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Report of the Sixth Methane Reference Gas Inter-comparison Experiment for Asia from 2018 to 2019

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Research Infrastructure Quality Assurance series

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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

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Chair, Publications Board
World Meteorological Organization (WMO)
7 bis, avenue de la Paix
P.O. Box 2300
CH-1211 Geneva 2, Switzerland

Tel.: +41 (0) 22 730 84 03
Fax: +41 (0) 22 730 81 17
Email: Publications@wmo.int

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

Prepared by

Teruo Kawasaki[1], Atsuya Kinoshita[1], Yousuke Sawa[1], Shuangxi Fang[2], Haeyoung Lee[3], Yogesh K. Tiwari[4]

1. Japan Meteorological Agency (JMA), Tokyo, Japan;
2. China Meteorological Administration (CMA), Beijing, China;
3. Korea Meteorological Administration (KMA)/National Institute of Meteorological Sciences (NIMS), Jeju, Republic of Korea;
4. Indian Institute of Tropical Meteorology (IITM), Pune, India.

Compiled by

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)

If you have any questions, please contact atenv@met.kishou.go.jp

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1. INTRODUCTION

The Japan Meteorological Agency (JMA) serves as the World Calibration Centre (WCC) for methane (CH_4) and the Quality Assurance/Science Activity Centre (QA/SAC) for carbon dioxide (CO_2) and methane (CH_4) 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 CH_4 reference gas inter-comparison experiments from 2001 to 2019 to quantify differences among CH_4 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 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).

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 6th round-robin inter-comparison for Asia, two reference gas cylinders were circulated in turn to JMA, CMA, KMA/NIMS, IITM, and JMA during January 2018 to September 2019. Table 2 provides details about the cylinders used in this round-robin experiment. Two cylinders were commercially available CH_4 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 CH_4 mole fractions were 1 780 ppb and 1 940 ppb.

Table 2. Cylinders used in the 6th Asia round-robin inter-comparison

Cylinder ID	Fill date	Fill pressure at 35°C (MPa)	Matrix gas	CH_4 Nominal value (ppb)	Manufacturer
CPD00241	2017-01–22	11.8	Purified natural air	1 780	JFP
CPD00242	2017-01–22	11.8	Purified natural air	1 940	JFP

2. MEASUREMENT METHODS AND RESULTS

Table 3 provides details of the CH_4 analytical methods used by each laboratory. All participants used wavelength-scanned cavity ring-down spectroscopy (WS-CRDS) to measure CH_4 mole fractions. CMA also measured the cylinders using a gas chromatograph equipped with a flame ionization detector (GC/FID). WCC-JMA, CMA and KMA/NIMS adopt the WMO CH_4 X2004A scale, and IITM adopts the previous WMO CH_4 X2004 scale.

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	1 611.38 ~ 2 164.63
CMA (CRDS)	CRDS	Picarro G2301	WMO CH_4 X2004A	1 645.11 ~ 2 376.29
CMA (GC/FID)	GC/FID	Agilent 6890N	WMO CH_4 X2004A	1 721.92 ~ 2 579.0
KMA/NIMS	CRDS	Picarro G2301	WMO CH_4 X2004A	1 674.25 ~ 2 329.67
IITM	CRDS	Picarro G2201-I	WMO CH4 X2004	1 652.22 ~ 1994.48

Table 4 lists the CH_4 mole fractions measured by each laboratory. WCC-JMA measurements showed that the differences in CH_4 between the beginning and end of the experiment for both cylinders were less than 0.2 ppb. Thus, no correction for drift during the experimental period was applied to the CH_4 values reported by the laboratories.

Table 4. CH_4 mole fractions measured by each laboratory

Laboratory	Measurement date	CPD00241			CPD00242		
		Mole fraction (ppb)	SD (ppb)	ND	Mole fraction (ppb)	SD (ppb)	ND
WCC-JMA	2018-01-10	1 776.49	0.03	5	1 938.19	0.05	5
CMA (CRDS)	2018-04-04	1 775.7	0.13	3	1 938.3	0.06	3
CMA (GC/FID)	2018-04-09	1 775.1	0.2	4	1 937.7	0.3	4
KMA/NIMS	2018-07-25	1 776.23	0.196	120	1 938.3	0.189	120
IITM	2018-10-08	1 779.85	0.50	61	1 941.01	0.49	61
WCC-JMA	2019-09-30	1 776.67	0.08	5	1 938.31	0.06	5

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

Figure 1 shows differences between measurements of CH_4 by each laboratory and the WCC-JMA. The measurement uncertainty (σ) in this experiment indicated by the error bars is defined as follows:

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

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

The inter-comparison results confirmed that the differences between each laboratory and WCC-JMA were within the GAW network extended compatibility goal of ±5 ppb. Results from CMA and KMA/NIMS agree within the GAW network compatibility goal of ±2 ppb.

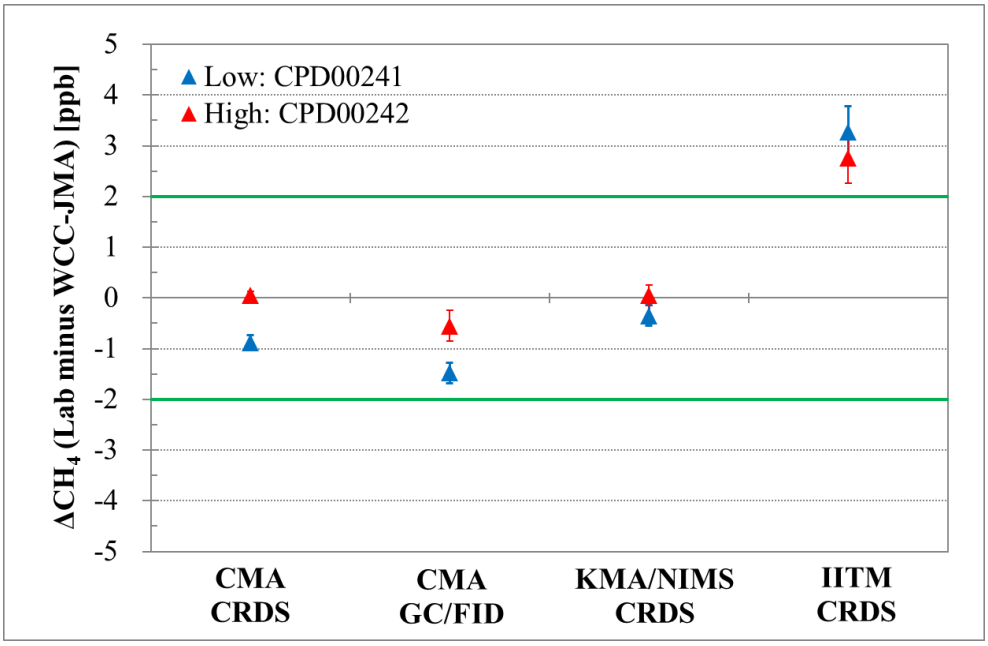

Figure 1. CH_4 differences (Laboratory X minus WCC-JMA) for each cylinder. The mean value of WCC-JMA measurements at the beginning and end of the experiment was used as WCC-JMA results. Error bars are measurement uncertainties calculated from the standard deviations reported by each laboratory [See equation (1)]. The two green lines identify the WMO recommended network compatibility goal (±2ppb) for atmospheric CH_4 measurements.

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For more information, please contact:

World Meteorological Organization

Science and Innovation Department

7 bis, avenue de la Paix – P.O. Box 2300 – CH 1211 Geneva 2 – Switzerland

Tel.: +41 (0) 22 730 81 11 – Fax: +41 (0) 22 730 81 81

Email: GAW@wmo.int

Website: https://public.wmo.int/en/programmes/global-atmosphere-watch-programme

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