## 6. iceGGO-5 ($N_2O$)

### *6.1. Round-robin cylinders (iceGGO-5)*

The focus of the fifth experiment (iceGGO-5), which took place in 2016, was on a comparison of $N_2O$ standard gas scales by circulating high-pressure gas cylinders. Table 14 provides details about the six sample cylinders used for this round-robin experiment. Five cylinders contained commercially available $N_2O$ standard gases, which were filled by the JFP. The five gases were prepared using purified natural air as a matrix gas; their $N_2O$ concentrations ranged from about 280 ppb to 340 ppb. The $N_2O$ concentrations in the five cylinders had been previously calibrated twice by using the WMO X2006A scale (Hall et al., 2007) at NOAA in December 2006 and during September–October 2010. Their values have been published on the NOAA website (http://www.esrl.noaa.gov/gmd/ccl/refgas.html). Another cylinder (CPB31357) with a $N_2O$ concentration of about 334 ppb was prepared from pure $N_2O$ and purified natural air by the NMIJ gravimetric method. A four-step dilution was used to make the mixtures. The $N_2O$ concentrations at each step were 19,000 ppm, 443 ppm, 14 ppm, and 330 ppb. Pure $N_2$ gas was used as the dilution gas in the first and second steps, and purified natural air was used as the dilution gas in the third and fourth steps. Three mixtures were prepared at each step. Table 15 lists the concentrations of the gases ($N_2$, $O_2$, Ar, and $CO_2$) in the mixtures. The expanded uncertainty of the gravimetric value ($k$ = 2), ~0.18 ppb, was mainly associated with the determination of the $N_2O$ concentration in the purified natural air.

**Table 14.** The six cylinders used for the iceGGO-5.

| Cylinder Identification | $N_2O$ Concentration (ppb) | Matrix gas | Manufacturer | Filling method | Date of filling |
|---|---|---|---|---|---|
| CQC00239 | 280.62 ±0.64* | Purified natural air | JFP | Volmetric | July, 27, 2006 |
| CQC00238 | 295.69 ±0.18* | Purified natural air | JFP | Volmetric | July, 27, 2006 |
| CQC00237 | 310.62 ±0.04* | Purified natural air | JFP | Volmetric | July, 27, 2006 |
| CQC00236 | 325.88 ±0.25* | Purified natural air | JFP | Volmetric | July, 27, 2006 |
| CQC00235 | 340.60 ±0.70* | Purified natural air | JFP | Volmetric | July, 27, 2006 |
| CPB31357 | 333.88 ±0.18** | Purified natural air[$] | NMIJ | Gravimetric | March 4, 2016 |

*Averaged value measured in 2006 and 2010 by NOAA

**Gravimetric value from NMIJ with the expanded uncertainty ($k$ = 2) after the ± symbols

[$]Detailed composition in Table 15

**Table 15.** Concentrations of gases in the iceGGO-5 cylinder prepared by the NMIJ gravimetric method. The numbers after the ± symbols indicate the expanded uncertainty ($k$ = 2).

| Cylinder Identification | $N_2O$ ppb | $CO_2$ ppm | $N_2$ ppm | $O_2$ ppm | Ar ppm |
|---|---|---|---|---|---|
| CPB31357 | 333.88 ±0.18 | 398.38 ±0.08 | 780890 ±47.7 | 209389 ±41.7 | 9321.7 ±23.2 |

### *6.2. Measurement methods (iceGGO-5)*

Five laboratories (JMA, AIST, MRI, NIES, and TU) participated in the iceGGO-5 round-robin measurements from March to October 2016. Table 16 provides details of the $N_2O$ analytical methods used by the five laboratories. Three laboratories (JMA, NIES, and TU) used a gas chromatograph with an electron capture detector (GC/ECD) to measure $N_2O$ concentrations, whereas three laboratories (JMA, AIST, and MRI) used a laser-based analyzer of Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS, LGR Inc.). The JMA measurements were based on the WMO X2006A scale (Hall et al., 2007), which has

been propagated from the NOAA. The other four laboratories carried out their measurements using different standard gas scales (AIST, MRI2014, NIES96, and TU2006) that were developed independently. The calibration gases for the AIST, NIES, and TU covered a relatively wide range of $N_2O$ concentrations, whereas the range of concentrations in the calibration gases used by the JMA and MRI was not wide enough to include the lowest concentration in one of the round-robin cylinders. To evaluate the stability of $N_2O$ concentrations during the experimental period, the AIST assayed the NMIJ cylinder at the beginning and end of the experiment.

**Table 16.** The five laboratories that participated in the iceGGO-5 and their analytical methods, instruments, and calibration scales for $N_2O$.

| Laboratory | Method | Instrument | Standard scale | Range of calibration gases | Number of calibration gases | Date of measurements |
|---|---|---|---|---|---|---|
| AIST(Laser) | ICOS | ICOS 907-0015, LGR | AIST Scale | 270 ppb - 380 ppb | 5 | April 10-17, 2016 |
| MRI(Laser) | ICOS | N2O/COAnalyzer, LGR | MRI 2014 Scale | 300 ppb - 350 ppb | 5 | March 9, 2016 |
| NIES(GC) | GC/ECD | Agilent 6890 (ECD), Agilent | NIES 96 Scale | 250 ppb - 400 ppb | 4 | June 4-5, 2016 |
| TU(GC) | GC/ECD | Agilent 6890 (ECD), Agilent | TU2006 Scale | 120 ppb - 370 ppb | 3 | June 17 - July 20, 2016 |
| JMA (GC) | GC/ECD | GC-2014 (ECD), Shimadzu | WMO X2006A Scale | 300 ppb - 360 ppb | 5 | August 9 & October 13-14, 2016 |
| JMA(Laser) | ICOS | DLT-100 Fast, LGR | WMO X2006A Scale | 300 ppb - 360 ppb | 5 | August 19-20, 2016 |

### *6.3. Results of iceGGO-5*

Table 17 lists the $N_2O$ concentrations measured in the six round-robin cylinders by the five laboratories that used the GC/ECD and laser-based analyzers together with NMIJ's gravimetric value. No corrections for drift have been applied to the concentrations reported by any of the laboratories. The analytical precision of most of the measurements by four of

the laboratories was less than 0.5 ppb; the precision of the JMA measurements made by the GC/ECD method was larger. In general, the precision of the laser-based analyzer, ICOS, was better than that of the GC/ECD. The JMA concentrations differed between the two analytical methods, although the same calibration standard gases were used for both of the methods.

**Table 17.** $N_2O$ concentrations (ppb) during the iceGGO-5. The reported analytical precisions are shown in parentheses.

| | Cylinder Identifications | | | | | |
|---|---|---|---|---|---|---|
| Laboratory | CPB31357 | CQC00239 | CQC00238 | CQC00237 | CQC00236 | CQC00235 |
| AIST (ICOS) | 333.54 (0.03) | 280.43 (0.06) | 295.17 (0.05) | 310.12 (0.05) | 325.30 (0.05) | 339.94 (0.05) |
| MRI (ICOS) | - | 280.58 (0.25) | 295.87 (0.53) | 310.55 (0.03) | 325.99 (0.34) | 339.97 (0.04) |
| NIES (GC/ECD) | 332.97 (0.13) | 279.72 (0.20) | 294.25 (0.16) | 309.17 (0.18) | 324.26 (0.18) | 338.87 (0.01) |
| TU (GC/ECD) | 334.37 (0.27) | 280.79 (0.53) | 295.54 (0.48) | 310.05 (0.23) | 325.55 (0.36) | 339.79 (0.23) |
| JMA (GC/ECD) | 335.15 (0.53) | 280.92 (0.67) | 295.61 (0.56) | 310.65 (0.42) | 325.95 (0.28) | 340.56 (0.39) |
| JMA (ICOS) | 333.84 (0.08) | 280.59 (0.21) | 295.41 (0.14) | 310.52 (0.10) | 325.84 (0.11) | 340.54 (0.19) |
| NMIJ | 333.88 (0.18)* | - | - | - | - | - |

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

Figure 6 shows the differences in the $N_2O$ concentrations measured by each laboratory (Laboratory X) and the NMIJ or NOAA for the six cylinders. The differences (Laboratory X minus NMIJ/NOAA) among the laboratories ranged from –1.7 ppb to +1.5 ppb. The differences from the NOAA values clearly depended on the $N_2O$ concentrations for the measurements made by the AIST, NIES, and TU. In contrast, the values measured with ICOS analyzers by the MRI and JMA were similar to the NOAA values. These results

reflect mainly differences in the $N_2O$ calibration standard gas scales among the laboratories. The NMIJ gravimetric value was within ±1 ppb of the region of most of the $N_2O$ measurements, except for the JMA measurement made with the GC/ECD.

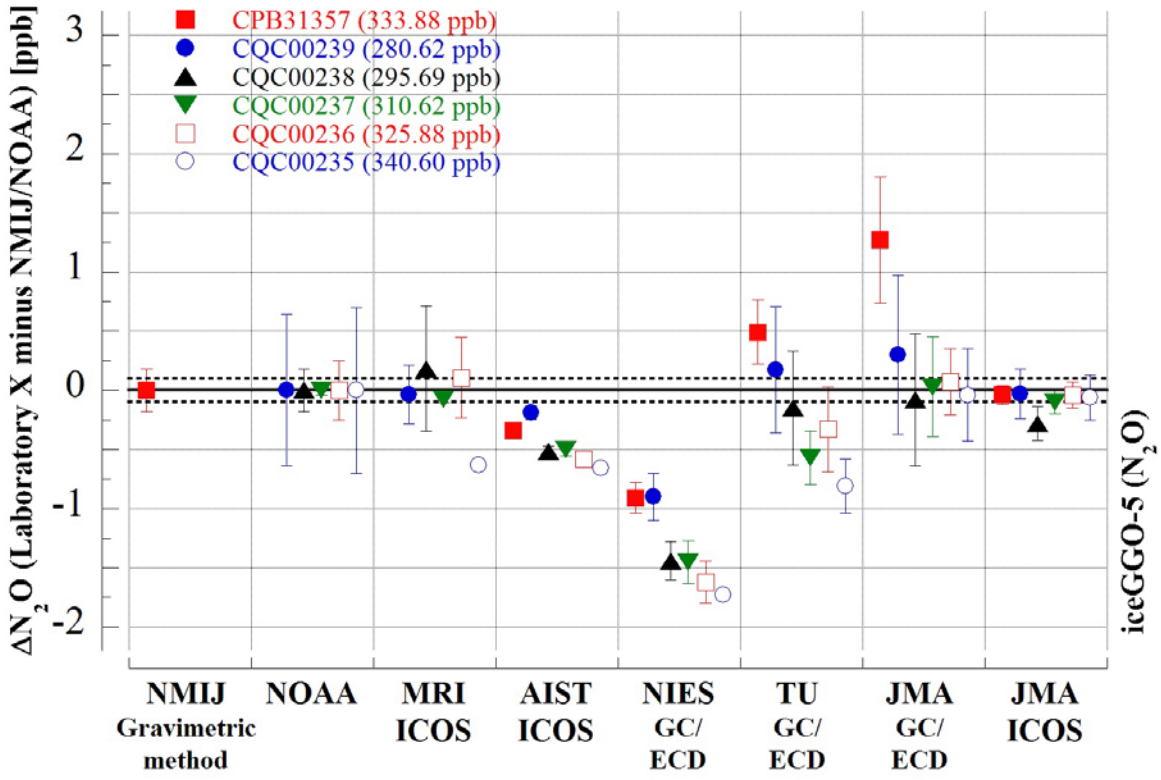


**Figure 6.** Differences (Laboratory X minus NOAA/NMIJ) of $N_2O$ concentrations for each round-robin cylinder assayed during the iceGGO-5. The error bars represent the ± measurement uncertainty reported by each laboratory, although the error bar of the NMIJ indicates the ± expanded uncertainty of the gravimetric method ($k$ = 2). The dashed lines around the zero line identify the WMO recommended criterion (±0.1 ppb) for $N_2O$ measurement compatibility.