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CCQM-K90, Formaldehyde in nitrogen, 2 µmol mol^{-1} Final report

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Summary

The CCQM-K90 comparison is designed to evaluate the level of comparability of National Metrology Institutes (NMI) or Designated Institutes (DI) measurement capabilities for formaldehyde in nitrogen at a nominal mole fraction of 2 µmol mol^{-1}.

The comparison was organised by the BIPM using a suite of gas mixtures prepared by a producer of specialty calibration gases. The BIPM assigned the formaldehyde mole fraction in the mixtures by comparison with primary mixtures generated dynamically by permeation coupled with continuous weighing in a magnetic suspension balance. The BIPM developed two dynamic sources of formaldehyde in nitrogen that provide two independent values of the formaldehyde mole fraction: the first one based on diffusion of trioxane followed by thermal conversion to formaldehyde, the second one based on permeation of formaldehyde from paraformaldehyde contained in a permeation tube.

Two independent analytical methods, based on Cavity Ring Down Spectroscopy (CRDS) and Fourier Transform Infrared spectroscopy (FTIR) were used for the assignment procedure.

Each participating institute was provided with one transfer standard and value assigned the formaldehyde mole fraction in the standard based on its own measurement capabilities.

The stability of the formaldehyde mole fraction in transfer standards was deduced from repeated measurements performed at the BIPM before and after measurements performed at participating institutes. In addition, 5 control standards were kept at the BIPM for regular measurements during the course of the comparison.

Temporal trends that approximately describe the linear decrease of the amount-of-substance fraction of formaldehyde in nitrogen in the transfer standards over time were

[*] N. Aoki was added on 13 Sept 2017, V. Ferracci and R.C. Brown were added on 26 Sept. 2017, after the first publication of the report on 1st Sept. 2017.

estimated by two different mathematical treatments, the outcomes of which were proposed to participants. The two treatments also differed in the way measurement uncertainties arising from measurements performed at the BIPM were propagated to the uncertainty of the trend parameters, as well as how the dispersion of the dates when measurements were made by the participants was taken into account.

Upon decision of the participants, the Key Comparison Reference Values were assigned by the BIPM using the largest uncertainty for measurements performed at the BIPM, linear regression without weight to calculate the trend parameters, and not taking into account the dispersion of dates for measurements made by the participant. Each transfer standard was assigned its own reference value and associated expanded uncertainty. An expression for the degree of equivalence between each participating institute and the KCRV was calculated from the comparison results and measurement uncertainties submitted by participating laboratories. Results of the alternative mathematical treatment are presented in annex of this report.

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2 Purpose

The CCQM-K90 comparison was designed to evaluate the level of comparability of National Metrology Institutes (NMI) or Designated Institutes (DI) measurement capabilities for formaldehyde in nitrogen at a nominal mole fraction of 2 µmol mol^{-1}.

3 Measurand, quantities and Units

The measurand was the mole fraction of formaldehyde in nitrogen, with measurement results being expressed in mol mol^{-1} (or one of its submultiples mmol mol^{-1}, µmol mol^{-1} or nmol mol^{-1}).

4 Participants

The comparison included 9 participants: D.I. Mendeleyev Institute for Metrology (VNIIM), Korea Research Institute of Standards and Science (KRISS), Laboratoire National de métrologie et d'Essais (LNE), National Institute of Metrology (NIM), National Metrology Institute of Japan (NMIJ), National Physical Laboratory (NPL), National Institute of Science and Technology (NIST), Van Swinden Laboratory (VSL), and the Bureau International des Poids et Mesures (BIPM).

5 Measurement schedule

The comparison was organised by the BIPM following the schedule displayed in Table 1.

Date	Event
Aug 2014	Delivery of transfer standards at the BIPM / purity analysis
Oct 2014	Protocol distributed within GAWG, deadline for registration 05/12/14
20 Jan 2015	Start of mixtures stability study
Apr 2015	Shipment of participants cylinders to NIST
June 2015	Shipment of cylinders from NIST to participants
Aug-Sep 2015	Analysis of mixtures by participants
Oct 2015	Shipment of cylinders from participants to NIST
Jan 2016	Shipment of cylinders from NIST to BIPM Results forms received from participants Re-verification of participants mixtures together with control mixtures
Mar 2016	Last measurements of all cylinders at BIPM
Apr 2016	Draft A report available

Table 1: schedule of events in CCQM-K90 organisation

6 Transfer standards

The BIPM acquired 14 mixtures of formaldehyde in nitrogen in high pressure cylinders at the nominal mole fraction of 2 µmol mol^{-1}. All standard mixtures were obtained from the same commercial producer of specialty calibration gases and were delivered at the same time. The mixtures were purchased by the BIPM with the requirement to obtain identical mixtures as previously validated in the framework of a testing agreement between the BIPM, the VSL, and the specialty gases producer[†]. They were delivered at the BIPM on 14 August 2014.

6.1 Cylinders characteristics

Cylinders were tracked at the BIPM with their reference as provided by the company, as well as with a label used in measurement data files. All pressures were measured upon their arrival, before their shipment to the NIST in April 2015 and after their return at the BIPM in January 2016. References, labels and pressures are listed in Table 2.

lab	Ref	label	*P1*	*P2*
BIPM	CC435866	C6	112	50
KRISS	CC435857	C12	115	70
LNE	CC435928	C13	115	80
NIM	CC435863	C7	115	107
NIST	CC435922	C9	115	N/A
NMIJ	CC433246	C14	115	100
NPL	CC435939	C2	107	65
VNIIM	CC435864	C11	115	100
VSL	CC435862	C8	115	N/A

Table 2: list of transfer standards with their company reference, label given at BIPM, pressure before and after shipment in bar.

6.2 Purity analysis

As part of the comparison, the mixtures were analysed by Fourier Transformed Infrared Spectroscopy (FTIR), to deduce the formaldehyde amount fraction but also to quantify possible impurities. A typical spectrum is displayed in Figure 1. Formaldehyde (HCHO) is clearly visible, but also carbon monoxide (CO), carbon dioxide (CO_2), water (H_2O), and trioxane ($(HCHO)_3$) in small amounts. The absorbance takes negative values in the figure due to a numerical shift in the FTIR quantification software. It was verified that this did not impact the results.

[†] See for example document GAWG/13-15

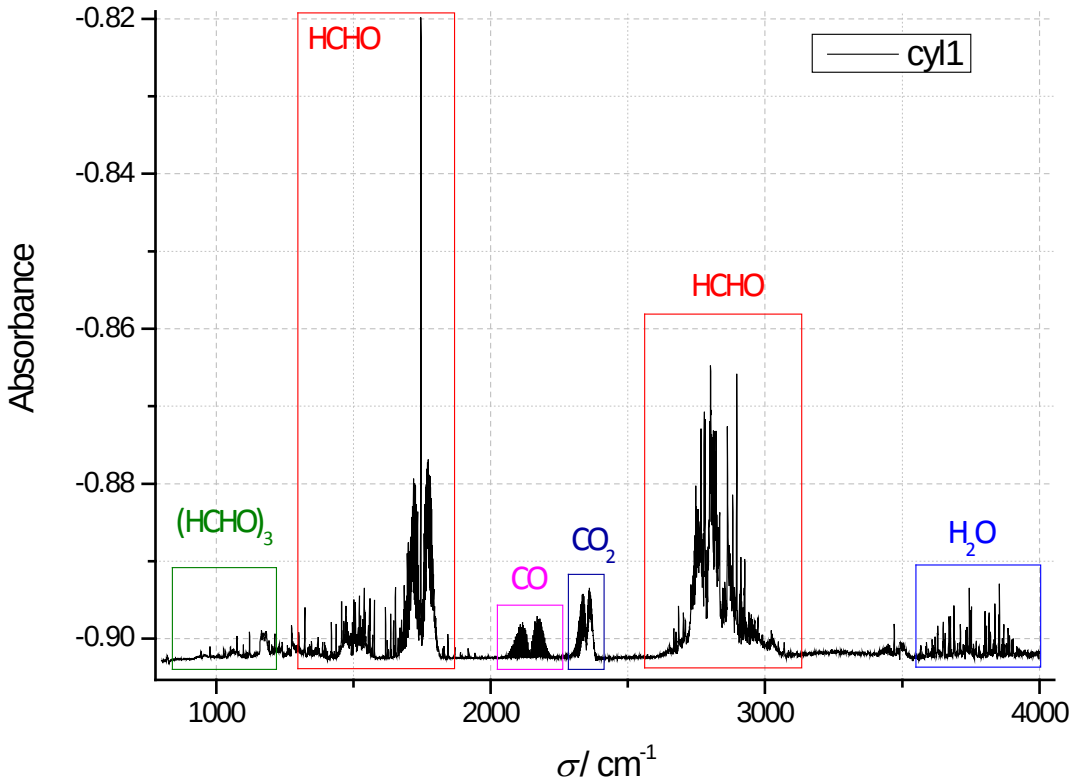

Figure 1: typical FTIR spectrum recorded on one of the set of 14 cylinders acquired for the comparison showing the region where absorption features could be attributed to an absorbing species for further quantification.

The detected impurities do not constitute a source of bias in the comparison. They were nevertheless measured and quantified during each FTIR analysis, using a quantification method based on synthetic calibration for CO, CO_2 and H_2O, with molecular parameters from the HITRAN 2012 database. Quantification of trioxane was based on previous calibration of the FTIR with known amounts of trioxane generated in the same system used for formaldehyde, with the trioxane to formaldehyde converter turned off.

All cylinders were found to have similar levels of impurities. The levels quantified in the spectrum displayed in Figure 1 are reported here. Values for all cylinders measured during the first series can be found in Annex 3 – FTIR impurity analysis. They are all provided for information only, without an associated uncertainty.

Table 3: impurities measured by FTIR in one of the set of 14 cylinders acquired for the comparison.

compound	mole fraction / (µmol mol^{-1})
$(HCHO)_3$	0.016
CO	0.249
CO_2	0.043
H_2O	0.559

7 Measurement protocol

The comparison was performed following the protocol sent to participants on 25 October 2014, described with more details below. The series of measurements is also summarised in Table 5 at the end of this section.

7.1 Preparation of cylinders

On receipt by the BIPM, all cylinders were allowed to equilibrate at laboratory temperature for at least 24 hours. All cylinders were then rolled for at least 1 hour to ensure homogeneity of the mixture.

Each cylinder was connected to one inlet of a 16-inlet automatic gas sampler connected to the gas analysers and the formaldehyde dynamic generation facility based on paraformaldehyde.

The pressure reducer of each cylinder was flushed nine times with the mixture. The cylinder valve was then closed leaving the high pressure side of the pressure reducer at the cylinder pressure and the low pressure side of the pressure reducer at ~300 kPa (abs). The cylinders were left to stand for at least 24 hours, to allow conditioning of the pressure reducers.

Immediately prior to an analysis, each cylinder valve was opened again and the pressure reducer flushed a further three times.

7.2 Series of analysis versus the paraformaldehyde source

The first two series of analysis was performed with the BIPM dynamic source of formaldehyde in nitrogen based on permeation of paraformaldehyde. Before the analysis of all cylinders, the amount fraction of water co-emitted with formaldehyde from the permeation tube was evaluated from measurements performed with and without the permeation tube inside the chamber, using a Cavity Ring Down Spectroscopy (CRDS) Halo+ analyser calibrated by NPL. This value was further introduced in calculations of the HCHO amount fraction in dynamic mixtures.

The suite of cylinders was analysed sequentially, each of them in between the analysis of a minimum of two dynamic mixtures of formaldehyde mole fractions chosen so as to bracket the cylinder value. Both dynamic and cylinder mixtures were analysed with the same two following analytical techniques and associated measurement procedures:

- Cavity Ring Down Spectroscopy (CRDS): the analyser was flushed with the mixture to analyse during a minimum of 35 minutes followed by 5 minutes of measurement, taking the average of the response over these 5 minutes as the instrument response to the mixture.
- Fourier Transformed Infrared spectroscopy (FTIR): the analyser was flushed with the mixture to analyse during sufficient time to let twenty times the gas cell volume pass through the cell before starting the measurements. During spectra acquisition, 120 scans were co-added over a period of 5 minutes to provide one single beam spectrum of a sample. This single beam spectrum was ratioed with a similar spectrum of ultra-pure nitrogen collected under similar conditions to provide an absorbance spectrum to be used for the quantification of the formaldehyde mole fraction.

7.3 Series of analysis versus the trioxane source

Two additional series of analysis were performed with the BIPM dynamic source of formaldehyde in nitrogen based on diffusion of trioxane followed by dissociation of formaldehyde in a converter. The same procedure described above was used to perform measurements with the 2 analytical instruments, FTIR and CRDS.

7.4 Calculation of formaldehyde mole fractions

During each series of measurement, each cylinder was analysed once in a measurement sequence following always the same pattern described below:

Table 4: measurement sequence followed during the analysis of one cylinder. The mixture is either BIP nitrogen, a standard mixture generated dynamically or the standard cylinder to analyse. x_{nom} is the nominal mole fraction of formaldehyde in the mixture in µmol mol^{-1}.

Mixture	x_{nom}
BIP nitrogen	0
dynamic standard 1	1
dynamic standard 2	1.5
Cylinder	2
dynamic standard 3	2.5
dynamic standard 4	3
BIP nitrogen	0

The formaldehyde mole fraction in dynamically generated mixtures was deduced from the measurement equation corresponding to the generation method (paraformaldehyde permeation or trioxane diffusion), as described in more detailed in Annex 5 – Measurement uncertainties (BIPM).

Following the regression analysis principles developed in ISO 6143, measurement results acquired during one cylinder analysis with each analytical method (FTIR and CRDS) were first modelled by performing a generalised least-squares regression between the analytical values and the dynamically generated gravimetric values to determine the analysis function. The analysis function was then used to calculate a predicted value for each cylinder. A program developed in Labview was used in conjunction with *B_least* to perform these calculations.

7.5 Stability testing of transfer standards (TS)

From the trends of the HCHO amount fraction measured in all cylinders between January to March 2015, a selection was performed to send the most stable 8 mixtures to the participants.

The remaining cylinders were kept as control standards (CS) and monitored using the exact same procedure between April 2015 and January 2016, versus the trioxane source at the BIPM.

After receipt of transfer standards from participants in January 2016, all standards were again monitored during three months, first versus the trioxane source, then versus the paraformaldehyde source. The date of the measurement of each cylinder was recorded so as to calculate the exact number of days since the start of the comparison. The

number of days was used as time scale to model the HCHO loss versus time with a linear decrease, as observed.

Table 5: series of measurements performed at the BIPM for the comparison CCQM-K90

Analysis	Dates	Cylinders	Source of HCHO	Comment/event
1	20-30 Jan 2015	14 (all)	Paraformaldehyde	4 analyses discarded
2	16-24 Feb 2015	14	Paraformaldehyde	
3	10-13 Mar 2015	13	Trioxane	1 cylinder empty
4	24-25 Mar 2015	4 CS	Trioxane	
5	23-24 Apr 2015	5 CS	Trioxane	
6	28 May-02 Jun 2015	5 CS	Trioxane	Analysis discarded
7	16-17 July 2015	5 CS	Trioxane	Analysis discarded
8	02-03 Sep 2015	5 CS	Trioxane	
9	21-22 Oct 2015	5 CS	Trioxane	
10	15-16 Dec 2015	5 CS	Trioxane	
11	27 Jan- 03Feb 2016	11	Trioxane	2 TSs not back
12	17-23 Mar 2016	11	Paraformaldehyde	Analysis discarded
13	29 Mar-01 Apr 2016	11	Trioxane	

8 Deviations from the protocol

During the course of the comparison, which included measurements at the BIPM starting in September 2014 and ending in April 2016, a number of technical events happened, with various impacts on the measurements. They are listed below in chronological order:

- 20 January 2015, FTIR pressure stability:
  after the analysis of 4 cylinders, pressure instability was detected in the FTIR. A connection was modified and the analysis of the 11 other cylinders continued. The FTIR values for the first 4 cylinders were discarded.
- 10 March 2015, one cylinder empty:
  cylinder C4 was found to be empty during the third series of analysis. It was removed from the comparison.
- 20 March 2015, CRDS out of specifications:
  the CRDS instruments showed an increasing instability problem. It was returned to the factory for a complete repair. It returned to the BIPM 7 months later, in October 2015. It was decided not to use these CRDS recorded values in the comparison result, rather use them as a validation tool when the instrument was operating within its specifications.
- 28 May 2015, CO in the trioxane source:
  unexpected HCHO values calculated by FTIR on cylinders kept at the BIPM were observed, about 2.5% higher than obtained from five previous analysis performed between January and April 2015. This was considered as abnormal and triggered further investigations on the status of the facility as well as on the calculation method. It was found that the facility used to generate reference standards was not in its normal state: the trioxane to formaldehyde converter was not operating correctly, as observed from levels of carbon monoxide higher than before. It was concluded

that the efficiency of this converter was altered, causing an error in the mole fraction of formaldehyde in the samples calculated when applying the usual equation, in which a conversion factor equal to 1 is assumed. Investigations showed that changing the tubing of the converter was the appropriate solution to recover a conversion of factor of 1. This was implemented on 25/08/2015 and a new analysis was performed. As the conversion factor resulting from an altered converter could not be calculated, it was decided to discard all the measurement values obtained during the period from May 2015 to August 2015, when carbon monoxide levels higher than 20 ppb as measured by the FTIR were observed. The level of CO in dynamic mixtures was continued to be monitored and found to be below that level during the rest of the comparison.

- 17 March 2016, CRDS out of specifications:
  after having moved the CRDS analyser from one room (trioxane source facility) to the other (paraformaldehyde source facility), the analyser showed very unstable values. It was again declared out of specification and was not used for the remainder of the study.
- 20 March 2016, impurities in the paraformaldehyde source:
  during the analysis of all cylinders with the paraformaldehyde source, unexpected HCHO values were observed, with up to 15% increase compared to the previous analysis of January 2016. After investigation, an unknown impurity was observed in the FTIR spectra recorded on the paraformaldehyde source. As the FTIR analytical values recorded on cylinders were consistent with previous values, it was concluded that the source was generating 15% less formaldehyde than expected, either due to an impurity in the permeation tube, or loss of formaldehyde by reaction inside the chamber. It was decided to discard this series of measurements, to declare the paraformaldehyde source out of specification, and to perform a last series of measurements with the trioxane source.

In addition to the above list, two participants experienced technical issues impacting the measurement results:

- VSL:
  after the analysis a final pressure test was carried out at VSL. After that the liner used for the pressure test could not be removed. A pressure regulator could also not be attached since it would leak as the liner itself can rotate freely. It was jointly decided not to return the cylinder to BIPM, but that VSL could submit its measured values for the comparison. In view of the very consistent linear decrease of the HCHO mole fraction observed on all other mixtures, it was decided to calculate the average loss per month on other cylinders and use this as the most probable loss for VSL transfer standard.
- NIST:
  the dynamic generation system maintained by NIST experienced a major failure at the expected time of analysis of K90 transfer standards. NIST could not report a value before the end of measurements performed at the BIPM. NIST cancelled its participation in this key comparison.

9 Measurement results and uncertainty budgets

With about one series of measurement per month during 14 months, the total number of measurements is large. Results are therefore summarised in this section, presented in graphs, with all supporting data provided in Annex 2 – Measurements results by FTIR. The uncertainty budget associated with formaldehyde mole fractions generated dynamically at the BIPM is presented in Annex 5 – Measurement uncertainties (BIPM). The results of measurements performed on the set of 5 control standards kept at the BIPM are presented first, followed by the transfer standards measurements. Only the values that were not discarded for technical reasons are displayed in the graphs. Discarded values can be seen in the Table 9 and Table 10 displayed in Annex 2 – Measurements results by FTIR. All results are displayed first, followed by discussion on selection of appropriate data to calculate reference values.

9.1 Measurements at the BIPM

A total of 13 series of measurements were performed at the BIPM, of which 3 had to be discarded for technical reasons discussed in section 7. Both the FTIR and the CRDS analysers were used at the start of the study. However, due to the failure of the CRDS analyser after 3 months of measurements, values obtained with this instrument have all been discarded from the comparison and all values are based on FTIR measurements only. For information only, a comparison between the CRDS and FTIR results is presented in Annex 4 – Measurements results by CRDS. A selection of three series of measurements performed with the CRDS within its specification demonstrates good agreement between the two techniques, well within the uncertainties.

9.1.1 Control standards

5 control standards were kept at the BIPM and monitored during the entire course of the comparison. For each of them, the formaldehyde mole fraction measured in the control standard by FTIR calibrated with dynamically generated standard mixtures is plotted in Figure 2 versus the time since 14/08/2014 in days. This arbitrary choice corresponds to the date of arrival of all cylinders, allowing some consideration on the initial content of all mixtures.

This figure includes measurements performed with the two dynamic sources, following the measurement series detailed in Table 5.

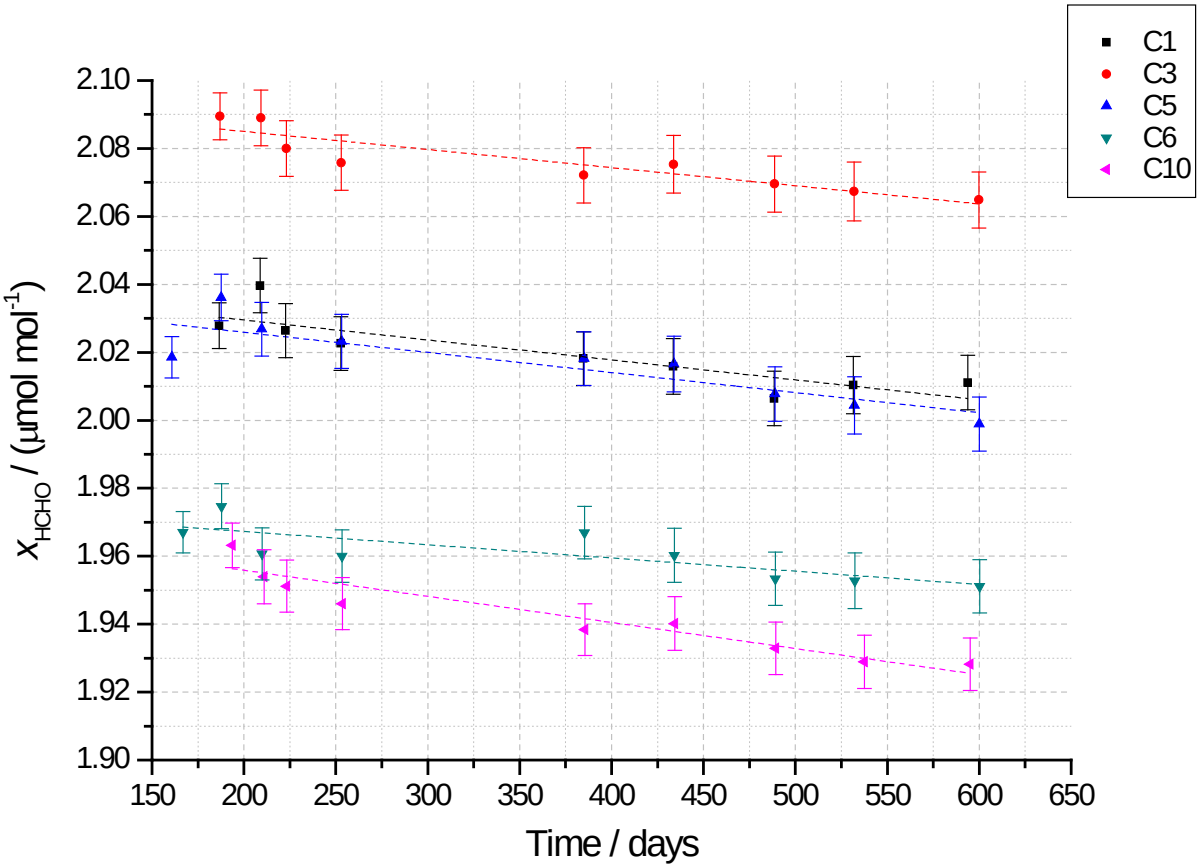

Figure 2: formaldehyde mole fraction measured in control standards during the course of the comparison versus the time since 24/08/2014 in days. Uncertainties are expressed at 95% confidence level (k = 2).

The above graph shows very consistent trends on all control standards, which all appear to be well fitted with a linear decrease. In addition there is no evidence that switching permeation source causes a change in reported BIPM values, which would be evident at a time equals to 200 days if it did.

9.1.2 Transfer Standards

A total of 8 transfer standards were sent to participants after the fourth series of analyses. Only 6 came back after analysis by participants, before the 11th series of analyses. For each of them, the formaldehyde mole fraction measured by FTIR calibrated with dynamically generated standard mixtures is plotted in Figure 3 versus the number of days.

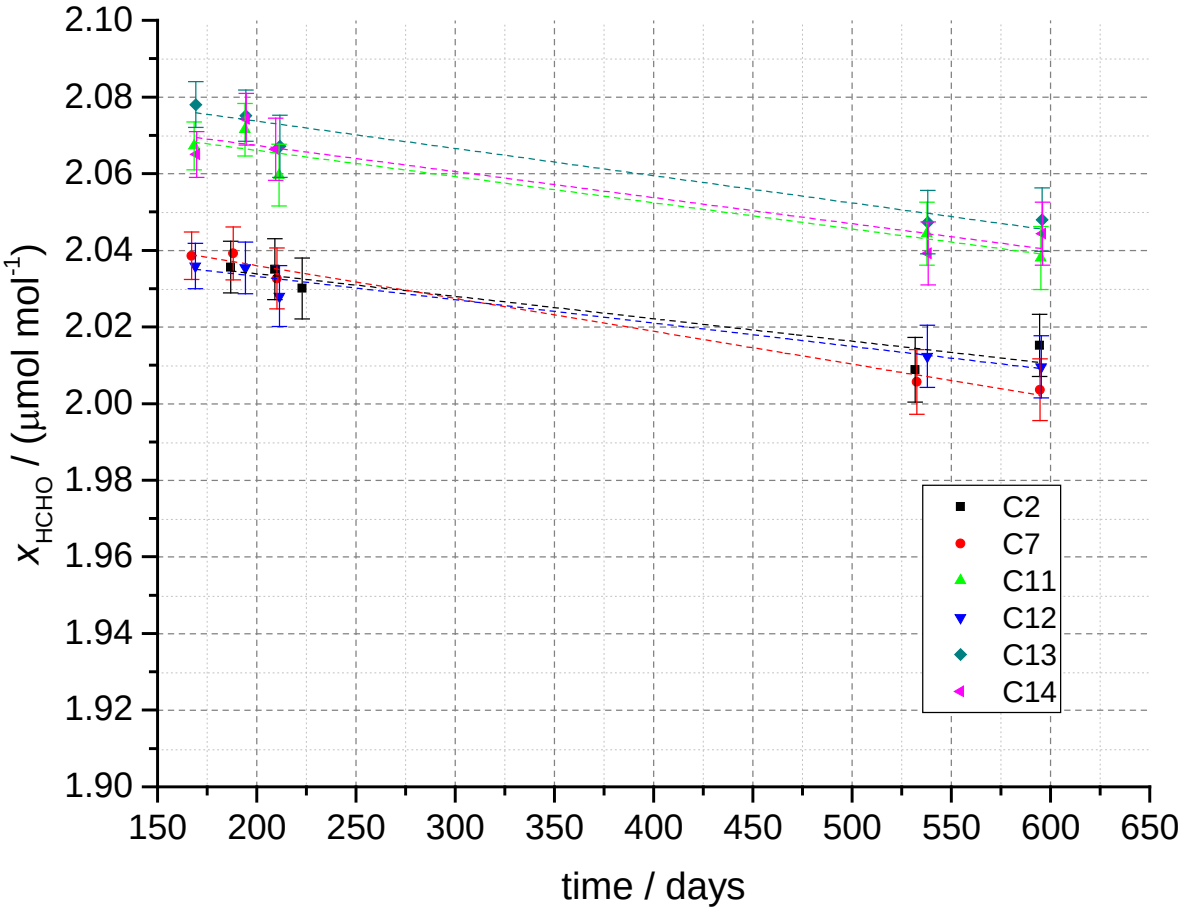

Figure 3: formaldehyde mole fraction measured in transfer standards during the course of the comparison versus the time in days.

This graph again shows a consistent linear decrease on the 6 transfer standards that came back after measurements by the participants.

9.1.3 Loss of HCHO versus time

From all valid series of measurements (10 for the control standards and 5 for the transfer standards), the loss of HCHO was calculated after linear regression of *x*(HCHO) versus the number of days. They are all plotted in Figure 4, expressed here in µmol mol^{-1} day^{-1} for an easier comparison with the nominal mole fraction.

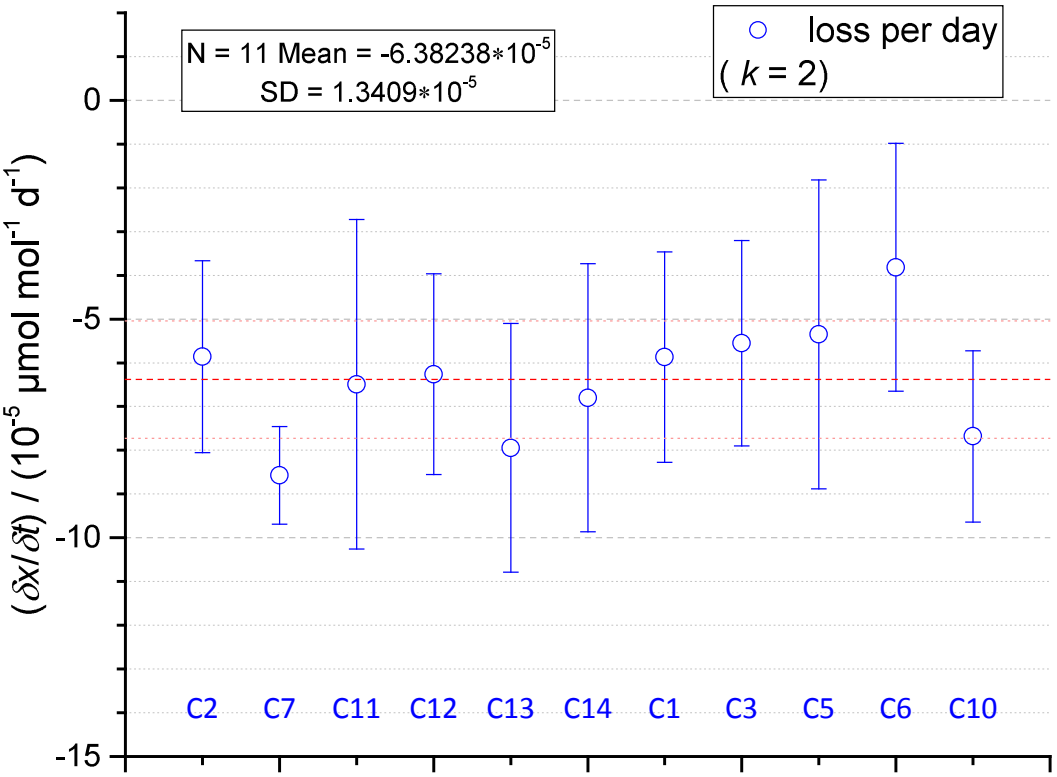

Figure 4: loss of HCHO in 10^{-5} µmol mol^{-1} d^{-1} calculated in control and transfer standards from linear regressions of all series of measurements. Standards are identified by their label C*i*.

This graph shows that all cylinders demonstrated very consistent trends, with an average loss calculated on 11 mixtures of -6.38×10^{-5} µmol mol^{-1} d^{-1}, equivalent to -0.1% in 30 days.

9.2 Measurements by participants

Participants were asked to use their usual procedure to measure the formaldehyde mole fraction in transfer standards, and to carefully report the date of analysis to the pilot laboratory in results forms. All results forms can be found in Annex 4. Table 6 below summarises the following information:

- Lab — participant acronym
- Analyser — type of analytical method.
- Source — raw material used to generate formaldehyde
- T /°C — temperature at which the raw material was maintained
- n_C — number of calibration point
- n_S — number of measurement series

Lab	Analyser	Source	T / °C	n_C	n_s
BIPM	FTIR	Trioxane	20	4	1
KRISS	CRDS	paraformaldehyde	110	1	1
LNE	QCL	trioxane	35	1	5
NIM	CRDS	trioxane	40	1	3
NMIJ	FTIR	paraformaldehyde	75	4	5
NPL	CRDS	Trioxane*	35	1 & 2	8
VNIIM	CRDS	trioxane		1	5
VSL	CRDS	paraformaldehyde	60	1	4

Table 6: summary of measurement methods used by participants.

Participants used three different analytical methods: most of them chose Cavity Ring-Down Spectroscopy (CRDS) implemented in commercial instruments, with the exception of VSL, which has developed a home-made version; two of them used a FTIR, and one used a commercial Quantum Cascade Laser (QCL) based analyser.

All participants generated calibration gases dynamically, based on two different raw materials: paraformaldehyde or trioxane. Only NPL produced calibration mixtures in high pressure cylinders, in addition to dynamic mixtures. The temperature at which the raw material was maintained during the measurement is indicated for information.

Most of the participants generated calibration mixtures at one HCHO mole fraction close to the nominal value to value assign the transfer standards. Only NMIJ and BIPM generated 4 different values to bracket the transfer standard. NPL used 2 calibration mixtures in high pressure cylinder, and 1 dynamic calibration gas mixture.

The BIPM measurement result is the value measured on the standard labelled C6 during the measurement series performed in September 2015, using the trioxane source to generate the calibration gas.

Individual measurements performed by participants are reported together with measurements at the BIPM and the deduced linear fits in the two following figures: cylinders C2, C6, C12 and C14 in Figure 5 and cylinders C7, C8, C11 and C13 in Figure 6.

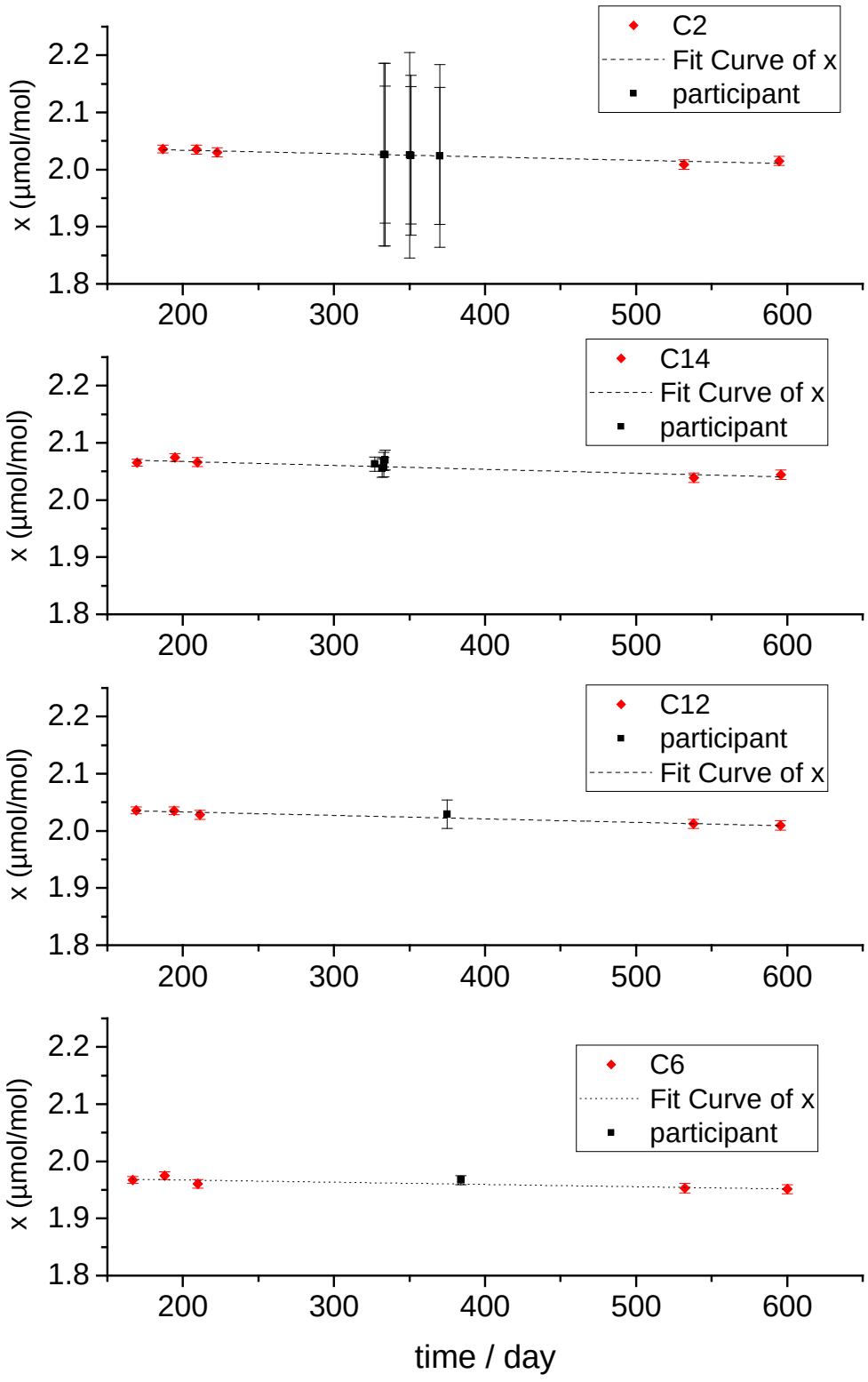

Figure 5: formaldehyde mole fraction measured in transfer standards C2, C14, C12 and C6 during the course of the comparison versus the time in days. Red diamonds : measurements at the BIPM; black squares: measurements by the participant; dotted line: linear fit of measurements performed at the BIPM.

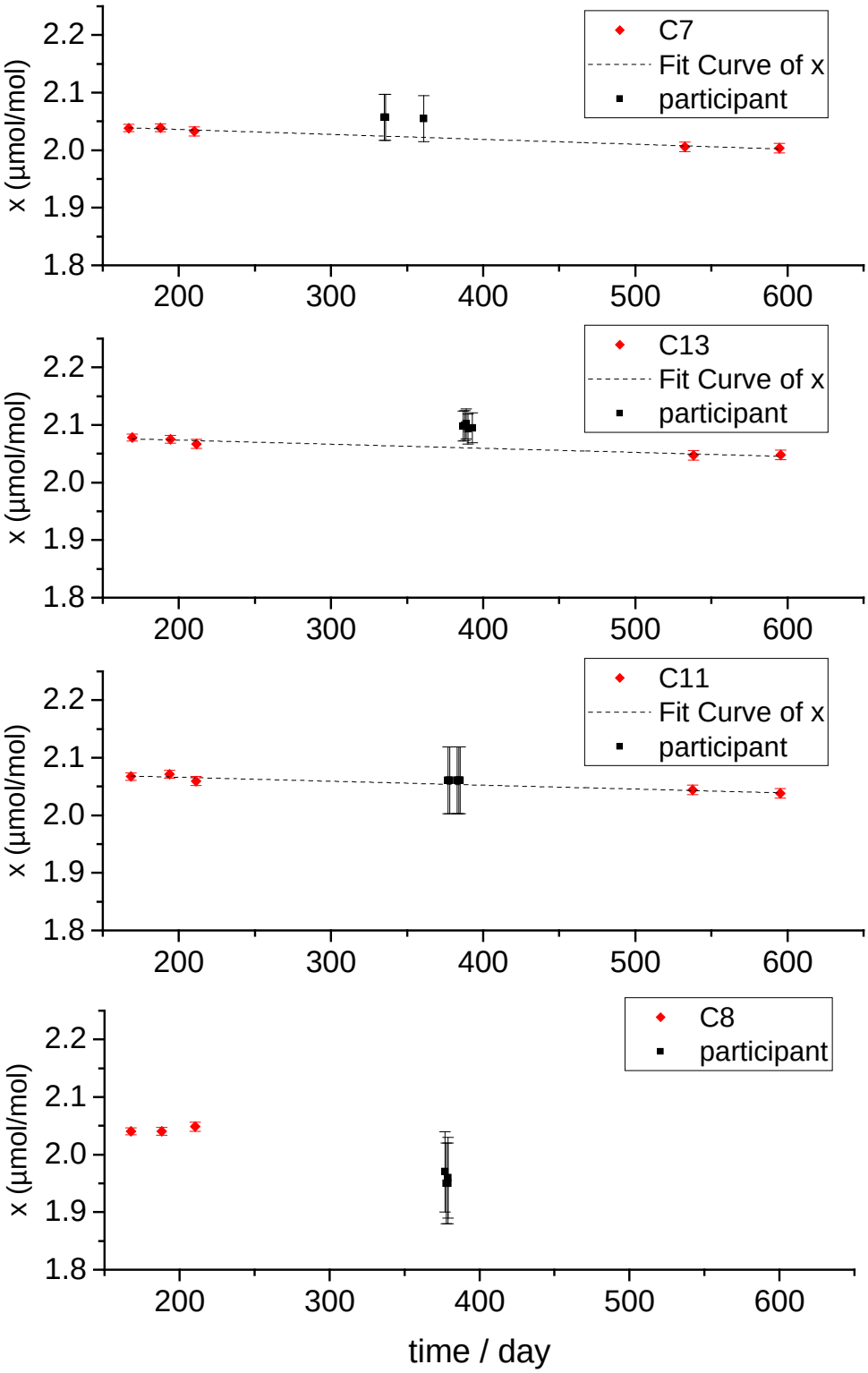

Figure 6: formaldehyde mole fraction measured in transfer standards C7, C13, C11 and C8 during the course of the comparison versus the time in days. Red diamonds: measurements at the BIPM; black squares: measurements by the participant; dotted line: linear fit of measurements performed at the BIPM.

10 Key comparison reference values

Considering that the two dynamic sources maintained by the BIPM provided consistent results, the reference values were calculated from all series of measurements performed during the course of the comparison (except those discarded for technical reasons).

For each transfer standard, the mole fraction of formaldehyde x_{HCHO} was modelled by a linear equation $x_{HCHO}(t) = x_0 + a_1 t$, where t is the time in days, x_0 is the HCHO mole fraction extrapolated to the starting date of 14/08/2014, and a_1 is the loss of HCHO in µmol mol^{-1} d^{-1}. The reference value x_R was then deduced at the date of the analysis reported by the participant. When the participant report indicated several days of measurements, it was checked that all measurement dates provided consistent results with the final result. No inconsistency was noticed.

Considering that the measurement uncertainty associated with values obtained by both dynamic sources were very similar and reproducible, typically 0.003 µmol mol^{-1} for the paraformaldehyde source and 0.004 µmol mol^{-1} for the trioxane source, the conservative value of 0.004 µmol mol^{-1} was chosen for the standard uncertainty $u(x_R)$ associated with all reference values, except for VSL.

For the VSL, as the transfer standard could not be returned, only three series of measurements could be performed at the BIPM before shipment of the cylinder. The loss calculated on those three results was positive and close to zero, not consistent with other values. The loss in this cylinder was then estimated from the average of all other cylinders (controls and transfers): $a_1 = -6.11\times10^{-5}$ µmol mol^{-1} d^{-1}. As three measurements were available, a possible intercept was calculated from each of them and the mean of these three values was taken as the final intercept: $a_0 = 2.055$ µmol mol^{-1}. An additional uncertainty component was estimated for the VSL cylinder, to reflect the fact that its loss was estimated from the others. A maximum reference value of 2.036 µmol mol^{-1} was first calculated, using the maximum observed loss and the associated mean intercept. Similarly, a minimum reference value of 2.027 µmol mol^{-1} was calculated using the minimum observed loss and associated intercept. The standard uncertainty was estimated from a rectangular distribution of total width equals to the difference between the maximum and minimum values, resulting in $u_m = 0.003$ µmol mol^{-1}. This was further combined with the uncertainty of 0.004 µmol mol^{-1} to result in a final standard uncertainty of 0.005 µmol mol^{-1}.

Applying the above calculations, the degrees of equivalence are plotted in Figure 7 and all details listed in two table: Table 7 lists the details of the calculation of the reference values, and Table 8 gives the values of the degrees of equivalence.

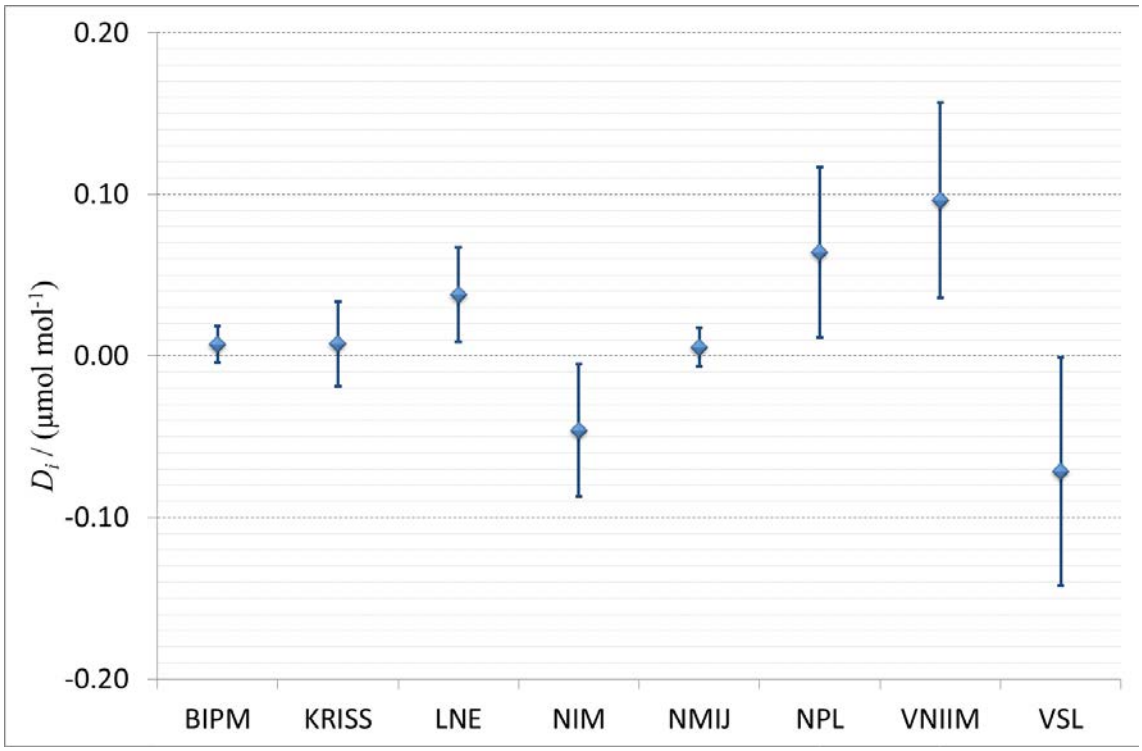

Figure 7: degrees of equivalence

NMI	Label	Day M	t	a_1	x_0	x_R	$u(x_R)$
BIPM	C6	02/09/2015	384.00	-3.81×10^{-5}	1.9682	1.960	0.004
KRISS	C12	03/09/2015	385.00	-5.95×10^{-5}	2.0345	2.022	0.004
LNE	C13	17/09/2015	399.00	-6.89×10^{-5}	2.0750	2.059	0.004
NIM	C7	10/08/2015	361.00	-8.54×10^{-5}	2.0386	2.022	0.004
NMIJ	C14	24/07/2015	344.00	-6.91×10^{-5}	2.0697	2.058	0.004
NPL	C2	19/08/2015	370.00	-5.87×10^{-5}	2.0361	2.024	0.004
VNIIM	C11	25/08/2015	376.00	-6.73×10^{-5}	2.0678	2.054	0.004
VSL	C8	28/08/2015	379.00	-6.11×10^{-5}	2.0546	2.031	0.005

Table 7 : calculation of reference values, where t is the time at the date M since 14/08/2014 in days, a_1 the loss in µmol mol^{-1} d^{-1}, x_0 is the HCHO mole fraction extrapolated to day 0, x_R is the reference value deduced at time t, and $u(x_R)$ its associated standard uncertainty, all expressed in µmol mol^{-1}.

NMI	x_R	$u(x_R)$	x_i	$u(x_i)$	D_i	$U(D_i)$
BIPM	1.960[‡]	0.004	1.967	0.004	0.007	0.011
KRISS	2.022	0.004	2.029	0.013	0.007	0.026
LNE	2.059	0.004	2.097	0.014	0.038	0.029
NIM	2.022	0.004	1.976	0.020	-0.046	0.041
NMIJ	2.058	0.004	2.063	0.005	0.005	0.012
NPL	2.024	0.004	2.088	0.026	0.064	0.053
VNIIM	2.054	0.004	2.150	0.030	0.096	0.061
VSL	2.031	0.005	1.960	0.035	-0.071	0.071

Table 8 : reference values x_R and standard uncertainty $u(x_R)$, reported values x_i and standard uncertainty $u(x_i)$, and degrees of equivalence D_i, and expanded uncertainty $U(D_i)$, all expressed in µmol mol^{-1}.

11 Supported claims

The results of the comparison may be used to underpin laboratories calibration and measurement capability claims for formaldehyde in nitrogen at mole fractions between 1 µmol mol^{-1} and 10 µmol mol^{-1}.

12 Annex 1 – Alternative mathematical treatment of results

The following pages describe the second mathematical treatment presented to participants (PDF version only).

[‡] There was a typing error on this value in the report as published on 1st Sept. 2017, which has been corrected in this version, dated 6 Sept. 2017.

MEMORANDUM

TO:	Joële Viallon	(BIPM)
CC:	George Rhoderick	(NIST)
	Robert Wielgosz	(BIPM)
SUBJECT:	**Reference values, associated uncertainties, and degrees of equivalence for CCQM-K90**	
FROM:	Antonio Possolo	(NIST)
DATE:	January 27, 2017	

1 Purpose

This memorandum describes the estimation of the temporal trends that approximately describe the decrease of the amount-of-substance fraction of formaldehyde in nitrogen (measurand) over time. These trends are used to compute the laboratory-specific reference values used for the key comparison. The corresponding unilateral degrees of equivalence are computed, and the associated uncertainties are evaluated taking into account the uncertainties reported by the participants, as well as the uncertainties surrounding those trends and the dispersion of the dates when measurements were made by the participants.

2 Trends

2.1 Trends — Patterns

The measurements that were made repeatedly over time, in five control cylinders (C01, C03, C05, C06, and C10) and in seven transfer standards (C02, C07, C08, C11, C12, C13, and C14), show that the amount-of-substance fraction of formaldehyde in nitrogen decreased approximately linearly in the course of the 765 days that elapsed since the cylinders first arrived at the BIPM, and until the most recent measurement was made.

In this conformity, I denote $x_C(t) = \alpha_C + \beta_C t + \varepsilon_C(t)$ the value of the measurand on day t in cylinder C. Days are counted from August 14, 2014, when the cylinders first arrived at the BIPM. The choice of this particular, common origin for the time scale facilitates assessing differences between the original amount-of-substance fractions of formaldehyde in the different cylinders.

For example, Table 7 of the Draft A Report for CCQM-K90 indicates that "Day 0" for cylinder C12 was January 29, 2015, and Table 10 indicates that 25 days later

the BIPM determined that the amount-of-substance fraction of formaldehyde in it was 2.035 μmol/mol. Since there are 168 days between August 14, 2014, and January 29, 2015, the corresponding value of t is $168\,\mathrm{d} + 25\,\mathrm{d} = 193\,\mathrm{d}$. The calculations involving dates were performed using facilities provided by R package `lubridate` (R Core Team, 2016; Grolemund and Wickham, 2011).

I will show that there are statistically significant differences between the estimates of the intercepts $\{\alpha_C\}$, hence that the compositions of the cylinders were not identical at the time of delivery to the BIPM. This is of no practical consequence for the comparison, but it is worth nothing nonetheless.

Figure 1 on Page 3 shows the data used to estimate the slopes and intercepts for the trends in the value of the measurand. The data comprise the values measured by the BIPM, and the associated uncertainties, as listed in Tables 9 and 10 of the Draft A Report for CCQM-K90, but excluding the values that appear in italic gray font in these tables, which have been discarded for the technical reasons noted in that report.

Each plot in Figure 1 depicts the measured values $\{x_C(t)\}$ as blue dots, and $\{x_C(t) \pm U_{95\,\%}(x_C(t))\}$ as blue, vertical line segments. It also shows two estimates of the trend: one depicted as a green line, the other as a red line. The following facts are worth noting:

(a) In most of the plots, the red line lies essentially underneath the green line, hence is invisible;

(b) In those few cases (C10 being the most striking) where the two lines are distinct, this may be attributable to the influence of one or two measurement results that are out of alignment with the bulk of the others;

(c) The estimates of the intercepts $\{\alpha_C\}$, which are the amount-of-substance fractions on August 14, 2014, differ appreciably from one another;

(d) The trends of all cylinders except C08 have negative slopes, and the trend for CO8 is unreliable because it is based on only three early determinations, while all the others are based either on measurements distributed fairly evenly in time or on two groups of determinations widely separated in time.

2.2 Trends — Robust Estimation

The dotted lines in Figure 1 correspond to weighted least squares estimates of the slopes and intercepts, with weights inversely proportional to the squared measurement uncertainties associated with the individual determinations. Not

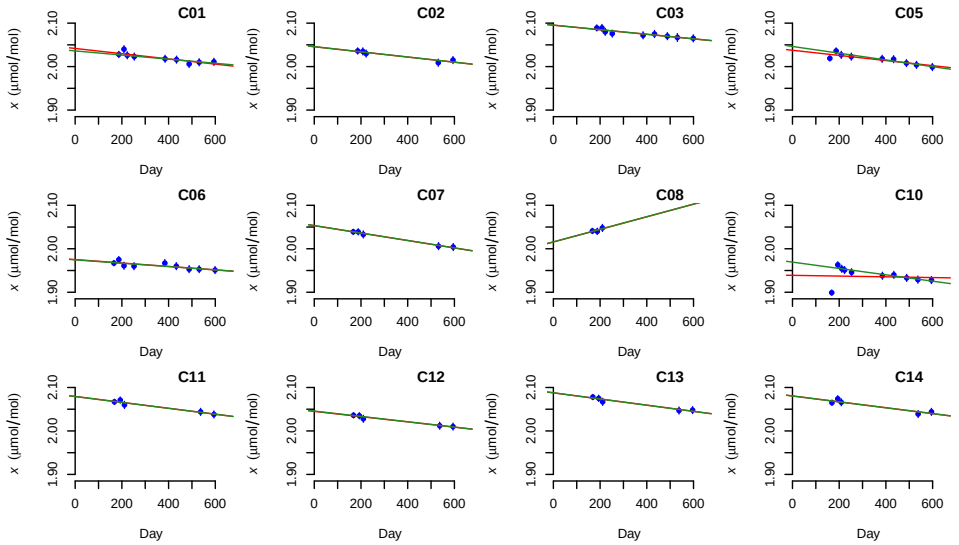

Figure 1: Measurement results used to estimate the temporal trends for the amount-of-substance fraction of formaldehyde in nitrogen. The blue dots represent the measured values $\{x_C(t)\}$, and the blue, vertical line segments represent $x_C(t) \pm U_{95\,\%}(x_C(t))$. The red lines represent the linear trends fit by ordinary least squares, and the green lines represent their counterparts fit using a robust method. All the plots have the same horizontal and vertical scales. Day 0 is August 14, 2014. Both the least squares and robust fits used weights inversely proportional to the squared standard uncertainties.

surprisingly, least squares trends are highly vulnerable to measurement results that are out of alignment with the bulk of the others, and that have high leverage: for example, the result of the earliest measurement made on C10.

The solid lines correspond to a robust fit based on an estimator described by Yohai (1987) and Koller and Stahel (2011) and implemented in R function `lmrob` defined in package `robustbase` (Maechler et al., 2016), also with weights inversely proportional to the squared measurement uncertainties associated with the individual determinations.

Given the intrinsic advantages of this robust procedure, and the fact that it produces clearly more reasonable trends than the least squares procedure in those cases where they differ, I have adopted the robust estimates for all subse-

quent data reductions, which are listed in Table 1, together with the associated standard uncertainties evaluated as described in §2.3. The estimates and uncertainties for C08 were computed as described in §2.4.

Both the intercepts and the slopes are significantly heterogeneous: that is, they are more dispersed than their associated uncertainties suggest they should be. This conclusion is based on Cochran's Q-test of heterogeneity (Cochran, 1954), and on the values of the heterogeneity index I^2 suggested by Higgins and Thompson (2002), both computed using R function `rma` defined in package `metafor` (Viechtbauer, 2010), based on random effects models fitted to the intercepts and slopes using the DerSimonian-Laird procedure (DerSimonian and Laird, 1986).

Both p-values, of Cochran's Q-test of homogeneity, for the intercepts and for the slopes, are less than 0.0001. I^2 is 99 % for the intercepts and 77 % for the slopes: these are the proportions of the total variability of the estimated intercepts and slopes that are attributable to heterogeneity.

Therefore, the original amount-of-substance fraction of formaldehyde appears to have differed markedly between some of the cylinders, and similarly for the rates at which formaldehyde will have been lost subsequently. Figures 2 and 3, on Pages 6 and 7 support the same conclusion.

	C01	C02	C03	C05	C06	C07
α /(μmol/mol)	2.036	2.046	2.095	2.046	1.975	2.053
$u(\alpha)$ /(μmol/mol)	0.002	0.003	0.006	0.007	0.005	0.001
β /(10^{-5}μmol/mol/d)	−4.700	−5.900	−5.300	−7.700	−3.900	−8.500
$u(\beta)$ /(10^{-5}μmol/mol/d)	0.700	1.200	1.100	1.700	0.900	0.400

	C08	C10	C11	C12	C13	C14
α /(μmol/mol)	2.055	1.969	2.079	2.046	2.088	2.080
$u(\alpha)$ /(μmol/mol)	0.005	0.006	0.003	0.003	0.003	0.005
β /(10^{-5}μmol/mol/d)	−6.400	−7.300	−6.800	−6.200	−7.100	−6.800
$u(\beta)$ /(10^{-5}μmol/mol/d)	1.600	1.300	0.500	0.400	0.700	1.200

Table 1: Robust estimates of the intercepts (α) and slopes (β), and associated uncertainties, of the linear trends that approximately describe the decrease of the amount-of-substance fraction of formaldehyde in nitrogen over time.

2.3 Trends — Uncertainty Evaluation

The uncertainty associated with the slopes and intercepts of the robust trends defined in §2.2 was evaluated by application of the parametric statistical bootstrap (Efron and Tibshirani, 1993), which, in the nomenclature of the GUM Supplement 1, is a Monte Carlo method for "propagation of distributions" (Joint Committee for Guides in Metrology, 2008).

Let a_{C} and b_{C} denote the robust estimates of the intercept α_{C} and slope β_{C} of the trend for cylinder C, and define the fitted values as $\widehat{x}_{\mathrm{C}}(t_1) = a_{\mathrm{C}} + b_{\mathrm{C}} t_1, \ldots, \widehat{x}_{\mathrm{C}}(t_{m_{\mathrm{C}}}) = a_{\mathrm{C}} + b_{\mathrm{C}} t_{m_{\mathrm{C}}}$, where $t_1, \ldots, t_{m_{\mathrm{C}}}$ denote the numbers of days elapsed since August 14, 2014, when the m_{C} measurements of cylinder C were made. The parametric bootstrap involved repeating the following steps $K = 25\,000$ times for each cylinder C:

(1) Draw $x^*_{\mathrm{C}}(t_i)$ from a Gaussian distribution with mean $\widehat{x}_{\mathrm{C}}(t_i)$ and standard deviation $U_{95\,\%}(x_{\mathrm{C}}(t))/2$, for $i = 1, \ldots, m_{\mathrm{C}}$;

(2) Compute robust estimates, $a_{k,\mathrm{C}}$ and $b_{k,\mathrm{C}}$, of the intercept and slope of the linear trend fitted to the m_{C} pairs $\{(t_i, x^*_{\mathrm{C}}(t_i))\}$.

Figures 2 and 3 on Pages 6 and 3, show smooth histograms of the $\{a_{k,\mathrm{C}}\}$ and $\{b_{k,\mathrm{C}}\}$, and substantiate the aforementioned claim of there being significant differences at least between some of them. In particular, the cylinders seem to be arranged in three groups based on their original amount-of-substance fractions of formaldehyde.

2.4 Trends — Imputation for C08

The three early determinations of the amount-of-substance fraction of formaldehyde in cylinder CO8 are insufficient to produce a reliable estimate of the corresponding trend. In fact, as already noted, those determinations suggest an increase of the amount-of-substance fraction of formaldehyde over time, when it is known that the opposite should have been the case.

Based on the reasonable assumption that the rate of decrease of this amount-of-substance fraction in C08 is similar to the rates of decrease in the other cylinders, I have estimated β_{C08} by applying the Linear Pool (Stone, 1961) to the estimates of the slopes for the other cylinders.

This procedure produces a sample from the probability distribution that describes the uncertainty associated with the slope imputed for C08, whose average and standard deviation are listed in Table 1 as the imputed value of the slope

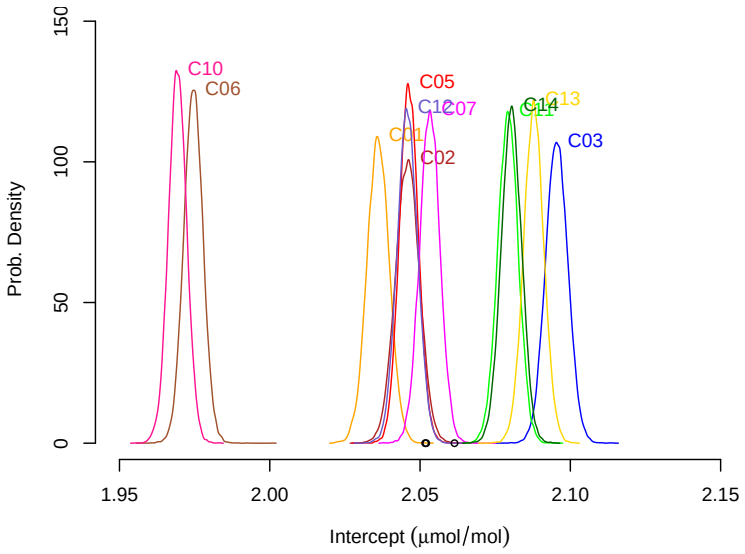

Figure 2: Smooth histograms, indeed kernel density estimates (Silverman, 1986), of the Monte Carlo samples of the intercepts of the linear trends that describe how the amount-of-substance fractions of formaldehyde have decreased over time in the different cylinders. The intercepts estimate the amount-of-substance fractions at the time the cylinders first arrived at the BIPM. The three (black) open circles indicate imputed alternative values of the intercept corresponding to C08, computed as described in §2.4.

for C08 and its associated uncertainty: $\beta_{C08} = -6.415 \times 10^{-5}\,\mu\text{mol/mol/d}$ and $u(\beta_{C08}) = 1.604 \times 10^{-5}\,\mu\text{mol/mol/d}$.

The Linear Pool is preferable to the average of the slopes for the other cylinders because the uncertainty of the average would be $\sqrt{11} \approx 3.3$ times smaller than the typical uncertainty of the 11 slopes being averaged, while the uncertainty of the slope imputed for C08 obviously should be larger than the typical uncertainty of the slopes for the other cylinders.

When the imputed slope is coupled with the three early determinations of the amount-of-substance fraction, three versions of the corresponding intercept α_{C08} are obtained: 2.052 μmol/mol, 2.052 μmol/mol, and 2.061 μmol/mol. Their average is the value imputed for α_{C08}, and their standard deviation is the associated uncertainty, both listed in Table 1.

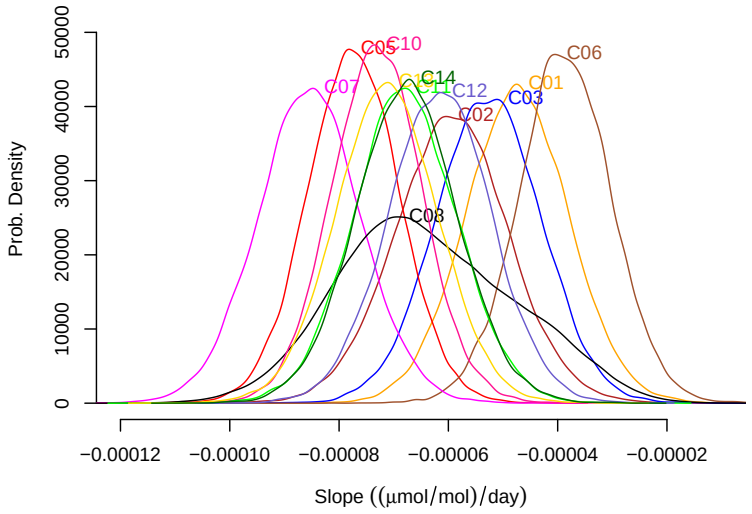

Figure 3: Smooth histograms, indeed kernel density estimates (Silverman, 1986), of the Monte Carlo samples of the rates of decrease (slopes) of the amount-of-substance fractions of formaldehyde in the different cylinders. The black curve summarizes the Monte Carlo sample drawn from the probability distribution of the slope imputed for C08 as described in §2.4.

3 Reference Values

Reference values and their associated uncertainties are computed taking into account the trends discussed in §2, and their associated uncertainties, as well as the dispersion in time of the days in which measurements were made that contributed to the measurement result stated by each participating laboratory.

Take C07, for example, which was measured by NIM. The measurement result was based on determinations made on three different days: July 15 and 16, and August 10, 2015. These are 335, 336, and 361 days after August 14, 2014, the day when the cylinders first arrived at the BIPM.

The uncertainty evaluation described in §2.3 produced samples of size $K = 25\,000$ drawn from the probability distributions that describe the uncertainty associated with the intercept α_{C07} and slope β_{C07}. Pairing these with a sample of the same size, drawn with replacement from $\{335\,\mathrm{d}, 336\,\mathrm{d}, 361\,\mathrm{d}\}$, pro-

duces a sample from the distribution of the reference value corresponding to C07 as measured by NIM. The mean and standard deviation of this sample are the corresponding reference value, $x_R(\text{C07}) = 2.024\,\mu\text{mol/mol}$ and associated standard uncertainty $u(x_R(\text{C07})) = 0.002\,\mu\text{mol/mol}$.

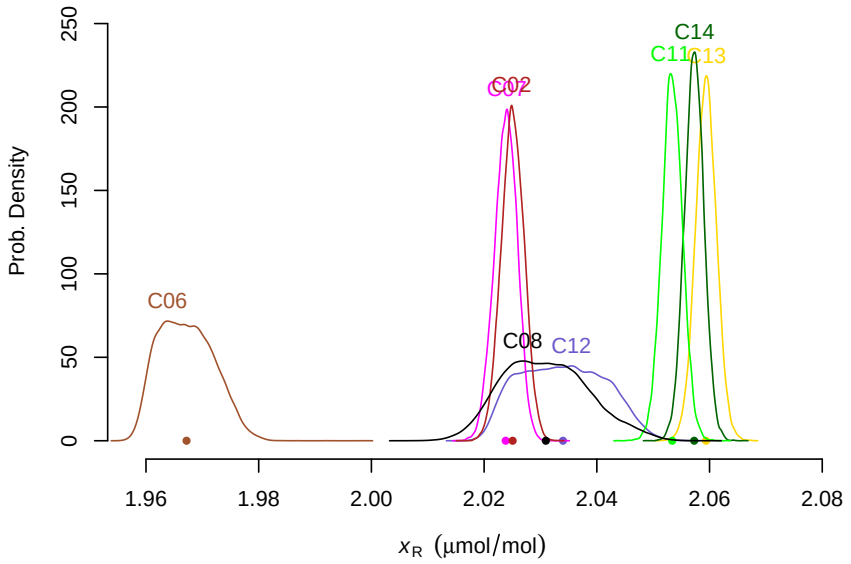

Figure 4: Smooth histograms of the Monte Carlo samples of the reference values, expressing the uncertainty associated with the trends of the amount-of-substance fraction of formaldehyde in the transfer standards, and the dispersion in time of the days when each of them was measured. The dots indicate the means of the samples, which are the reference values listed in Table 2 on Page 9.

4 Degrees of Equivalence

Figure 5 on Page 10 depicts the unilateral degrees of equivalence that are listed in Table 2 on Page 9, comprising the differences $\{D(C) = x_M(C) - x_R(C)\}$, and the associated, expanded uncertainties $U_{95\,\%}(D(C)) = [u^2(x_M(C)) + u^2(x_R(C))]^{1/2}$, where $x_M(C)$ denotes the value measured for cylinder C, and $u(x_M(C))$ denotes

		x_R	$u(x_R)$	D	$U_{95\,\%}(D)$	/(μmol/mol)
BIPM	C06	1.967	0.005	0.000	0.012	
KRISS	C12	2.034	0.007	−0.005	0.030	
LNE	C13	2.059	0.002	0.038	0.028	
NIM	C07	2.024	0.002	−0.048	0.040	
NMIJ	C14	2.057	0.002	0.006	0.011	
NPL	C02	2.025	0.002	0.063	0.052	
VNIIM	C11	2.053	0.002	0.097	0.060	
VSL	C08	2.031	0.008	−0.071	0.072	

Table 2: Reference values and associated standard uncertainties, and unliateral degrees of equivalence.

the associated uncertainty reported by the laboratory that made the measurement.

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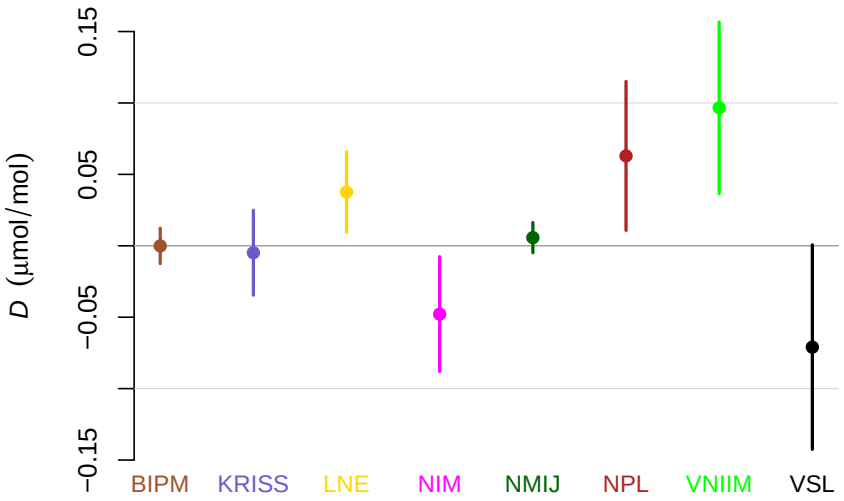

Figure 5: Unilateral degrees of equivalence.

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13 Annex 2 – Measurements results by FTIR

Results of all 13 series of measurements performed at the BIPM are presented in Table 9 and Table 10 below, where x is the formaldehyde mole fraction, and $U(x)$ its associated expanded uncertainty (k=2), both expressed in µmol mol^{-1}.

C1			**C3**			**C5**		
days	*x*	*U*(*x*)	*days*	*x*	*U*(*x*)	*days*	*x*	*U*(*x*)
159	*1.953*	*0.005*	*160*	*2.051*	*0.006*	*161*	2.019	0.006
187	2.028	0.007	188	2.089	0.007	188	2.036	0.007
209	2.040	0.008	210	2.089	0.008	210	2.027	0.008
223	2.026	0.008	223	2.080	0.008			
253	2.023	0.008	253	2.076	0.008	253	2.023	0.008
288	*2.137*	*0.008*	*288*	*2.166*	*0.008*	*288*	*2.094*	*0.008*
336	*2.118*	*0.009*	*337*	*2.161*	*0.009*	*337*	*2.093*	*0.009*
385	2.018	0.008	385	2.072	0.008	385	2.018	0.008
434	2.016	0.008	434	2.075	0.008	434	2.017	0.008
489	2.006	0.008	489	2.070	0.008	489	2.008	0.008
531	2.010	0.008	532	2.067	0.009	532	2.004	0.008
582	*2.260*	*0.000*	*582*	*2.329*	*0.000*	*582*	*2.254*	*0.006*
594	2.011	0.008	600	2.065	0.008	600	1.999	0.008
C6			**C10**			**C4**		
days	*x*	*U*(*x*)	*days*	*x*	*U*(*x*)	*days*	*x*	*U*(*x*)
167	1.967	0.006	*168*	*1.899*	*0.006*	*161*	*2.209*	*0.007*
188	1.975	0.007	194	1.963	0.007	*187*	*2.278*	*0.008*
210	1.961	0.008	211	1.954	0.008			
			223	1.951	0.008			
253	1.960	0.008	254	1.946	0.008			
292	*2.107*	*0.008*	*289*	*1.993*	*0.008*			
337	*2.033*	*0.000*	*337*	*2.006*	*0.008*			
385	1.967	0.008	386	1.938	0.008			
434	1.960	0.008	434	1.940	0.008			
489	1.953	0.008	489	1.933	0.008			
532	1.953	0.008	537	1.929	0.008			
582	*2.195*	*0.006*	*586*	*2.156*	*0.007*			
600	1.951	0.008	595	1.928	0.008			

Table 9: measurement results of the 6 control cylinders kept at the BIPM. The number of days since the first measurement is indicated with the corresponding formaldehyde mole fraction x and the expanded uncertainty $U(x)$, both expressed in µmol mol^{-1}. Values in italic grey indicate values that were discarded for technical reasons.

C2			C7			C8		
days	*x*	*U*(*x*)	*days*	*x*	*U*(*x*)	*days*	*x*	*U*(*x*)
160	*1.993*	*0.006*	167	2.039	0.006	168	2.041	0.006
187	2.036	0.007	188	2.039	0.007	188	2.040	0.007
209	2.035	0.008	210	2.033	0.008	210	2.048	0.008
223	2.030	0.008						
532	2.009	0.008	533	2.006	0.008			
582	*2.267*	*0.000*	*583*	*2.262*	*0.006*			
595	2.015	0.008	595	2.004	0.008			
			C11			**C12**		
			days	*x*	*U*(*x*)	*days*	*x*	*U*(*x*)
			169	2.067	0.006	169	2.036	0.006
			194	2.071	0.007	194	2.035	0.007
			211	2.060	0.008	211	2.028	0.008
			538	2.044	0.008	538	2.012	0.008
			587	*2.275*	*0.007*	*587*	*2.246*	*0.007*
			595	2.038	0.008	595	2.010	0.008
C13			**C14**					
days	*x*	*U*(*x*)	*days*	*x*	*U*(*x*)			
169	2.078	0.006	170	2.065	0.006			
195	2.075	0.007	195	2.074	0.007			
212	2.067	0.008	209	2.066	0.008			
538	2.047	0.008	538	2.039	0.008			
587	*2.284*	*0.007*	*587*	*2.282*	*0.007*			
596	2.048	0.008	596	2.044	0.008			

Table 10: measurement results of the 7 transfer standards sent to participants (NIST standard is not reported). The number of days since 14/08/2014 is indicated with the corresponding formaldehyde mole fraction *x* and the expanded uncertainty *U*(*x*), both expressed in µmol mol^{-1}. Values in italic grey indicate values that were discarded for technical reasons.

The loss of formaldehyde in all standards, deduced from the linear regression of measured values versus the time of analysis, expressed in 10^{-5} µmol mol^{-1} d^{-1}, is reported in Table 11.

Label	d*x*/d*t*	Label	d*x*/d*t*	Label	d*x*/d*t*
C1	-5.970	C2	-5.866	C13	-6.886
C3	-5.179	C7	-8.535	C14	-6.913
C5	-6.302	C8	0.000		
C6	-3.808	C11	-6.733		
C10	-7.419	C12	-5.953		

Table 11: loss of formaldehyde in control and transfer standards, d*x*/d*t*, deduced from linear regressions of 10 (or 5) series of measurement during 450 days, expressed in 10^{-5} µmol mol^{-1} d^{-1}.

14 Annex 3 – FTIR impurity analysis

Mole fractions of impurities detected by FTIR in all cylinders measured during the first series can be found in Table 12. They are provided for informational purposes only, without an associated uncertainty.

mixture	$(HCHO)_3$	CO	CO_2	H_2O
1	0.016	0.243	0.156	0.563
2	0.015	0.183	-0.020	0.303
3	0.020	0.253	-0.034	0.351
4	0.018	0.210	0.014	3.286
5	0.017	0.192	-0.027	0.474
6	0.016	0.341	0.115	0.489
7	0.019	0.184	0.062	0.672
8	0.016	0.226	0.040	0.528
10	0.020	0.207	-0.049	0.311
11	0.015	0.323	-0.043	0.578
12	0.016	0.204	0.012	0.447
13	0.017	0.356	0.051	0.550
14	0.017	0.191	0.013	0.459

Table 12: amount fractions of impurities detected by FTIR in each standard mixture during the first series of measurements performed at the BIPM.
All values are in μmol mol^{-1}.

15 Annex 4 – Measurements results by CRDS

The protocol of the comparison included measurements performed with two analytical techniques, FTIR and CRDS. However the CRDS instrument was out of specifications at two occasions during the course of the comparison, and was unavailable during seven months for repair. It was therefore decided to discard measurements performed with that instrument. Measurement results displayed in Table 13 are provided for information only.

During the series performed before October 2015, the instrument already suffered from an increased instability, with a typical Allan deviation of 20 nmol mol^{-1} for 5 minutes averaging measured on nitrogen, compared to 2 nmol mol^{-1} for the FTIR. After October 2015, the instrument was stable again, with Allan deviations of about 4 nmol mol^{-1}. However, it started to be even more unstable after February 2016 and was not used for the remainder of the study.

date	C1	C2	C3	C5	C6	C7	C8	C10	C11	C12	C13	C14
15/01/2015				2.057	2.054	2.067	2.106	1.976	2.132	2.139	2.106	2.099
15/02/2015	2.046	2.125	2.139	2.023	2.014	2.065	2.045	1.945	2.168	2.086	2.093	2.062
16/02/2015	2.005	2.008	2.143	2.026	1.918	2.126	2.066	2.032	2.083	2.030	2.179	2.135
17/02/2015	2.033	2.085	2.128					2.003				
21/10/2015	2.027		2.087	2.027	1.976			1.948				
15/12/2015	2.024		2.077	2.016	1.964			1.945				
27/01/2016	2.010	2.020	2.070	2.010	1.960	2.010		1.941	2.045	2.022	2.054	2.054

Table 13: HCHO mole fractions measured in all standards by CRDS calibrated with dynamic calibration gas mixtures, expressed in µmol mol^{-1}.

Measurements performed between October 2015 and January 2016 could be analysed and compared with results obtained by FTIR. The difference between values obtained with the two techniques is plotted in Figure 8 for the three series of measurements performed, versus the cylinder number. They demonstrate a good agreement between the two analytical techniques, well within their uncertainties.

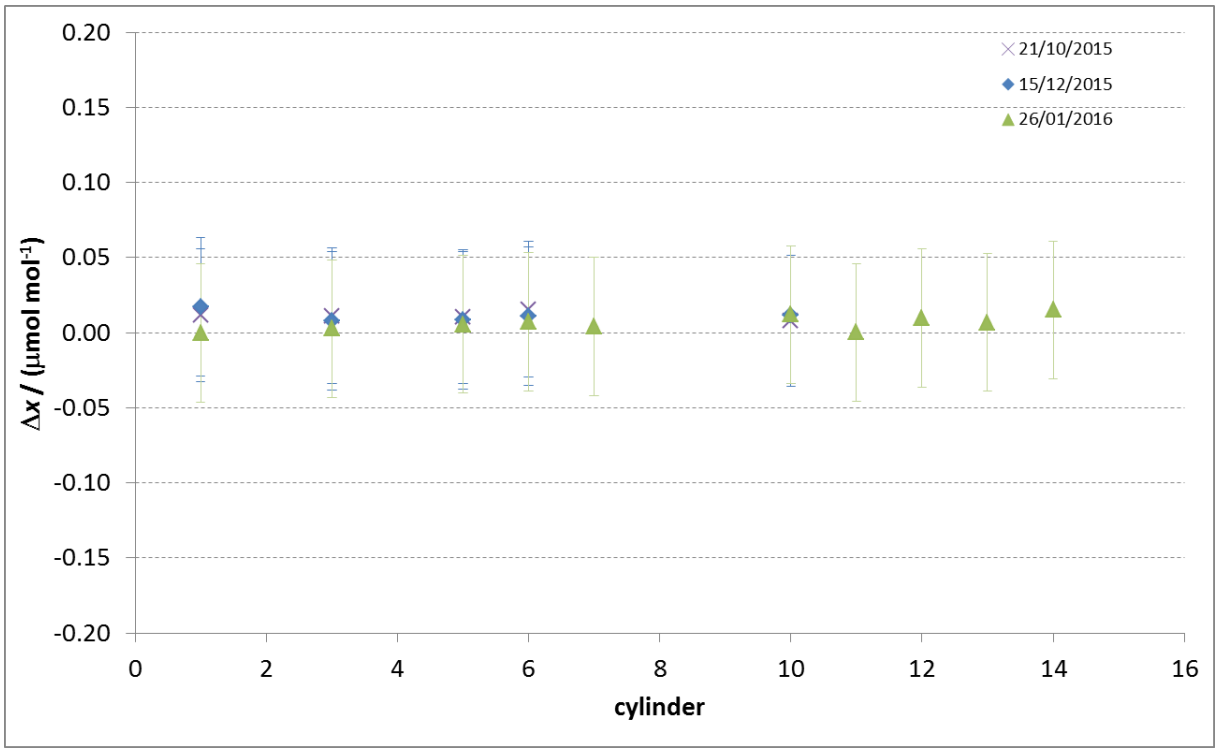

Figure 8: difference between HCHO mole fractions obtained by FTIR and CRDS on three series performed between October 2015 and January 2016.

16 Annex 5 – Measurement uncertainties (BIPM)

16.1 Trioxane diffusion source

The HCHO mole fraction in the gas mixtures produced by diffusion of trioxane followed by thermal conversion, x(HCHO) in µmol mol^{-1}, is determined according to the following equation:

$$x(\mathrm{HCHO}) = \frac{3 q_\mathrm{m} V_\mathrm{m}}{q_\mathrm{v} M_{(\mathrm{HCHO})_3}} \beta_\mathrm{conv} \qquad (1)$$

where:

q_m is the mass loss rate of the diffusion cell containing $(HCHO)_3$ in ng min^{-1};

V_m = 22.4038 L mol^{-1}, is the molar volume of air/N_2 at standard conditions (273.15 K, 101.3 kPa);

$M_{(HCHO)3}$ = 90.0779 g mol^{-1}, is the molar mass of $(HCHO)_3$;

q_v is the total flow rate of N_2 given by the molbloc®/molbox® in L min^{-1};

β_conv = 1 is the conversion factor of $(HCHO)_3$ to HCHO;

Uncertainties associated with each HCHO mole fraction x_PT in gas mixtures produced by diffusion of trioxane followed by thermal conversion, $u(x_\mathrm{PT})$, are automatically calculated by a program developed in house. An example of the uncertainty budget is listed below:

Quantity	Typical value	Standard uncertainty
q_m	6700 ng min^{-1}	8.51 ng min^{-1}
V_m	22.4038 L mol^{-1}	0.34×10^{-3} L mol^{-1}
q_v	2.5 L min^{-1}	1.96 mL min^{-1}
M_HCHO3	90.078 g mol^{-1}	2×10^{-3} g mol^{-1}
β	1	1.73×10^{-3}
x_PT	**2.0 µmol mol^{-1}**	**0.005 µmol mol^{-1}**

16.2 Paraformaldehyde permeation source

The HCHO mole fraction in the gas mixtures produced by permeation from paraformaldehyde, x(HCHO) in µmol mol^{-1}, is determined according to the following equation:

$$x(\mathrm{HCHO}) = \frac{q_\mathrm{m} V_\mathrm{m}}{q_\mathrm{v} M_\mathrm{HCHO}} - \frac{M_\mathrm{H2O}}{M_\mathrm{HCHO}} x(\mathrm{H_2O}) \qquad (2)$$

where:

q_m is the mass loss rate of the permeation tube containing paraformadehyde in ng min^{-1};

V_m = 22.4038 L mol^{-1}, is the molar volume of air/N_2 at standard conditions (273.15 K, 101.3 kPa);

q_v is the total flow rate of N_2 given by the molbloc®/molbox® in L min^{-1};

M_{HCHO} = 30.026 g mol^{-1}, is the molar mass of HCHO;

M_{H2O} = 18.053 g mol^{-1}, is the molar mass of H_2O;

$x(H_2O)$ is the mole fraction of water in the sample produced by permeation from the paraformaldehyde permeation tube.

Uncertainties associated with each HCHO mole fraction x_{PT} in gas mixtures produced by permeation from paraformaldehyde, $u(x_{PT})$, are automatically calculated by a program developed in house. An example of the uncertainty budget is listed below:

Quantity	Typical value	Standard uncertainty
q_m	7 µg min^{-1}	8.5 ng min^{-1}
V_m	22.4038 L mol^{-1}	0.34×10^{-3} L mol^{-1}
q_v	2.5 L min^{-1}	1.28 mL min^{-1}
M_{HCHO}	30.026 g mol^{-1}	2×10^{-3} g mol^{-1}
x_{H2O}	0.012 µmol mol^{-1}	0.006 µmol mol^{-1}
M_{H2O}	18.053 g mol^{-1}	0.5×10^{-3} g mol^{-1}
x_{PT}	**2.082 µmol mol^{-1}**	**0.005 µmol mol^{-1}**

16.3 Correlations

The covariance between two dynamic gravimetric gas mixtures of mole fractions $x_{,i}$ and $x_{,j}$ is calculated as follows:

$$u\left(x_i, x_j\right) = \gamma u\left(x_i\right)^2 \tag{3}$$

where $u(x_i)$ is the standard uncertainty of the more concentrated mixture and,

$$\gamma = \frac{q_{v\,j}}{q_{v\,i}} \tag{4}$$

is the dilution factor between the total flow rate q_{vi} (resp. q_{vj}) used to generate the gas mixture of mole fraction x_i (resp. x_j).

16.4 Analytical instruments:

The standard uncertainty associated with the CRDS analytical values y_{CRDS} is the Allan deviation σ_{Allan_CRDS} measured prior to a series of measurements. Values of 20 nmol mol^{-1} were observed between January and March 2016, improved to 4 nmol mol^{-1} between October 2015 and February 2016.

The standard uncertainty associated with the FTIR analytical values y_{FTIR} is the Allan deviation σ_{Allan_FTIR} measured prior to a series of measurements. It was always close to 2 nmol mol^{-1} during measurements performed for the comparison.

17 Annex 6 – Participants reports

All reports are displayed entirely in the following pages (PDF version only).

Result Form
CCQM K90, Formaldehyde in nitrogen, 2 µmol mol ^{1}

- This form should be completed by participants in the key comparison CCQM-K90 after completion of the measurements described in the protocol of the comparison.

- Comparison coordinator: Dr Joële Viallon
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Return of result form:

- Please complete and return the form by email to jviallon@bipm.org

Participant information			
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Email	dhkim@kriss.re.kr		

Transfer standard information	
Date of reception	June 29, 2015
Serial number of cylinder received	CC435857
Cylinder pressure as received	1600 psi
Cylinder pressure before shipment to BIPM	1000 psi

Results of measurements

Please indicate the date of analysis and the value and associated expanded uncertainty of the formaldehyde mole fraction measured in the transfer standard.

Date of analysis	Formaldehyde mole fraction x(HCHO) / µmol mol^{-1}	Expanded uncertainty U(x(HCHO)) / µmol mol^{-1}	Coverage factor
Sept 3, 2015	2.029	0.025	2

Description of measurements

Please provide below a description of the measurements performed, including the description of national/working standards, analytical instrument(s), handling of the transfer standard, and the calibration procedure followed to deduce the formaldehyde mole fraction in the transfer standard.

Permeation system

The permeation system for dynamic thermogravimetry consisted of a magnetic suspension balance (MSB) and permeation chamber (Rubotherm GmbH, Konard-Zuse-Street, Bochum, Germany). To generate the formaldehyde standard gas, a paraformaldehyde permeation tube (VICI Metronics, Poulsbo, Washington, USA) was used as the formaldehyde source. To control the supply of pure nitrogen, mass flow controller (MFC) was used. The total nitrogen flow to the permeation system was accurately measured with a molbloc-L laminar flow element (Molbox 1+, Fluke Corp., Phoenix, Arizona, USA).

Generation of formaldehyde standard gas

A paraformaldehyde permeation tube was placed inside the permeation chamber at 110 °C. Pure nitrogen was introduced at a constant flow rate of 500 mL/min. The mass loss of the permeation tube was determined by weighing the tube with the magnetic suspension balance (MSB). The mole fraction of the formaldehyde in the generated gas mixture was calculated from the permeation rate (i.e., the sum of formaldehyde and water permeated from the permeation tube) and the total flow rate of nitrogen introduced to the permeation system. In the calculation, the influence of the water permeation on the net mole fraction of formaldehyde was corrected. For this correction, the mole fraction of the water generated from the paraformaldehyde in the permeation tube was measured using a CRDS (HALO+, Tiger Optics LLC, Warrington, Pennsylvania, USA).

Measurement of formaldehyde

Formaldehyde was mesured by CRDS (G1107, Picarro, Santa Clara, California, USA). The CRDS was calibrated based on the formaldehyde standard gas. Both the standard gas and the study materials in cylinders were analyzed under the same experimental conditions. The inlet flow and pressure of the formaldehyde standard gas and the transfer standard gas into the CRDS was maintained at 400 mL/min and 135 kPa, respectively.

Uncertainty budget

Please provide below the uncertainty budget used to calculate the uncertainty associated with the measurement of the formaldehyde mole fraction.

Model equations

- The equation for calculating the mole fraction of formaldehyde in the generated gas mixture

$$x_{HCHO,PT} = \frac{P \cdot V_m}{F_T \cdot M_{HCHO}} - \frac{M_{H_2O}}{M_{HCHO}} x_{H_2O}$$

- $x_{HCHO,PT}$ (μmol/mol) : mole fractions of formaldehyde in the generated gas mixture
- P (μg/min) : permeation rate (i.e., the sum of formaldehyde and water permeated from the permeation tube)
- V_m (L/mol) : molar volume of an ideal gas at standard temperature and pressure (STP)
- M_{HCHO} (g/mol) and M_{HCHO} (g/mol) : molar mass of formaldehyde and water, respectively
- F_T (L/min) : total flow rate of nitrogen introduced to the system
- x_{H2O} (μmol/mol) : mole fraction of water generated from paraformaldehyde in the permeation tube

- The equation for calculating the mole fraction of formaldehyde in the CCQM-K90 transfer standard.

$$x_{HCHO,K90} = \frac{x_{HCHO,PT} \cdot R_{HCHO,K90,CRDS}}{R_{HCHO,PT,CRDS}}$$

- $x_{HCHO,\,K90}$**:** mole fraction of formaldehyde in the CCQM-K90 transfer standard
- R: response of CRDS

Uncertainty Budgets

#	Quantity	Value	Standard Uncert., *u*	Expended Uncert., *Uexp*	Coverage Factor, *k*	Relative Expended Uncert., %	Source
1	*Vm*, L/mol	24.45	negligible	-	-	-	-
2	F_T, mL/min	4967	4.25	8.5	2	0.17	result of calibration
3	M_{HCHO}, g/mol	30.026	negligible	-	-	-	-
4	M_{HCHO}, *g/mol*	18.0152	negligible	-	-	-	-
5	X_{H2O}, μmol/mol	0.015	0.0008	0.0015	2	10	reproducibility of $CRDS_{H2O}$ measurement
6	*P*, ng/min	14297	41	82	2	0.57	reproducibility of MSB measurement
7	$X_{HCHO,PT}$, μmol/mol	2.3335	0.007	0.014	2	0.6	combined uncertaity (#1-6)
8	$X_{HCHO,K90}$, μmol/mol	2.029	0.01	0.02	2	1	reproducibility of $CRDS_{HCHO}$ measurement
9	$X_{HCHO,K90}$, μmol/mol	2.029	0.012	0.025	2	1.2	combined uncertaity (#7-8)

Result Form

CCQM-K90, Formaldehyde in nitrogen, 2 μmol/mol

Participants information

Institute	National Institute of Metrology		
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Telephone	(0)86-(0)10-84252306	Fax	(0)86-(0)10-84252306
Email	zhouzy@nim.ac.cn		
Transfer standard information			
Date of reception	July 10, 2015		
Serial number of cylinder received	CC435863		
Cylinder pressure as received	115 Bar		
Cylinder pressure before shipment to BIPM	107 Bar		

Results of measurement

Please indicate the date of analysis and the value and associated expanded uncertainty of the formaldehyde mole fraction measured in the transfer standard.

Date of analysis	**Formaldehyde mole fraction X(HCHO)/ μmol mol^{-1}**	**Expanded uncertainty U(X(HCHO))/ μmol mol^{-1}**	**Coverage factor, *k*.**
2015/07/15	1.976	0.040	2
2015/07/16	1.977	0.040	2
2015/08/10	1.976	0.040	2
Report result	**1.976**	**0.040**	**2**

Description of measurements

Please provide below a description of the measurements performed, indicating the description of national/working standards, analytical instrument(s), handing of the transfer standard, and the calibration procedure followed to deduce the formaldehyde mole fraction in the transfer standard.

Table 1 listed the description of national standard, analytical instrument and measurement method.

Table 1 Description of measurements

Items	Description
Instrument used for HCHO measurement	CRDS, Picarro G1107
Techniques used for HCHO STD gas mixtures preparation	Diffusion tube of dynamic voulmetric method, national standard (home made).
Compound used for production HCHO	Trioxane, 99% (purity)
Diffusion tube rate,μg/min	(1.963 ±0.023) μg/min, which was determined by weighing the trioxane diffusion tube during a period time.
Temperature of thermol decomposition	180 ^{o}C
Decomposition rate of trioxiane	100%
Temperature of diffusion tube	40^{o}C
Carried gas flow rate (nitrogen that passed into the diffusion system using a mass flow controller)	80 ml/min
Dilution gas flow rate (nitrogen that used to mix with the carried gas)	(1~3) L/min
Approximate mole fraction of HCHO gas generated above conditions	(1.4~2.0) μmol/mol.
Techniques used for flow rate measurement	Dry-Cal Flow Calibration.
H2O concentration	H_2O was measured by CRDS as 0. (Picarro CRDS Model G1107) and final results were not corrected.
Calibration procedure	Single point calibration was used to calculate the mole fraction of the target compound in a comparison cylinder, when analyzing the sample gas mixture, “A-B-A” type calibration procedure was used. It means that the sample and calibration gas mixtures were measured in the order of Calibration-Sample-Calibration. This procedure was carried out 3 times on different days.
Environmental conditions	We did not considered the effect of the temperature, moisture and pressure changes of lab`s environment on the measurement results.

Uncertainty budget

Please provide below the uncertainty budget used to calculate the uncertainty associated with the measurement of the formaldehyde mole fraction.

The uncertainty of calibration gas mixtures (C_0) were evaluated according to" ISO 6145-8 Gas analysis - Preparation of calibration gas mixtures using dynamic volumetric methods - Part 8: Diffusion method".

The C_0 can be calculated with equation (1) as below:

$$C_0 = \frac{P_0 V_0 T}{T_0 P M Q} \times R_m \times 10^3 = 276.699 \times \frac{T}{PQ} \times R_m \qquad (1)$$

Where,

C_0- mole fraction of calibration standard prepared by dynamic volumetric method （μmol/mol）,

P_0- Pressure value in a standard state 101.325 kPa.

V_0- Volume value in a standard state 22.4 L/mol.

T_0- Temperature value in a standard state 273.15 K.

T- Temperature of gas mixture cell where the carried gas (contained trioxane) mixed with dilution gas (K).

P- pressure of gas mixture cell where the carried gas (contained trioxane) mixed with dilution gas (kPa).

M- molecular of trioxane （g/mol）.

R_m- diffusion rate of troxiane（μg/min）.

Q- total flow rate of carried gas and dilution gas （ml/min）.

The carried gas and dilution gas are nitrogen. Table 2 listed the purity assay of nitrogen used in the experiments.

Table 2 Purity of Nitrogen

Component	Purity of N_2 (mol/mol)	Standard uncertainty (mol/mol)
H_2O	1.2×10^{-8}	1.0×10^{-8}
O_2	1.4×10^{-8}	0.5×10^{-8}
H_2	3.0×10^{-7}	1.0×10^{-7}
CO	5.3×10^{-8}	3.0×10^{-8}
CO_2	1.3×10^{-7}	1.0×10^{-7}
CH_4	1.0×10^{-8}	1.0×10^{-8}
Ar	4.90×10^{-5}	0.12×10^{-5}
N_2	0.999970	0.000002

The standard relative uncertainty of (C_0) can be calculated with equation (2), which derived from equation (1).

$$\left[\frac{u(C_0)}{C_0}\right]^2 = \left[\frac{u(Q)}{Q}\right]^2 + \left[\frac{u(T)}{T}\right]^2 + \left[\frac{u(P)}{P}\right]^2 + \left[\frac{u(R_m)}{R_m}\right]^2 \qquad (2)$$

Table 3 listed the uncertainty budget for the calibration gas mixtures (C_0):

Table 3 Uncertainty budget of the calibration gas mixtures

Component	distribution	Sensitivity coefficient	Relative standard uncertainty, $u(x_i)$
Q	Rectangle	1	0.60%
T	Rectangle	1	0.23%
P	Rectangle	1	0.26%
R_m	Normal	1	0.60%
Combined relative standard uncertainty			0.92%

"A-B-A" type calibration procedure was used in this measurement. The calibration uncertainty was evaluated based on the equation (3):

$$C_S = \frac{A_S}{A_0} * C_0 \qquad (3)$$

where,

C_s - mole fraction of sample gas mixture;

A_s - responding of sample cylinder in CRDs;

C_0 - mole fraction of calibration gas mixtures;

A_0 - responding of calibration gas mixtures in CRDs

Table 4 listed the uncertainty budget for this comparison sample cylinder measurement:

Table 4 Uncertainty budget for the sample cylinder measurement

Component	**distribution**	**Sensitivity coefficient**	**Relative standard uncertainty, $u(x_i)$**
A_s	Normal	1	0.20%
A_0	Normal	1	0.20%
C_0	Rectangle	1	0.92%
^1f	Normal	1	0.22%
Combined relative standard uncertainty			1.00%

^1f - the reproducibility of the measurement for different days, considering the stability of formaldehyde in cylinder.

The measurement result (C_s) relative standard uncertainty u_{C_s} can be calculated with equation (4)

$$u_{C_s}{}^2 = u_{C_0}{}^2 + u_{A_0}{}^2 + u_{A_s}{}^2 + u_f{}^2 \quad (4)$$

Where,

u_{C_s}- The combined relative standard uncertainty of the measurement result.

u_{C_0}- The relative standard uncertainty of the calibration gas mixtures.

u_{A_0}- The relative standard uncertainty of responding of sample cylinder in CRDs.

u_{A_s}- The relative standard uncertainty of responding of calibration gas mixtures in CRDs.

$u_{C_s}=\sqrt{(0.20\%)^2+(0.20)^2+(0.92\%)^2+(0.22\%)^2}=0.99\%$

The expanded relative uncertainty with 95% confidence and a coverage factor k=2 is:

$U_{C_s}=k*u_{C_s}=2.00\%$

For the sample cylinder, the measurement result with an absolute uncertainty is: (1.976±0.040) μmol/mol

Result Form
CCQM -K90, Formaldehyde in nitrogen, 2 µmol mol ^{1}
-

- This form should be completed by participants in the key comparison CCQM-K90 after completion of the measurements described in the protocol of the comparison.

- Comparison coordinator: Dr Joële Viallon
  Chemistry Section
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Return of result form:

- Please complete and return the form by email to
  jviallon@bipm.org

Participant information			
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Contact person	Takuya Shimosaka		
Telephone	+81-29-861-6851	**Fax**	+81-29-861-6854
Email	t-shimosaka@aist.go.jp		

Transfer standard information	
Date of reception	June 6, 2015
Serial number of cylinder received	CC433246
Cylinder pressure as received	11.5 MPa
Cylinder pressure before shipment to BIPM	9.5 MPa

Results of measurements

Date of analysis yyyy/mm/dd	Formaldehyde mole fraction x(HCHO) / µmol mol^{-1}	Expanded uncertainty U(x(HCHO)) / µmol mol^{-1}	Coverage factor
2015/07/17-2015/07/24	2.063	0.009	2

The analysis was done in a week. The date of analysis is summarized in Table 4.

Description of measurements

National standards

The primary standard gases were prepared by the permeation method basically according to ISO 6145-10. Experimental conditions of the permeation method are summarized in Table 1.

Table 1 Experimental conditions of the permeation method

Instrument for weighing permeation tube	Magnetic suspension balance (MSB)
Instrument for measuring water in standard gas	Cavity Ring-Down Spectroscopy (CRDS)
Instrument for measuring mass flow rate of carrier gas	Mass flow controller (MFC)
Permeation tube	8 mm OD× 10cm long
Source material for formaldehyde	Paraformaldehyde
Temperature of permeation tube	74 ºC
Flow rate of carrier gas to the generation cell	300 SCCM
Total flow rate of carrier gas	300 SCCM, 400 SCCM, 600 SCCM, 1000 SCCM

The apparatus for preparing the standard gases is composed of a magnetic suspension balance (MSB) with a generation cell in which the permeation tube supplied from GASTEC Corporation is set, two mass flow controllers (MFCs), and a moisture meter (Cavity Ring-Down Spectroscopy (CRDS)). The MSB, MFCs, and CRDS were used to measure the mass of the permeation tube, the flow rate of carrier gases, and water mole fraction in the gas from the generation cell, respectively.

The standard gases were prepared by mixing the gaseous formaldehyde generated from the permeation tube and the carrier gas (high purity nitrogen of 99.9995%). The formaldehyde mole fraction ($x_{\mathrm{HCHO,STD}}$) in the standard gases was calculated by the following formula.

$$x_{\mathrm{HCHO,STD}} = \frac{\Delta m_{\mathrm{HCHO}}/M_{\mathrm{HCHO}}}{F_{\mathrm{total\ carrier}}/M_{\mathrm{N_2}}}, \quad (1)$$

where Δm_{HCHO} is the permeability of formaldehyde, $F_{\mathrm{Total\ carrier}}$ total mass flow rate of the carrier gas, M_{HCHO} and M_{N2} are molar mass of formaldehyde and nitrogen (carrier gas), respectively. Because water is generated when formaldehyde is produced from paraformaldehyde, the permeability of formaldehyde is expressed by the following equation,

$$\Delta m_{\mathrm{HCHO}} = \Delta m_{\mathrm{tube}} - \Delta m_{\mathrm{H_2O}}, \quad (2)$$

where Δm_{tube} and $\Delta m_{\mathrm{H_2O}}$ are the mass loss rate of the permeation tube and the permeability of water, respectively. Mass loss rate of the permeation tube (Δm_{tube}) was measured by the MSB. The permeability of water ($\Delta m_{\mathrm{H_2O}}$) is given as

$$\Delta m_{\mathrm{H_2O}} = \frac{x_{\mathrm{H_2O}} F_{\mathrm{cell\ carrier}} M_{H_2O}}{M_{\mathrm{N_2}}}, \quad (3)$$

where x_{H_2O} is the mole fraction of water in the gas from the generation cell, $F_{\text{cell carrier}}$ is mass flow rate of the carrier gas through the generation cell, and M_{H_2O} is the molar mass of water.

The uncertainty ($u(x_{\text{HCHO}})$) of formaldehyde mole fraction is given as

$$u^2(x_{\text{HCHO,STD}}) = x^2_{\text{HCHO,STD}}\left[\frac{u^2(\Delta m_{\text{tube}})+u^2(\Delta m_{\text{H}_2\text{O}})}{(\Delta m_{\text{tube}}-\Delta m_{\text{H}_2\text{O}})^2} + \left(\frac{u(M_{\text{HCHO}})}{M_{\text{HCHO}}}\right)^2 + \left(\frac{u(F_{\text{total carrier}})}{F_{\text{total carrier}}}\right)^2 + \left(\frac{u(M_{\text{N}_2})}{M_{\text{N}_2}}\right)^2\right], \quad (4)$$

where

$$u^2(\Delta m_{\text{H}_2\text{O}}) = \Delta m^2_{\text{H}_2\text{O}}\left[\left(\frac{u(x_{\text{H}_2\text{O}})}{x_{\text{H}_2\text{O}}}\right)^2 + \left(\frac{u(F_{\text{cell carrier}})}{F_{\text{cell carrier}}}\right)^2 + \left(\frac{u(M_{\text{H}_2\text{O}})}{M_{\text{H}_2\text{O}}}\right)^2 + \left(\frac{u(M_{\text{N}_2})}{M_{\text{N}_2}}\right)^2\right]. \quad (5)$$

The four primary standards were prepared by controlling carrier gas flow rate at 300 SCCM, 400 SCCM, 600 SCCM, and 1000 SCCM. Examples of the mole fractions of formaldehyde in the primary standards and their uncertainties are shown in Table 2.

Table 2 Examples of the mole fractions of formaldehyde in the four primary standards and their standard uncertainties

Number	Total flow rate (SCCM)	Mole fraction (μmol/mol)
1	300	4.2395 ± 0.0099
2	400	3.1740 ± 0.0074
3	600	2.1123 ± 0.0049
4	1000	1.2656 ± 0.0030

Analytical instruments

A sample of CCQM-K90 was analyzed by a FTIR spectrometer of which analytical conditions are shown in Table 3. The formaldehyde mole fraction was determined using the strongest absorption line of 1745.50 cm^{-1}.

Table 3. Analytical conditions of a FTIR spectrometer used to measure formaldehyde in nitrogen

Instrument	JASCO FT/IR 6100
Detector	MCT
Path length	12 m
Resolution	1 cm^{-1}
Number of Integrations	256 times
Sample flow rate	100~200 mL/min
Absorption line	1745.50 cm^{-1}

Handling the transfer standard and the calibration procedure

The CCQM-K90 cylinder had been in the analytical room over a day before it was measured. The mole fraction in the CCQM-K90 sample was determined using the four primary standard gases. The standard gases and the sample were measured in the following measurement sequence:

STD_1 - STD_2 – sample – STD_3 – STD_4

The sample and standard gases were measured seven times in a sequence. The formaldehyde mole

fraction in the sample was determined in every sequence using the generalized least-square method in which uncertainties for the standard gases and measurement were considered to estimate the mole fraction and its uncertainty.

The sequence was repeated 5 times and the mole fraction and its uncertainty were determined in every sequence. The mole fraction in the sample ($x_{\mathrm{HCHO,sample}}$) to be reported was the weighted mean of the mole fractions of formaldehyde in five sequences ($x_i (i = 1\sim5)$).

$$x_{\mathrm{HCHO,sample}} = \frac{\sum_{i=1}^{5} w_i x_i}{\sum_{i=1}^{5} w_i}. \tag{6}$$

The weighing factor w_i is described in the next section.

Uncertainty budget

The mole fraction for each sequence (x_i) has a correlation with one another because the mole fraction in the standard gases for each sequence is calculated from the mass flow rate measured using the same mass flow controller. The standard uncertainty of $x_{\mathrm{HCHO,sample}}$ was therefore calculated using the following formula.

$$u\left(x_{\mathrm{HCHO,sample}}\right) = \sqrt{\sigma^2_{x_{\mathrm{HCHO,sample}}} + u_s^2}, \tag{7}$$

where u_s is the common uncertainty and $\sigma_{x_{\mathrm{HCHO,sample}}}$ is the standard uncertainty due to the other factors. $\sigma_{x_{\mathrm{HCHO,sample}}}$ is given as

$$\sigma^2_{x_{\mathrm{HCHO,sample}}} = \frac{1}{\sum_{i=1}^{5} w_i}, \tag{8}$$

where w_i is the weighting factor. The weighting factor w_i is given as

$$w_i = \frac{1}{(u_i^2 - u_s^2)} = \frac{1}{u_{r_i}^2}, \tag{9}$$

where u_i is the standard uncertainty of x_i derived from eq.(4), u_{r_i} is the statistical dispersion not to depend on the common uncertainty.

The determined mole fraction ($x_{\mathrm{HCHO,sample}}$) and the standard uncertainty ($u\left(x_{\mathrm{HCHO,sample}}\right)$) in the CCQM-K90 sample were 2.0626 μmol/mol and 0.044 μmol/mol as shown in Table 4.

Table 4 Results of the determination of the formaldehyde mole fraction in the CCQM-K90 sample

Analytical date (yyyy/mm/dd)	Mole fraction ($\boldsymbol{x_i}$) (μmol/mol)	Standard uncertainty($\boldsymbol{u_i}$) (μmol/mol)		
			u_{r_i}	u_s
2015/7/17	2.0627	0.0064	0.0057	
2015/7/22	2.0558	0.0080	0.0075	
2015/7/23	2.0674	0.0080	0.0074	0.0030
2015/7/23	2.0574	0.0083	0.0078	
2015/7/24	2.0697	0.0087	0.0082	
$\boldsymbol{x_{\mathrm{HCHO,sample}}}$		**2.0626 μmol/mol**		
$\boldsymbol{u\left(x_{\mathrm{HCHO,sample}}\right)}$		**0.0044 μmol/mol**		
	$\boldsymbol{\sigma_{x_{\mathrm{HCHO,sample}}}}$	0.0032 μmol/mol		
	$\boldsymbol{u_s}$	0.0030 μmol/mol		

VNIIM report
CCQM-K90, Formaldehyde in nitrogen, 2 µmol mol^{-1}

Participant information			
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Transfer standard information			
Date of reception	20.08.2015		
Serial number of cylinder received	CC435864		
Cylinder pressure as received	11.5 MPa		
Cylinder pressure before shipment to BIPM	10.0 MPa		

Results of measurements

Dates of analysis	**Formaldehyde mole fraction *x*(HCHO) / µmol mol^{-1}**	**Expanded uncertainty *U*(x(HCHO)) / µmol mol^{-1}**	**Coverage factor**
25.08.2015 - 03.09.2015	2.15	0.06	2

1 Description of measurements

1.1 Preparation of calibration standards

Characteristics of pure substances used for preparation of the calibration gas mixtures are shown in the table 1.

Table 1

Substance	Mole* fraction (10^{-2} mol/mol)	Standard uncertainty (10^{-2} mol/mol)
Nitrogen	99.999848	0.000003
1,3,5- Trioxane	99.0**	0.6
* - Mass fraction for Trioxane ** - Moisture content in Trioxane – 0.060 % (U=10 % rel., k=2) measured by coulometric Karl Fisher titration		

Dynamic calibration gas mixtures were prepared on the base of trioxane permeation tube (PT) and Magnetic Suspension balance (Rubotherm, Germany).

Trioxane permeation tube was designed as polyethylene ampoule (d=8 mm, l=15 mm) with wall thickness 0.3 mm. PT was thermostated at 30°C, and it generated vapour phase trioxane at a rate approximately 2 µg/min. A flow of dry nitrogen (set at 0.100 dm^3/min by mass flow controller) as a balance gas was purged through the system.

Trioxane in the vapour phase was removed from the thermostat cell by the balance gas flow to the thermal convertor, where trioxane was converted to formaldehyde. The convertor was designed as a stainless steel tube with electropolished surface (d=1/8 inch, l=3.5 m), located in the oven at 250°C. This temperature was chosen as optimum temperature for conversion. The efficiency of conversion was estimated

(1) by means of CRDS analyzer by choosing conditions for which the maximum formaldehyde signal was obtained and

(2) by means of chromato-mass-spectrometry by monitoring of relative change of trioxane content before and after conversion and also by monitoring of other substances, which could present in the mixture after conversion.

At the output of the convertor the obtained gas mixture (formaldehyde/nitrogen) was diluted to approximately 0.8 dm^3/min (set by mass flow controller and measured accurately by flow calibrator (Cal=Trak SL800, Sierra Instruments Inc., USA) in order to receive a mixture of the target amount of substance level - 2 µmol/mol.

The amount fraction of formaldehyde (C, µmol/mol) in generated dynamic calibration gas mixture was calculated in accordance with the formula: $C = \frac{G \cdot V_m \cdot K}{W \cdot M_F}$

Where

G – trioxane permeation rate, µg/min;

V_m – molar volume of the ideal gas at standard temperature and pressure. dm^3/mole;

W – total flow rate through the dynamic system, dm^3/min;

M_F – molar mass of formaldehyde, g/mole

K – conversion coefficient, K was estimated as 0.999.

The exact values of formaldehyde amount fraction in the calibration gas mixtures and associated standard uncertainties are shown in the table 2.

Table 2

Date of preparation	Mole fraction (µmol/mol)	Standard uncertainty (µmol/mol)
26/08/2015	2.148	0.029
27/08/2015	2.144	0.029
01/09/2015	2.082	0.029
02/09/2015	2.076	0.029
03/09/2015	2.096	0.029

1.2 Handling of the transfer standard

The comparison cylinder (transfer standard) was rolled for about 1 hour to ensure homogeneity of the mixture. Prior to measurements, it was hold at laboratory temperature for more than 24 hours.

1.3 Calibration and measurement procedure

Measurements were carried out by CRDS analyzer (Picarro G 2107, Picarro Inc. USA) using one point calibration method.

5 independent measurements in 5 days were performed.

Each measurement consisted of 5 sub-measurements with a sequence in the order:

Calibration mixture – Transfer standard – Calibration mixture.

Operating mode for CRDS analyzer

Averaging time: 5 min

Measurement cell temperature: 45°C

Measurement cell pressure: 18,665 kPa

Sample flow rate: 0.4 dm^3/min

Each measurement was followed by control of conversion coefficient by chromato-mass-spectrometry (Agilent 7890A, Agilent Technologies, USA).

Operating mode for Chromato-mass-spectrometer

Detector: MSD

Mode: SIM

Column: DB-1, 30 m × 0,32 mm, 5 µm

Temp. program of the column thermostat: 60°C – 1.45 min, 100°C/min, 160°C – 0.8 min

Carrier gas: He

Gas flow: 1.5 ml/min -1.45min, 2.5 ml/min – till 3.3 min

Sample loop volume: 0.25 cm^3

Temperature of sampling valve: 100 °C

Sample splitting: 3:1

2 Uncertainty budget

Uncertainty source		Estimate x_i	Units	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution $u_i(y)$ µmol/mol
Calibration standard	Trioxane permeation rate	1.90	µg/min	0.0228	1.13	0.0258
	Flow rate	0.730	dm^3/min	0.0021	2.95	0.0062
	Conversion coefficient	0.999	-	0.005	2.2	0.011
Scatter of the results		2.15	µmol/mol	0.007	1	0.007
Combined standard uncertainty						0.0296
Expanded uncertainty k=2						0.06

Date: 17/09/2015

Authors: L.A. Konopelko, Y.A. Kustikov, A.V. Malginov, I.K. Chubchenko, A.Y. Klimov, O.V. Efremova

Result Form

CCQM-K90, Formaldehyde in nitrogen, 2 µmol mol^{-1}

- This form should be completed by participants in the key comparison CCQM-K90 after completion of the measurements described in the protocol of the comparison.
- Comparison coordinator: Dr Joële Viallon
Chemistry Section
Bureau International des Poids et Mesures
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Return of result form:

- Please complete and return the form by email to jviallon@bipm.org

Participant information			
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Transfer standard information	
Date of reception	08/06/2015
Serial number of cylinder received	CC435928
Cylinder pressure as received	100
Cylinder pressure before shipment to BIPM	80

Results of measurements

Please indicate the date of analysis and the value and associated expanded uncertainty of the formaldehyde mole fraction measured in the transfer standard.

Date of analysis	Formaldehyde mole fraction x(HCHO) / nmol mol^{-1}	Standard uncertainty U(x(HCHO)) / nmol mol^{-1}	Coverage factor
15/09/15	2098	13	1
16/09/15	2099	13	1
17/09/15	2102	13	1
18/09/15	2093	13	1
21/09/15	2095	13	1

Final result

Formaldehyde mole fraction x(HCHO) / nmol mol^{-1}	Expanded uncertainty U(x(HCHO)) / nmol mol^{-1}	Coverage factor
2097	27	2

Description of measurements

Please provide below a description of the measurements performed, including the description of national/working standards, analytical instrument(s), handling of the transfer standard, and the calibration procedure followed to deduce the formaldehyde mole fraction in the transfer standard.

The reference standard of formaldehyde is based on a diffusion tube of trioxane in an oven heated at 35°C flushing by pure nitrogen. The gas mixture generated with the diffusion tube is then converted in formaldehyde with an electropolished stainless steel tube (3 meters) put into an oven at 240°C.
The diffusion tube is weighed on a micro balance every 2 weeks to evaluate the diffusion rate and the nitrogen flow is measured by a Molbloc system. The purity is determined by gas phase chromatography with a HID detector.

The analyser (Aerodyne spectrometer) is first calibrated with the diffusion tube for one hour (one point calibration). The sample is then analysed for two hours. At last, the analyser is calibrated again for one hour. This procedure allows to prevent a possible drift.
Averages of the concentrations are calculated on one hour for the reference standard, on the last 30 minutes for the sample.

Uncertainty budget

The uncertainty budget is established by combining the uncertainty on the concentration of the reference gas mixture, the analytical uncertainty and the reproducibility standard deviation of the measurements.
The table sums up the uncertainties of one determination of the concentration gas mixture.

Variable	Unity	Value	u(Xi)	C(Xi)	C(Xi).u(Xi)	weight %
Cylinder response	nmol/mol	1868.9	0.3	1.120855	0.3362565	0.07%
Purity	%	99.59	0.2367136	21.03385	4.978999	16.19%
Permeation rate	ng/min	3411.55	11	0.6140204	6.754224	29.79%
Evolution of the permeation rate	ng/min	0	10	0.6140204	6.140204	24.62%
Temperature variation	ng/min	0	9.848297	0.6140204	6.047055	23.88%
Molecular mass	g/mol	30.026	6.00E-04	-69.76491	-0.0418589	0.00%
Nitrogen flow	l/min	1.204	0.001	-869.0056	-0.8690056	0.49%
Flow calibration	l/min	0.0012	0.0012	-1738.104	-2.085725	2.84%
Molar volume	liter	22.414	1.90E-04	93.45772	0.017757	0.00%
Standard 1 response	nmol/mol	1877.6	2	-0.5578016	-1.115603	0.81%
Nitrogen flow	l/min	1.204	0.001	-869.0982	-0.8690982	0.49%
Standard 2 response	nmol/mol	1877.4	2	-0.5579204	-1.115841	0.81%

Concentration	2095 ± 13 nmol/mol (k=1)

The formaldehyde mole fraction given in the paragraph “Results of measurements” is the average of the five determinations and the uncertainty is the quadratic sum of the uncertainty of the measurement and the standard deviation of the five determinations.

C = 2097 ± 27 nmol/mol (k=2)

Report Form: K90 - Formaldehyde in nitrogen

Laboratory: National Physical Laboratory

Cylinder Number: CC435938

Measurement #1: CRDS (dynamic reference standard)

Component	Date (dd/mm/yy)	Result (µmol/mol)	standard uncertainty (µmol/mol)	No. of replicates
CH_2O	13/07/2015	2.08	0.08	4

Measurement #2: CRDS (CC450885)

Component	Date (dd/mm/yy)	Result (µmol/mol)	standard uncertainty (µmol/mol)	No. of replicates
CH_2O	14/07/2015	2.08	0.06	3

Measurement#3 : CRDS (CC450781)

Component	Date (dd/mm/yy)	Result (µmol/mol)	standard uncertainty (µmol/mol)	No. of replicates
CH_2O	14/07/2015	2.09	0.08	3

Measurement#4 : CRDS (dynamic reference standard)

Component	Date (dd/mm/yy)	Result (µmol/mol)	standard uncertainty (µmol/mol)	No. of replicates
CH_2O	30/07/2015	2.10	0.09	4

Measurement#5 : CRDS (CC450885)

Component	Date (dd/mm/yy)	Result (µmol/mol)	standard uncertainty (µmol/mol)	No. of replicates
CH_2O	31/07/2015	2.09	0.06	3

Measurement#6: CRDS (CC450781)

Component	Date (dd/mm/yy)	Result (µmol/mol)	standard uncertainty (µmol/mol)	No. of replicates
CH_2O	31/07/2015	2.07	0.07	3

Measurement#7 : CRDS (CC450885)

Component	Date (dd/mm/yy)	Result (µmol/mol)	standard uncertainty (µmol/mol)	No. of replicates
CH_2O	19/08/2015	2.10	0.06	3

Measurement#8: CRDS (CC450781)

Component	Date (dd/mm/yy)	Result (µmol/mol)	standard uncertainty (µmol/mol)	No. of replicates
CH_2O	19/08/2015	2.11	0.08	3

Final Result:

Component	Date (dd/mm/yy)	Result (µmol/mol)	expanded uncertainty (µmol/mol)	coverage factor
CH_2O	**19/08/2015**	**2.088**	**0.052***	**2**

*The reported uncertainty is based on a standard uncertainty multiplied by a coverage factor *k* = 2, providing a coverage probability of 95 %.

Details of the measurement method used

Reference method

The amount fraction of formaldehyde in the comparison mixture was measured using a cavity ring-down spectrometer (Picarro G1107).

Calibration standards

Two NPL Primary Reference Gas Mixtures (PRGMs) of nominally 2 µmol/mol formaldehyde in nitrogen were prepared in accordance with ISO 6142. Solid trioxane was used as source of pure formaldehyde. The trioxane diffusing from a solid pellet was thermally converted into formaldehyde in a converter kept at 230 °C. The purity of the source formaldehyde (gas phase) was analysed and found to be (99.25 ± 0.75) %. The mixtures were prepared in Air Liquide/Scott 29.5 L cylinders with Aculife VIII passivation. The PRGMs were prepared in one stage by direct addition of formaldehyde to the cylinder followed by the addition of the nitrogen matrix (by direct filling).

Both mixtures were used to determine the amount fractions of the formaldehyde in the comparison mixture. The amount fraction of CC450781 was 1.994 ± 0.038 µmol/mol and CC450885 was 2.060 ± 0.033 µmol/mol. Expanded uncertainties are quoted.

In addition, a dynamic facility was also used to determine the amount fraction of the travelling standard. The dynamic standard is based on the diffusion of trioxane pressed into small rods (approximately 5 g) and placed in a borosilicate glass cell. The cell was placed in an oven at 35 °C along with a heat exchanger and a thermal converter operated at 230 °C. The heat exchanger consists of 2.5 m of 1/16" tubing (SilcoNert2000-coated) and was used to equilibrate the temperature of the incoming nitrogen to that of the oven before reaching the diffusion cell. The trioxane exiting the diffusion cell was diluted in a flow of nitrogen and was thermally converted to formaldehyde in the converter. The nitrogen flow was controlled using high-accuracy mass flow controllers (C-MOS, Sensirion) and was measured using a high accuracy Dry-Cal Flow Calibrator (ML-800, Bios International Corporation) under controlled conditions. The mass loss of trioxane from the diffusion cell was measured over a 6 month period; the diffusion rate was determined as the gradient of a linear fit through the mass loss data against time. The amount fraction of formaldehyde generated dynamically, x_f, was calculated as follows:

$$x_f = \frac{d \times V_m \times C}{M_f \times Q_A} + x_z$$

where d is the diffusion rate (g/min), V_m is the molar volume of an ideal gas at standard temperature and pressure (L/mol), C is the converter efficiency, M_f is the molar mass of formaldehyde (g/mol), Q_A is the total flow in the dynamic system (L/min) and x_z is the amount fraction of formaldehyde in the nitrogen balance gas (mol/mol).

Instrument calibration, data analysis and quantification

For each measurement, the comparison mixture and an NPL reference standard (static or dynamic) were connected to a CRDS analyser via stainless steel tubing and a 3-way valve for rapid switching between the two mixtures. Each sampling line was equipped with a vent line to allow the gas to flow when not being sampled. Needle valves were used to control the gas flow to the analyser. When a mixture was being measured, the flow was adjusted in order to provide an excess flow of approximately 0.2-0.4 L/min, as measured on a rotameter placed on the vent line. Prior to the measurement, the lines were thoroughly purged and flow rates were allowed to stabilise for approximately one hour. The method was set up to alternate between the NPL and the comparison mixture every 15 minutes. At least three measurements of the comparison mixture were carried out, with the NPL reference standard sampled before and after in each case. The value of the instrument reading used for each measurement was the average of the last 2 minutes of each sampling session (resulting in the average of 120 data points).

Uncertainty evaluation

The ratio of the CRDS response from the comparison mixture and the NPL PRGM was calculated using:

$$r = \frac{2A_{u,m}}{(A_{s,m} + A_{s,m+1})}$$

Where $A_{u,m}$ is the average instrument response from repeat *m* of the comparison mixture, and $A_{s,m}$ is the average instrument response from repeat *m* of the NPL PRGM.

And the average ratio ($\bar{r}$) is calculated by:

$$\bar{r} = \frac{\sum r}{n}$$

Where *n* is the number of ratios. The amount fraction of formaldehyde in the comparison mixture, x_u, is then calculated by:

$$x_u = x_s \bar{r}$$

Where x_s is the amount fraction of formaldehyde in the standard. The standard uncertainty of the measurand, $u(x_u)$, is calculated by:

$$\frac{u(x_u)}{x_u} = \sqrt{\frac{u(x_s)^2}{{x_s}^2} + \frac{u(\bar{r})^2}{\bar{r}^2}}$$

The table which follows details the uncertainty analysis for an example measurement.

quantity	unit	example value	standard uncertainty	sensitivity coefficient	uncertainty contribution	uncertainty type	distribution
x_s	nmol/mol	2.060	0.0163	1.0096	0.0164	A	normal
$\bar{f}$	-	1.0096	0.0285	2.0600	0.0588	A	normal
x_u	**nmol/mol**	**2.080**					
$u(x_u)$	**nmol/mol**	**0.0610**					
$U(x_u)$	**nmol/mol**	**0.1221**					

To obtain the final result for the comparison, an average was taken for the eight measurements. The following table shows the calculation of the final results and its uncertainty.

quantity	unit	value	standard uncertainty	sensitivity coefficient	uncertainty contribution	uncertainty type	distribution
x_1	nmol/mol	2.079	0.0816	0.13	0.0102	A	normal
x_2	nmol/mol	2.080	0.0610	0.13	0.0076	A	normal
x_3	nmol/mol	2.092	0.0802	0.13	0.0100	A	normal
x_4	nmol/mol	2.097	0.0900	0.13	0.0113	A	normal
x_5	nmol/mol	2.085	0.0624	0.13	0.0078	A	normal
x_6	nmol/mol	2.072	0.0731	0.13	0.0091	A	normal
x_7	nmol/mol	2.095	0.0616	0.13	0.0077	A	normal
x_8	nmol/mol	2.105	0.0751	0.13	0.0094	A	normal
x_f	**nmol/mol**	**2.088**					
$u(x_f)$	**nmol/mol**	**0.026**					
$U(x_f)$	**nmol/mol**	**0.052**					

Where x_1-x_8 is the measurement number and x_f is the final value of the amount fraction of formaldehyde in the comparison mixture.

Authorship

Valerio Ferracci, Richard J C Brown, Paul J Brewer

Participant information			
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Transfer standard information			
Date of reception	13 May 2015		
Serial number of cylinder received	3ALM139 (CC435862)		
Cylinder pressure as received	113 bar		
Cylinder pressure before shipment to BIPM	The cylinder was not returned to BIPM as the liner (as used for the pressure measurement before shipment) could not be removed anymore from the cylinder.		

Results of measurements

Date of analysis	Formaldehyde mole fraction x(HCHO) / µmol mol^{-1}	Expanded uncertainty U(x(HCHO)) / µmol mol^{-1}	Coverage factor
26-28 August 2015	1.96	0.07	k=2

Description of measurements

Measurements were performed using a home-built CRDS spectrometer operating in the mid-infrared wavelength region. The spectrometer is equipped with a quartz-coated measurement cell to reduce adsorption of formaldehyde. For this comparison the formaldehyde absorption feature centred at 2950 cm^{-1} (i.e., 3390 nm) was selected based on the expected absorption signal of a 2 µmol/mol formaldehyde mixture and due to the absence of significant H_2O and CO_2 absorption in this wavelength region. The light source was scanned over a nearly 3 cm^{-1} range in 1000 small wavelength steps and the ring down time was recorded. Typically 10 wavelength scans were made and then averaged (first 1 or 2 scans omitted).

For calibration formaldehyde was dynamically generated from paraformaldehyde in powder form following ISO-6145-8:2005. The paraformaldehyde is contained in diffusion cells which were stored in an oven kept at a temperature of 60 °C. The formaldehyde was diluted dynamically with nitrogen to achieve low µmol/mol levels. The mass loss of the paraformaldehyde was determined by manually weighing the diffusion cells over a period of 5 weeks.

A correction was made for the mass loss due to water contained in the paraformaldehyde [Aoki et al, 2013]. Therefore the water mole fraction was determined in the dynamically generated formaldehyde mixture and from this the background water level was subtracted which was determined by measuring without the diffusion cells installed.

Measurements

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
CH_2O	26/08/2015 27/08/2015 28/08/2015 28/08/2015	1.97 1.95 1.95 1.96	0.5	4

Figure 1 shows recorded spectra of the cylinder mixture, dynamically generated formaldehyde from a diffusion cell and nitrogen as used for the dynamic generation. In addition, a scaled spectrum (……) from the diffusion cell measurement is shown. This scaled diffusion cell spectrum shows a good match with the cylinder measurements (——). Hence in the used wavelength range there are no spectrally interfering species present in the cylinder mixture and the used wavelength range is thus suitable for the determination of the formaldehyde mole fraction.

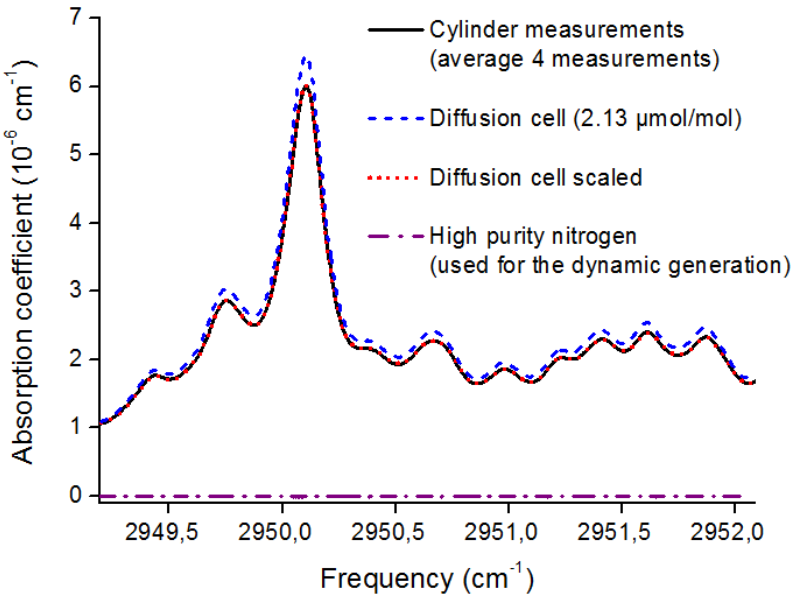

Figure 1 *Measured absorption spectra from the cylinder, a diffusion cell (normal and scaled) and high purity nitrogen.*

Sample Handling:

The sample cylinder was stored at room temperature before analysis.

Uncertainty Budget:

The main contribution stems from the dynamic generation of formaldehyde. This in turn is in particular due to the relatively large uncertainties in the measured diffusion rate of 1.3% and in the correction for the H_2O contained in the paraformaldehyde. Smaller uncertainty contributions include the nitrogen purity used for the dynamic generation and the uncertainty in the nitrogen flow rate. The expanded uncertainty (coverage factor k=2) is 3.7%.

Component	Relative uncertainty
Diffusion rate	1.3%
Flow rate	0.2%
H_2O correction	1.2%
Analytical measurement	0.5%
Total expanded uncertainty (k=2)	3.7%

References

N. Aoki, K. Kato, R. Aoyagi, M. Wakayama, *Evaluation of the permeability of formaldehyde and water through a permeation tube for the preparation of an accurate formaldehyde reference gas mixture.* Analyst 138, 6930 (2013)