

Evaluation of a new methane calibration system at JMA for WCC Round Robin experiments

by

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Abstract

A new calibration system of methane (CH₄) standard gases by using a wavelength-scanned cavity ring-down spectroscopy (WS-CRDS) analyzer was developed at the Japan Meteorological Agency (JMA) in collaboration with the Meteorological Research Institute. We used two sets of CH₄ primary standard gases with mole fractions assigned based on the World Meteorological Organization (WMO) CH₄ mole fraction scale maintained by the National Oceanic and Atmospheric Administration to test the performance of the new WS-CRDS calibration system. Our results showed high repeatability (0.06 nmol mol⁻¹) and reproducibility (0.07 nmol mol⁻¹) of measurements and good linearity against the WMO CH₄ mole fraction scale. The CH₄ calibration results for the new system agree well with those of the previous JMA calibration system, which employed a gas chromatograph with a flame ionization detector (GC/FID). These tests indicate that the new WS-CRDS CH₄ calibration system at JMA will provide results that are consistent with those of the previous GC/FID system but with precision that is one order of magnitude higher. We also evaluated the stability and consistency of the JMA calibrations over the past 10 years by examining data from the World Calibration Centre (WCC) Round Robin comparison experiments in Asia and the regions in the southwest Pacific. The results of our study clearly demonstrate that the new calibration system will provide more precise CH₄ measurements and improved traceability to the WMO scale of atmospheric CH₄ measurements for the JMA/WCC comparisons.

1. Introduction

During the past four decades, precise and systematic measurements of atmospheric methane (CH₄) by global observation networks have been collected from ground-based stations (e.g., Simpson *et al.*, 2006; Rigby *et al.*, 2008; Dlugokencky *et al.*, 2009), ships (e.g., Matsueda *et al.*, 1993, Terao *et al.*, 2011), and aircraft (e.g., Umezawa *et al.*, 2012; Sweeney *et al.*, 2015). These long-term observations have clearly shown that although the mean annual rate of increase of atmospheric CH₄ decreased from ~13 nmol mol⁻¹ yr⁻¹ during the early 1980s to near zero during 1999–2006, it began to increase again in 2007 (World Meteorological Organization,

2017). Recent CH₄ isotope studies have attributed the re-growth of atmospheric CH₄ since 2007 to increased microbial CH₄ emissions in the tropics from wetlands, ruminants, and rice paddies (e.g., Nisbet *et al.*, 2016; Schaefer *et al.*, 2016; Morimoto *et al.*, 2017). Because the reasons for such decadal changes of CH₄ emissions are poorly understood, more measurements are needed to resolve the divergence between top-down and bottom-up estimates of the global CH₄ budget (Nisbet *et al.*, 2014).

Global atmospheric measurements can be used in inversion modeling to constrain the spatiotemporal distributions of CH₄ sources and sinks (e.g., Kirschke *et al.*, 2013; Houweling *et al.*, 2017). It is essential to use global observation data in top-down estimations by various inversion methodologies, and for that purpose, atmospheric CH₄ measurements from different laboratories must be merged to produce an integrated global database. However, CH₄ mole fractions measured by different laboratories have been reported to differ by as

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much as $\sim 10 \text{ nmol mol}^{-1}$; this value is considerably larger than the analytical precisions of $\sim 1\text{--}2 \text{ nmol mol}^{-1}$ at individual laboratories (e.g., Matsueda *et al.*, 2004; Dlugokencky *et al.*, 2005; Tsuboi *et al.*, 2017). Careful and regular calibration of measuring devices and comparison of calibration scales among laboratories are fundamental requirements for analyses of global observation data.

The World Meteorological Organization (WMO) Global Atmosphere Watch (GAW) programme coordinates systematic observations and analyses of atmospheric CH_4 and other trace gas species (<http://www.wmo.int/gaw>). Measurement data are posted by WMO/GAW participating laboratories and archived and distributed by the World Data Centre for Greenhouse Gases (WDCGG) at the Japan Meteorological Agency (JMA). The WMO/GAW programme strives to achieve compatibility among participating laboratories of $\pm 2 \text{ nmol mol}^{-1}$ for measurements of CH_4 in well-mixed background air (WMO, 2016); this precision is deemed sufficient for detection of global trends related to climate change. The WMO/GAW requires datasets to be traceable to a common reference. The National Oceanic and Atmospheric Administration (NOAA) Earth System Research Laboratory has developed a gravimetric scale (NOAA04) that has been accepted as the WMO CH_4 mole fraction scale (Dlugokencky *et al.*, 2005). NOAA operates the Central Calibration Laboratory (CCL) for CH_4 , which maintains and distributes the WMO mole fraction scale to GAW partners around the world. The traceability of data from GAW stations to the WMO scale is evaluated at several World Calibration Centres (WCCs).

JMA has been designated the WCC for CH_4 in Asia and the regions of the southwest Pacific and, in collaboration with the NOAA CCL, propagates the WMO CH_4 scale to the GAW network within its WCC jurisdiction. To do this, JMA established a CH_4 calibration system in 2000 (Matsueda *et al.*, 2004) that has been used for regional WCC- CH_4 Round Robin (RR) comparison experiments (details available at <https://ds.data.jma.go.jp/wcc/wcc.html>). In addition, the system has been used to calibrate the CH_4 working standard gases that are used for atmospheric CH_4 measurements at three JMA/GAW stations (Wada *et al.*, 2013), from a C-130 aircraft (Tsuboi *et al.*, 2013; Niwa *et al.*, 2014), and onboard JMA research vessels.

Beginning in 2000, CH_4 standard gas calibrations at JMA were made by using a gas chromatograph equipped with a flame ionization detector (GC/FID) (Matsueda *et al.*, 2004; Tsuboi *et al.*, 2016). However, over the past few years laser-based spectroscopic techniques such as wavelength-scanned cavity ring-down spectroscopy (Crosson, 2008) and cavity-enhanced off-axis integrated cavity output spectroscopy (O'Shea *et al.*, 2013) have become commercially available for measurement of atmospheric CH_4 . These techniques provide higher precision, improved stability, lower maintenance, and easier operation than the GC/FID method. In 2017, JMA replaced their GC/FID CH_4 calibration system with a new

laser-based spectroscopy system. To date, few comparisons of the laser-based spectroscopic and GC/FID techniques have been published (Tsuboi *et al.*, 2013; Rella *et al.*, 2013; Vardag *et al.*, 2014; Flores *et al.*, 2015; Zellweger *et al.*, 2016). It is therefore important to evaluate the compatibility of past GC/FID CH_4 calibrations with those of the new JMA/WCC calibration system.

In this paper, we examine the reliability of JMA's new laser-based spectroscopy CH_4 calibration system for use within the JMA/WCC RR comparison experiment program. First, we describe the new calibration method and the JMA primary standard gases. We then present the results of performance tests we ran on the new system to determine the repeatability and reproducibility, linearity, and traceability of calibrations to the WMO scale. Next, we investigate the consistency of calibration results from the GC/FID and new calibration systems. Finally, we validate the JMA CH_4 calibrations on the basis of the results of the JMA/WCC RR comparison experiments.

2. Calibration method and standards

2.1 Previous and new calibration systems

Two previous reports on the JMA GC/FID CH_4 calibration system (Matsueda *et al.*, 2004; Tsuboi *et al.*, 2016) gave its measurement precision as $\sim 1.2 \text{ nmol mol}^{-1}$. Note that in this study, GC/FID calibration data with standard deviations greater than 2 nmol mol^{-1} ($n = 11$) were excluded.

In collaboration with the Meteorological Research Institute (MRI), JMA developed a new high-precision calibration system for the mole fractions of CH_4 in standard gas samples for JMA/WCC RR comparison experiments and in reference gases for atmospheric measurements of JMA/GAW observations. The main component of the new calibration system is a laser-based spectroscopic instrument in a wavelength-scanned cavity ring-down spectroscopy (WS-CRDS) analyzer (Picarro, Inc., CA, USA; model G2301) for CH_4 and CO_2 (Crosson, 2008), although CO_2 output signals are not recorded during routine CH_4 standard gas calibrations.

Figure 1 shows a plumbing diagram of the new CH_4 calibration system installed at JMA headquarters in Tokyo. It automatically measures CH_4 mole fractions in 12 high-pressure gas cylinders by using a commercially available control unit (CONTEC, Co., Osaka, Japan; model CPU-CA20(FIT)GY) connected to a personal computer installed with custom-made software. For routine JMA calibrations, five primary standard gases in 48-L aluminum high-pressure cylinders are used to measure up to seven gas samples per analytical run. Before introducing the gas sample into the airflow line, a 2-way valve (Fijikin Inc. Japan; model FP-91-6.35) connected to a gas vent line is opened to flush out any remaining gas in the pressure regulator attached to the high-pressure cylinder (Fig. 1).

A stainless steel filter of $2 \mu\text{m}$ mesh size (Swagelok; model

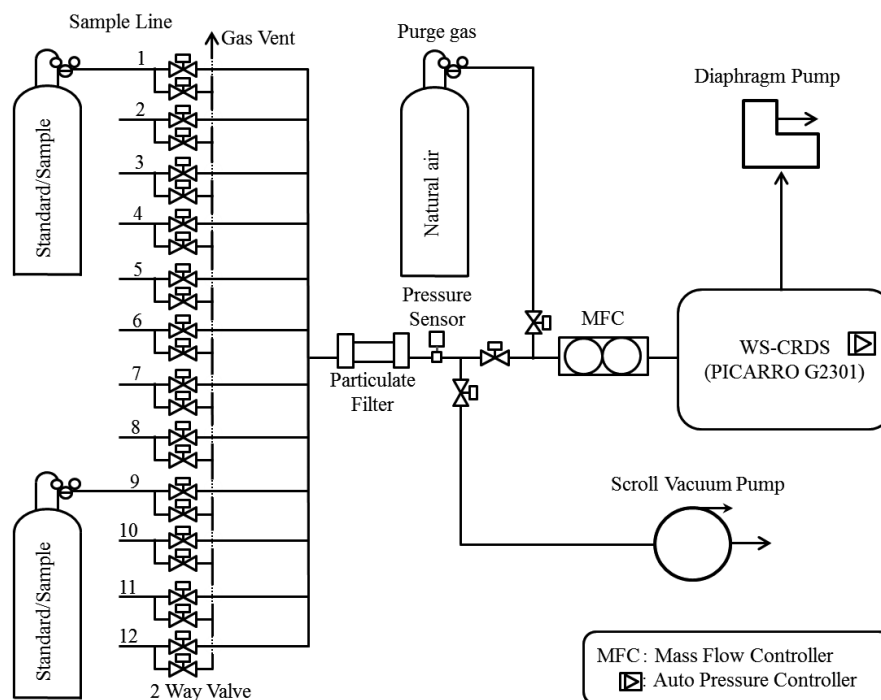


Fig. 1 Schematic of the new WS-CRDS system developed at JMA for calibration of CH_4 standard gases. The analytical procedure for this system is described in detail in the text.

SS-2F-2) and a pressure sensor with a range from -100 to 300 kPa (Nagano Keiki Co., Ltd.; model ZT-60-A3N) are connected to the airflow line. The flow rate into the WS-CRDS analyzer cell is kept constant at $100 \pm 2 \text{ ml min}^{-1}$ by a mass flow controller (Fijikin Inc. Japan; model FCST1005ML-4J2-F200-AIR). To remove water vapor, a bypass airflow line equipped with a cold-trap unit cooled at -60°C by a Stirling cooler (Twinbird Co., Niigata, Japan; model SC-UE15R) is placed upstream of the mass flow controller. The bypass airflow line (not shown in Fig. 1) is not used for calibrations of standard gases with very low water vapor content ($\sim -80^\circ\text{C}$ dew point). Sample pressure within the analyzer cell is maintained at precisely 18.7 kPa by an internal pressure controller, with cell temperature kept at 45°C . Sample flow into the analyzer is kept constant for 10 min to ensure stabilization of the analyzer responses. During the 10 min of sample flow, output signals from the analyzer are recorded at ~ 3 s intervals and the last 1 min of recorded data points are averaged to calculate the CH_4 mole fraction.

After each analysis, the airflow line up to the 2-way valve that precedes the mass flow controller is evacuated by a scroll vacuum pump (Edwards Ltd., UK; model nXDS 10i) for 110 s. To avoid drift of the analyzer signal associated with changes in flow rate and cell pressure (Tsuboi *et al.*, 2013), a pre-prepared purge gas of similar CH_4 mole fraction to that of the dry ambient air is flowed through the mass flow controller and analyzer during evacuation (Fig. 1). This continuous air-supply system by using purge gas is essential for high-precision analysis in the new CH_4 calibration system.

2.2 Standard gases

Because details of the two sets of primary standard gases and their CH_4 mole fractions (Table 1) have been reported elsewhere (Matsueda *et al.*, 2004; Tsuboi *et al.*, 2016), only a brief description is given here. Both sets of primary standard gases were volumetrically prepared in 48 -L aluminum high-pressure cylinders by JMA in cooperation with a Japanese gas company Japan Fine Products (JFP) (formerly Nippon Sanso Corporation, Japan). The CH_4 mole fractions in the primary standard gases range from approximately 1610 to $2160 \text{ nmol mol}^{-1}$, thus covering the natural variability of CH_4 in well-mixed background air. Other reference gases in aluminum high-pressure cylinders were prepared by the same volumetric method JFP for use in the calibration performance tests described in Section 3.

The first and second sets of five primary standard gas cylinders were sent to NOAA in 2006 and 2011, respectively, to determine their CH_4 mole fractions by GC/FID calibration. Their mole fractions were re-calculated according to the updated WMO X2004A scale (updated 7 July 2015). The average change (± 1 SD) due to this scale revision was reported to be $-0.3 \pm 0.3 \text{ nmol mol}^{-1}$ (see https://www.esrl.noaa.gov/gmd/cc1/ch4_scale.html). We downloaded the updated mole fractions of the JMA primary standard gases from the NOAA website (<https://www.esrl.noaa.gov/gmd/cc1/refgas.html>) and compared them with those calibrated on the previous WMO X2004 scale (Table 1). The average difference between the old and new scales was $-0.4 \pm 0.1 \text{ nmol mol}^{-1}$ for the 10 primary standard gases, which is similar to the aforementioned

Table 1. Details of JMA's two sets of the primary standard gases and their CH₄ mole fractions calibrated on the WMO X2004 (NOAA04) and X2004A scales.

Cylinder ID	Cylinder Volume L	Preparation Date	Calibration Date at CCL of NOAA	X2004 Scale (A) nmol mol ⁻¹	Sdev nmol mol ⁻¹	X2004A Scale (B) nmol mol ⁻¹	Scale Difference (B)–(A) nmol mol ⁻¹
First-set Primary Standard Gases							
CQB11442	48	NOV 8, 1999	SEP 19–OCT 3, 2006	1621.94	0.38	1621.52	–0.42
CQB11443	48	NOV 8, 1999	SEP 13–25, 2006	1749.77	0.51	1749.31	–0.46
CQB11444	48	NOV 8, 1999	SEP 13–28, 2006	1867.19	0.19	1866.70	–0.49
CQB11446	48	NOV 15, 1999	SEP 13–28, 2006	1982.57	0.43	1982.06	–0.51
CQB11447	48	NOV 15, 1999	SEP 19–OCT 2, 2006	2108.48	0.28	2107.93	–0.55
Second-set Primary Standard Gases							
CQB18737	48	MAR 7, 2011	NOV 17–28, 2011	1611.65	0.20	1611.38	–0.27
CQB18738	48	MAR 7, 2011	OCT 27–NOV 14, 2011	1760.51	0.16	1760.21	–0.30
CQB18739	48	MAR 7, 2011	OCT 27–NOV 14, 2011	1898.07	0.91	1897.75	–0.32
CQB18740	48	MAR 7, 2011	OCT 27–NOV 14, 2011	2030.35	0.10	2030.01	–0.34
CQB18741	48	MAR 7, 2011	NOV 17–28, 2011	2165.00	0.30	2164.63	–0.37

value reported by NOAA. In this study, we used CH₄ mole fractions revised according to the updated WMO X2004A scale, with the exception of the JMA/WCC results discussed in Section 3.5, which have not yet been updated.

2.3 WCC Round Robin comparison experiments

JMA organized four rounds of the CH₄ RR comparison experiments from 2001 to 2016 as part of the JMA/WCC-CH₄ activities in Asia and regions of the southwest Pacific; the fifth and sixth rounds are still in progress. This WCC program has collaborated with the Inter-Comparison Experiment for Greenhouse Gases Observation (iceGGO) project in Japan since 2012 (Tsuboi *et al.*, 2017). Details of the JMA/WCC RR experiments and their results are available from the WCC website (<https://ds.data.jma.go.jp/wcc/wcc.html>). In the RR experiments, two cylinders of reference gas with different CH₄ mole fractions are circulated in turn to participating laboratories for measurement of their mole fractions; the measured values are then reported to the WMO/GAW Secretariat.

Twelve laboratories have participated in the RR experiments: the China Meteorological Administration, the Commonwealth Scientific and Industrial Research Organization (Australia), the Indian Institute of Tropical Meteorology, the Korea Meteorological Administration (South Korea), the Korea Research Institute of Standards and Science (South Korea), the National Institute of Water and Atmospheric Research Ltd. (New Zealand), the NOAA/Earth System Research Laboratory (United States), the National Institute of Advanced Industrial Science and Technology (Japan), the Meteorological Research Institute (Japan), the National Institute for Environmental Studies (Japan), the National Institute of Polar Research (Japan), and Tohoku University (Japan).

It should be noted that several measurements from the RR program that have been posted on the WCC website are

preliminary and will be revised in the future. Because we used only statistics derived from the JMA/WCC RR results to evaluate the JMA calibration, individual measured values from each laboratory are not identified here.

3. Results and discussion

3.1 Analytical procedure

In the new calibration system, the output signals of CH₄ from the WS-CRDS analyzer, pressure and temperature inside the analyzer cell, and pressure and flow rate in the airflow line are measured at about 3 s intervals. Figure 2 shows an example of the WS-CRDS CH₄ output signals for the second set of five primary standard gases and five sample gases measured at a flow rate of 100 ml min⁻¹. To calibrate the sample gases, the five primary standard gases were introduced before and after five successive sample gas analyses. This frequency of introduction of the primary standard gases is sufficient to precisely calibrate the sample gases because WS-CRDS analyzer drift was negligible within this time interval. For routine JMA operations, this analysis is repeated five times to obtain five measured CH₄ mole fractions for each sample gas cylinder. We then calculate the average of the five measurements and their standard deviation to get one calibration result.

Each analysis run for a sample gas or a primary standard gas takes 11.8 min (710 s); evacuation and purge of the airflow line takes 1.8 min, and the sample or standard gas is flowed through the WS-CRDS analyzer for 10 min. When the output CH₄ signals from the analyzer are averaged every 1 min, we find no significant fluctuations (less than ±0.2 nmol mol⁻¹) during the last 3 min of the 10 min of sample flow. The high flow rate (100 ml min⁻¹) we used was chosen to ensure stabilization of the analyzer signal within 10 min. Note that a lower flow rate, for instance 50 ml min⁻¹, cannot

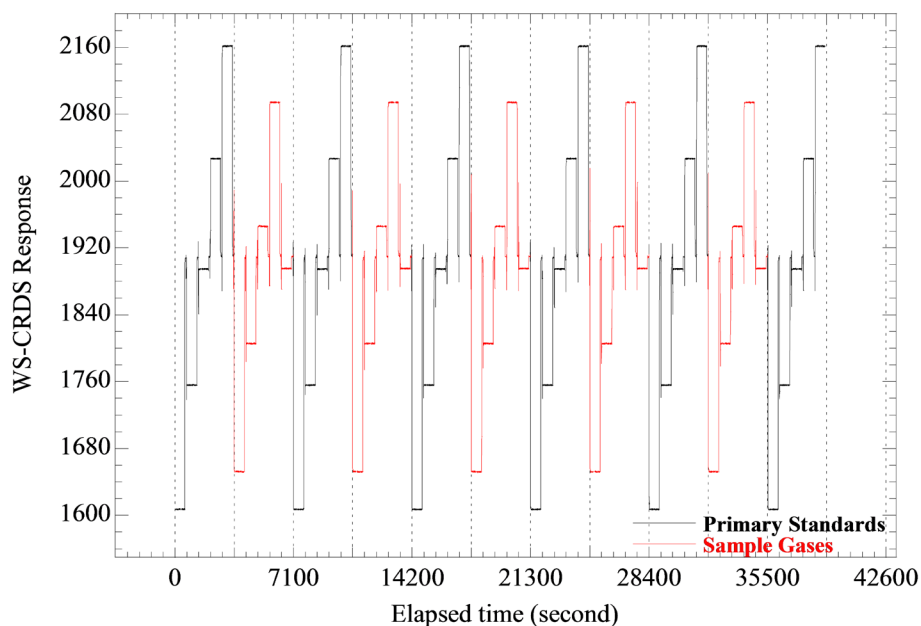


Fig. 2 Example of a time series of CH_4 output signals from the WS-CRDS analyzer of the new calibration system for analyses of five primary standard gases and five sample gases.

stabilize the analyzer signal within 10 min. After completion of each sample flow, the purge gas is introduced into the analyzer during the 1.8 min evacuation step. Peaks appear in the WS-CRDS response curves at the introduction of the purge gas for each analysis run (at $1920 \text{ nmol mol}^{-1}$; Fig. 2). Water vapor (H_2O) output signals from the WS-CRDS analyzer showed very low H_2O content ($<0.005\%$) for all of the primary standard gases and sample gases, which strongly suggests that the H_2O content had no significant influence on our analyses (Chen *et al.*, 2010).

3.2 Analytical precision

Figure 3 shows the frequency distribution of SDs for five repetitive measurements of CH_4 with the new WS-CRDS system for several reference gas samples calibrated during March–October in 2017. 88% of the SDs were less than $0.1 \text{ nmol mol}^{-1}$; SDs larger than $0.16 \text{ nmol mol}^{-1}$ were obtained for only 3 of the 199 calibrations done. We evaluated the measurement repeatability of the new calibration system to be $0.06 \text{ nmol mol}^{-1}$ (median of the SDs). Thus, the introduction of the WS-CRDS calibration system at JMA improved the repeatability of CH_4 standard gas calibrations conducted there by one order of magnitude, compared with the previous GC/FID with the repetitive analytical precision of $\sim 1.2 \text{ nmol mol}^{-1}$ (Matsueda *et al.*, 2004).

We also evaluated the measurement reproducibility of the new calibration system by comparing the CH_4 mole fractions of reference gases measured from the same cylinder on two consecutive days. Figure 4 shows the frequency distribution for the differences of 111 pairs of measurements of CH_4 mole fraction (range, 1530 to 2210 nmol mol^{-1}) collected from

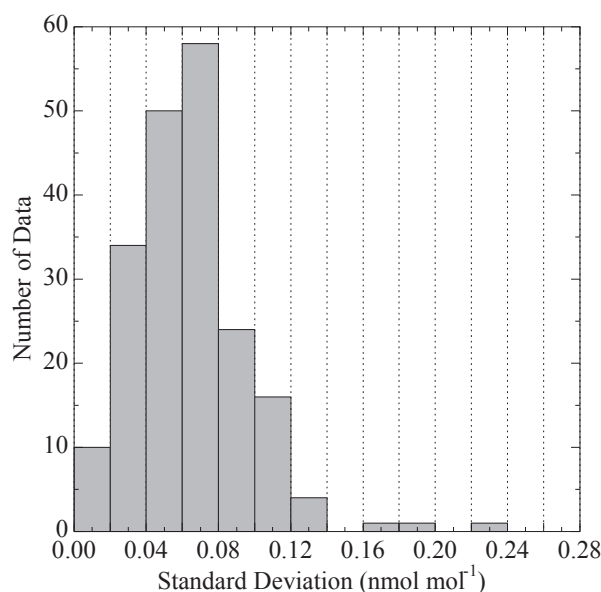


Fig. 3 Frequency distribution of standard deviations for five repetitive measurements of CH_4 mole fractions in one calibration run using the new WS-CRDS calibration system during March–October 2017.

calibrations during April 2017–March 2018. 98% of the pairs agreed within $0.25 \text{ nmol mol}^{-1}$, although two pairs differed by $0.53 \text{ nmol mol}^{-1}$. Exclusion of outliers ($>0.25 \text{ nmol mol}^{-1}$) gave a measurement reproducibility for the new calibration system of $0.07 \text{ nmol mol}^{-1}$ (mean of 109 pair differences). Note that if a difference between a pair of measurements of $>0.25 \text{ nmol mol}^{-1}$ is obtained during routine operations at JMA, an additional measurement is made. Investigation of

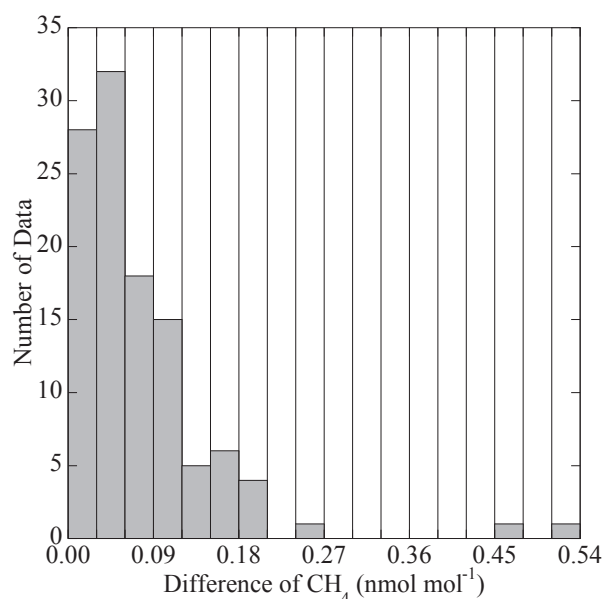


Fig. 4 Frequency distribution of differences of CH_4 mole fractions for pairs of measurements made on consecutive days by the new WS-CRDS calibration system.

the differences of 22 pairs of measurements separated by longer time intervals (2–11 months) gave a slightly higher measurement reproducibility (mean of $0.08 \text{ nmol mol}^{-1}$), but all of the results were $<0.3 \text{ nmol mol}^{-1}$. This longer-term reproducibility is not quantitatively verifiable because of possible drift of CH_4 content in the gas cylinders. More experimental data are needed to evaluate the longer-term reproducibility of the new calibration system.

3.3 Linearity of the WS-CRDS calibration system

To examine the linearity of the WS-CRDS calibration system we compared the CH_4 output signals for the five primary standard gases to the CH_4 mole fractions of the WMO X2004A scale assigned to the second set of five primary standard gases (Fig. 5). In this analysis we used averaged values from five repetitive measurements of one calibration result for which the SD was $<0.1 \text{ nmol mol}^{-1}$. The residuals of the measured values with respect to the linear fit curve were 0.1 – $0.5 \text{ nmol mol}^{-1}$ (Fig. 5, lower panel). Similar residuals were determined from the linear fit curves for an additional 16 repeat calibration measurements. Because the stability of the CH_4 contents in all of the primary gas cylinders has been carefully monitored since 2011 (Tsuboi *et al.*, 2016), we are confident that these deviations do not represent drift of the standard CH_4 mole fractions. Rather, they suggest that there may be internal inconsistencies of the assigned mole fractions among the five primary standards because of the greater analytical uncertainty (precision of $\sim 1.2 \text{ ppb}$) of the GC/FID calibrations by NOAA (Dlugokencky *et al.*, 2005). Nonetheless, the deviations we measured are one order magnitude lower than the WMO CH_4 measurement compatibility goal

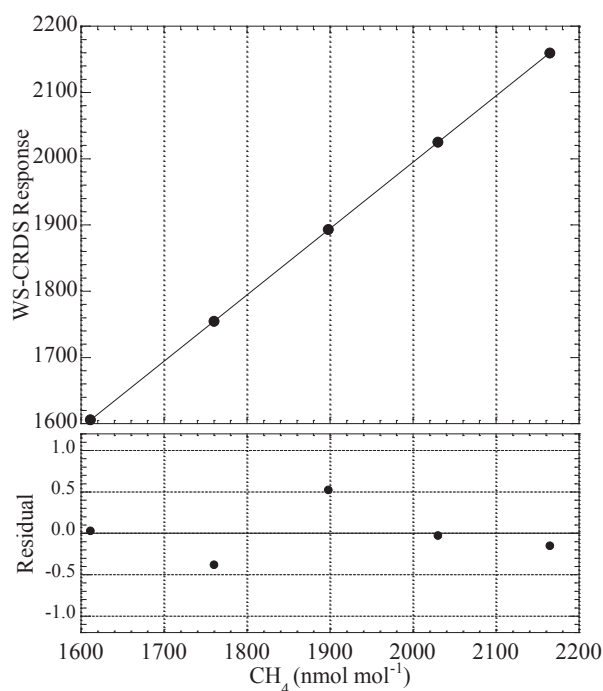


Fig. 5 WS-CRDS analyzer responses versus CH_4 mole fractions assigned on the WMO mole fraction scale of the second-set primary standards. Measurements were made by using the WS-CRDS calibration system on 31 March 2017. The solid line represents the linear least-squares fit to all the data points. Residuals of the fit are plotted in the lower panel.

of $\pm 2 \text{ nmol mol}^{-1}$. Thus, we are confident that the new WS-CRDS calibration system improves our ability to precisely evaluate the internal consistency of the current standard CH_4 mole fractions.

3.4 Comparison of previous and new calibrations

We examined the consistency of standard gas calibration results for the previous GC/FID system with those of the new WS-CRDS systems by comparing time series from 2011 to 2017 of their CH_4 calibrations. Figure 6 shows an example of calibration results for two reference gases (cylinders CPB31288 and CPB31289). We examined three categories of CH_4 calibrations: (1) GC/FID system calibrations with first-set primary standards, (2) GC/FID system calibrations with second-set primary standards, and (3) WS-CRDS system calibrations with second-set primary standards. All of the measured mole fractions are on the same WMO X2004A scale.

JMA changed from first-set to second-set primary standard gases for routine GC/FID calibrations in April 2014, after which the first-set standards were occasionally used for comparison until the end of 2016. The record of GC/FID calibrations with first-set standards shows relatively consistent mole fractions for both reference gases during the 6 years from 2011 to 2016 (Fig. 6). The variability of measurements during that period was within the WMO CH_4 measurement com-

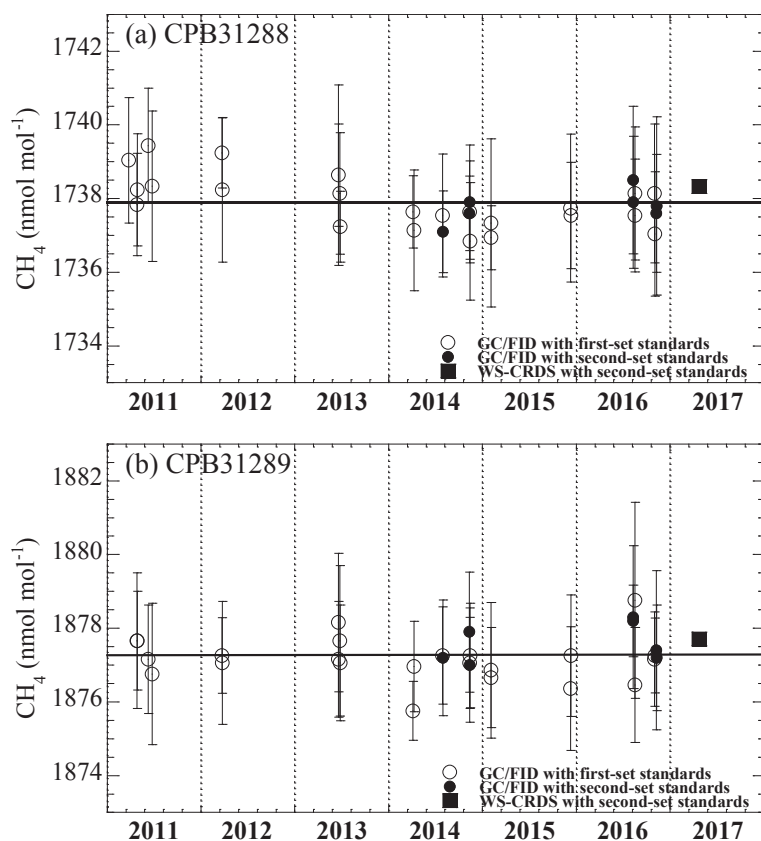


Fig. 6 Comparison of CH_4 mole fractions of reference gas cylinders (a) CPB31288 and (b) CPB31289 measured by JMA's GC/FID calibration system with first- and second-set standard gases and by the WS-CRDS calibration system with second-set standard gases. Error bars show standard deviations of the calibration measurements. The solid horizontal lines represent the average CH_4 mole fractions of all measurements by the GC/FID calibration system from 2011 to 2016.

patibility goal of $\pm 2 \text{ nmol mol}^{-1}$, indicating that the GC/FID calibration system at JMA was well maintained and there were no significant drifts for either the primary standards or the reference gases. Calibration results obtained by the GC/FID system after April 2014 with the second-set primary standards were consistent with those previously obtained with the first-set standards for both reference gases. These results indicate that the two sets of the primary standards have provided consistent and unbiased calibration results.

Measurements of the two reference gases that used the WS-CRDS calibration system with the second-set primary standards in 2017 (Fig. 6) obtained CH_4 mole fractions of $1738.33 \pm 0.05 \text{ nmol mol}^{-1}$ for cylinder CPB31288 and $1877.71 \pm 0.02 \text{ nmol mol}^{-1}$ for cylinder CPB31289. These results agree well with those obtained by GC/FID calibration, which averaged $1737.9 \pm 1.6 \text{ nmol mol}^{-1}$ ($n = 31$) and $1877.3 \pm 1.6 \text{ nmol mol}^{-1}$ ($n = 30$) for cylinders CPB31288 and CPB31289, respectively. The differences between the two calibration methods ($< 0.4 \text{ nmol mol}^{-1}$) were statistically insignificant given the greater measurement uncertainty of the GC/FID calibration system.

We measured another 13 reference gases with the WS-CRDS calibration system to allow comparison with past measurements by the GC/FID calibration system. The CH_4

mole fractions for all 15 reference gases covered the range from 1600 to 2200 nmol mol^{-1} . The GC/FID mole fraction used to determine the difference between the WS-CRDS and GC/FID mole fractions obtained for each reference gas was calculated by using the average value for all calibrations by the GC/FID method. The differences between the results of the two calibration methods for the 15 reference gases ranged from -0.35 to $+0.57 \text{ nmol mol}^{-1}$ (Fig. 7) and showed no dependency on CH_4 mole fraction. These results indicate consistency of standard gas calibrations by both methods with a combined analytical uncertainty of ± 0.4 to $\pm 1.3 \text{ nmol mol}^{-1}$ (Fig. 7). The average of the differences for all the reference gas measurements was $+0.21 \pm 0.27 \text{ nmol mol}^{-1}$ ($n = 15$), indicating a small but statistically insignificant positive bias. These results strongly suggest that instrument bias of the WS-CRDS analyzer caused by the isotope effect (e.g., Chen *et al.*, 2010) and the pressure-broadening effect (e.g., Nara *et al.*, 2012) were minimal. We attribute the instrument bias mainly to differences in the isotopic compositions of the CH_4 and matrix gases (N_2 , O_2 , Ar) of the samples and standards. However, the similarity of the compositions of the reference and standard gases used in this study likely reduced the influence of WS-CRDS instrument biases (Tsuboi *et al.*, 2013).

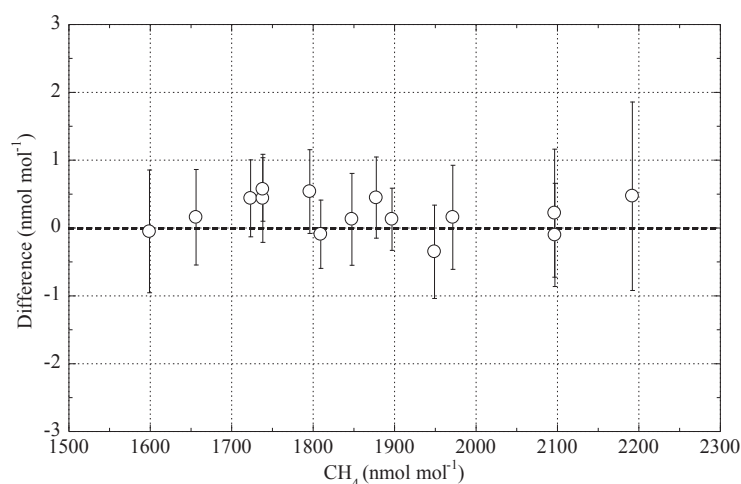


Fig. 7 Differences between CH_4 mole fractions measured by the WS-CRDS and GC/FID calibration systems for 15 reference cylinders with mole fractions covering the range 1600–2200 nmol mol^{-1} . Error bars show combined measurement uncertainty calculated from the standard deviations of both calibration measurements.

3.5 WCC Round Robin comparison results

The JMA/WCC RR comparison allows evaluation of the long-term performance of calibrations by JMA and other participating laboratories and their consistent traceability to the WMO mole fraction scale by comparison of direct measurements of reference gas samples from the same cylinders. We examined the results of the second, third, and fourth rounds of the JMA/WCC RR experiments, which were carried out between 2006 and 2016. We did not use the first round results (2001–2005) because at that time the WMO CH_4 scale had not been established.

The historical differences (2006–2016) of the CH_4 mole fractions measured by participating laboratories from those measured by JMA for gas from two RR cylinders (one with CH_4 mole fraction 1650–1750 nmol mol^{-1} , the other with CH_4 mole fraction 1850–1880 nmol mol^{-1}) are shown in Figure 8. Measurements of samples from the two cylinders by the JMA calibration system before and after one round experiment showed no significant drift of the CH_4 mole fraction. These JMA measurements were averaged for the comparisons with the CH_4 mole fractions measured by the other laboratories. It is noted that some of the JMA measurements on the WMO X2004A scale during the fourth round were re-calculated to unify all of the JMA data on the WMO X2004 scale. The differences of the CH_4 mole fractions measured by participating laboratories from those measured by JMA ranged from $-5.1 \text{ nmol mol}^{-1}$ to $+4.8 \text{ nmol mol}^{-1}$. The averaged combined measurement uncertainties for all participating laboratories was $2.3 \text{ nmol mol}^{-1}$ (with the exception of one measurement which differed from the JMA measurement by $5.4 \text{ nmol mol}^{-1}$), indicating that the calibration systems of all of the laboratories were well maintained over the period from 2006 to 2016.

Measurements by some of the participating laboratories were made on independent CH_4 standard scales. To evaluate

the influence of the different standard scales, we identified the data from laboratories that used the WMO X2004 scale and those from laboratories that used different scales (Fig. 8). Thirty-one of 36 data points from laboratories that based their measurements on the WMO scale lie within the range of the WMO compatibility goal of $\pm 2 \text{ nmol mol}^{-1}$. The five data points outside that range were from the cylinders of reference gases of lower CH_4 content measured in 2008 and 2009; measurements from the higher CH_4 content cylinders in those years were within the compatibility goal. The reason for this discrepancy is unclear, although the JMA calibration system was found to be well maintained during 2008–2009 when other time-series measurements were examined (Tsuboi *et al.*, 2016).

There were more outliers with positive differences greater than 2 nmol mol^{-1} in data from the laboratories that did not use the WMO standard scale. This is clearly evident in the frequency distributions of the data points grouped by standard scale used (Fig. 9). The frequency distributions show average differences ($\pm 1 \text{ SD}$) of $-0.5 \pm 1.5 \text{ nmol mol}^{-1}$ ($n = 36$) between measurements on the WMO standard scale, but differences of $+1.9 \pm 1.9 \text{ nmol mol}^{-1}$ ($n = 28$) for data measured on other standard scales. Kawasaki *et al.* (2016) reported that conversion factors between scales are useful to harmonize data based on markedly different standard scales. Tsuboi *et al.* (2017) converted measurements from all of the Japanese laboratories that used independent standard scales to the WMO scale according to empirical equations that were precisely determined during several inter-comparison experiments of the iceGGO program conducted in Japan from 2012 to 2016. Further comparison experiments are needed to better understand inter-laboratory scale conversions and thus to improve the compatibility of atmospheric CH_4 measurements among different laboratories.

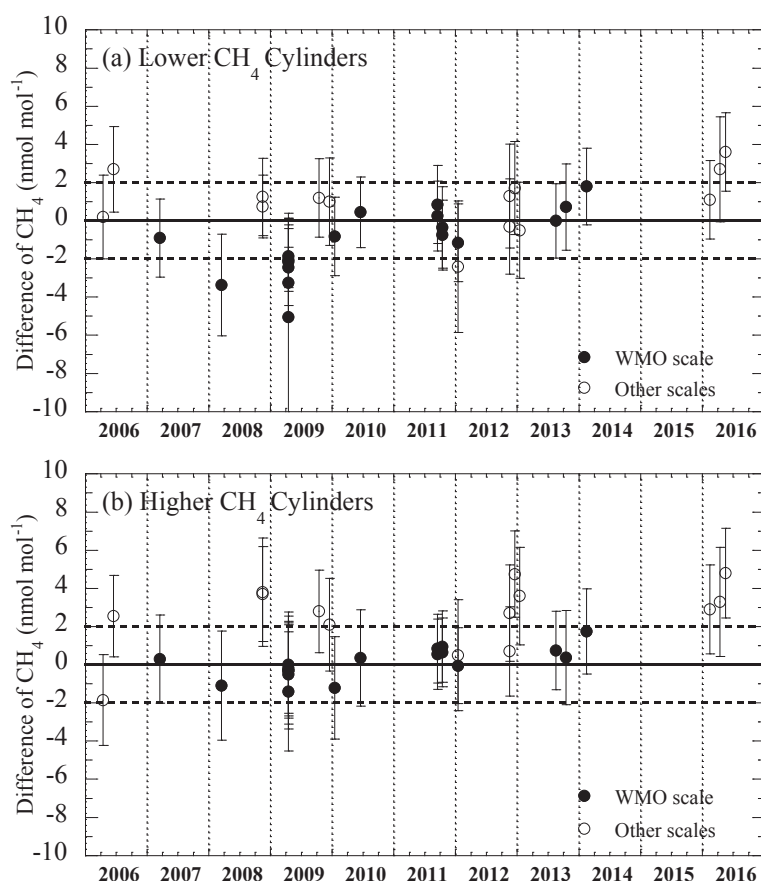


Fig. 8 Results of JMA/WCC Round Robin comparison experiments (2006–2016). Differences of calibrated CH_4 mole fractions determined by participating laboratories from those determined by JMA for (a) a cylinder with a CH_4 mole fraction of 1650–1750 nmol mol⁻¹ (Lower CH_4 cylinder) and (b) one with a CH_4 mole fraction of 1850–1880 nmol mol⁻¹ (Higher CH_4 cylinder). Error bars show the combined measurement uncertainty calculated from the standard deviations of both measurements.

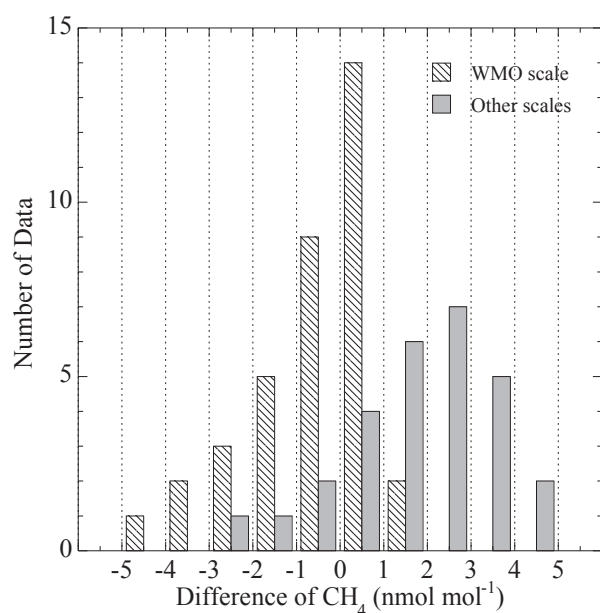


Fig. 9 Frequency distributions of differences of calibrated CH_4 mole fractions determined by participating laboratories from those determined by JMA for the results of JMA/WCC Round Robin comparison experiments (2006–2016). Data from participants who use the WMO mole fraction scale are differentiated from those who use other scales.

4. Summary and conclusions

In collaboration with the MRI, JMA developed a new system for calibration of CH_4 standard gases by using a WS-CRDS analyzer with the intention of replacing the existing GC/FID calibration system. Using two sets of CH_4 primary standard gases assigned according to the WMO CH_4 mole fraction scale, we demonstrated that the WS-CRDS calibration system had high measurement repeatability (0.06 nmol mol⁻¹) and reproducibility (0.07 nmol mol⁻¹) and that replacement of the GC/FID calibration system by the WS-CRDS system would improve the precision of CH_4 standard gas calibrations at JMA by one order of magnitude.

Comparison of calibrations by the new WS-CRDS system with those of the previous GC/FID system at JMA showed good agreement with a mean difference of $+0.21 \pm 0.27$ nmol mol⁻¹ ($n = 15$), well within the WMO compatibility goal of ± 2 nmol mol⁻¹. Thus, we demonstrated that calibrations with the new system are consistent with historic CH_4 calibrations by JMA using the GC/FID system.

Our comparison of CH_4 calibrations by JMA with those made by other laboratories in WCC RR international exper-

iments in Asia and the regions of the southwest Pacific over the past 10 years has demonstrated that the results of the JMA/WCC RR experiments will be useful for assessment of the difference in standard gas scales used by the participating laboratories.

The improvement in the precision of CH₄ standard gas calibrations gained by using the WS-CRDS calibration system at JMA will provide better traceability of atmospheric CH₄ measurements to the WMO mole fraction scale for the ongoing JMA/WCC RR comparison experiments.

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WCC 巡回実験のための JMA における新メタン検定装置の評価

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気象庁（JMA）はメタン標準ガス検定装置の更新のために、レーザー光を用いた波長スキャンキャビティリングダウン分光法（WS-CRDS）を導入した新たな検定装置を気象研究所と共同で開発した。検定に用いる JMA の一次標準ガスは 2 組準備し、それらのメタン濃度は米国海洋大気庁において世界気象機関（WMO）のスケールで値付けされた。WS-CRDS を用いた新検定装置の性能試験を実施した結果、0.06 nmol mol⁻¹ の高い繰り返し測定精度（repeatability）を有し、検定の再現性（reproducibility）は 0.07 nmol mol⁻¹ と評価された。また、検定装置の高い直線性も確認された。新検定装置で得られる検定結果は、水素炎検出器を備えたガスクロマトグラフを用いた旧型検定装置と良い一致を示した。WMO の全球大気監視計画（GAW）の基で、JMA が過去 10 年間にアジア・南西太平洋地域を対象として実施してきた全球大気監視校正センター（WCC）の巡回比較実験の結果を調査した。その結果、JMA/WCC 実験は、この地域の GAW 観測所の大気測定に対する WMO スケールのトレーサビリティを確認するために有効であり、新検定装置によりスケールをより正確に評価できることが検証された。