7. iceGGO-6 (CH_4)

7.1. Round-robin cylinders (iceGGO-6)

The sixth experiment (iceGGO-6), which took place in 2016, focused on a comparison of CH_4 standard gas scales by circulating high-pressure gas cylinders. Table 18 provides details about the four sample cylinders used in this round-robin experiment. Two cylinders contained commercially available CH_4 standard gases and were filled by the JFP. These two gas samples were prepared using purified natural air as the matrix gas, and the CH_4 concentrations were about 1738 ppb and 1877 ppb, respectively. They had previously been used for the fourth round-robin experiment of the GAW/WCC for CH_4 in Asia and the southwest Pacific region during 2011–2014 (http://ds.data.jma.go.jp/wcc/ch4/rusult_4th.html). The other two cylinders (CPB28035 and CPB28219) contained samples with CH_4 concentrations of about 1797 ppb and 2198 ppb, respectively. The samples were prepared by the NMIJ gravimetric method during the CIPM CCQM-K82 experiment. The cylinders were filled using a synthetic air diluent consisting of a mixture of pure N_2, O_2, Ar, and CO_2 (Table 19). The expanded uncertainty of the gravimetric values (k = 2), ±1.3 ppb, was associated mainly with the determination of the CH_4 in the matrix gases (pure O_2 and N_2). The details of the NMIJ gravimetric method have been reported elsewhere (Flores et al., 2015).

Table 18. The four cylinders used for the iceGGO-6.

Cylinder Identification	CH_4 Concentration (ppb)	Matrix gas	Manufacturer	Filling method	Date of filling
CPB28035	1797.3*	Synthetic air[$]	NMIJ	Gravimetric	August 28, 2012
CPB28219	2198.3*	Synthetic air[$]	NMIJ	Gravimetric	June 6, 2012
CPB31288	1740.1**	Purified natural air	JFP	Gravimetric	February 25, 2011
CPB31289	1878.6**	Purified natural air	JFP	Gravimetric	February 25, 2011

*Gravimetric value from NMIJ

**Measured by JMA/CRDS

[$]Detailed composition in Table 19

Table 19. Details of the compositions of the two cylinders prepared by the NMIJ gravimetric method. The numbers after the ± symbols indicate the expanded uncertainty (k = 2).

Cylinder Identification	CH_4 ppb	CO_2 ppm	N_2 ppm	O_2 ppm	Ar ppm
CPB28035	1797.3 ±1.32	386.66 ±0.091	779814 ±6.33	210538 ±6.45	9259.76 ±0.715
CPB28219	2198.3 ±1.33	383.39 ±0.087	780898 ±6.55	209276 ±6.68	9439.93 ±0.757

7.2. Measurement methods (iceGGO-6)

Four laboratories (JMA, AIST, MRI, and NIES) participated in the iceGGO-6 round-robin measurements from February 2016 to September 2016. Table 20 provides details of the CH_4 analytical methods used by the five laboratories. The JMA and MRI used a laser-based analyzer and wavelength-scanned cavity ring-down spectroscopy (WS-CRDS, Picarro Inc.) to measure CH_4 concentrations. Three laboratories (JMA, AIST, and NIES) used a GC/FID, although the instruments they used differed. The JMA measurements were based on the WMO X2004A scale, which has been propagated from the NOAA

(Dlugokencky et al., 2005). The other three laboratories carried out their measurements using different standard gas scales (AIST, MRI, and NIES94), which were developed independently. The calibration gases used by the AIST and NIES covered a relatively wide range of CH_4 concentrations, whereas the range of concentrations in the calibration gases used by the JMA and MIR was not wide enough to measure the highest concentration in the round-robin cylinder. To assess the gases for drift during the experimental period, the AIST measured the CH_4 concentrations in the two NMIJ cylinders at the beginning and end of the round-robin experiment.

Table 20. The four laboratories that participated in the iceGGO-6 and their analytical methods, instruments, and calibration scales for CH_4.

Laboratory	Method	Instrument	Standard scale	Range of calibration gases	Number of calibration gases	Date of measurements
AIST	GC/FID	GC-14BPF (FID), Shimadzu	AIST Scale	1010 ppb - 2530 ppb	4	April 2-9, 2016
MRI	CRDS	G2301 (CRDS), Picarro	MRI Scale	1600 ppb - 2100 ppb	5	February 12, 2016
NIES	GC/FID	HP7890 (FID), Agilent	NIES94 Scale	1250 ppb - 2500 ppb	6	May 18-19, 2016
JMA	GC/FID	GC-14BPF (FID), Shimadzu	WMO X2004A Scale	1620 ppb - 2110 ppb	5	August 15, 2016
JMA	CRDS	G2301 (CRDS), Picarro	WMO X2004A Scale	1610 ppb - 2160 ppb	5	August 4, 2016

7.3. Results of iceGGO-6

Table 21 lists the CH_4 concentrations measured in the four gas cylinders by the four laboratories. The AIST measurements at the end of the experiment revealed no change of CH_4 concentration in the two NMIJ cylinders. Thus, no correction for drift during the experimental period was applied to the concentrations reported by the laboratories. The

analytical precision of most of the measurements in all the laboratories was less than ~2 ppb. The measurement precision of the laser-based analyzer, CRDS, was generally better than that of the GC/FID.

Table 21. CH_4 concentrations (ppb) measured during the iceGGO-6. The reported analytical precisions are indicated in parentheses.

	Cylinder Identifications			
Laboratory	CPB28035	CPB28219	CPB31288	CPB31289
AIST (GC/FID)	1797.8 (1.3)	2198.0 (1.4)	1741.1 (1.8)	1880.9 (1.7)
MRI (CRDS)	1796.3 (0.1)	2199.5 (0.1)	1739.5 (0.1)	1880.5 (0.1)
NIES (GC/FID)	1798.8 (0.6)	2200.1 (0.3)	1742.0 (0.1)	1882.4 (0.2)
JMA (GC/FID)	1793.3 (1.0)	2192.8 (2.0)	1738.1 (1.5)	1876.9 (1.6)
JMA (CRDS)	1796.4 (0.1)	2192.2 (0.2)	1740.1 (0.5)	1878.6 (0.3)
NMIJ	1797.3 (1.3)*	2198.3 (1.3)*	-	-

*Gravimetric value (Expanded uncertainty of gravimetric method (k = 2))

Figure 7 shows the differences between the CH_4 concentrations in the four cylinders measured by each laboratory (Laboratory X) and the NMIJ or NOAA. The NMIJ values for the two cylinders are based on the gravimetric method, whereas the NOAA values for the other two cylinders at 1740.0 ± 0.7 ppb (CPB31288) and 1879.7 ± 1.0 ppb (CPB31289) were measured during the fourth round-robin experiment of the JMA/WCC for CH_4 from

January to February 2014 (http://ds.data.jma.go.jp/wcc/ch4/rusult_4th.html). The differences (Laboratory X minus NMIJ/NOAA) among the laboratories ranged from –6 ppb to +7 ppb.

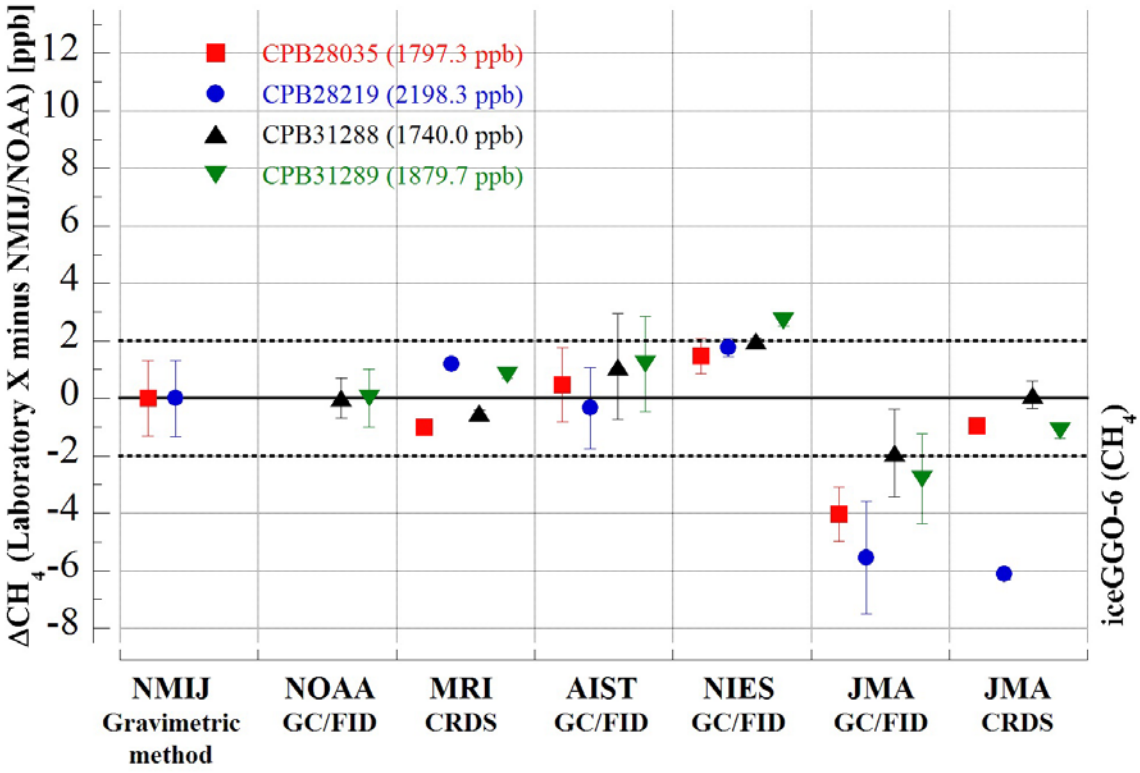

Figure 7. Differences (Laboratory X minus NOAA/NMIJ) of CH_4 concentrations for each round-robin cylinder measured during the iceGGO-6. The error bars represent the ± measurement precision reported by each laboratory, although the error bar of the NMIJ indicates the ± expanded uncertainty of the gravimetric method (k = 2). The dashed lines around the zero line identify the WMO recommended criterion (±2 ppb) for CH_4 measurement compatibility.