

Figure 3. Differences (Laboratory X minus NIES) of CO₂ concentrations for three round-robin cylinders measured for the iceGGO-2. The error bars represent the ± measurement precisions reported by each laboratory. The dashed lines around the zero line identify the WMO criterion (±0.1 ppm) in the Northern Hemisphere for network compatibility.

4. iceGGO-3 (CO₂)

4.1. Round-robin cylinders (iceGGO-3)

The third experiment (iceGGO-3), which took place in 2014, was a comparison of CO₂ concentrations in high-pressure cylinders. Table 8 provides details about the three sample cylinders used in the round-robin experiment. The samples in these three cylinders contained CO₂ at concentrations of about 380 ppm, 400 ppm, and 418 ppm, respectively. The samples were prepared from pure CO₂ and purified natural air with a three-step

dilution by the gravimetric method in accordance with ISO 6142:2001 during the time interval from November 28, 2013, to December 19, 2013. At each step of the dilution, three mixtures were prepared. The CO₂ concentrations at each step were 60000 ppm, 5000 ppm, and 400 ppm. The purity of the CO₂ and the concentrations of N₂, O₂, and Ar in the purified natural air were determined by gas chromatography, Fourier-transform infrared spectrometry and so on. The expanded uncertainty of the CO₂ gravimetric values, about 0.05 ppm, was associated mainly with weighing the filling gas. The $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values of the pure CO₂ used to prepare these gases, determined precisely by isotope ratio mass spectrometry (IRMS) at the AIST and TU, were about -8.9‰ and -13‰ , respectively. This isotopic composition differed from that of the calibration gases prepared with combusted petroleum CO₂ (around -30‰ for $\delta^{13}\text{C}$) that was used for measurements by all participants.

Table 8. Mean concentrations of gases in the three cylinders used for CO₂ analyses during the iceGGO-3. The numbers after the \pm symbols indicate the expanded uncertainty ($k = 2$).

Cylinder Identification	CO ₂ ppm	N ₂ ppm	O ₂ ppm	Ar ppm	$\delta^{13}\text{C}(\text{CO}_2)^*$ ‰	$\delta^{13}\text{C}(\text{CO}_2)^{**}$ ‰	$\delta^{18}\text{O}(\text{CO}_2)^*$ ‰	$\delta^{18}\text{O}(\text{CO}_2)^{**}$ ‰
CPD00070	379.88 ±0.056	781049 ±24	209214 ±16	9357 ±18	-8.907 ±0.012	-8.881 ±0.024	-13.099 ±0.011	-13.006 ±0.056
CPD00076	399.57 ±0.049	781044 ±29	209209 ±16	9347 ±24	-8.964 ±0.012	-8.874 ±0.024	-13.173 ±0.022	-13.064 ±0.027
CPD00069	418.12 ±0.051	781017 ±24	209209 ±15	9356 ±18	-8.908 ±0.006	-8.897 ±0.018	-13.088 ±0.012	-13.048 ±0.011

*Measured by IRMS of AIST

**Measured by IRMS of TU

4.2. Measurement methods (iceGGO-3)

Five laboratories (AIST, TU, JMA, MRI, and NIES) participated in the iceGGO-3 round-robin experiment from January to September 2014. Table 9 lists the participating laboratories and details of their CO₂ analytical methods.

All participants used a NDIR analyzer to measure CO₂ concentrations, but the models of the NDIR instruments differed. The TU used three different NDIR models: VIA-500R (Horiba), VIA-510R (Horiba), and LI-6252 (LI-COR). The other laboratories used only one NDIR model for the CO₂ measurements. The CO₂ scales were different from each other (Table 9). To check for CO₂ concentration drift during the experimental period, the AIST measured the CO₂ concentrations in all cylinders at both the beginning and the end of the round-robin experiment.

Table 9. The five laboratories and their analytical methods, instruments, and calibration scales for CO₂ during the iceGGO-3.

Laboratory	Method	Instrument	Standard scale	Range of calibration gases	Number of calibration gases	Date of Measurements
AIST	NDIR	VIA-500R, Horiba	TU2010 Scale	370 ppm - 450 ppm	6	January 22 - March 12, 2014
TU	NDIR	VIA-500R, Horiba	TU2010 Scale	370 ppm - 430 ppm	4	March 25 - 27, 2014
TU	NDIR	VIA-510R, Horiba	TU2010 Scale	370 ppm - 430 ppm	4	March 26, 2014
TU	NDIR	LI-6252, Licor	TU2010 Scale	370 ppm - 430 ppm	4	March 25 - 27, 2014
JMA	NDIR	VIA-510R, Horiba	WMO X2007 Scale	350 ppm - 440 ppm	7	June 4 - 5, 2014
MRI	NDIR	LI-6252, Licor	MRI 1987 Scale	350 ppm - 430 ppm	6	July 30 - August 1, 2014
NIES	NDIR	LI-6252, Licor	NIES09 Scale	340 ppm - 450 ppm	8	August 11-12, 2014
AIST	NDIR	VIA-500R, Horiba	TU2010 Scale	360 ppm - 450 ppm	6	September 2 - 5, 2014

4.3. Results of iceGGO-3

Table 10 shows results of the CO₂ analyses of the three round-robin cylinders by five laboratories using several NDIR models together with the gravimetric values. The precision of most of the results was less than 0.02 ppm. The AIST measurements at both the beginning and the end of the round-robin experiment revealed a slight increase for all three cylinders of 0.02–0.03 ppm, but this drift was not significant compared to the measurement precisions. Thus, no correction for drift was applied to the measurement results reported by the laboratories. The NIES measurements were corrected by the isotope effect (+0.066 ppm) in accord with Tohjima et al. (2009), but the isotope effect was not considered in the measurements made by other laboratories.

Table 10. CO₂ concentrations (ppm) determined during the iceGGO-3. The reported precisions are shown in parentheses.

Laboratory	Cylinder Identifications		
	CPD00070	CPD00076	CPD00069
AIST (VIA-500R)	379.68 (0.013)	399.33 (0.008)	417.92 (0.013)
TU (VIA-500R)	379.76 (0.007)	399.39 (0.005)	417.97 (0.005)
TU (VIA-510R)	379.67 (0.010)	399.33 (0.008)	417.91 (0.007)
TU (LI-6252)	379.66 (0.008)	399.28 (0.011)	417.88 (0.008)
JMA (VIA-510R)	379.60 (0.017)	399.15 (0.012)	417.80 (0.022)
MRI (LI-6252)	379.45 (0.011)	399.08 (0.008)	417.62 (0.002)
NIES (LI-6252)	379.55* (0.009) (+0.066)**	399.18* (0.014) (+0.066)**	417.78* (0.010) (+0.066)**
AIST (VIA-500R)	379.71 (0.013)	399.35 (0.006)	417.94 (0.011)
NMIJ	379.88 [#] (0.056) ^{###}	399.57 [#] (0.049) ^{###}	418.12 [#] (0.051) ^{###}

*Corrected by isotope effect

**Isotope effect

[#]Gravimetric value

^{###}Expanded uncertainty of gravimetric value ($k = 2$)

Figure 4 shows differences in the CO₂ concentrations measured in the three cylinders by each laboratory (Laboratory X) and the NIES. The differences (Laboratory X minus NIES) among the laboratories and NDIR models ranged from -0.15 ppm to +0.2 ppm for the three cylinders. The gravimetric values from the NMIJ were higher than the CO₂ concentrations measured by all the laboratories, but the reason for this difference is unknown. The TU measurements clearly showed a difference among the concentrations determined with the three NDIR models; the concentrations differed by about 0.1 ppm. These results strongly reflect not only differences in the CO₂ calibration standard scales but

also isotope effects between the NDIR models. Details of the isotope effect are described in section 9.5.

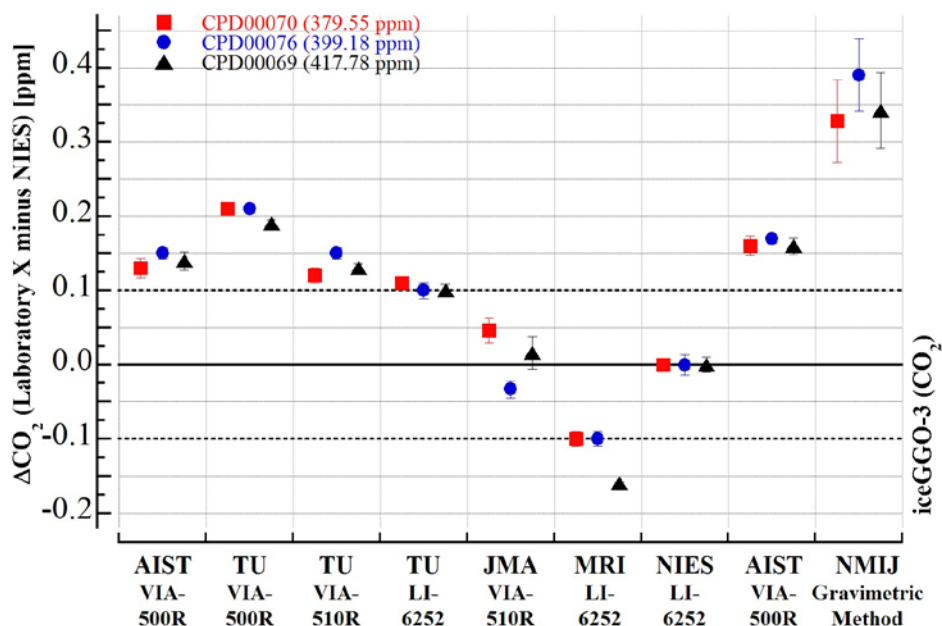


Figure 4. Differences (Laboratory X minus NIES) of CO₂ concentrations in three round-robin cylinders measured during the iceGGO-3. The error bars represent the ± measurement uncertainty reported by each laboratory, although the error bar for the NMIJ indicates the ± expanded uncertainty of the gravimetric method. The dashed lines around the zero line identify the WMO criterion (±0.1 ppm) in the Northern Hemisphere for network compatibility.

5. iceGGO-4 (CO)

5.1. Round-robin cylinders (iceGGO-4)

The fourth experiment (iceGGO-4), which took place in 2013-2014, focused on comparison of CO standard gas scales by circulating high-pressure cylinders. Table 11 provides details about the two sample cylinders used for this round-robin experiment. The samples in these two cylinders contained CO at concentrations of about 346 ppb and 249