Isotopic ratio measurement results are here expressed as deviations from an agreed-upon international reference measurement standard in per mil (‰) units. δ^{13}C and δ^{18}O of CO_2 are defined as follows:

$$\delta^{13}C = \left\{ \frac{\left({}^{13}C/{}^{12}C \right)_{sa}}{\left({}^{13}C/{}^{12}C \right)_{st}} - 1 \right\} \times 1000 \text{ ,} \qquad (1)$$

$$\delta^{18}O = \left\{ \frac{\left({}^{18}O/{}^{16}O \right)_{sa}}{\left({}^{18}O/{}^{16}O \right)_{st}} - 1 \right\} \times 1000 \text{ ,} \qquad (2)$$

where the subscripts sa and st denote the sample and the standard, respectively. In this study, all measured δ^{13}C and δ^{18}O values of CO_2 are reported based on the Vienna Pee Dee Belemnite (VPDB) scale.

2. iceGGO-1 (CH_4)

2.1. Round-robin cylinders (iceGGO-1)

The first experiment (2012–2013), the iceGGO-1, focused on a comparison of CH_4 standard gas scales by circulating high-pressure gas cylinders. Details of the six sample cylinders used in this round-robin experiment are listed in Table 1. Four cylinders were commercially available CH_4 standard gases, which were filled by Japan Fine Products (JFP;

formerly Nippon Sanso Corporation, Japan). These four gases were prepared using purified natural air as a matrix gas, and their CH_4 concentrations ranged from ~1660 ppb to ~1920 ppb. Two of the four cylinders (CPB13002 and CPB13003) had been used previously by the JMA during 2008–2011 for the third round-robin experiment of the Global Atmosphere Watch (GAW) World Calibration Centre (WCC) for CH_4 in Asia and the southwest Pacific region (http://ds.data.jma.go.jp/wcc/ch4/rusult_3rd.html). The other two standard gases (CPB28218 and CPB28042), with CH_4 concentrations of about 1810 ppb and 2240 ppb, were prepared gravimetrically with a four-step dilution from pure N_2, O_2, Ar, and CO_2, and CH_4 (Table 2). These gases are SI-traceable standards prepared by the gravimetric method of the NMIJ. The expanded uncertainties of the gravimetric values, ~1.3 ppb (k = 2), were associated mainly with the determination of the concentration of CH_4 in the matrix gases (pure O_2 and N_2). Details of the NMIJ gravimetric method have been reported elsewhere (Flores et al., 2015).

Table 1. The six cylinders used for the iceGGO-1.

Cylinder Identification	CH_4 Concentration (ppb)	Matrix gas	Manufacturer	Filling method	Date of filling
CPB13002	1664.2*	Purified natural air	JFP	Gravimetric	April, 1, 2008
CPB00786	1779.6*	Purified natural air	JFP	Gravimetric	November 16, 1999
CPB13003	1844.8*	Purified natural air	JFP	Gravimetric	April, 1, 2008
CPB00787	1918.8*	Purified natural air	JFP	Gravimetric	November 16, 1999
CPB28218	1813.8**	Synthetic air[$]	NMIJ	Gravimetric	May 31 - June 1, 2012
CPB28042	2240.1**	Synthetic air[$]	NMIJ	Gravimetric	September 4-6, 2012

*Measured by JMA

**Gravimetric value from NMIJ

[$]Detailed composition in Table 2

Table 2. Details of the compositions of two cylinders prepared with the NMIJ gravimetric method. These values were calculated according to ISO-6142:2001. The numbers after the ± symbols indicate the expanded uncertainty (k = 2).

Cylinder Identification	CH_4 ppm	CO_2 ppm	N_2 ppm	O_2 ppm	Ar ppm
CPB28218	1.81381 ±0.00133	390.209 ±0.092	774381 ±6.68	215882 ±6.82	9344.69 ±0.7579
CPB28042	2.24013 ±0.00134	390.677 ±0.087	773710 ±6.31	216277 ±6.43	9619.48 ±0.7198

2.2. Measurement methods (iceGGO-1)

Six laboratories (JMA, NIPR, AIST, MRI, NIES, and TU) participated in the iceGGO-1 round-robin experiment from October 2012 to February 2013. Table 3 provides details of the CH_4 analytical methods used by the six laboratories. All participants used a gas chromatograph equipped with a flame ionization detector (GC/FID) to measure CH_4 concentrations; the instruments, however, differed between laboratories. Five laboratories carried out the measurements using different standard gas scales (NIPR, AIST, MRI, NIES94, and TU2008), which were independently developed and maintained for a long period of time. In contrast, the JMA measurements were based on the WMO X2004 scale, which has been propagated from the Global Monitoring Division (GMD) of the NOAA Earth System Research Laboratory (Dlugokencky et al., 2005; Tsuboi et al., 2016). The calibration gases used by the NIPR, AIST, NIES, and TU cover a relatively wide range of CH_4 concentrations, whereas the range of the JMA and MRI calibration gases was not wide enough to measure the highest concentration in the round-robin cylinder. To evaluate the

drift of the CH_4 concentration during the experimental period, the JMA measured all cylinders at the beginning and end of the round-robin experiment.

2.3. Results of iceGGO-1

The CH_4 concentrations in the six gas cylinders reported by the six laboratories are given in Table 4. The analytical precision of most of the measurements from all laboratories was less than ~2 ppb. The relatively large analytical precision reported by the JMA for the cylinder with the highest CH_4 concentration reflects extrapolation of the calibration curve. The JMA measurements showed that the differences in concentrations between the beginning and end of the experiment for all four cylinders were less than 0.8 ppb, which is smaller than the JMA analytical precision. Thus, no correction for drift during the experimental period has been applied to the concentrations reported by the laboratories.

Table 3. The six laboratories and the analytical methods, instruments, and calibration scales they used to measure CH_4 during the iceGGO-1 experiment.

Laboratory	Method	Instrument	Standard scale	Range of calibration gases	Number of calibration gases	Date of measurements
JMA	GC/FID	GC-14BPF (FID), Shimadzu	WMO X2004 Scale	1620 ppb - 2110 ppb	5	October 11-12, 2012
NIPR	GC/FID	GC-8A (FID), Shimadzu	NIPR Scale	1390 ppb - 2280 ppb	4	October 18-23, 2012
AIST	GC/FID	GC-14BPF (FID), Shimadzu	AIST Scale	1010 ppb - 2530 ppb	4	November 11-17, 2012
MRI	GC/FID	AG-1F (FID), Yanaco	MRI Scale	1600 ppb - 2100 ppb	5	November 2 - December 6, 2012
NIES	GC/FID	HP5890 (FID), Agilent	NIES94 Scale	1250 ppb - 2500ppb	6	December 14-17, 2012
TU	GC/FID	6890NF (FID), HP	TU2008 Scale	900 ppb - 2500 ppb	5	January 12-24, 2013
JMA	GC/FID	GC-14BPF (FID), Shimadzu	WMO X2004 Scale	1620 ppb - 2110 ppb	5	February 7-20, 2013

Table 4. CH_4 concentrations (ppb) reported by the indicated laboratories as a part of the iceGGO-1. Reported analytical precisions are indicated in parentheses.

	Cylinder Identifications					
Laboratory	CPB13002	CPB00786	CPB13003	CPB00787	CPB28218	CPB28042
JMA	1664.2 (1.5)	1779.6 (1.8)	1844.8 (1.1)	1918.8 (1.7)	1811.2 (1.0)	2234.6 (3.9)
NIPR	1661.7 (2.6)	1780.2 (1.7)	1845.7 (1.9)	1920.4 (1.4)	1810.8 (2.0)	2238.9 (1.4)
AIST	1665.4 (1.5)	1782.1 (1.5)	1847.9 (1.3)	1923.2 (1.3)	1813.9 (1.9)	2240.7 (1.9)
MRI	1663.8 (1.1)	1781.4 (0.9)	1845.9 (0.8)	1921.2 (1.0)	1812.5 (0.8)	2241.5 (0.8)
NIES	1665.8 (0.9)	1785.3 (1.2)	1850.0 (0.5)	1924.1 (0.8)	1816.3 (1.8)	2240.8 (0.6)
TU	1663.6 (1.1)	1781.8 (1.2)	1848.8 (1.3)	1922.5 (1.2)	1815.7 (0.9)	2243.2 (1.5)
JMA	1664.0 (1.7)	1779.4 (1.8)	1845.6 (1.9)	1918.6 (1.2)	1810.8 (2.1)	2234.4 (4.3)
NMIJ	-	-	-	-	1813.8 (1.3)*	2240.1 (1.3)*

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

Figure 1 shows the differences between the CH_4 concentrations measured in the six round-robin cylinders by each laboratory (Laboratory X) and by the JMA. The differences (Laboratory X minus JMA) among the laboratories ranged from –2 ppb to +9 ppb. This range of differences reflects mainly differences in the reference CH_4 standard scales among the laboratories. The differences of the concentrations reported by all five laboratories and the JMA concentrations clearly increased with increasing CH_4 concentration. These increased differences often exceeded the criterion for compatibility of CH_4 measurements (±2 ppb) recommended by the WMO (WMO, 2016b). The gravimetric values determined by ISO 6142:2001 for the two cylinders were higher than the JMA measurements based on

the WMO X2004 scale. The differences between the two gravimetric scales tended to increase with increasing CH_4 concentration. These results agree well with the difference between the NMIJ and WMO X2004 scales for the CCQM-K82 comparison as a part of the CIPM program (Flores et al., 2015). Tsuboi et al. (2016) have reported more details about the differences between the two scales.

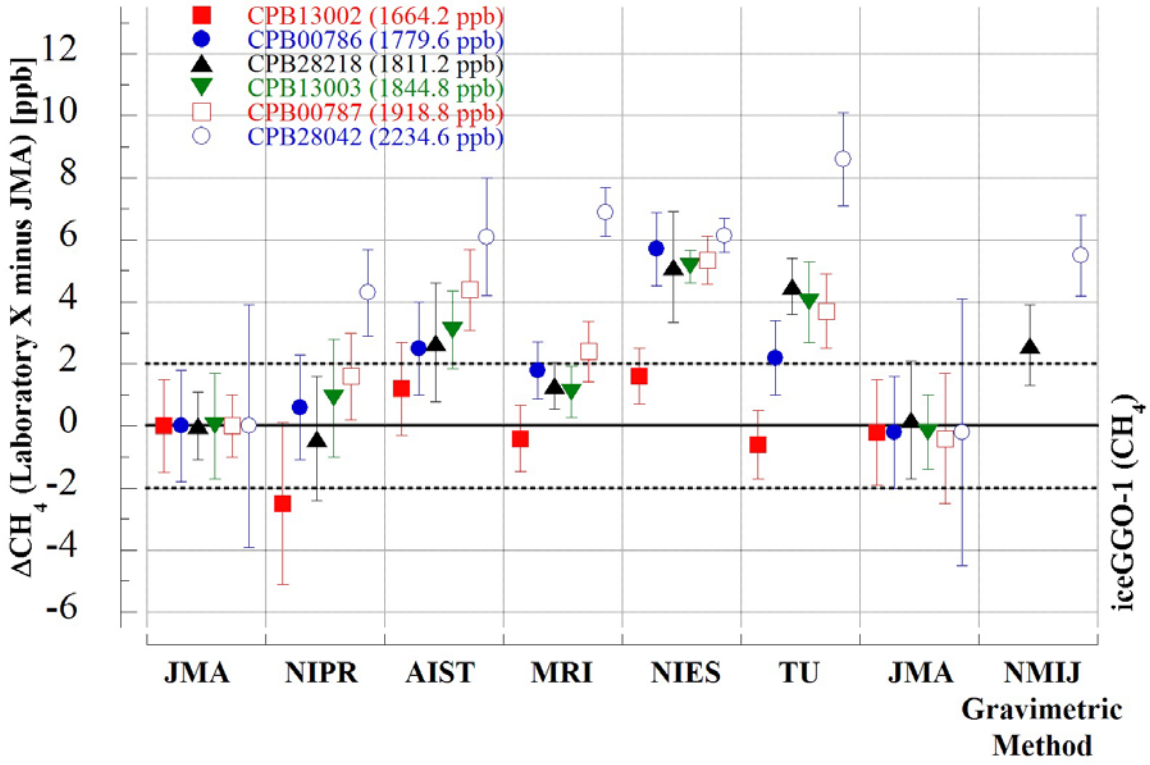

Figure 1. Differences (Laboratory X minus the JMA) of CH_4 concentrations for each round-robin cylinder measured as a part of the iceGGO-1. The error bars represent the ± measurement precision reported by each laboratory, although the error bar of the NMIJ indicates the ± expanded uncertainty of the gravimetric method (k = 2). The dashed lines around the zero line identify the WMO recommended criterion (±2 ppb) for CH_4 measurement compatibility.