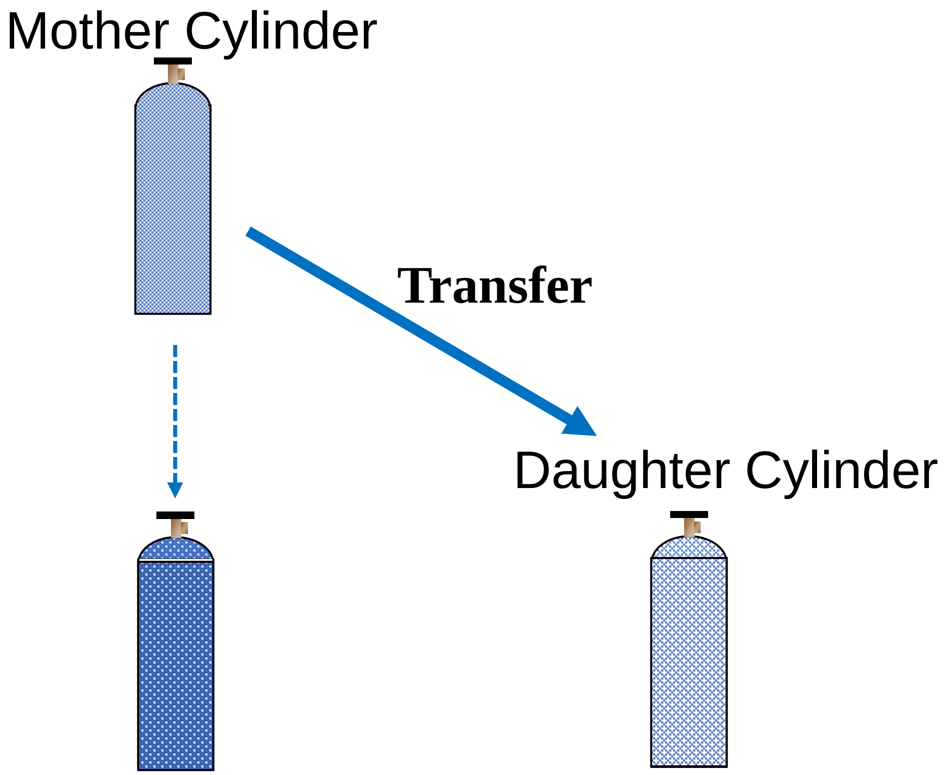


Deviations of CO_2 molar fractions from initial values for Daughter cylinder

The deviations of CO_2 molar fraction in daughter cylinders from initial values were independent from transfer volume, cylinder pressure and transfer speed.

Fractionation effect by transfer of a CO_2/air mixture is constant regardless transfer conditions.

Results of Mother-daughter transfer experiment



CO_2 molar fraction

Increase = decrease

Mass balance was good agreement

We performed mother-daughter transfer experiments twelve times. The fractionation factor (α) in transfer of the mixtures was estimated using the following equation.

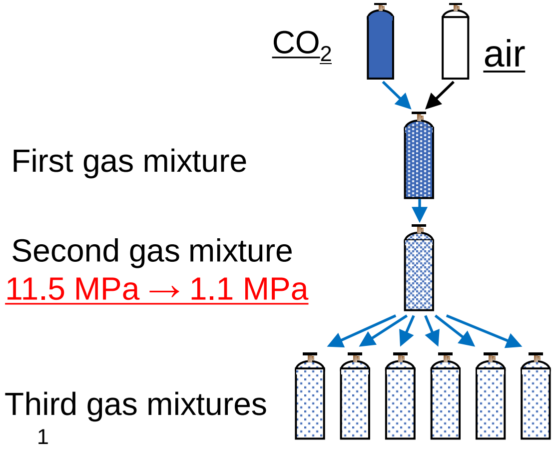
$$X_{out} = \alpha X_0.$$

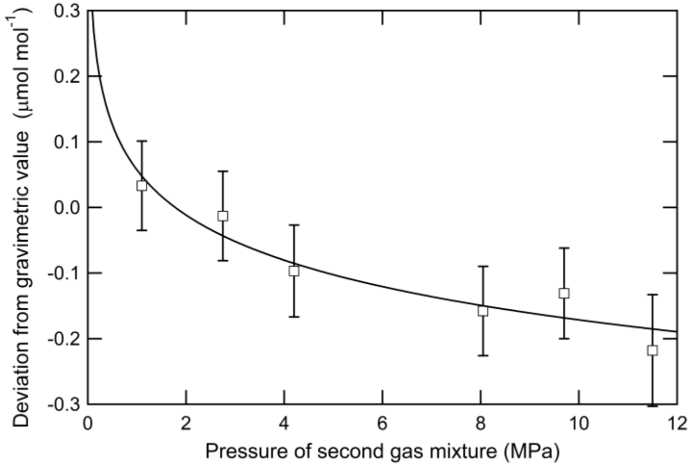
Where X_{out} and X_0 is the initial CO_2 molar fractions.

The fractionation factor (α) was estimated to be **0.99968 ± 0.00010.**

CO_2 change in source gas by fractionation

(a) Change of CO_2 molar fraction in second gas mixture with its consumption





Rayleigh fractionation model

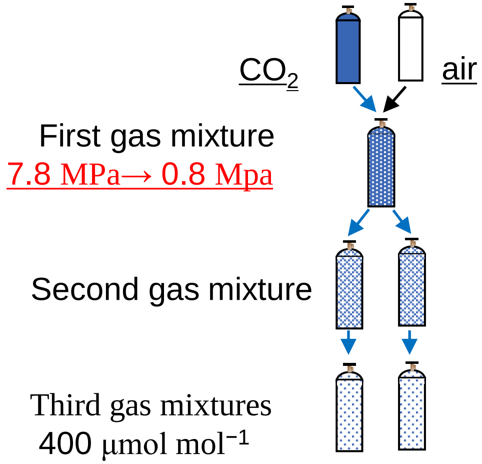
$$\frac{X}{X_0} = \left(\frac{P}{P_0}\right)^{\alpha-1}$$

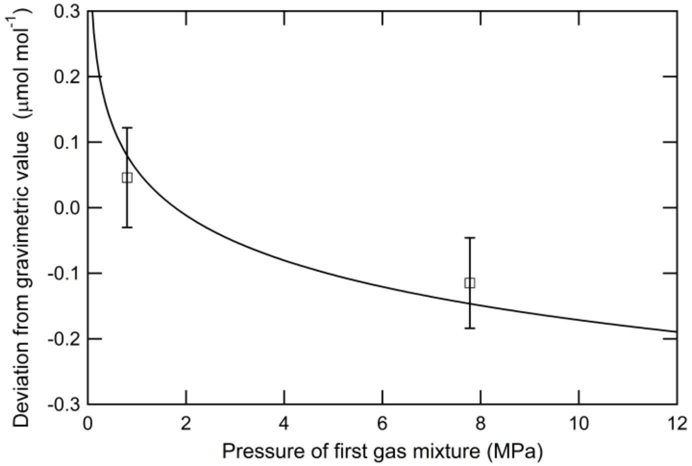
X : CO_2 molar fraction in a cylinder
X_0: CO_2 molar fraction at P_0

P: Pressure in a cylinder
P_0: Initial pressure in a cylinder
α: Fraction factor

Fraction factor obtained by fitting using the Rayleigh fractionation model is 0.99976 ± 0.00004.

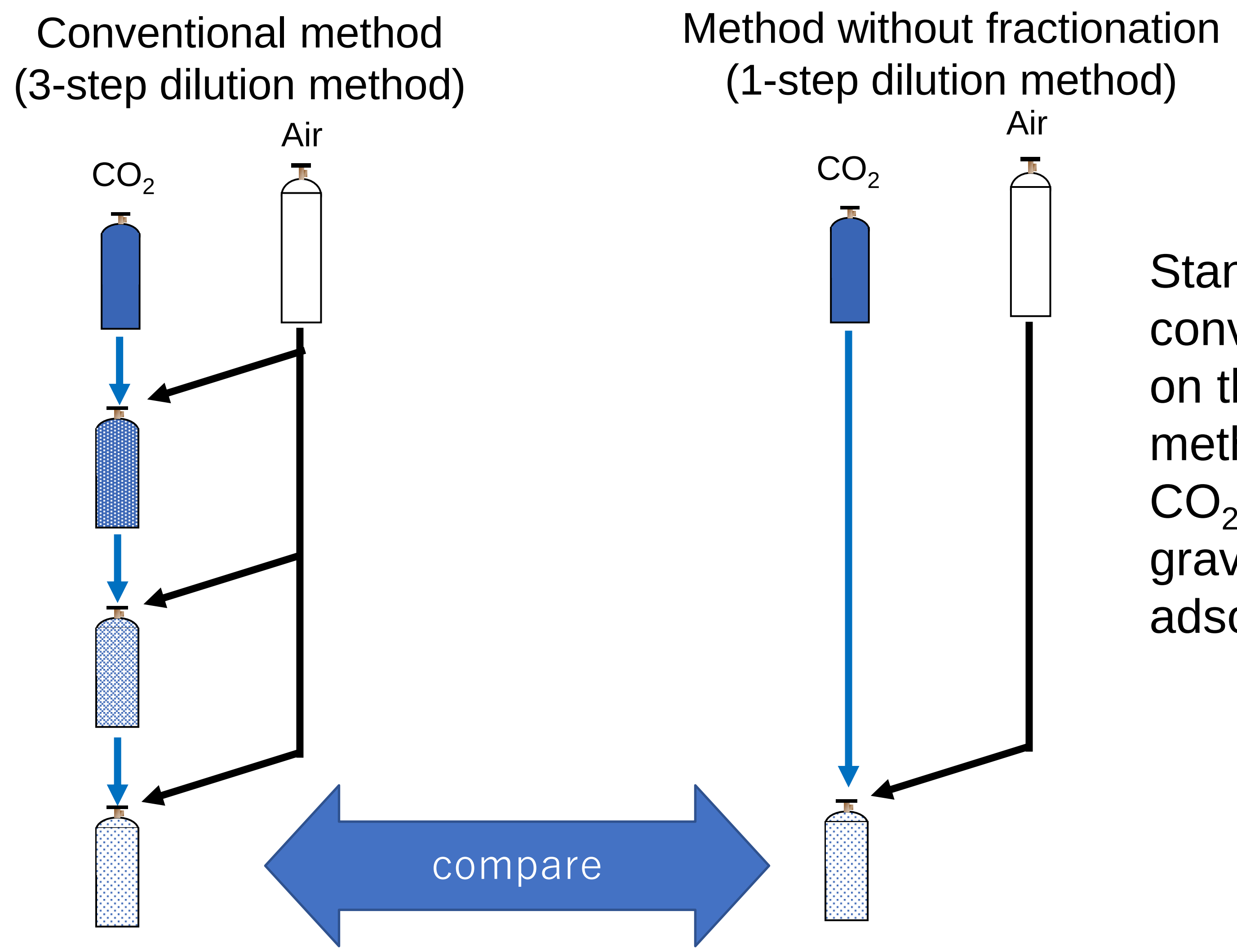
(b) Change of CO_2 molar fraction in first gas mixture with its consumption





Measurement values were agreement within the equation of Rayleigh fractionation model calculated using fraction factor obtained by above experiment (a).

Evaluation of fractionation effect in actual preparation

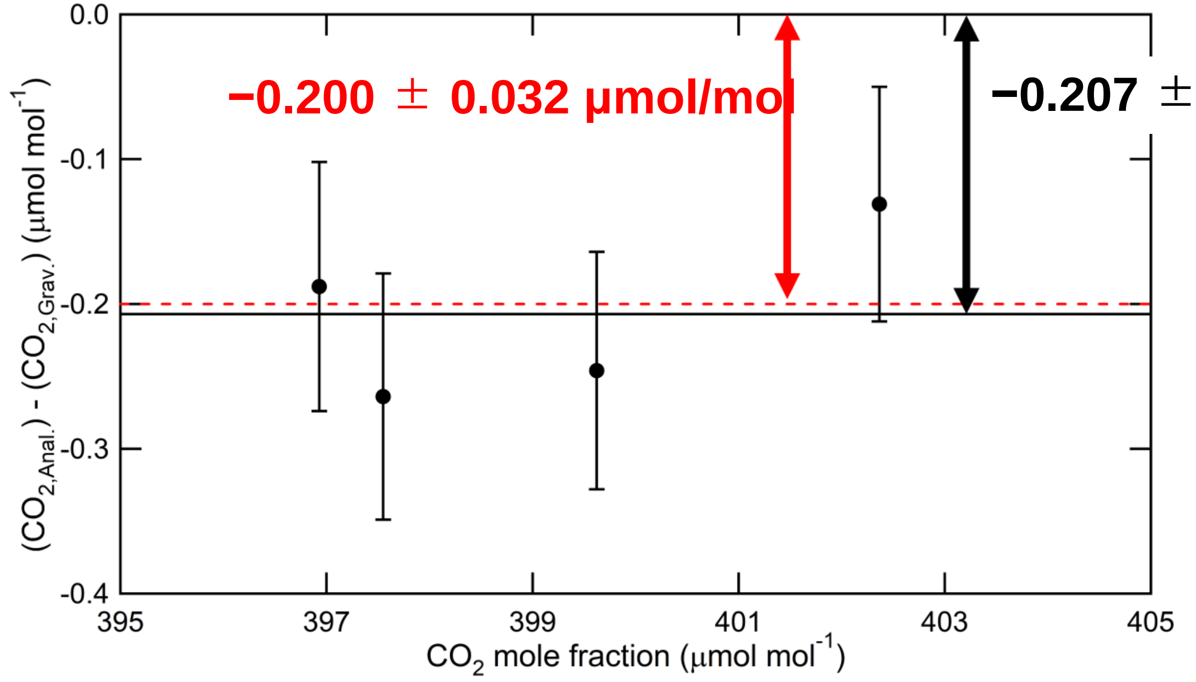


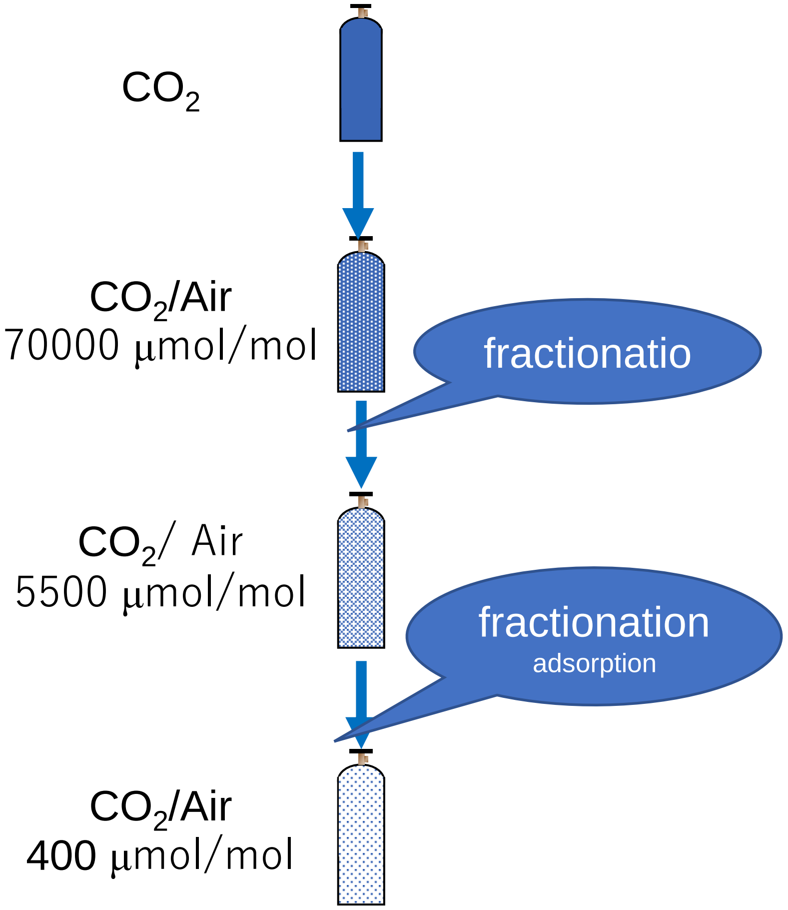
Standard gas mixtures prepared by conventional method were measured based on the standard gas mixtures prepared by the method without fractionation. The measured CO_2 molar fractions were compared with the gravimetric values which corrected adsorption effect.

Validation of conventional method by 1 step dilution

Deviation calculated using the fractionation factor

Deviation from gravimetric values in standard gas mixtures





CO_2 in standard gas mixtures prepared by a conventional method should be subject to influence of the fractionation effect in 2 or 3-step dilutions.

Conclusion

- A technique to prepare CO_2 standard gases by 1-step dilution, which was not affected by the fractionation, was developed. CO_2 molar fractions and its uncertainties in the standard gas mixtures prepared by the technique were less than the recommended value of WMO.
- Decanting experiment identified that CO_2 to adsorb on inner surface of a cylinder was estimated to be 0.027±0.004 μmol/mol.
- Mother-daughter transfer experiment showed that fractionation of CO_2 and air increased and decreased CO_2 molar fractions in source gas and in a receiving daughter cylinder, respectively, by transfer of CO_2/air gas mixture. Fractionation factor in transfer of source gas estimated to be 0.99976 ± 0.00004 by evaluating change of CO_2 molar fraction in source gas due to its consumption.
- CO_2 molar fractions in standard gases prepared by 3-step dilution deviated from gravimetric values. The deviated amount was good agreement with the values calculated using fractionation factor.