Global Atmosphere Watch
World Calibration Centre for Surface Ozone
Carbon Monoxide and Methane

Laboratory Air Pollution / Environmental Technology

WCC-Empa REPORT 05/4 – Part B

Submitted to the

World Meteorological Organization

SYSTEM AND PERFORMANCE AUDIT

FOR SURFACE OZONE AND METHANE

AT JMA GAW FACILITIES

PART B

JMA CENTRAL CALIBRATION FACILITIES

JAPAN, NOVEMBER 2005

Submitted by

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WMO World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane
Empa Dübendorf, Switzerland

Empa is accredited as a calibration laboratory for ozone measuring instruments in accordance with ISO/IEC 17025

S schweizerischer kalibrierdienstdienst

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swiss calibration service

SCS accreditation-No. SCS 089

CONTENTS

ASSESSMENT AND RECOMMENDATIONS

This report summarises the assessment and recommendations of the first system and performance audit at the Central Calibration Facilities of the Japan Meteorological Agency (JMA). The audit was conducted by WCC-Empa[1] from 28 thru 30 November 2005 in agreement with the WMO/GAW quality assurance system [*WMO*, 2001]. The results of the audit at the Regional GAW station Ryori are published in a separate report and are also part of this audit [*Zellweger, et al.*, 2005].

People present during the audit included

Dr. Christoph Zellweger	Empa Dübendorf, WCC-Empa
Dr. Jörg Klausen	Empa Dübendorf, QA/SAC Switzerland
Mr. Hideyuki Sasaki	JMA, Director of Atmospheric Environment Division
Mr. Kazuhiro Tsuboi	JMA, Head of Greenhouse Gas Observations Section
Mr. K. Umehara	JMA, WCC for Methane
Ms. Hikaru Doi	JMA, Operator (Surface Ozone)

Our assessment of the Central Calibration Facilities for surface ozone and methane at JMA is summarized below. The assessment criteria for the ozone inter-comparison were developed by WCC-Empa and QA/SAC Switzerland [*Hofer, et al.*, 2000; *Klausen, et al.*, 2003].

This report is distributed to JMA and the World Meteorological Organization in Geneva. The executive summaries will be posted on the internet.

The recommendations found in this report are complemented with a priority (*** indicating highest priority) and a suggested completion date.

JMA Calibration Facilities

JMA maintains calibration facilities for surface ozone and methane at the headquarters in Tokyo. JMA also acts as a World Calibration Centre for Methane in Asia and the South-West Pacific and as a Regional Dobson Calibration Centre (RDCC) for Asia.

Recommendation 1 (, 2007)**
The JMA Calibration Facilities are an important contribution to GAW. WCC-Empa encourages JMA to explore the possibility of acting as a Regional Calibration Centre for Surface Ozone.

Recommendation 2 (*, 2007)
The close collaboration between JMA and NIES should be continued. Inter-comparisons between the NIES SRP and the JMA ozone calibrator should be carried out at regular, e.g. yearly intervals.

Management and Operation

All GAW activities of JMA are coordinated by the Global Environment and Marin Department's Atmospheric Environment Division (AED) of JMA. These activities include in addition to the calibration facilities also the World Data Centre for Greenhouse Gases (WDCGG), QA/SAC Japan, and three GAW stations (Minamitorishima, Ryori, Yonagunijima).

[1] WMO/GAW GAW World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane. WCC-Empa was assigned by WMO and is hosted by the Laboratory for Air Pollution and Environmental Technology of the Swiss Federal Laboratories for Materials Testing and Research (Empa). The mandate is to conduct system and performance audits at Global GAW stations every 2 – 4 years based on mutual agreement.

Recommendation 3 (*, on-going)
Japan contributes significantly to the GAW programme of WMO. These contributions are important for GAW and should be continued.

Surface Ozone Calibration Facilities

Instrumentation. The ozone calibration facilities at JMA consist of two ozone calibrators (TEI 49C-PS) and an ozone analyser (TEI 49C). Alternatingly, one of the TEI 49 C-PS is directly compared to the GAW reference at NIST on a yearly basis.

Intercomparison (Performance Audit). The two calibrators of JMA were inter-compared with the WCC-Empa travelling standard. The inter-comparisons of the calibrators extended over a period of 16 hours. The results of the assessment are summarised below and are presented in Figure 1.

TEI 49C-PS #72971-372 (JMA-1):	0 – 90 ppb good agreement	
Unbiased O3 mixing ratio (ppb)	X_{O3} (ppb) = ([OC] + 0.22 ppb) / 0.987	(1a)
TEI 49C-PS #72972-372 (JMA-2):	0 – 90 ppb good agreement	
Unbiased O3 mixing ratio (ppb)	X_{O3} (ppb) = ([OC] + 0.17 ppb) / 0.986	(1b)

Here, [OC] represents surface ozone readings obtained from the JMA ozone calibrators.

The two ozone calibrators of JMA agree extremely well when compared to each other. However, lower readings of approximately 1.1% are observed when compared to WCC-Empa. Approximately 0.4% of this difference may be explained by differences of the WCC-Empa SRP#15 and the GAW reference SRP#2, while the remaining 0.7% cannot be explained.

Recommendation 4 (*, 2006)**
WCC-Empa recommends to perform another inter-comparison between the JMA ozone calibrators and an external references, e.g. NIST SRP#2 or NIES SRP#35. The comparison that was made after the audit at NIST could not explain the remaining difference because the instrument was serviced and the calibration settings were set back before shipment to NIST.

The inter-comparisons at JMA were made without using the JMA external glass manifold. During the inter-comparisons an ozone loss of approximately 0.5% was observed when the external manifold was used. This is most probably due to the design of the manifold.

Recommendation 5 (*, 2006)**
The external glass manifold should be re-designed to avoid ozone loss.

Recommendation 6 (, 2006)**
Direct inter-comparisons of the two ozone calibrators are encouraged. Until now comparisons were made only indirect using the TEI 49C ozone analyser.

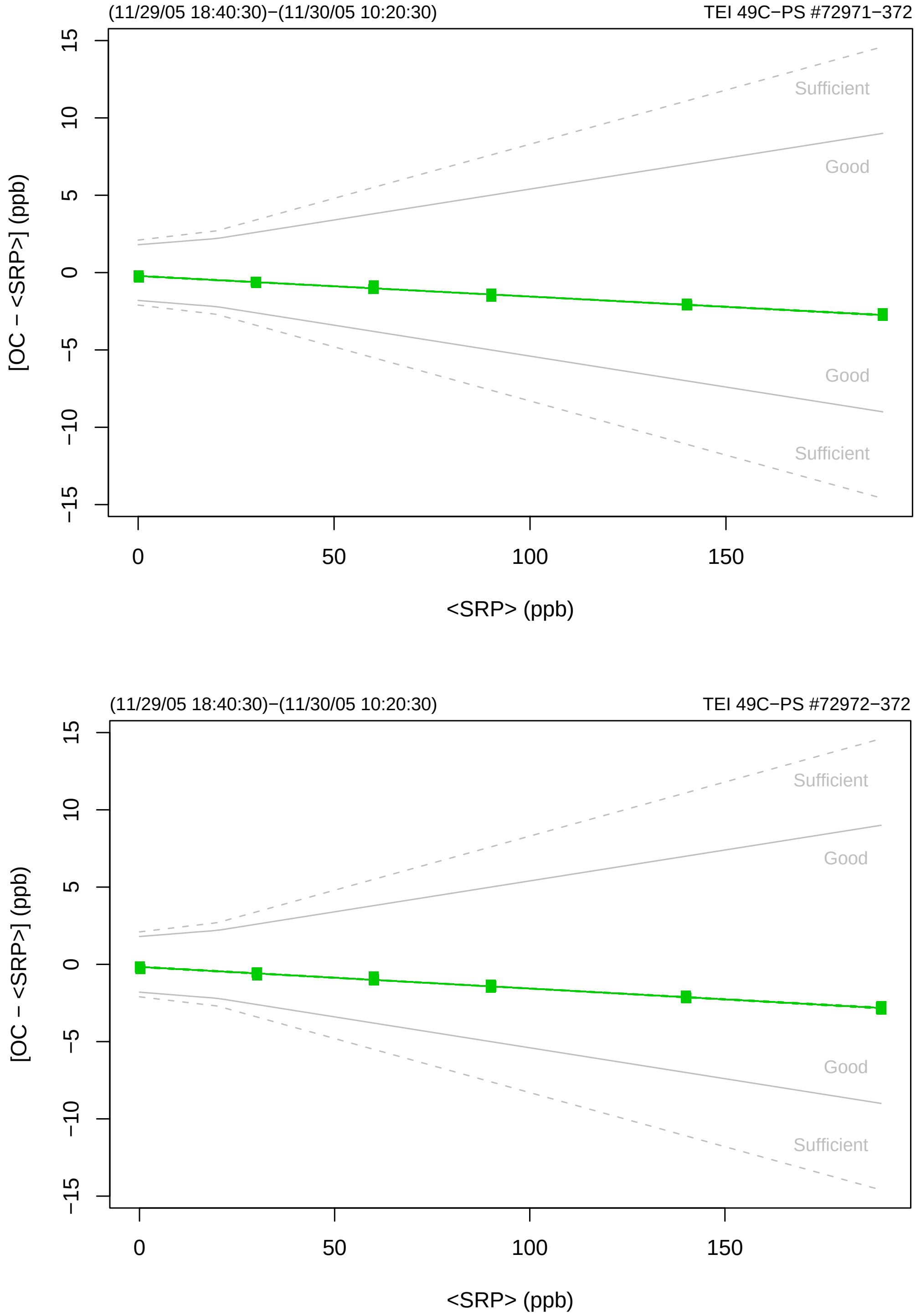

Figure 1. Bias of the JMA ozone calibrators with respect to the SRP as a function of concentration. Each point represents the average of the last 10 one-minute values at a given level. Areas defining 'good' and 'sufficient' agreement according to GAW assessment criteria [*Klausen, et al.*, 2003] are delimited by gray lines. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. Upper panel: TEI 49C-PS #72971-372 (JMA-1), lower panel: TEI 49C-PS #72972-372 (JMA-2).

Methane Calibration Facilities

Instrumentation. JMA operates a GC/FID system for methane calibrations. The system is automated and can easily be used to calibrate laboratory standards. The instrumentation is adequate for the intended purpose.

Standards. Primary gravimetric standards and secondary standards are available at JMA. The primary standards were prepared with the Tohoku University (TU) method. Currently five primary and five secondary standards purchased from Nippon Sanso in 1999 are available and cover the concentration range from 1600 to 2100 nmol/mol. With this equipment, adequate calibration of the methane measurements is possible; however the possibility of a direct link to the NOAA04 methane scale would be preferable.

> **Recommendation 7 (*, 2006-2007)**
> *NOAA/GMD is providing the official methane scale for the GAW programme (NOAA04 scale). JMA is encouraged to maintain traceability of the TU scale to NOAA04. It should be considered to purchase NOAA/GMD methane standards in addition to the available standards from Nippon Sanso.*

Intercomparison (Performance Audit). The inter-comparison involved repeated measurements of WCC-Empa travelling standards with the JMA instrument. In the absence of formal data quality objectives, the results cannot be formally assessed, however, the following equation characterises the instrument bias (cf. Figure 2). The regression was forced through zero.

Unbiased CH_4 mixing ratio (ppb): X_{CH4} (ppb) = $[CH_4]$ / 1.0008 (2)

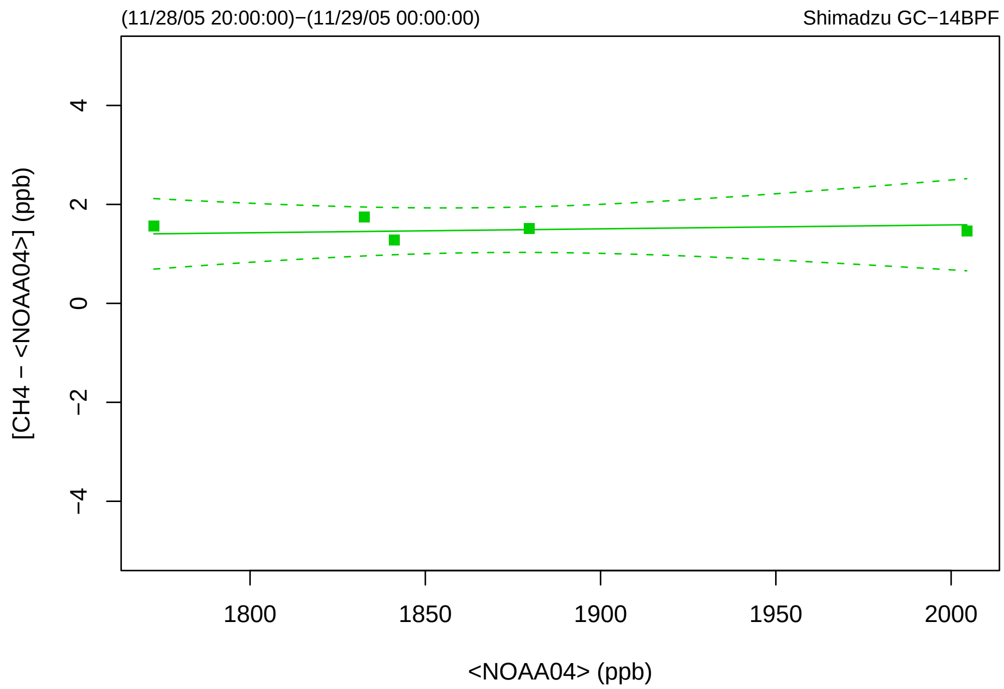

Figure 2. Bias of the JMA methane GC (Shimadzu GC-14BPF) with respect to the NOAA04 reference scale as a function of concentration. Each point represents the average of data at a given level from a specific run. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands.

Data Acquisition and Management

Surface Ozone: The data acquisition consists of a custom made data acquisition system which acquires the digital output of the TEI instruments via RS-232. The system is able to fully control the TEI 49C-PS ozone calibrators, and inter-comparisons can be run automatically. In addition, all relevant instrument parameters are acquired.

Methane: GC control software from Shimadzu is used. Calibrations can be run automatically.

Both data acquisition systems are adequate for the intended purpose.

Conclusions

The JMA calibration facilities contribute significantly to the GAW programme. It should be explored if the activities could be expanded with a Regional Calibration Centre for Surface Ozone in addition to the existing facilities for methane.

Dübendorf, June 2007

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APPENDIX

GAW Calibration Facilities at JMA

Organization and Contact Persons
The JMA calibration facilities are part of the Global Environment and Marine Department's Atmospheric Environment Division (AED). The responsibilities for calibration issues are with QA/SAC Japan (general), the World Calibration Centre for Methane for Asia and South-West Pacific (WCC, calibrations for methane), and the Greenhouse Gas Observation Unit (calibrations for surface ozone). Further details about the organisation of GAW activities in Japan can be found in Part A of this report [*Zellweger, et al.*, 2005].

Surface Ozone Calibration Facilities
The ozone calibration facilities at JMA consist of two ozone calibrators (TEI 49C-PS) and an ozone analyser (TEI 49C). Alternatingly, one of the TEI 49 C-PS is directly compared to the GAW reference at NIST on a yearly basis. A picture of the system is shown in Figure 3.

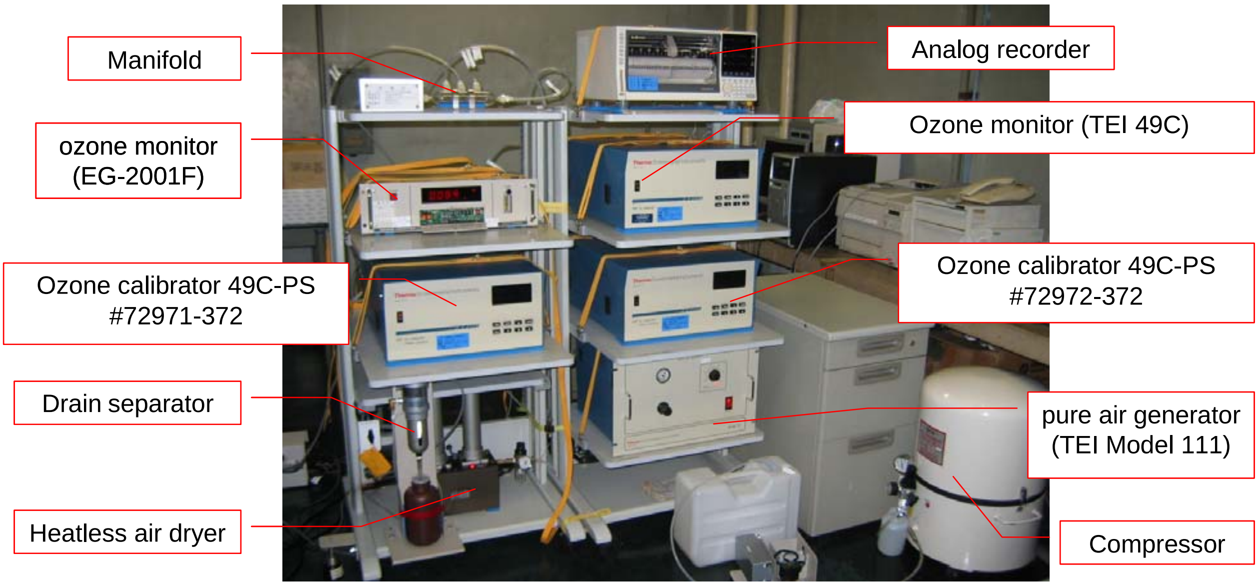


Figure 3. Ozone calibration facilities at JMA

Instrument Set-up and Procedures

Air Conditioning
The laboratories of the JMA calibration facilities are air conditioned. All instruments are installed in the basement of JMA headquarters.

Instrumentation
Two TEI 49C-PS ozone calibrators and a TEI 49C ozone analyser are available. The two ozone calibrators have been modified using a common glass manifold for ozone distribution to other instruments. This manifold was subject to significant ozone loss due to imperfect mixing of the air. It should be re-designed (cf. Recommendation 5).

Data Acquisition and Data Transfer
The custom made data acquisition acquires the digital signals of the ozone calibrators and guest instruments and fully controls the ozone generators of the TEI 49C-PS. Additional instrument parameters can also be acquired.

Inter-Comparison of Ozone Analyzer

All procedures were conducted according to the Standard Operating Procedure [*WMO*, 2006] and included inter-comparisons of the transfer standard with the Standard Reference Photometer at Empa before and after the inter-comparison of the calibrators.

Setup and Connections
Table 1 details the experimental setup during the inter-comparison of the JMA calibrators. The data used for the evaluation was recorded by the JMA data acquisition system. No further corrections were applied to the data.

Table 1. Experimental details of the ozone inter-comparison.

Transfer standard (TS)	Model, S/N	TEI 49C-PS #54509-300 (WCC-Empa)
	Settings	BKG = 0.0; COEFF = 1.012
Ozone calibrator (OC) JMA-1	Model, S/N	TEI 49 C-PS #72971-372
	Principle	UV absorption
	Range	0-1000 ppb
	Settings	BKG +0.1 ppb, COEF 1.008
Ozone calibrator (OC) JMA-2	Model, S/N	TEI 49 C-PS #72972-372
	Principle	UV absorption
	Range	0-1000 ppb
	Settings	BKG +0.2 ppb, COEF 1.006
Ozone source		Internal generator of TS
Zero air supply		Custom built, consisting of: silica gel - inlet filter 5 μm - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 μm (WCC-Empa)
Connection between instruments		Ca. 2.5 meter of 1/4" PFA tubing between TS manifold and OC. The inter-comparison was made without the JMA external glass manifold.
Data acquisition	TS and CO	One minute aggregates from JMA data acquisition
Pressure readings at beginning of inter-comparison (hPa)	Ambient	1011.9 hPa (WCC-Empa reference)
	TS	1011.9 hPa
	OC JMA-1	1012.0 hPa (no adjustments were made)
	OC JMA-2	1011.9 hPa (no adjustments were made)
Levels (ppb)		0, 30, 60, 90, 140, 190
Duration per level (min)		20
Sequence of levels		Repeated runs of randomised fixed sequence
Runs		8 runs (29 thru 30 November, 2005)

Results

Each ozone level was applied for 20 minutes, and the last 10 one-minute averages were aggregated. The results are shown in Table 2 for TEI 49C-PS # 72971-372 and in Table 3 for TEI 49C-PS # 72972-372. These aggregates were used in the assessment of the inter-comparison as described elsewhere *[Klausen, et al., 2003]*. All results refer to the calibration factors as given in Table 1 above. The readings of the transfer standard (TS) were compensated for bias with respect to the Standard Reference Photometer (SRP) prior to the evaluation of the ozone calibrator (OC) values.

Table 2. Ten-minute aggregates computed from the last 10 of a total of 20 one-minute values for the inter-comparison of the JMA ozone calibrator (OC) TEI 49C-PS # 72971-372 (JMA-1) with the WCC-Empa transfer standard (TS).

DateTime (UTC+1)	Run	Level	TS (ppb)	OA (ppb)	Flag[#]	sdTS (ppb)	sdOA (ppb)
2005-11-30 10:25	1	0	0.01	-0.10	0	0.09	0.04
2005-11-30 10:05	1	30	29.98	29.40	0	0.09	0.04
2005-11-30 09:45	1	90	89.91	88.68	0	0.06	0.05
2005-11-30 09:25	1	140	139.88	137.94	0	0.05	0.04
2005-11-30 09:05	1	60	60.04	59.19	0	0.05	0.06
2005-11-30 08:45	1	190	189.82	187.28	0	0.07	0.05
2005-11-30 08:25	2	0	0.12	-0.15	0	0.09	0.03
2005-11-30 08:05	2	60	59.95	59.02	0	0.06	0.03
2005-11-30 07:45	2	30	29.99	29.45	0	0.09	0.04
2005-11-30 07:25	2	90	89.92	88.65	0	0.11	0.05
2005-11-30 07:05	2	190	189.80	187.22	0	0.05	0.09
2005-11-30 06:45	2	140	139.91	138.00	0	0.05	0.05
2005-11-30 06:25	3	0	0.06	-0.12	0	0.07	0.03
2005-11-30 06:05	3	90	89.93	88.62	0	0.09	0.03
2005-11-30 05:45	3	30	30.01	29.49	0	0.08	0.03
2005-11-30 05:25	3	190	189.76	187.23	0	0.04	0.06
2005-11-30 05:05	3	60	60.00	59.08	0	0.08	0.03
2005-11-30 04:45	3	140	139.84	137.96	0	0.09	0.03
2005-11-30 04:25	4	0	0.04	-0.11	0	0.12	0.03
2005-11-30 04:05	4	30	29.95	29.46	0	0.07	0.05
2005-11-30 03:45	4	90	89.91	88.70	0	0.09	0.05
2005-11-30 03:25	4	140	139.85	137.99	0	0.04	0.05
2005-11-30 03:05	4	60	59.98	59.19	0	0.10	0.05
2005-11-30 02:45	4	190	189.79	187.24	0	0.06	0.07
2005-11-30 02:25	5	0	0.07	-0.11	0	0.07	0.03
2005-11-30 02:05	5	60	59.94	59.22	0	0.07	0.04
2005-11-30 01:45	5	30	30.03	29.45	0	0.09	0.05
2005-11-30 01:25	5	90	89.92	88.69	0	0.06	0.03
2005-11-30 01:05	5	190	189.77	187.27	0	0.08	0.04
2005-11-30 00:45	5	140	139.90	137.96	0	0.09	0.05
2005-11-30 00:25	6	0	0.06	-0.15	0	0.11	0.04
2005-11-30 00:05	6	90	89.95	88.67	0	0.06	0.05
2005-11-29 23:45	6	30	30.01	29.51	0	0.09	0.03
2005-11-29 23:25	6	190	189.75	187.30	0	0.08	0.07
2005-11-29 23:05	6	60	59.99	59.06	0	0.09	0.05
2005-11-29 22:45	6	140	139.85	137.92	0	0.11	0.05
2005-11-29 22:25	7	0	0.00	-0.13	0	0.09	0.03
2005-11-29 22:05	7	30	29.99	29.48	0	0.08	0.03
2005-11-29 21:45	7	90	89.94	88.65	0	0.06	0.05
2005-11-29 21:25	7	140	139.84	138.02	0	0.06	0.04
2005-11-29 21:05	7	60	59.99	59.12	0	0.02	0.05
2005-11-29 20:45	7	190	189.79	187.40	0	0.09	0.07
2005-11-29 20:25	8	0	0.04	-0.12	0	0.12	0.03

DateTime (UTC+1)	Run	Level	TS (ppb)	OA (ppb)	Flag#	sdTS (ppb)	sdOA (ppb)
2005-11-29 20:05	8	60	59.92	58.99	0	0.07	0.04
2005-11-29 19:45	8	30	29.99	29.45	0	0.09	0.05
2005-11-29 19:25	8	90	89.91	88.49	0	0.07	0.04
2005-11-29 19:05	8	190	189.74	187.17	0	0.09	0.05
2005-11-29 18:45	8	140	139.84	138.03	0	0.10	0.04

#0: valid data

Table 3. Ten-minute aggregates computed from the last 10 of a total of 20 one-minute values for the inter-comparison of the JMA ozone calibrator (OC) TEI 49C-PS # 72972-372 (JMA-2) with the WCC-Empa transfer standard (TS).

DateTime (UTC+1)	Run	Level	TS (ppb)	OA (ppb)	Flag#	sdTS (ppb)	sdOA (ppb)
2005-11-29 18:45	1	0	0.01	-0.12	0	0.09	0.03
2005-11-29 19:05	1	30	29.98	29.45	0	0.09	0.05
2005-11-29 19:25	1	90	89.91	88.55	0	0.06	0.05
2005-11-29 19:45	1	140	139.87	137.92	0	0.05	0.03
2005-11-29 20:05	1	60	60.03	59.12	0	0.05	0.04
2005-11-29 20:25	1	190	189.82	187.17	0	0.07	0.05
2005-11-29 20:45	2	0	0.12	-0.12	0	0.09	0.04
2005-11-29 21:05	2	60	59.94	59.07	0	0.06	0.05
2005-11-29 21:25	2	30	29.99	29.52	0	0.09	0.04
2005-11-29 21:45	2	90	89.92	88.68	0	0.11	0.07
2005-11-29 22:05	2	190	189.79	187.10	0	0.06	0.05
2005-11-29 22:25	2	140	139.91	137.90	0	0.05	0.06
2005-11-29 22:45	3	0	0.05	-0.05	0	0.07	0.06
2005-11-29 23:05	3	90	89.93	88.65	0	0.09	0.04
2005-11-29 23:25	3	30	30.01	29.59	0	0.08	0.03
2005-11-29 23:45	3	190	189.76	187.14	0	0.04	0.05
2005-11-30 00:05	3	60	60.00	59.16	0	0.08	0.05
2005-11-30 00:25	3	140	139.84	137.93	0	0.09	0.06
2005-11-30 00:45	4	0	0.04	-0.10	0	0.12	0.03
2005-11-30 01:05	4	30	29.94	29.48	0	0.07	0.04
2005-11-30 01:25	4	90	89.91	88.74	0	0.09	0.07
2005-11-30 01:45	4	140	139.84	138.01	0	0.04	0.04
2005-11-30 02:05	4	60	59.98	59.14	0	0.10	0.04
2005-11-30 02:25	4	190	189.79	187.22	0	0.06	0.04
2005-11-30 02:45	5	0	0.07	0.01	0	0.07	0.04
2005-11-30 03:05	5	60	59.94	59.28	0	0.07	0.03
2005-11-30 03:25	5	30	30.03	29.41	0	0.09	0.03
2005-11-30 03:45	5	90	89.92	88.58	0	0.06	0.05
2005-11-30 04:05	5	190	189.77	187.25	0	0.08	0.07
2005-11-30 04:25	5	140	139.90	137.91	0	0.09	0.06
2005-11-30 04:45	6	0	0.06	-0.09	0	0.11	0.03
2005-11-30 05:05	6	90	89.95	88.72	0	0.06	0.05
2005-11-30 05:25	6	30	30.01	29.41	0	0.09	0.06
2005-11-30 05:45	6	190	189.75	187.22	0	0.08	0.05
2005-11-30 06:05	6	60	59.99	59.07	0	0.09	0.04
2005-11-30 06:25	6	140	139.85	137.88	0	0.11	0.04
2005-11-30 06:45	7	0	0.00	-0.10	0	0.09	0.04
2005-11-30 07:05	7	30	29.99	29.51	0	0.08	0.04
2005-11-30 07:25	7	90	89.94	88.64	0	0.06	0.05
2005-11-30 07:45	7	140	139.84	137.90	0	0.06	0.06
2005-11-30 08:05	7	60	59.98	59.12	0	0.02	0.03
2005-11-30 08:25	7	190	189.79	187.32	0	0.09	0.04
2005-11-30 08:45	8	0	0.04	-0.07	0	0.12	0.02
2005-11-30 09:05	8	60	59.92	59.03	0	0.07	0.05

DateTime (UTC+1)	Run	Level	TS (ppb)	OA (ppb)	Flag#	sdTS (ppb)	sdOA (ppb)
2005-11-30 09:25	8	30	29.99	29.48	0	0.09	0.03
2005-11-30 09:45	8	90	89.91	88.55	0	0.07	0.06
2005-11-30 10:05	8	190	189.74	187.13	0	0.09	0.07
2005-11-30 10:25	8	140	139.84	137.96	0	0.09	0.03

#0: valid data

Figure 4 and Figure 5 show the regression residuals of the two ozone calibrators with respect to the SRP as a function of ozone concentration and time for the range 0 – 90 ppb.

Based on these inter-comparison results, unbiased ozone volume mixing ratios X_{O3} and an estimate for the remaining combined standard uncertainty u_{O3} can be computed from the one-minute data [OC] of the ozone calibrators using equations (1a) and (1b) [*Klausen, et al.*, 2003].

TEI 49C-PS #72971-372 (JMA-1):

$$X_{O3}\ (ppb) = ([OC] + 0.22\ ppb) / 0.987$$

$$u_{O3}\ (ppb) = sqrt(0.28\ ppb^2 + 2.67e\text{-}05 * X_{O3}^2) \quad (1a)$$

TEI 49C-PS #72972-372 (JMA-2):

$$X_{O3}\ (ppb) = ([OC] + 0.17\ ppb) / 0.986$$

$$u_{O3}\ (ppb) = sqrt(0.28\ ppb^2 + 2.67e\text{-}05 * X_{O3}^2) \quad (1b)$$

Changes Made to Instrument

No changes were made to the instruments, all settings remained.

Conclusions

The two ozone calibrators of JMA agree extremely well when compared to each other. However, lower readings of approximately 1.1% are observed when compared to WCC-Empa. Approximately 0.4% of these lower readings may be explained by differences of the WCC-Empa SRP#15 and the GAW reference SRP#2, while the remaining 0.7% cannot be explained. WCC-Empa therefore strongly suggests that the ozone calibrators are again inter-compared against NIST SRP#2 or another SRP (cf. Recommendation 4). The inter-comparison should be done with JMA-1, because JMA-2 was serviced sent to NIST already after the audit. During the servicing the calibration settings of JMA-2 were set to BKG 0.0 ppb and COEF 1.000. With these settings JMA-2 was reading 1.1% lower compared to NIST SRP#2. Assuming that the instrument calibration remained unchanged during the servicing this would explain most of the lower readings during the inter-comparisons with WCC-Empa.

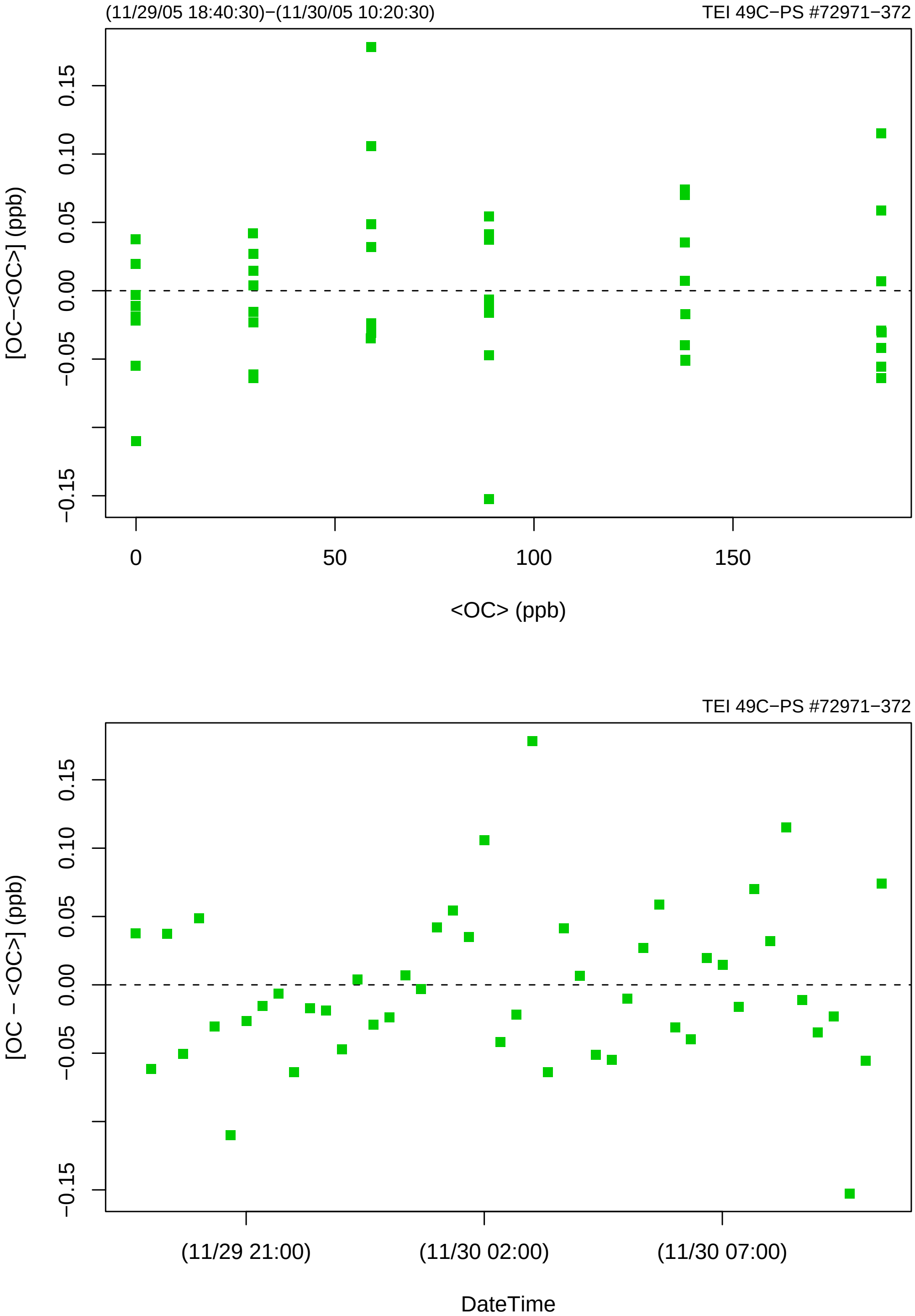
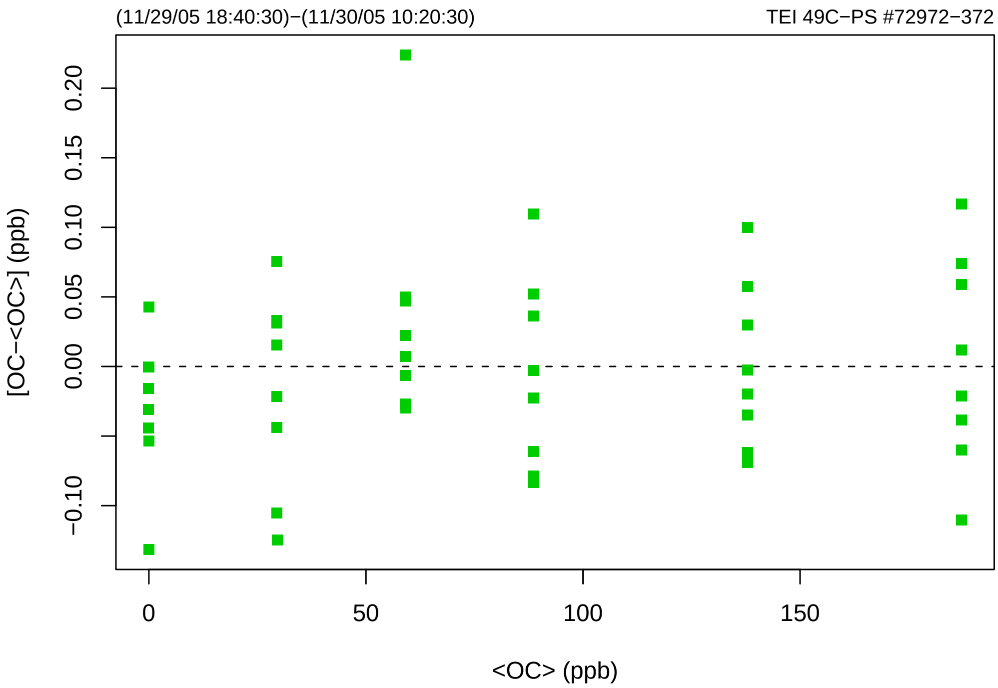


Figure 4. Regression residuals of the JMA-1 ozone calibrator as a function of concentration (upper panel) and time (lower panel).



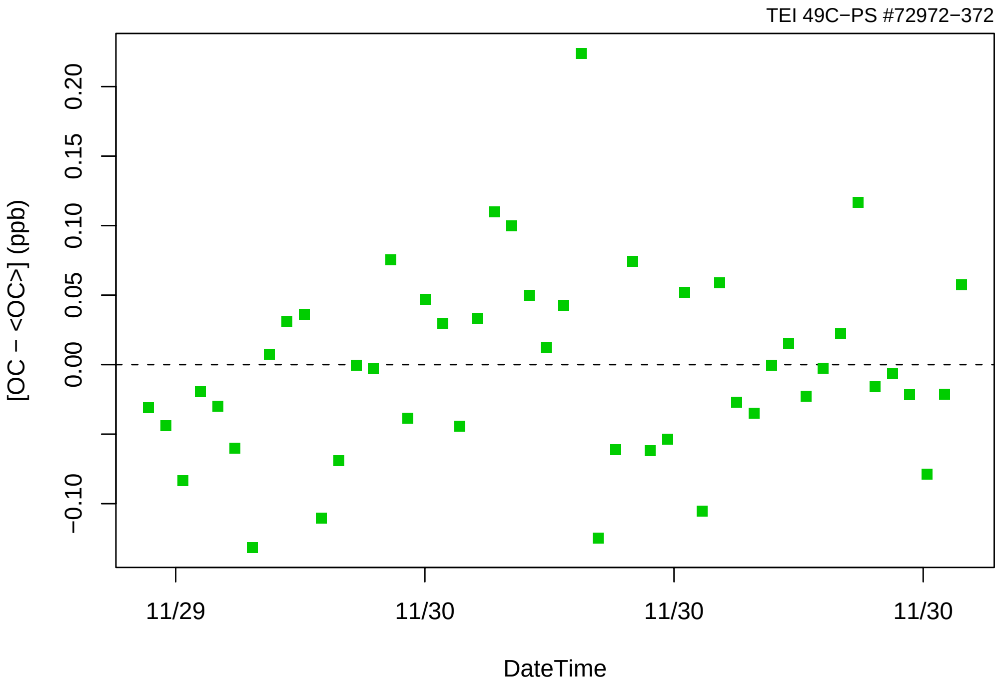


Figure 5. Regression residuals of the JMA-2 ozone calibrator as a function of concentration (upper panel) and time (lower panel).

Methane Calibration Facilities

The World Calibration Centre (WCC) for Methane in Asia and the South-West Pacific was established in the framework of the Global Atmosphere Watch (GAW) programme of the World Meteorological Organization (WMO), and is operated by the Japan Meteorological Agency (JMA) in Tokyo. The activities include the calibration of methane standard gases, on request from GAW operators in the region, against the standards maintained by JMA, as well as the organisation of methane reference gas inter-comparison experiments.

All inter-comparisons during the audit by WCC-Empa were done according to Standard Operating Procedures [*WMO*, in preparation].

Instrument Set-up and Procedures

Air Conditioning

The laboratories of the JMA calibration facilities are air conditioned. All instruments are installed in the basement of JMA headquarters.

Instrumentation

The analytical system for methane at JMA is a gas chromatographic system from Shimadzu. Instrumental details are listed in Table 5.

Standards and Calibration

In contrast to WCC-Empa, the methane scale of JMA is based on a set of gravimetrically prepared standards in natural purified air (by Nippon Sanso, 1999) based on a method described by [*Aoki, et al.*, 1992]. The standards are regularly inter-compared with primary standards maintained by the Meteorological Research Institute (MRI), Tsukuba, Japan [*Matsueda*, 1993], and have also been inter-compared with the scale maintained by NOAA [*Dlugokencky, et al.*, 2005]. Table 4 gives an overview of the primary and secondary methane standards available at JMA. All standards were purchased in 1999 and are in use since then. No uncertainties have been assigned to the primary standards. The secondary standards were calibrated using the primary standards.

Table 4. Methane standards available at the JMA calibration facilities for methane

Manufacturer, S/N, Use	CH_4 Content (ppb) and matrix	Calibration		In service	
		Date	By	From	To
Nippon Sanso CPB12986 Primary standard	1600.1 ppb, CH_4 in natural purified air	1999	Nippon Sanso	1999	continues
Nippon Sanso CPB12987 Primary standard	1700.5 ppb, CH_4 in natural purified air	1999	Nippon Sanso	1999	continues
Nippon Sanso CPB12988 Primary standard	1850.5 ppb, CH_4 in natural purified air	1999	Nippon Sanso	1999	continues
Nippon Sanso CPB12989 Primary standard	1998.4 ppb, CH_4 in natural purified air	1999	Nippon Sanso	1999	continues
Nippon Sanso CPB12990 Primary standard	2100.3 ppb, CH_4 in natural purified air	1999	Nippon Sanso	1999	continues
Nippon Sanso CQB11442 Secondary standard	1620.7±1.4 ppb, CH_4 in natural purified air	1999	Nippon Sanso	1999	continues
Nippon Sanso CQB11443 Secondary standard	1750.4±1.3 ppb, CH_4 in natural purified air	1999	Nippon Sanso	1999	continues
Nippon Sanso CQB11444 Secondary standard	1869.7±1.5 ppb, CH_4 in natural purified air	1999	Nippon Sanso	1999	continues
Nippon Sanso CQB11446 Secondary standard	1986.3±1.5 ppb, CH_4 in natural purified air	1999	Nippon Sanso	1999	continues
Nippon Sanso CQB11447 Secondary standard	2113.1±1.6 ppb, CH_4 in natural purified air	1999	Nippon Sanso	1999	continues

Inter-Comparison of Methane Analysers

All procedures were conducted according to the Standard Operating Procedure [*WMO*, in preparation] and included inter-comparisons of the travelling standards at Empa before and after the inter-comparison of the analyser.

Setup and Connections

Table 5 shows details of the experimental setup during the inter-comparison of the transfer standard and the JMA calibration system. The data used for the evaluation was recorded by the JMA data acquisition system, and no further corrections were applied.

Table 5. Experimental details of the methane inter-comparison.

Travelling standard (TS)		WCC-Empa Travelling standards (6 l aluminium cylinder containing natural air)
Field instrument	Model, S/N	Shimadzu GC-14BPF
	Principle	GC / FID Detector
	Sample loop	10 ml
	Column	Packed fused silica: Molecular sieve 5 Å (60/80 mesh) length 400 cm, ID 3.0 mm
	Carrier gas	N_2 99.99995%
	Temperatures	Sample loop: 70°C, Column: 70°C
	Instrument specials	A few seconds before injection, the flow through the loop is stopped to equilibrate pressure. The sample loop and injection valve reside inside GC oven
Connection of TS to field instrument		TS were connected to the sample selection valve of the JMA system
Data Acquisition		Shimadzu GC control software; peak area was used for data evaluation
Levels (ppb)		Level / Cylinder / Reference / St. Uncert. 1 / 050419_FA02482 / 1772.54 / 0.21 2 / 050701_FA02505 / 1832.65 / 0.24 3 / 050419_FA02488 / 1841.22 / 0.49 4 / 050419_FA02479 / 1879.59 / 0.21 5 / 050415_FA02466 / 2004.49 / 0.25
Number of injections		Each TS was analysed twice with 10 injections per analysis
Sequence of levels		Randomised sequence
Runs		2 runs (28 thru 29 November, 2005)

Results

Each TS was analysed twice with 10 injections per analysis, which resulted in 2 useable values per level. These were further aggregated by level before use in the assessment (cf. Table 6).

Table 6. CH_4 computed from two analyses, each aggregated from 10 single injections (mean and standard uncertainty of mean) for each level during the inter-comparison of the JMA methane calibration system with the WCC-Empa travelling standards (TS).

Date Time (UTC+1)	TS (ppb)	sdTS (ppb)	CH_4 (ppb)	sd CH_4 (ppb)	No. of values
2005-11-28 20:00	1772.54	0.21	1774.10	0.30	20
2005-11-28 21:00	1832.65	0.24	1834.40	0.40	20
2005-11-28 22:00	1841.22	0.49	1842.50	0.40	20
2005-11-28 23:00	1879.59	0.21	1881.10	0.00	20
2005-11-29 00:00	2004.49	0.25	2005.95	0.65	20

Figure 6 shows the regression residuals of the Shimadzu GC-14BPF GC system plotted against the concentration. The absence of concentration dependence (lower pane) indicates linearity of the instrument.

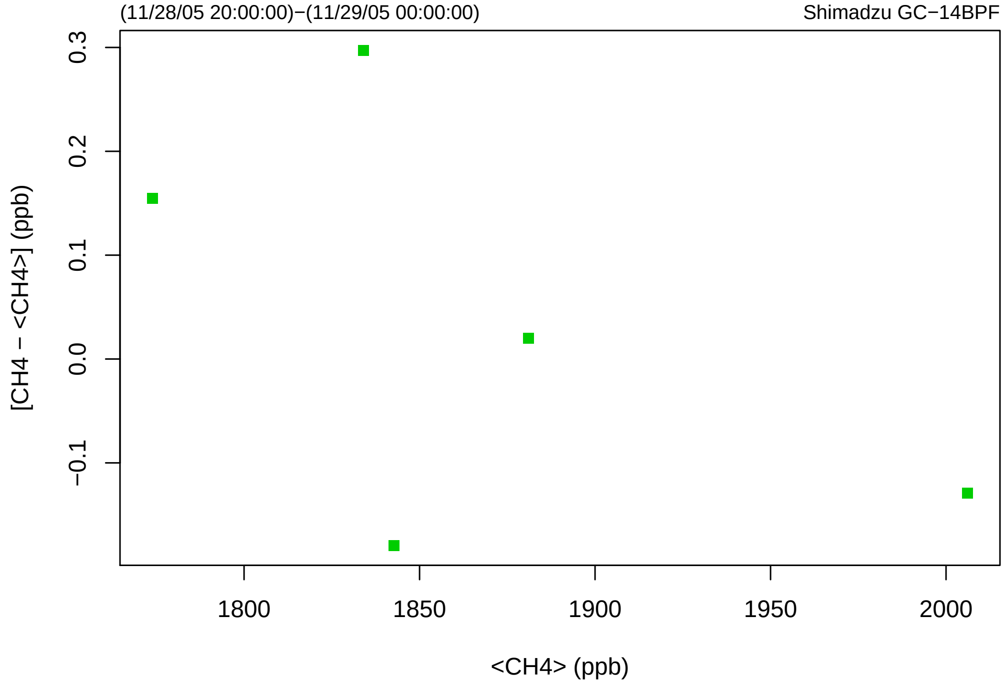


Figure 6. Regression residuals of the JMA methane calibration system versus the methane concentration. Points represent averages of valid aggregates of 20 single injections.

Based on these inter-comparison results, unbiased methane volume mixing ratios of the Shimadzu GC-14BPF GC calibration system X_{CH4} and an estimate for the remaining combined standard uncertainty u_{CH4} can be computed using equation (2).

$$X_{CH4}\,(ppb) = [CH_4] / 1.0008$$
$$u_{CH4}\,(ppb) = sqrt(0.12\,ppb^2 + 1.70e\text{-}08 * X_{CH4}^2) \qquad (2)$$

Conclusions
The CH_4 inter-comparison between WCC-Empa and JMA agreed very well in the concentration range between 1770 and 2000 ppb methane. The deviation from the transfer standards is less than 0.1 %. The good result of the inter-comparison measurements shows that the whole measurement system is appropriate for the measurement of methane. Therefore no further technical recommendations are made by WCC-Empa. However, it should be considered to maintain a direct link of the TU methane scale to the GAW reference (NOAA04) (cf. Recommendation 7).

WCC-Empa Transfer Standards
The Traceability of the WCC-Empa transfer standards to the GAW reference is described in WCC-Empa Report 05/4 - Part A [Zellweger, et al., 2005].

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Ozone Audit Executive Summary (JMA)

0.1	Station Name:	NA (JMA Central Calibration Facilities, Tokyo)
0.2	GAW ID:	NA
0.3	Coordinates/Elevation:	NA
Parameter:		Surface Ozone

1.1	Date of Audit:	28 November, 2005
1.2	Auditors:	Dr. C. Zellweger, Dr. J. Klausen
1.3	Station staff involved in audit:	K. Tsuboi (JMA), H. Doi (JMA)
1.4	Ozone Reference [SRP]:	NIST SRP#15
1.5	Ozone Transfer Standard [TS]	
1.5.1	Model and serial number:	TEI 49C PS #54509-300
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	(0.9991±0.0010) × [SRP] - (0.07±0.09)
1.6	Ozone Calibrator [OC]	
1.6.1	Model:	TEI 49 C-PS #72971-372
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	BKG +0.1 ppb, COEF 1.008
1.6.4	Calibration at start of audit (ppb):	[OC] = (0.9867±0.0000) × [SRP] - (0.22±0.09)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X = ([OC] + 0.22) / 0.9867
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.28\ ppb^2 + 2.67e\text{-}5 \times X^2)^{1/2}$
1.6.7	Coefficients after audit	unchanged
1.6.8	Calibration after audit (ppb):	unchanged
1.6.9	Unbiased ozone mixing ratio (ppb) after audit:	unchanged
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	unchanged
1.7	Comments:	JMA internal instrument ID: JMA-1
1.8	Reference:	WCC-Empa Report 05/4 – Part B

[OC]: Instrument readings; [SRP]: SRP readings; X: mixing ratios on SRP scale
NA: Not applicable

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Ozone Audit Executive Summary (JMA)

0.1	Station Name:	NA (JMA Central Calibration Facilities, Tokyo)
0.2	GAW ID:	NA
0.3	Coordinates/Elevation:	NA
Parameter:		Surface Ozone

1.1	Date of Audit:	28 November, 2005
1.2	Auditors:	Dr. C. Zellweger, Dr. J. Klausen
1.3	Station staff involved in audit:	K. Tsuboi (JMA), H. Doi (JMA)
1.4	Ozone Reference [SRP]:	NIST SRP#15
1.5	Ozone Transfer Standard [TS]	
1.5.1	Model and serial number:	TEI 49C PS #54509-300
1.5.2	Range of calibration:	0 – 200 ppb
1.5.3	Mean calibration (ppb):	(0.9991±0.0010) × [SRP] - (0.07±0.09)
1.6	Ozone Calibrator [OC]	
1.6.1	Model:	TEI 49 C-PS #72972-372
1.6.2	Range of calibration:	0 – 100 ppb
1.6.3	Coefficients at start of audit	BKG +0.2 ppb, COEF 1.006
1.6.4	Calibration at start of audit (ppb):	[OC] = (0.9860±0.0000) × [SRP] - (0.17±0.09)
1.6.5	Unbiased ozone mixing ratio (ppb) at start of audit:	X = ([OC] + 0.17) / 0.9860
1.6.6	Standard uncertainty remaining after compensation of calibration bias (ppb):	$u_X \approx (0.28\ ppb^2 + 2.67e\text{-}5 \times X^2)^{1/2}$
1.6.7	Coefficients after audit	unchanged
1.6.8	Calibration after audit (ppb):	unchanged
1.6.9	Unbiased ozone mixing ratio (ppb) after audit:	unchanged
1.6.10	Standard uncertainty remaining after compensation of calibration bias (ppb):	unchanged
1.7	Comments:	JMA internal instrument ID: JMA-2
1.8	Reference:	WCC-Empa Report 05/4 – Part B

[OC]: Instrument readings; [SRP]: SRP readings; X: mixing ratios on SRP scale
NA: Not applicable

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Methane Audit Executive Summary (RYO)

0.1	Station Name:	NA (JMA Central Calibration Facilities, Tokyo)
0.2	GAW ID:	NA
0.3	Coordinates/Elevation:	NA
Parameter:		Methane

1.1	Date of Audit:	28 November, 2005	
1.2	Auditors:	Dr. C. Zellweger, Dr. J. Klausen	
1.3	Station staff involved in audit:	K. Tsuboi (JMA), K. Umehara (JMA)	
1.4	CH_4 Reference:	NOAA04	
1.5	CH_4 Transfer Standard [TS]		
1.5.1	CH_4 Cylinders:	050419_FA02482	1772.54±0.21 ppb
	050701_FA02505	1832.65±0.24 ppb	
	050419_FA02488	1841.22±0.49 ppb	
	050419_FA02479	1879.59±0.21 ppb	
	050415_FA02466	2004.49±0.25 ppb	
1.6	CH_4 analyzer [CA]		
1.6.1	Model:	Shimadzu GC-14BPF	
1.6.2	Range of calibration:	1770 –2005 ppb	
1.6.3	Coefficients at start of audit	NA	
1.6.4	Calibration at start of audit (ppb):	$CH_4 = (1.00079 \pm 0.00007) \times X$	
1.6.5	Unbiased CO mixing ratio (ppb) at start of audit:	$X = CH_4 / 1.00079$	
1.6.6	Standard uncertainty after compensation of calibration bias at start of audit(ppb):	$u_X \approx (0.12\ ppb^2 + 1.70e\text{-}08 \times X^2)^{1/2}$	
1.6.7	Coefficients after audit	NA	
1.6.8	Calibration after audit (ppb):	unchanged	
1.6.9	Unbiased CH_4 mixing ratio (ppb) after audit:	unchanged	
1.6.10	Standard uncertainty after compensation of calibration bias after audit(ppb):	unchanged	
1.7	Comments:		
1.8	Reference:	WCC-Empa Report 05/4 – Part B	

[CH_4]: Instrument readings; X: mixing ratios on the NOAA04 CH_4 scale.
NA: Not applicable

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