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

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Acknowledgements

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TABLE OF CONTENTS

1. INTRODUCTION ........................................................................................................1

2. MEASUREMENT METHODS AND RESULTS.........................................................3

3. REFERENCES ............................................................................................................5
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).
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 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 1 780 ppb and 1 940 ppb.

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

<table>
<thead>
<tr>
<th>Cylinder ID</th>
<th>Fill date (Y-M-D)</th>
<th>Fill pressure at 35°C (MPa)</th>
<th>Matrix gas</th>
<th>CH₄ Nominal value (ppb)</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPD00241</td>
<td>2017-01-22</td>
<td>11.8</td>
<td>Purified natural air</td>
<td>1 780</td>
<td>JFP</td>
</tr>
<tr>
<td>CPD00242</td>
<td>2017-01-22</td>
<td>11.8</td>
<td>Purified natural air</td>
<td>1 940</td>
<td>JFP</td>
</tr>
</tbody>
</table>
2. **MEASUREMENT METHODS AND RESULTS**

Table 3 provides details of the CH₄ analytical methods used by each laboratory. All participants used wavelength-scanned cavity ring-down spectroscopy (WS-CRDS) to measure CH₄ 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 CH₄ X2004A scale, and IITM adopts the previous WMO CH₄ X2004 scale.

<table>
<thead>
<tr>
<th>Laboratory</th>
<th>Method</th>
<th>Instrument</th>
<th>Calibration scale</th>
<th>Range of calibration gases (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WCC-JMA</td>
<td>CRDS</td>
<td>Picarro G2301</td>
<td>WMO CH₄ X2004A</td>
<td>1 611.38 ~ 2 164.63</td>
</tr>
<tr>
<td>CMA (CRDS)</td>
<td>CRDS</td>
<td>Picarro G2301</td>
<td>WMO CH₄ X2004A</td>
<td>1 645.11 ~ 2 376.29</td>
</tr>
<tr>
<td>CMA (GC/FID)</td>
<td>GC/FID</td>
<td>Agilent 6890N</td>
<td>WMO CH₄ X2004A</td>
<td>1 721.92 ~ 2 579.0</td>
</tr>
<tr>
<td>KMA/NIMS</td>
<td>CRDS</td>
<td>Picarro G2301</td>
<td>WMO CH₄ X2004A</td>
<td>1 674.25 ~ 2 329.67</td>
</tr>
<tr>
<td>IITM</td>
<td>CRDS</td>
<td>Picarro G2201-I</td>
<td>WMO CH₄ X2004</td>
<td>1 652.22 ~ 1994.48</td>
</tr>
</tbody>
</table>

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 0.2 ppb. Thus, no correction for drift during the experimental period was applied to the CH₄ values reported by the laboratories.

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

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

\[ \sigma = \sqrt{\sigma_{\text{lab}}^2 + \sigma_{\text{WCC}}^2} \]  

(1)

where \( \sigma_{\text{lab}} \) and \( \sigma_{\text{WCC}} \) 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. 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.](image-url)
3. REFERENCES

Indian Institute of Tropical Meteorology (IITM)


Japan Meteorological Agency (JMA)


