

Research Infrastructure Quality Assurance

GAW Report No. 263

Report of the Fifth Methane Reference Gas Inter-comparison Experiment for Japan from 2018 to 2019

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World Calibration Centre for methane and the Quality Assurance/Science
Activity Centre for carbon dioxide and methane in Asia and the South-West
Pacific, c/o Japan Meteorological Agency, April 2021



**Report of the Fifth Methane Reference Gas Inter-comparison experiment for Japan,
from 2018 to 2019**

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**Report of the Fifth Methane Reference Gas Inter-comparison experiment for Japan,
from 2018 to 2019**

CONTENTS

1.	INTRODUCTION.....	1
2.	MEASUREMENT METHODS AND RESULTS.....	3
3.	REFERENCES.....	5

Report of the Fifth Methane Reference Gas Inter-comparison experiment for Japan, from 2018 to 2019

1. INTRODUCTION

The Japan Meteorological Agency (JMA) serves as the World Calibration Centre (WCC) for methane (CH₄) and the Quality Assurance/Science Activity Centre (QA/SAC) for carbon dioxide (CO₂) and methane (CH₄) in Asia and the South-West Pacific within the framework of the Global Atmosphere Watch (GAW) Programme of the World Meteorological Organization (WMO). As part of the WMO/GAW quality assurance system, the WCC-JMA has a fundamental role in helping to ensure the traceability of GAW network measurements to the WMO scale through inter-comparison campaigns.

The WCC-JMA organized six rounds of the CH₄ reference gas inter-comparison experiments from 2001 to 2019 to quantify differences among CH₄ standard scales implemented at each participating laboratory as well as to monitor the long-term stability of standard gases in Asia and the South-West Pacific in collaboration with the National Oceanic and Atmospheric Administration (NOAA, WMO/CCL), Commonwealth Scientific and Industrial Research Organisation (CSIRO), National Institute of Water and Atmospheric Research (NIWA), China Meteorological Administration (CMA), Korea Meteorological Administration (KMA)/National Institute of Meteorological Sciences (NIMS), Korea Research Institute of Standards and Science (KRISS), Indian Institute of Tropical Meteorology (IITM), Meteorological Research Institute (MRI), National Institute for Environmental Studies (NIES), National Institute of Advanced Industrial Science and Technology (AIST), National Institute of Polar Research (NIPR), Tohoku University (TU), and Japan Agency for Marine-Earth Science and Technology (JAMSTEC); the sixth round is currently in progress (Table 1).

**Report of the Fifth Methane Reference Gas Inter-comparison experiment for Japan,
from 2018 to 2019**

Table 1. List of Methane Reference Gas Inter-comparisons organized by WCC-JMA

Round-Robin #	Region	Experimental period
1	Asia	2001/04 ~ 2001/11
	South-West Pacific	2002/04 ~ 2003/12
	Japan	2004/09 ~ 2005/03
2	Asia	2005/07 ~ 2006/08
	South-West Pacific	2006/12 ~ 2008/08
	Japan	2009/06 ~ 2010/01
3	Asia	2008/05 ~ 2009/07
	South-West Pacific	2010/04 ~ 2011/02
	Japan	2012/10 ~ 2013/02
4	Asia	2011/06 ~ 2012/03
	South-West Pacific	2013/06 ~ 2014/04
	Japan	2015/12 ~ 2016/08
5	Asia	2014/07 ~ 2016/11
	South-West Pacific	2018/01 ~ 2018/09
	Japan	2018/09 ~ 2019/04
6	Asia	2018/01 ~ 2019/09

In the 5th round-robin inter-comparison for Japan, two reference gas cylinders were circulated in turn to JMA, JAMSTEC, TU, AIST, NIES, MRI, and JMA during September 2018 to April 2019. Table 2 provides details about the cylinders used in this round-robin experiment. Two cylinders were commercially available CH₄ standard gases, which were filled by Japan Fine Products (JFP; formerly Nippon Sanso Corporation, Japan). These two gas samples were prepared using purified natural air as the matrix gas, and the nominal CH₄ mole fractions were 1740 ppb and 1900 ppb.

Table 2. Cylinders used in the 5th Japan round-robin inter-comparison

Cylinder ID	Fill Date	Fill Pressure at 35°C (MPa)	Matrix gas	CH ₄ Nominal value (ppb)	Manufacturer
CPB13002	2014-01-24	11.8	Purified natural air	1740	JFP
CPB13003	2014-01-24	11.8	Purified natural air	1900	JFP

**Report of the Fifth Methane Reference Gas Inter-comparison experiment for Japan,
from 2018 to 2019**

2. MEASUREMENT METHODS AND RESULTS

Table 3 provides details of the CH₄ analytical methods used by each laboratory. WCC-JMA, JAMSTEC and MRI used wavelength-scanned cavity ring-down spectroscopy (WS-CRDS) to measure CH₄ mole fractions, and other laboratories used a gas chromatograph equipped with a flame ionization detector (GC/FID). WCC-JMA and JAMSTEC reported their measurements on the WMO CH₄ X2004A scale, and other laboratories adopt their own scales.

Table 3. Methods, instruments, and calibration scales used by each laboratory

Laboratory	Method	Instrument	Calibration Scale	Range of calibration gases (ppb)
WCC-JMA	CRDS	Picarro G2301	WMO CH ₄ X2004A	1611.38 ~ 2164.63
JAMSTEC	CRDS	LGR GGA-30r-EP	WMO CH ₄ X2004A*	1611.05 ~ 2119.54
TU	GC/FID	Agilent 6890	TU 1987 Scale	896.1 ~ 2500.4
AIST	GC/FID	GC-14BPF (SHIMADZU)	AIST Scale	1006.5 ~ 2534.0
NIES	GC/FID	Agilent 7890A	NIES 94 CH ₄ scale	1310.62 ~ 2486.92
MRI	CRDS	Picarro G1301	MRI Scale	1598.7 ~ 2102.1

* Calibrated by JMA primary standards

Table 4 lists the CH₄ mole fractions measured by each laboratory. WCC-JMA measurements showed that the differences in CH₄ between the beginning and end of the experiment for both cylinders were less than 0.1 ppb. Thus, no correction for drift during the experimental period was applied to the CH₄ values reported by the laboratories.

Table 4. CH₄ mole fractions measured by each laboratory

Laboratory	Measurement Date	CPB13002			CPB13003		
		Mole fraction (ppb)	SD (ppb)	ND	Mole fraction (ppb)	SD (ppb)	ND
WCC-JMA	05 Sep. 2018	1738.33	0.10	5	1897.09	0.05	5
JAMSTEC	18 Oct. ~ 22 Oct. 2018	1738.69	0.27	2	1897.35	0.30	2
TU	23 Nov. ~ 26 Nov. 2018	1739.6	1.4	26	1898.5	2.3	28
AIST	18 Dec. ~ 19 Dec. 2018	1741.4	0.88	16	1899.9	1.52	17
NIES	26 Feb. ~ 04 Mar. 2019	1739.85	0.93	17	1900.87	1.37	17
MRI	27 Mar. 2019	1739.3	0.1	3	1900.2	0.0	3
WCC-JMA	05 Apr. 2019	1738.34	0.03	5	1897.11	0.04	5

SD: Standard deviation, ND: Number of data used for averaging purposes

**Report of the Fifth Methane Reference Gas Inter-comparison experiment for Japan,
from 2018 to 2019**

Figure 1 shows differences between measurements of CH₄ by each laboratory and the WCC-JMA. The measurement uncertainty (σ) in this experiment indicated by the error bars is defined as follows:

$$\sigma = \sqrt{\sigma_{lab}^2 + \sigma_{WCC}^2} \quad (1)$$

where σ_{lab} and σ_{WCC} are the standard deviations reported by each laboratory.

The measurement results of JAMSTEC and WCC-JMA have shown a good agreement with differences of less than 0.4 ppb for two cylinders, whereas the differences between other laboratories and WCC-JMA ranged from 0.96 to 3.77 ppb, mainly due to differences of CH₄ calibration scales.

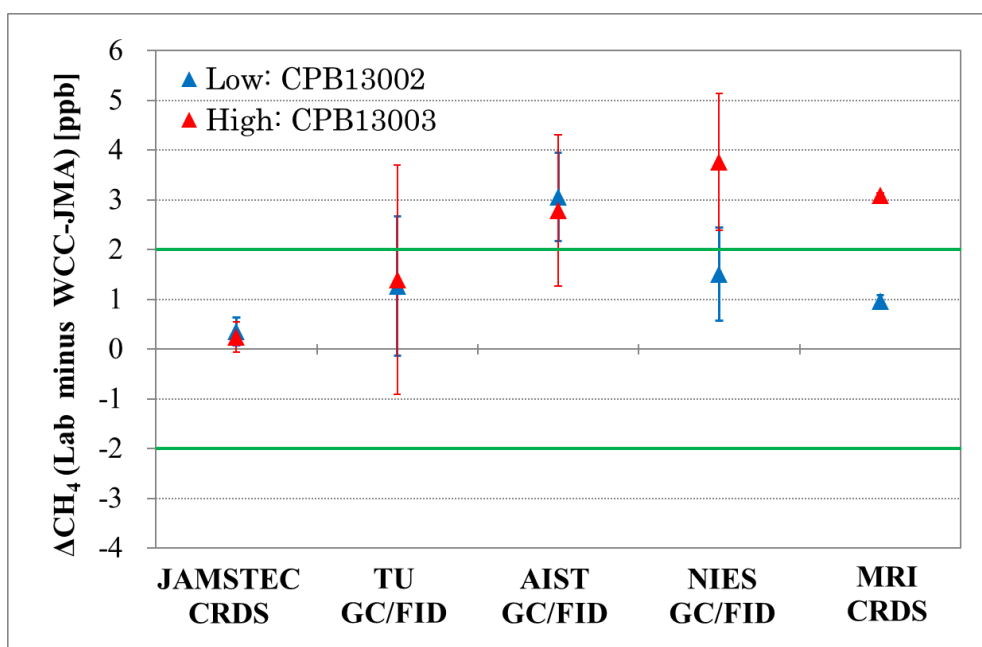


Figure 1. CH₄ differences (Laboratory X minus WCC-JMA) for each cylinder. The mean value of WCC-JMA measurements at the beginning and end of the experiment was used as WCC-JMA results. Error bars are measurement uncertainties calculated from the standard deviations reported by each laboratory [See equation (1)]. The two green lines identify the WMO recommended network compatibility goal (± 2 ppb) for atmospheric CH₄ measurements.

**Report of the Fifth Methane Reference Gas Inter-comparison experiment for Japan,
from 2018 to 2019**

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