Scale and stability of methane standard gas in JMA and comparison with MRI standard gas

by

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Abstract

We examined the standard gas scales and the stability of methane (CH₄) standard gases that have been used for atmospheric measurements at the Japan Meteorological Agency (JMA) since 2000. Calibration of the JMA standards at the National Oceanic and Atmospheric Administration (NOAA) using the NOAA04 gravimetric scale, which is the accepted World Meteorological Organization (WMO) CH₄ mole fraction scale, showed that CH₄ mole fractions in the NOAA04 scale differ by +1.3 to −4.5 nmol mol⁻¹ from those in the gravimetric scale in use at JMA. We established a linear relationship between the differences, which can be used for conversion between the two scales. Stability tests showed significant drift of ~1 nmol mol⁻¹ yr⁻¹ for the mole fractions of two of the standard gases tested; all other standards were shown to be stable. Experiments comparing the results obtained for standards used at JMA and the Meteorological Research Institute (MRI) between 2000 and 2014 verified the conversion to the WMO scale and the drift correction used. The Inter-Comparison Experiments for Greenhouse Gases Observation (icceGGO) program in Japan can provide a useful means of validating the MRI/JMA CH₄ scale and comparing it with other gravimetric scales used in Japan.

1. Introduction

Atmospheric methane (CH₄) is an important greenhouse gas in the climate system because of its infrared properties (e.g., Montzka et al., 2011). CH₄ is a key trace constituent in the chemistry of both the troposphere and stratosphere and has an important role in determining the oxidizing capacity of the troposphere related to the budgets of many trace gases such as carbon monoxide and ozone. CH₄ is emitted to the atmosphere from biogenic, thermogenic, and pyrogenic sources including wetlands, enteric fermentation, rice paddies, landfill, natural gas leakage, and biomass burnings. The atmosphere is a major sink of CH₄ because of the oxidative reaction of CH₄ with OH; soil is a minor sink because of oxidation of CH₄ by bacteria in the soil. Although changes in global CH₄ sources and sinks over the past three decades have been reviewed by Kirschke et al. (2013), uncertainties of decadal variability of emissions prevent us from reaching definitive conclusions about future levels of atmospheric CH₄.

For the past 30 years, accurate and systematic measurements have been taken by global atmospheric observation networks around the world (e.g., Rigby et al., 2008; Dlugokencky et al., 2009). Long-term monitoring of atmospheric CH₄ under the Global Atmosphere Watch (GAW) program of the World Meteorological Organization (WMO) has clearly shown prolonged periods of increasing atmospheric CH₄ over the past three decades, albeit with some interannual variability. However, from 1999 to 2006 the rate of increase slowed to almost zero before beginning to increase again in 2007 (WMO, 2013). The reasons for these changes are unclear because of our limited understanding of the controls of the global CH₄ budget (Nisbet et al., 2014). Thus, more long-term measurements are necessary to predict future trends of the atmospheric CH₄ burden.

Global atmospheric CH₄ measurements are useful to constrain the geographical distribution of CH₄ sources and sinks and their temporal changes by using inversion modeling (e.g., Kirschke et al., 2013). To improve our current understanding,
it is necessary to consolidate all of the atmospheric CH₄ measurements taken at ground-based stations (e.g., Dlugokencky et al., 2009) and on ships (e.g., Terao et al., 2011) and aircraft (e.g., Umezawa et al., 2012) around the world. However, measurements of CH₄ mole fractions by various laboratories can differ by as much as ~2%, which is considerably greater than analytical precision of ~0.1% (e.g., Matsueda et al., 2004; Dlugokencky et al., 2005). These differences are due in large part to differences in the standard gases used in the analyses. Thus, the WMO/GAW program has set a goal for all participating institutions measuring atmospheric CH₄ to report data on a common CH₄ standard scale (WMO, 2005).

In 2000, the Japan Meteorological Agency (JMA) established a CH₄ standard gas scale with a new calibration system based on independent gravimetric standards purchased from a Japanese gas company (Matsueda et al., 2004). On the other hand, the National Oceanic and Atmospheric Administration (NOAA) Earth System Research Laboratory has developed a new gravimetric scale (NOAA04), which has been accepted by the WMO as the CH₄ mole fraction scale (Dlugokencky et al., 2005). In 2006, JMA standard gases were sent to NOAA for calibration with NOAA04 and to facilitate conversion of past CH₄ measurements from the JMA gravimetric scale to the new WMO scale. Since then, the WMO scale has been maintained at JMA to calibrate CH₄ reference gases used for atmospheric monitoring at three ground-based stations (Wada et al., 2013) and by a C-130H aircraft (Tsutoh et al., 2013; Niwa et al., 2014). In addition, JMA is now the WMO World Calibration Center (WCC) for CH₄ standard gases in the Asia and southwest Pacific regions. WMO has required the JMA/WCC to maintain the WMO scale and to propagate its use throughout the regional WMO/GAW network.

To evaluate the quality of the CH₄ standard gases maintained by JMA, we examined the standard scale and investigated its long-term stability. In this paper, we first describe the conversion from the original JMA gravimetric scale to the new NOAA04 scale. We then report on the stability of the CH₄ content of the JMA standard gases. Finally, we compare the results of inter-comparison experiments of CH₄ standard gases at the Meteorological Research Institute (MRI) and other laboratories.

2. Standards and measurement method

2.1 Standard gases

Table 1 lists the CH₄ mole fractions for previous and current primary standard gases held by MRI and JMA. All of the standard gases were prepared with dry purified air as the diluent gas by Japan Fine Products (JFP; formerly Nippon Sanso Corporation, Japan). Details of the original sets (“First sets” in Table 1) of standards held at MRI and JMA have been reported elsewhere (Matsueda, 1993; Matsueda et al., 2004), so only a brief description is given here.

At MRI, the first set of eight standard gases was gravimetrically prepared by JFP with CH₄ mole fractions ranging from about 1540 to 2200 nmol mol⁻¹. At JMA, the first set of five standards gases, similarly prepared by JFP, had CH₄ mole fractions of about 1600 to 2100 nmol mol⁻¹. Previous comparisons have shown that the gravimetric values of the first set MRI standards agree well, within analytical error of less than 1.4 nmol mol⁻¹, with those of the JMA standards (Matsueda et al., 2004). The gravimetric values assigned for those standard gases are referred to here as the MRI/JMA scale.

Because several of the standards in the JMA first set were found to be unstable (Matsueda et al., 2004), JMA set up second and third sets of standard gases for long-term use as the primary scale (Table 1). The 10 standards of the second and third JMA sets were sent to NOAA in 2006 and 2011 to determine their mole fractions by calibration with the NOAA04 scale (Dlugokencky et al., 2005). In 2000, the five standard gases of the second JMA set were assigned to the MRI/JMA gravimetric scale from measurements based on the first set of JMA standards, and these standards were used in 2011 to measure the five standard gases in the third JMA set to propagate the MRI/JMA scale.

At MRI in 2011, a second set of five primary standard gases was prepared in 48-L aluminum cylinders because the pressure in the cylinders of the first set had been lowered by long-term use over the past 20 years (Table 1). The CH₄ mole fractions for the MRI second set based on the NOAA04 scale were determined by using the JMA second set standard gases in 2011−2012. The MRI/JMA gravimetric values calculated based on the difference between the MRI/JMA and NOAA04 scales are also given in Table 1, and its difference is described below in Section 3.1.

2.2 Calibration method

Details of the CH₄ standard gas calibration systems at MRI and JMA have been reported elsewhere (Matsueda, 1993; Matsueda et al., 2004). Automated calibration systems were established at MRI in 1993 and at JMA in 2000 for analysis of CH₄ mole fractions of standard gases by using a gas chromatograph equipped with a flame ionization detector (GC/FID). The overall precision for both the MRI and JMA systems was estimated to be less than ~1.4 nmol mol⁻¹. We note that JMA data for 11 repeated measurements with standard deviations greater than 2 nmol mol⁻¹ were discarded in this study, but several data sets with fewer repeated measurements were included. NOAA also used a GC/FID method to calibrate CH₄ standard gases with an overall precision of less than 1.5 nmol mol⁻¹ (Dlugokencky et al., 2005).
Table 1. Primary standard gases at MRI (two sets) and JMA (three sets) and their CH$_4$ mole fractions on the MRI/JMA and NOAA04 scales.

| Cylinder ID | Volume (L) | Preparation Date | CH$_4$ MRI/JMA Scale | Sdev | Measurement Date | CH$_4$ NOAA04 Scale | Sdev | Measurement Date |
|-------------|------------|------------------|----------------------|------|------------------|----------------------|------|------------------|
| DF4728      | 10         | APR 1, 1991      | 1536.5               |      | (Gravimetric)    |                      |      |                  |
| DF4727      | 10         | APR 1, 1991      | 1637.1               |      | (Gravimetric)    |                      |      |                  |
| DF4797      | 10         | APR 1, 1991      | 1737.3               |      | (Gravimetric)    |                      |      |                  |
| DF4723      | 10         | APR 2, 1991      | 1838.6               |      | (Gravimetric)    |                      |      |                  |
| DF4737      | 10         | APR 2, 1991      | 1938.3               |      | (Gravimetric)    |                      |      |                  |
| CBP10250    | 10         | SEP 25, 1996     | 1798.2               |      | (Gravimetric)    |                      |      |                  |
| CBP10251    | 10         | SEP 25, 1996     | 1900.7               |      | (Gravimetric)    |                      |      |                  |
| CBP10252    | 10         | SEP 25, 1996     | 2198.3               |      | (Gravimetric)    |                      |      |                  |

First Set in MRI

| Cylinder ID | Volume (L) | Preparation Date | CH$_4$ MRI/JMA Scale | Sdev | Measurement Date | CH$_4$ NOAA04 Scale | Sdev | Measurement Date |
|-------------|------------|------------------|----------------------|------|------------------|----------------------|------|------------------|
| CBP03383    | 48         | JAN 13, 2011     | 1598.6               |      | (Calculated)     | 1600.4               | 0.37 | MAR 2011–SEP 2012|
| CBP09933    | 48         | JAN 13, 2011     | 1724.1               |      | (Calculated)     | 1723.8               | 0.60 | MAR 2011–SEP 2012|
| CBP09392    | 48         | JAN 12, 2011     | 1850.3               |      | (Calculated)     | 1848.3               | 0.47 | MAR 2011–SEP 2012|
| CBP12908    | 48         | JAN 12, 2011     | 1975.5               |      | (Calculated)     | 1972.1               | 0.47 | MAR 2011–SEP 2012|
| CBP15988    | 48         | JAN 12, 2011     | 2102.0               |      | (Calculated)     | 2097.6               | 0.35 | MAR 2011–SEP 2012|

Second Set in MRI

| Cylinder ID | Volume (L) | Preparation Date | CH$_4$ MRI/JMA Scale | Sdev | Measurement Date | CH$_4$ NOAA04 Scale | Sdev | Measurement Date |
|-------------|------------|------------------|----------------------|------|------------------|----------------------|------|------------------|
| CBP12986    | 10         | NOV 15, 1999     | 1600.1               |      | (Gravimetric)    |                      |      |                  |
| CBP12987    | 10         | NOV 15, 1999     | 1700.5               |      | (Gravimetric)    |                      |      |                  |
| CBP12988    | 10         | NOV 12, 1999     | 1850.5               |      | (Gravimetric)    |                      |      |                  |
| CBP12989    | 10         | NOV 12, 1999     | 1998.4               |      | (Gravimetric)    |                      |      |                  |
| CBP12990    | 10         | NOV 15, 1999     | 2100.3               |      | (Gravimetric)    |                      |      |                  |

Second Set in JMA

| Cylinder ID | Volume (L) | Preparation Date | CH$_4$ MRI/JMA Scale | Sdev | Measurement Date | CH$_4$ NOAA04 Scale | Sdev | Measurement Date |
|-------------|------------|------------------|----------------------|------|------------------|----------------------|------|------------------|
| CBP11442    | 48         | NOV 9, 1999      | 1620.6               | 0.58 | MAY 15–19, 2000  | 1621.94              | 0.38 | SEP 19–OCT 3, 2006|
| CBP11443    | 48         | NOV 9, 1999      | 1750.3               | 0.37 | MAY 15–19, 2000  | 1749.77              | 0.51 | SEP 13–25, 2006  |
| CBP11444    | 48         | NOV 9, 1999      | 1869.6               | 0.65 | MAY 15–19, 2000  | 1867.19              | 0.19 | SEP 13–28, 2006  |
| CBP11446    | 48         | NOV 17, 1999     | 1986.0               | 0.43 | MAY 15–19, 2000  | 1982.57              | 0.43 | SEP 13–28, 2006  |
| CBP11447    | 48         | NOV 17, 1999     | 2113.0               | 0.53 | MAY 15–19, 2000  | 2108.48              | 0.28 | SEP 19–OCT 2, 2006|

Third Set in JMA

| Cylinder ID | Volume (L) | Preparation Date | CH$_4$ MRI/JMA Scale | Sdev | Measurement Date | CH$_4$ NOAA04 Scale | Sdev | Measurement Date |
|-------------|------------|------------------|----------------------|------|------------------|----------------------|------|------------------|
| CBP18737    | 48         | APR–JUN, 2011    | 1611.2               |      |                  | 1611.65              | 0.20 | NOV 17–28, 2011  |
| CBP18738    | 48         | APR–JUN, 2011    | 1761.9               |      |                  | 1760.51              | 0.16 | OCT 27–NOV 14, 2011|
| CBP18739    | 48         | APR–JUN, 2011    | 1901.5               |      |                  | 1898.07              | 0.91 | OCT 27–NOV 14, 2011|
| CBP18740    | 48         | APR–JUN, 2011    | 2034.6               |      |                  | 2030.35              | 0.10 | OCT 27–NOV 14, 2011|
| CBP18741    | 48         | APR–JUN, 2011    | 2170.2               |      |                  | 2165.00              | 0.30 | NOV 17–28, 2011  |

CH$_4$ mole fractions on the MRI/JMA scale were assigned based on a gravimetric method of JFP.

CH$_4$ mole fractions on the NOAA04 scale were determined from measurements by using standard gases in the second set of JMA, while those on the MRI/JMA scale were calculated based on the difference between the NOAA04 and MRI/JMA scales, as shown in Figure 1.

CH$_4$ mole fractions on the MRI/JMA scale were assigned based on a gravimetric method of JFP.

CH$_4$ mole fractions on the NOAA04 scale were calibrated at NOAA, while those on the MRI/JMA scale were propagated from the first set of the JMA standards.

3. Results and discussion

3.1 Differences of the MRI/JMA and NOAA gravimetric standard scales

Comparison of the CH$_4$ mole fractions in the second set of JMA standards according to the independently prepared MRI/JMA and NOAA04 scales (Fig. 1, Table 1) showed that the CH$_4$ mole fractions according to the NOAA04 scale differed by +1.3 to −4.5 nmol mol$^{-1}$ from those of the MRI/JMA gravimetric scale. The difference clearly increases with increasing mole fraction of CH$_4$ according to the linear equation $C_{NOAA} - C_{MRI/JMA} = 20.5 - 0.012 (C_{MRI/JMA})$, where $C_{NOAA}$ and $C_{MRI/JMA}$ are the mole fractions measured according to the NOAA04 and MRI/JMA scales, respectively. This empirical equation can be used for conversion of all previous measurements based on the MRI/JMA scale to the NOAA04 scale. Although JMA/WCC uses a second-order polynomial fitting for this scale adjustment (http://ds.data.jma.go.jp/wcc/ch4/recalculation2.html), the difference between their and our results is not significant within analytical error.
Fig. 1 Differences in CH₄ mole fractions measured by the NOAA04 and MRI/JMA gravimetric scales versus mole fraction on the MRI/JMA scale. Closed circles are the five second-set JMA standards measured at NOAA in 2006 and the open square is a standard gas sample measured at NOAA in 1992. Error bars show overall uncertainty derived from the standard deviations of the measurements for the two scales. The solid line represents the least-squares fit to the five data points.

In 1992, MRI and NOAA carried out an inter-comparison experiment by using a standard gas cylinder with a CH₄ mole fraction of 1754.5 ± 1.7 nmol mol⁻¹ according to the MRI/JMA scale (Matsueda, 1993). NOAA used the old CMDL83 scale in 1992 and the difference between the two scales (MRI/JMA – CMDL83) was found to be 23.0 ± 1.7 nmol mol⁻¹. However, Dlugokencky et al. (2005) reported that NOAA had changed to the new NOAA04 gravimetric standard scale and inferred that the ratio of the MRI/JMA scale to the NOAA04 scale was 1.0009. Using this ratio, we calculated a difference of −1.6 ± 2.0 nmol mol⁻¹ from NOAA04 to MRI/JMA. Using this ratio, we calculated a difference of −1.6 ± 2.0 nmol mol⁻¹ from NOAA04 to MRI/JMA. This result indicates that the assigned CH₄ mole fractions on the MRI/JMA scale are internally consistent, and that the use of any combination of the five standards would provide the same calibration result.

### 3.2 Stability of JMA standard gases

Matsueda et al. (2004) pointed out that temporal drifts of CH₄ mole fractions were observed in several standards in the JMA first set, but the drifts were not accurately estimated due to the short stability test for 3 years. We therefore compared CH₄ mole fractions of the five first-set JMA standards with those of the JMA second set for the 6-year period from March 2000 to May 2006 (Fig. 2). The linear regression slopes for three of the standard gases ranged from −0.30 to +0.12 nmol mol⁻¹ yr⁻¹, suggesting that the observed drifts for these standards during this period were not significant. However, two standard gases showed large and statistically significant decreases during the same period. The drifts for cylinders CPB12989 and CPB12990 were −0.92 ± 0.08 nmol mol⁻¹ yr⁻¹ and −0.83 ± 0.09 nmol mol⁻¹ yr⁻¹, respectively. Considering these drifts, the previous JMA/WCC results for 2000–2006 based on the JMA first-set standards were then revised (http://ds.data.jma.go.jp/wcc/ch4/com_annex2.html).

For evaluation of the 2000–2006 drifts in the JMA first-set standards, it was assumed that there was no change of the CH₄ mole fractions of the standard gases in the JMA second set during this period. We therefore examined the long-term stability of the five standards of the JMA second set on the basis of internal consistency of the archived raw data of the GC/FID measurements over the 15 years from 2000 to 2014. For this test, the CH₄ mole fraction of each standard gas was re-calculated based on the measurements of the other four standard gases to create a time-series data set for March 2000 to July 2014 (Fig. 3). We excluded outliers (1% to 4% of values) that deviated by more than 4 nmol mol⁻¹ from the mean without significant effect on the observed drift. Linear regression slopes for the five standards gases showed a negligible drift (< 0.02 nmol mol⁻¹ yr⁻¹; insignificant at the 95% confidence level). These results indicate that the five second-set JMA standard gas cylinders have been stable over the 15 years we examined. Moreover, the averaged mole fractions for the five standard gases agreed well (within less than ±1 nmol mol⁻¹) with their assigned values. This result indicates that the assigned CH₄ mole fractions on the MRI/JMA scale are internally consistent, and that the use of any combination of the five standards would provide the same calibration result.

### 3.3 Comparison of MRI and JMA CH₄ standard gases

The stability of the first set of MRI CH₄ standard gases over a period of 10 years was established by Matsueda et al. (2004). To monitor the long-term stability of JMA CH₄ standard gases and to evaluate the performance of the JMA calibration system, the CH₄ mole fractions of the first-set MRI standard gases were measured by GC/FID at JMA twice each year between 2000 and 2014 by using the JMA calibration system (Fig. 4). All of the measurements were performed using the same MRI/JMA scale. The measurement periods for three of the MRI standards were shorter because of the lower pressure of those cylinders as a result of their long-term use. Measurements during 2000–2006 were calibrated using the first set of JMA standards, but included drift errors due to significant changes of CH₄ contents in two of the standard gas cylinders. Consequently, these measured values were corrected by the estimated linear drift as shown in Figure 2. The measurements during 2005–2014 were calibrated using the second set of JMA standards, which are known to have reasonably stable CH₄ contents, as previously discussed.

Comparison of the averaged mole fractions from the first-set (2000–2006) and second-set JMA standard gas
Fig. 2 Temporal variations (March 2000 to May 2006) of CH₄ mole fractions for five JMA first-set standard gases measured using the five standards of the JMA second set. For each standard, the solid line represents the linear least-squares fit to all measurements. Values in parentheses are drift estimated from the slope of the least-squares fit (+1σ).
Fig. 3 Temporal variations (March 2000 to July 2014) of CH₄ mole fractions for each of the five JMA second-set standard gases calculated based on measurements of the other four second-set standard gases. For each analysis, the black solid line is the linear least-squares fit to all data points and the red solid line is the mole fraction of the MRI/JMA scale on 9 November 1999.
Fig. 4 Temporal variations (March 2000 to July 2014) of CH₄ mole fractions for six of the first-set MRI standard gases measured using JMA standard gases. Red and blue closed circles are measurements from the first- and second-set JMA standards, respectively. Open circles are measurements without drift corrections based on the first-set JMA standard. For each standard, the solid line represents the linear least-squares fit to all measurements and the dashed line is the gravimetric value on the MRI/JMA scale. Values in parentheses are drift estimated from the slope of the least-squares fit (± 1σ).
calibrations (2005–2014) for all six MRI cylinders revealed no discontinuity between the two data sets, thus indicating that the standard gas scale is consistently assigned in both JMA standard sets. Linear regression analysis of all of the data from 2000 to 2014 to determine long-term drift for each standard (Fig. 4) showed no significant drift trend (slopes of \(-0.15\) to \(+0.15\) nmol mol\(^{-1}\) yr\(^{-1}\)), although the cylinders with the lowest and highest mole fractions of CH\(_4\) showed more drift, probably reflecting higher uncertainties in the more extreme measurements. Several outliers that deviated from the mean by more than 4 nmol mol\(^{-1}\) were excluded (not shown in Fig. 4), but this exclusion had no significant effect on the drift estimations. Furthermore, the averages of all of the measured mole fractions for each of the six standard gases agreed well with their assigned values (within \(\pm 1\) nmol mol\(^{-1}\)). These results indicate that the JMA CH\(_4\) calibration system has been well maintained over the past 14 years and provides an effective tool for the JMA/WCC inter-comparison experiments.

3.4 iceGGO experiments

In 2012, JMA, MRI, 4 major observation laboratories in Japan, and the National Metrology Institute of Japan (NMIJ) established an alliance to compare the standard gas scales used for measurement of greenhouse gases in Japan; they named the resultant program the Inter-Comparison Experiments for Greenhouse Gases Observation (iceGGO). Further details of the iceGGO program have been reported elsewhere (Takahashi et al., 2013, 2014).

In 2012–2013 as the first exercise of the iceGGO program, we conducted round robin experiments on CH\(_4\) standard gases. Six cylinders with a nominal range of mole fractions of 1660–2240 nmol mol\(^{-1}\) were prepared, four by JFP using purified air as a diluent gas and two by MIJM using the gravimetric method and a synthetic air diluent (a mixture of pure N\(_2\), O\(_2\), and Ar). Round-robin comparisons of the CH\(_4\) mole fractions measured at each of the six laboratories were reported by Takahashi et al. (2013, 2014). To check for drift during the experimental period, the CH\(_4\) contents of all of the gases were measured by JMA by using the NOAA04 scale before and after the round-robin measurements.

We re-examined the differences of the CH\(_4\) mole fractions identified in the iceGGO exercise for the six inter-comparison cylinders as measured by the NOAA04 scale used at JMA and the MRI/JMA scale used at MRI (Fig. 5). The difference between measurements based on the two gravimetric scales (NOAA04 – MRI/JMA) increased almost linearly from about 0 nmol mol\(^{-1}\) to about –6 nmol mol\(^{-1}\) as CH\(_4\) mole fraction increased from 1650 to 2240 nmol mol\(^{-1}\), albeit with larger analytical error at the highest mole fraction owing to uncertainties inherent in the extrapolated measurements. The slope of the regression line agrees well with that of the previous experiment described in Section 3.1 (Fig. 1), thus re-affirming that there was little difference in the results obtained using the NOAA04 and MRI/JMA gravimetric scales.

The uncertainties of the assigned values for the two cylinders prepared gravimetrically by NMIJ (CH\(_4\) mole fractions of about 1810 and 2240 nmol mol\(^{-1}\)) was \(\pm 1.3\) nmol mol\(^{-1}\), which was caused by the determination of CH\(_4\) in the matrix gases (pure oxygen and nitrogen gases). The CH\(_4\) mole fractions from the NMIJ gravimetric method for these two cylinders were higher than those measured according to the NOAA04 gravimetric scale used at JMA. The differences between the two gravimetric scales (NOAA04 – NMIJ) were –2.6 nmol mol\(^{-1}\) at the 1810 nmol mol\(^{-1}\) level and –5.5 nmol mol\(^{-1}\) at the 2240 nmol mol\(^{-1}\) level (Fig. 5). These results agree well with those of the CCQM-K82 comparison by Flores et al. (2015) under the Bureau International des Poides et Mesures (BIPM) program, for which the values of (NOAA – NMIJ) were –3.1 nmol mol\(^{-1}\) at the 1800 nmol mol\(^{-1}\) level and –5.7 nmol mol\(^{-1}\) at the 2200 nmol mol\(^{-1}\) level. These results indicate that the NOAA04 gravimetric scale is different from that of NMIJ, but the NMIJ and MRI/JMA scales are similar. The experimental uncertainties of the GC/FID analyses remain, so further and more accurate comparisons obtained by using a high-precision laser-based instrument (e.g., Tsuboi et al., 2013) are needed to validate the differences of the CH\(_4\) standard gas scales.

4. Summary and conclusions

We examined the standard gas scales and the stability of the standard gases used at JMA for atmospheric CH\(_4\) mea-
measurements for the past 14 years. Because the JMA standard gases were calibrated by NOAA in 2006, we converted the mole fractions of the MRI/JMA gravimetric scale that has been used since 2000 to the NOAA04 gravimetric scale, the accepted WMO CH₄ mole fraction scale. The conversion was done by using an empirically derived equation based on analyses of the differences between the two gravimetric scales.

Stability tests showed significant drifts of two of the standard gases used from 2000 to 2006; all other standards were shown to be stable within experimental error. The temporal drifts were quantitatively estimated to allow elimination of calibration errors due to instability of the standards in the first set of JMA standards.

Inter-comparison experiments conducted using MRI standard gases from 2000 to 2014 validated the scale conversion, including the drift correction, clearly indicating that our method of conversion provided a CH₄ dataset compatible with the NOAA04 gravimetric scale within the analytical precision of the GC/FID system. All JMA observations of atmospheric CH₄ measured in Japan, adjusted to the NOAA04 gravimetric scale as reported here have been posted at the WMO World Data Center for Greenhouse Gases (WDCGG) website, which is hosted by JMA in Tokyo (http://ds.data.jma.go.jp/gmd/wdcdg/wdcdg.html). As a result of their conversion to the NOAA04 gravimetric scale, the atmospheric CH₄ observed in Japan, adjusted to the NOAA04 gravimetric scale as reported here have been posted at the WMO World Data Center for Greenhouse Gases (WDCGG) website, which is hosted by JMA in Tokyo (http://ds.data.jma.go.jp/gmd/wdcdg/wdcdg.html).

The iceGGO and BIPM programs have provided opportunities to compare gravimetric scales prepared and used by different organizations, although further work is needed. More experiments in cooperation with WMO and BIPM will improve the accuracy of and conversion between CH₄ mole fraction scales for measurements of atmospheric CH₄.

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**JMAにおけるメタン標準ガスのスケールと安定性及びMRI標準との比較**

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気象庁（JMA）では大気観測のために1600～2100 nmol mol⁻¹の濃度範囲のメタン(CH₄)標準ガスを2000年以降使用しておりますが、本研究ではその標準ガスのスケールと安定性について調べた。JMAの標準ガスは米国の海洋大気庁（NOAA）において質量比混合法によるNOAA04スケールを用いて検定された。NOAA04スケールは世界気象機関（WMO）のCH₄標準ガス・スケールとして認定されている。NOAA04スケールで与えられた濃度値は、これまでJMAで使用していた質量比混合ガスのMRI/JMAスケールによる濃度と比べて+1.3～4.5 nmol mol⁻¹の違いがあることが判明した。同スケールの差はCH₄濃度の違いに依存しており、その関係は直線で回帰できることが分かった。標準ガスの安定性試験を行った結果、2本の標準ガスに濃度変化が起こっていたが、他の標準ガスの濃度は安定であることが確認され、MRI/JMAスケールによる濃度の変化は0.35−0.45 nmol mol⁻¹の変化であることが確認された。気象研究所（MRI）との標準ガス比較実験は2000年～2014年まで継続し、WMOスケールへの変換や標準ガスの濃度変化の補正の妥当性を評価することができた。また、日本における「温室効果ガス観測のための比較実験（iceGGO）」プロジェクトでは計量機関による質量比混合ガスの値の比較結果が得られ、CH₄スケールの検証に有効であることが分かった。