International Comparison CCQM-K116:
10 µmol mol^{-1} water vapour in nitrogen

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Field

Amount of substance

Subject

Comparison of the composition of water vapour in nitrogen (track C)

Table of Contents

1. Introduction

The measurement of trace amounts of water in process gases is of paramount importance to a number of manufacturing processes. Water is considered to be one of the most difficult impurities to remove from gas supply systems and there is strong evidence that the presence of water contamination in semiconductor gases has a measurable impact on the quality and performance of devices. Consequently, semiconductor manufacturers are constantly reducing target levels of water in purge and process gases. As the purity of gases improves, the problem of quantifying contamination and ensuring that the gases are within specification at the point of use becomes more challenging. There are several established techniques for detecting trace water vapour in process gases. These include instruments based on the chilled mirror principle which measures the dew-point of the gas and the quartz crystal adsorption principle which measures the adsorption of water vapour into a crystal with a hygroscopic coating. Most recently, spectroscopic instruments such as those employing cavity ring-down spectroscopy (CRDS) have become available. The calibration of such instruments is a difficult exercise because of the very limited availability of accurate water vapour standards.

This CCQM comparison aims to assess the analytical capabilities of laboratories for measuring the composition of 10 µmol mol^{-1} water vapour in nitrogen. Each participant measured a different mixture prepared at NPL with a nominal composition as shown in table 1.

2. Design and organisation of the comparison

2.1 List of participants

Table 1 provides a list of the participating laboratories.

Acronym	Country	Full Institute Name and address
KRISS	KR	Korea Research Institute of Standards and Science, Daejeon, Republic of Korea
METAS	CH	Federal Institute of Metrology, Lindenweg 50, CH-3003 Berne-Wabern
NPL	UK	National Physical Laboratory, Hampton Road, Teddington, Middlesex, TW11 0LW, United Kingdom
VNIIM	RU	D.I. Mendeleyev Institute for Metrology, St Petersburg, Russia
VSL	NL	Van Swinden Laboratorium, Delft, The Netherlands
NMIJ	JP	National Metrology Institute of Japan，1-1-1 Umezono, Tsukuba, Ibaraki, 305-8563, Japan
NIM	CN	National Institute of Metrology，Beijing Beisanhuan East road Nop.18, Beijing 100029, China
INMETRO	BR	Instituto Nacional de Metrologia, Qualidade e Tecnologia (INMETRO), Rua Nossa Senhora das Graças, 50, Prédio 4, Xerém RJ, CEP 25250-020, Brasil

Table 1 Participating laboratories

2.2 Schedule

The schedule for the key comparison is shown in table 2.

Date	Event
May 2014	Issue draft protocol
May 2014	Registration of participants
July 2014	Purchase mixtures
September 2014	Verification of mixture compositions
October 2014	Stability measurements
September 2015	Distribution of mixtures
January 2016	Return of mixtures to NPL
February 2016	Re-verification of the mixtures
February 2017	Draft A report available
April 2018	Draft B report available

Table 2 Key comparison schedule

2.3 Measurement standards

A batch of 15 gas mixtures with a nominal composition of 10 µmol mol^{-1} water in nitrogen was prepared by a speciality gas company for the comparison in 10 litre aluminium cylinders (Luxfer). On arrival at the coordinating laboratory (NPL), the batch was analysed by comparison to NPL primary reference materials (PRMs) over a 6 month period. From these measurements, the amount fraction and stability of the mixtures was determined. A sub-set was selected for use as travelling standards in the comparison. This was based on selecting an ensemble with the lowest drift rate and the closest proximity of measured amount fractions.

Cylinders were distributed with a pressure of at least 8 MPa. After analysis, participants returned the cylinders to NPL with a sufficient pressure (> 5 MPa) for re-analysis. When all mixtures were returned, each was re-analysed at least twice over a 6 month period. The travelling standards were certified against two systems maintained at NPL as described in sections 2.4 and 2.5 using a Cavity Ring Down Spectrometer as a comparator (Tiger Optics Lasertrace 6000).

2.4 Molbloc dilution facility

The dynamic gas mixture used for validating the travelling standards was produced by blending a 100.8 µmol mol^{-1} PRM of water in nitrogen (NPL 1346) with nitrogen (Air products, BIP). The diluent gas was passed through a purifier system (SAES Getter Monotorr) to ensure it was free from the target gas. The flows of the diluent and the PRM were regulated by a 20 mg/s full-scale Viton seal (Brooks SLA5850-SE1AB1B2A1) and a 2 mg/s full scale metal seal (Brooks SLA7950-S1EGG1B2A1) thermal mass flow controllers respectively. The mass flow of each gas was measured accurately with 'Molbloc-L' laminar mass flow elements (DHI, models 1E3-VCR-V-Q and 1E2-VCR-V-Q for the target and balance gases, respectively), located upstream, and matched to the full scale setting of the mass flow controllers. A schematic of the system is shown in Figure 1.

Each Molbloc measures the upstream and downstream pressure using built-in high precision reference pressure transducers (RPTs). An ohmic measurement system reads the resistance of the Molbloc

platinum resistance thermometers from which the temperature of the Molbloc is calculated. The mass flow of the gas through each Molbloc is calculated using the measured pressures and temperature. The pressures of the PRM and diluent gas are controlled by two pressure regulators (LNI Schmidlin SA) that are set to maintain equal input pressures of nominally 3.0 bar absolute to the Molblocs (to ensure they are operating at a pressure within the range in which they were calibrated). A two-way valve was used to either flow the generated reference gas or the travelling standard into an analyser. Two lines venting to atmosphere ensured that the blend and travelling standard were flowing continuously and an equilibrium was maintained. The excess flow of the blended gas was matched to that of the travelling standard to ensure there was no change in upstream pressure to the analyser. Two shut off valves on each input to the blending manifold allowed the Molblocs to be isolated under pressure for routine leak checks. All manifolds were constructed of stainless steel tubing and the surface area was kept to a minimum to reduce contamination effects from build-up or release of the target gas in the system. The components in the system have been mounted on a dual Molbloc mounting system (DHI, model Molstic) to reduce the ambient vibration levels.

Values were assigned to the travelling standards using a cavity ring-down spectroscopy instrument (Tiger Optics Lasertrace 6000). Gas samples were delivered to the analyser via a manifold comprising stainless steel Swagelok fittings, which was purged before analysis using a gas of the same nominal composition. The analyser response to the matrix gas was recorded. The analyser response to the gas generated from the dynamic system was then recorded for at least a 10 minute period followed by the travelling standard for the same time. This sequence was repeated four times. At the end of the experiment the analyser response to the matrix gas was recorded a second time. To minimise the effects from zero drift, a mean of the analyser response to the matrix gas before and after the experiment was used. The amount fractions of the travelling standards was then determined by multiplying the ratio of the analyser response to the travelling standard and the gas generated from the dynamic system (both were corrected for the analyser response to matrix gas) with the amount fraction of the gas generated from the dynamic system.
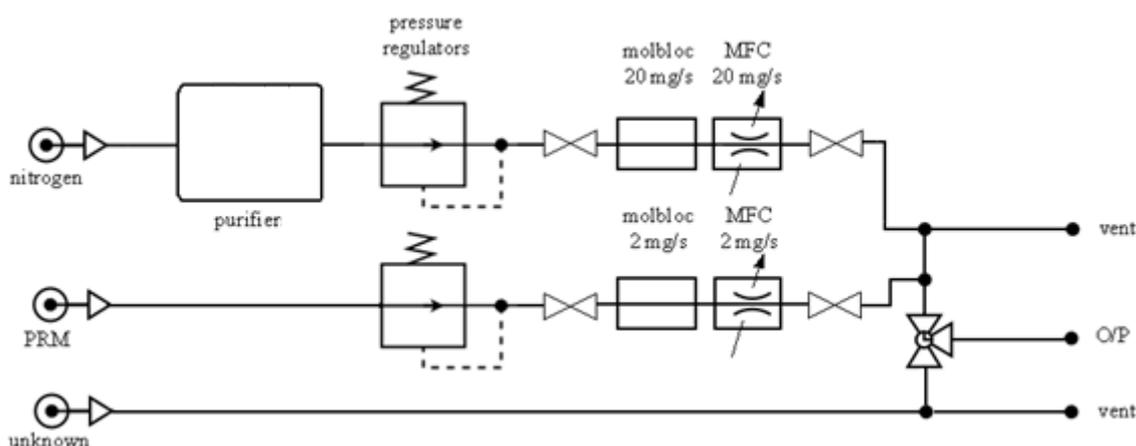

Figure 1 Schematic of the high accuracy dilution system. The output (O/P) is connected to a gas analyser. A two-way valve is used to alternate the flow of the blend and unknown to the analyser.

2.5 Chemical looping combustor

The travelling standards were also certified using NPL PRMs of hydrogen in nitrogen after conversion with a Chemical Looping Combustor (CLC) containing a bed of copper oxide (Gas Recovery and Recycle Ltd). This method, used in the fuel industry, generates water by oxidising hydrogen at 400 °C, following the reaction:

$$H_2 \text{ (g)} + CuO \text{ (s)} \quad \rightarrow \quad H_2O \text{ (g)} + Cu \text{ (s)} \tag{1}$$

This approach circumvents the challenges encountered in preparing static water standards in high-pressure cylinders, as hydrogen does not suffer the same adsorption losses. The stoichiometry of reaction 1 is dependent on the conversion efficiency of the CLC reactor. The conversion efficiency of the CLC was determined over the range from 10 to 1000 μmol mol^{-1} for a flow rate of 1 L/min. This was performed by comparing the response a quartz-crystal moisture analyser (Michell QMA 2030) to hydrogen PRMs converted to water with the CLC and static water standards in nitrogen. The hydrogen PRMs (NPL1602 9.9937 μmol mol^{-1} H_2 in N_2 and 232643SGR2 9.9839 μmol mol^{-1} H_2 in N_2) were prepared gravimetrically in accordance with ISO 6142 [1] using high purity hydrogen (BIP$^+$ grade, > 99.9999 %, Air Products) and nitrogen (BIP$^+$ grade, > 99.9999 %, Air Products) in 10 L Spectraseal cylinders (BOC). The mean conversion efficiency was 99.5 % with an expanded uncertainty (95 % level of confidence) of 0.5 %. The performance did not change with amount fraction of the PRM converted over the range tested. Values were assigned to the travelling standards using the procedure described in section 2.4. On average, the difference between the measurements from the two independent systems described in sections 2.4 and 2.5 was 0.41 % relative.

2.6. Stability of the travelling standards

To correct for drift in the amount fraction of water in the travelling standards, each was analysed four times (monthly) before distribution. Each travelling standard was re-analysed a further two times (monthly) after it was received back from the participant. Two control mixtures were also analysed at the same time as the travelling standards and during the distribution period. Figure 2 shows the stability data for the travelling standards and control mixtures. Due to issues with logistics, mixtures from NIM and INMETRO were received later than scheduled. Measurements on these mixtures to check for changes in composition were carried out 3 months later and are not shown here.
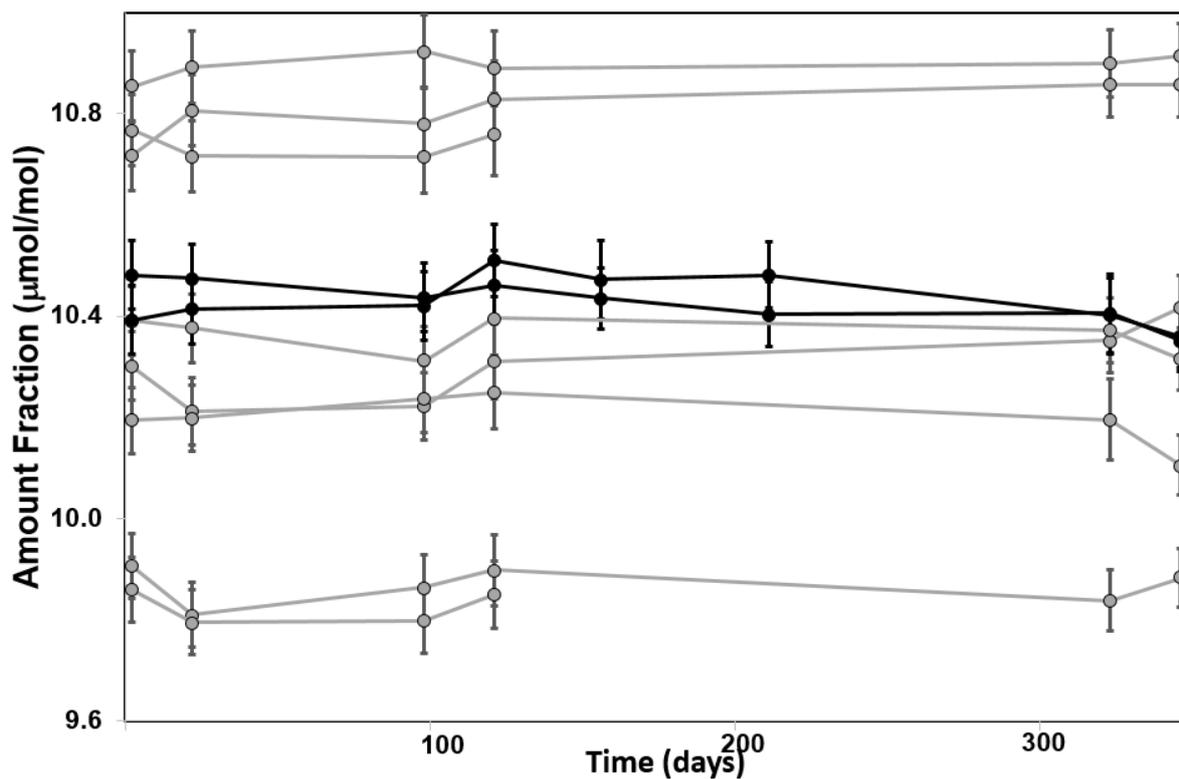
Figure 2 Stability data for all travelling standards (grey) and two control mixtures (black) held at NPL during the comparison. Bars show standard uncertainties.

The results of these analyses were plotted as a function of time and a linear squares fit was carried out using XLgenline software in each travelling standard before and after distribution. In Figure 3, an example of the amount fraction drift in one of the mixtures is given.
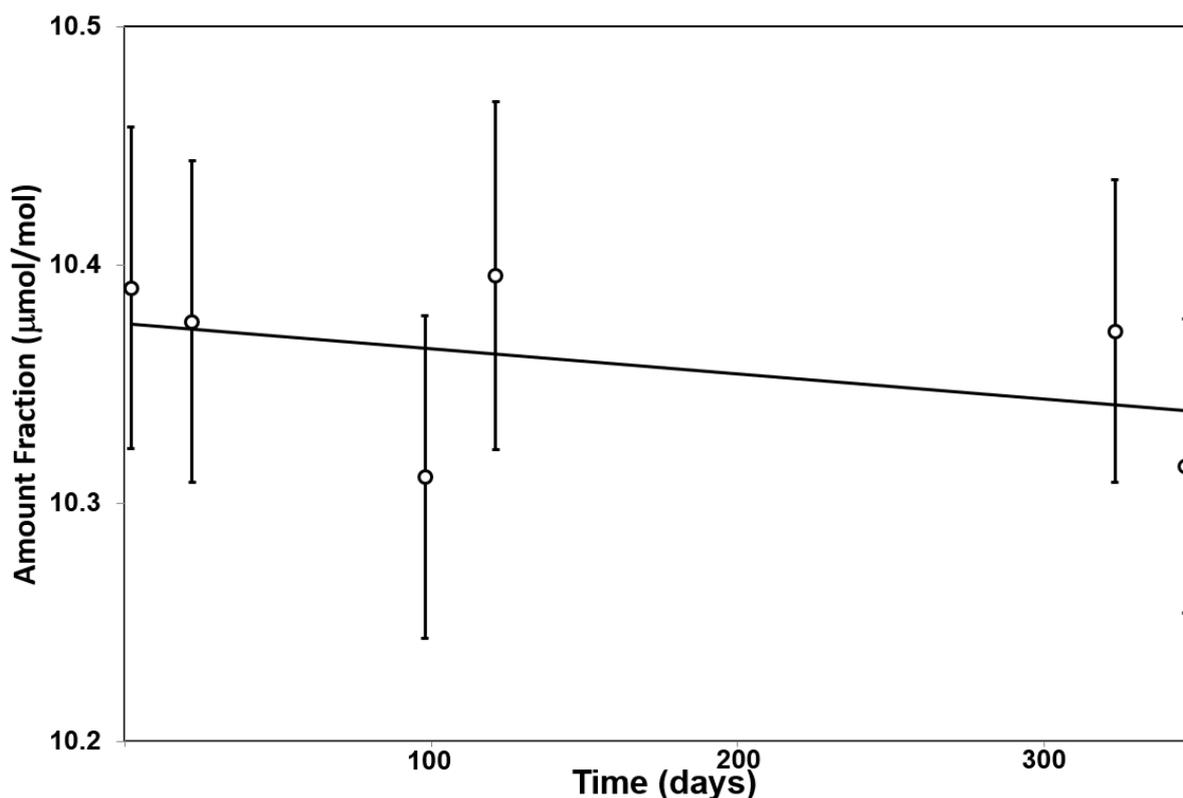
Figure 3 Example of the estimation of drift in the amount fraction in one of the travelling standards. The regression line has been fitted by ordinary least squares. The *x*-axis represents the time difference between measurements. The error bars indicate the standard uncertainty.

In all cases it was found that a straight line was a good fit to the data. The use of a straight line fit is further justified because it is consistent with typical chemical decay or absorption processes over a small range of amount fractions.[2] The assigned value for each travelling standard ($x_{i,b}$) was determined using:

$$x_{i,b} = x_{i,a} + x_{i,stab}$$

Where $x_{i,a}$ is the reference value assigned to the travelling standard analytically at t=0, prior to distribution and $x_{i,stab}$ is the drift correction determined from the gradient of the fitted line (*m*) and the time between t=0 and when the participant made a measurement. The uncertainties of the fit parameters were determined using XLGenline. The results are shown in table 3 where d_f is the difference between the participants submitted value (x_i) and the assigned value ($x_{i,b}$).

NMI	identifier	cylinder	x_a	$u(x_a)$	x_{stab}	u_{stab}	x_b	x	$u(x)$	*df*	$U(df)$
INMETRO	D	1154270	10.76	0.04	-0.029	0.028	10.73	11.02	0.37	0.29	0.74
VSL	F	1154280	9.90	0.04	-0.001	0.027	9.90	9.74	0.10	-0.16	0.22
VNIIM	G	1126470	10.31	0.04	0.027	0.012	10.34	10.54	0.19	0.20	0.38
NMIJ	I	1126478	10.39	0.04	-0.013	0.024	10.38	10.43	0.15	0.05	0.31
METAS	K	1154291	10.89	0.04	0.003	0.007	10.89	10.59	0.11	-0.30	0.23
KRISS	N	1126619	10.83	0.03	0.031	0.021	10.86	10.75	0.07	-0.11	0.17
NIM	O	1154281	9.85	0.03	-0.115	0.042	9.73	10.00	0.15	0.27	0.32
NPL	Q	1154294	10.25	0.03	-0.008	0.007	10.24	10.17	0.04	-0.07	0.10

Table 3 Assigned values to travelling standards in CCQM-K116, values are expressed in μmol mol^{-1}

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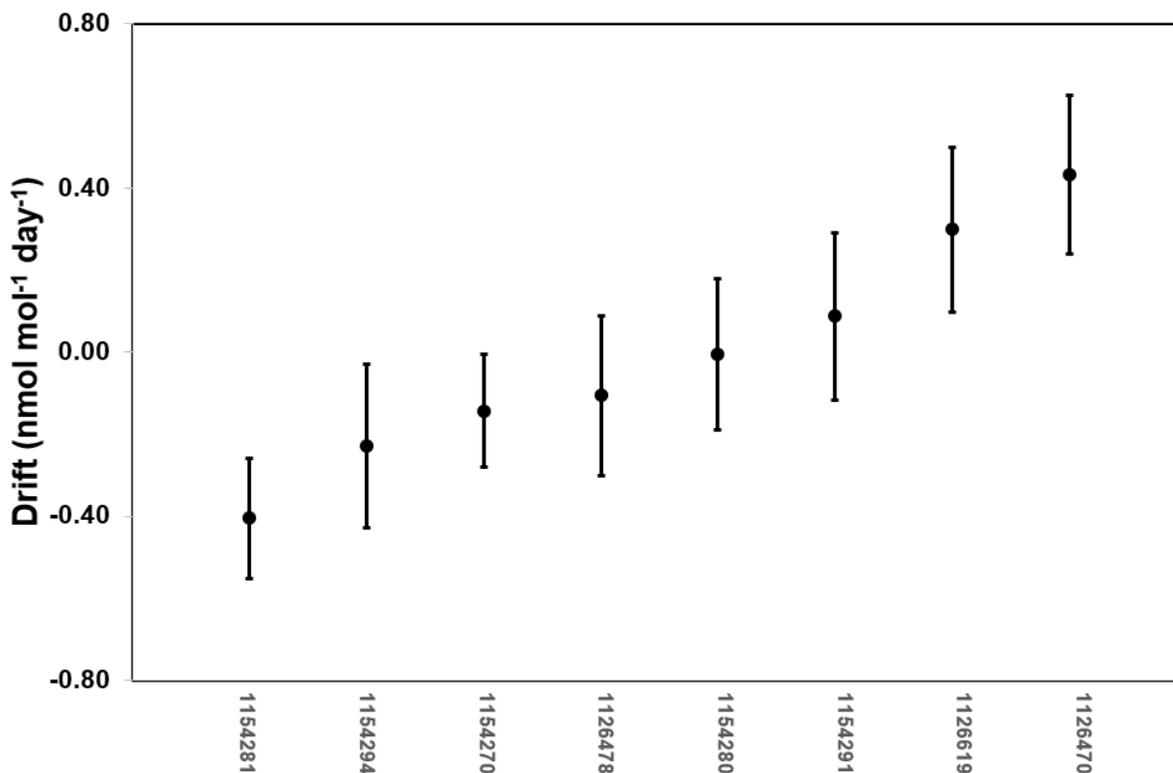
Figure 4 The estimated drift of each travelling standard and the standard error.

Figure 4 shows that the population has no significant outliers and that the estimated drifts are distributed around a median value of -0.056 nmol mol^{-1} day^{-1}. The maximum drift 0.43 nmol mol^{-1} day^{-1} corresponds to a drift of 0.8% over 6 months calculated at the nominal amount fraction of 10 µmol mol^{-1}.

3. Results

Table 4 presents the results from the comparison. Following discussion within the CCQM-GAWG, no technical reason could be found to explain the inconsistency between the reported results The reference values have been determined using a mean of the participants' results weighted by the submitted uncertainties. The mean was determined using the difference between the laboratories' reported results and the assigned value (d_f). An 'excess-variance' approach[3] has been used to allow for unexplained laboratory effects.

NMI	identifier	cylinder	x_{ref}	x	$u(x)$	d_i	$U(d_i)$
INMETRO	D	1154270	10.68	11.02	0.37	0.34	0.76
VSL	F	1154280	9.85	9.74	0.10	-0.11	0.28
VNIIM	G	1126470	10.29	10.54	0.19	0.25	0.41
NMIJ	I	1126478	10.33	10.43	0.15	0.10	0.36
METAS	K	1154291	10.84	10.59	0.11	-0.25	0.29
KRISS	N	1126619	10.81	10.75	0.07	-0.06	0.24
NIM	O	1154281	9.68	10.00	0.15	0.32	0.36
NPL	Q	1154294	10.19	10.17	0.04	-0.02	0.20

Table 4 Results of CCQM-K116, values are expressed in µmol mol^{-1}

A unilateral degree of equivalence in key comparisons is expressed as:

$$d_i = x_i - x_{i,ref}$$

Where, x_i is the reported amount fraction from laboratory i and $x_{i,ref}$ is the key comparison reference value for the mixture delivered to laboratory i. The combined uncertainty in this term can be expressed as:

$$u^2(d_i) = u^2(x_i) + u^2(x_{i,a}) + u^2(x_{i,stab})$$

Where $u(x_i)$ is the uncertainty submitted by the participant, $u(x_{i,a})$ is the uncertainty in assigning the reference value to each travelling standard at t=0 and $u(x_{i,stab})$ is the uncertainty of the stability correction which is determined from the standard error of the gradient.

A Graybill Deal mean[6] (used previously in key comparisons) of the participants' results weighted by the submitted uncertainties (x_{GD}) was determined using:

$$x_{GD} = \frac{1}{W_1} \sum_{i=1}^{p} w_i x_i, \quad w_i = 1/u_i^2, \ i=1,...,p, \quad W_1 = \sum_{i=1}^{p} w_i$$

Where the weights (w_i) are $1 / (u(x))^2$ and p is the number of participants. The inter-laboratory variance[5] (λ) was determined using:

$$\lambda = \max\left[0, \ \frac{\sum_{i=1}^{p} w_i (x_i - x_{GD})^2 - p + 1}{W_1 - W_2 / W_1} \right], \quad W_2 = \sum_{i=1}^{p} w_i^2$$

A DerSimonian-Laird mean[6] (x_{DL}) was calculated for the 8 participants ($N = 8$), using:

$$x_{DL} = \sum_{i=1}^{N} \tilde{w}_i x_i, \qquad \tilde{w}_i = \frac{(u_i^2 + \lambda)^{-1}}{\sum_{j=1}^{p} (u_j^2 + \lambda)^{-1}}.$$

The standard uncertainty[7] $u(x_{DL})$ was determined using:

$$u(x_{DL}) = \left[\sum_{i=1}^{p} \tilde{w}_i^2 (x_i - x_{DL})^2 \Big/ (1 - \tilde{w}_i) \right]^{1/2}.$$

As the data from all 8 laboratories was used to determine the KCRV, d_i and $u(d_i)$ were determined using[8]:

$$d_i = x_i - x_{DL}, \qquad u^2(d_i) = u_i^2 + \lambda - u^2(x_{DL}).$$

The full set of measurement data is provided in Annex B. The following values were determined from the analysis (x_{GD} = -0.069, $u(x_{GD})$ = 0.035, λ = 0.01, X_{DL} = -0.050, $u(x_{DL})$ = 0.057).

Figure 5 shows the degree of equivalence of the participating laboratories. The error bars are the expanded uncertainties obtained from the uncertainty of the results reported by each participant and the uncertainty in the KCRV.
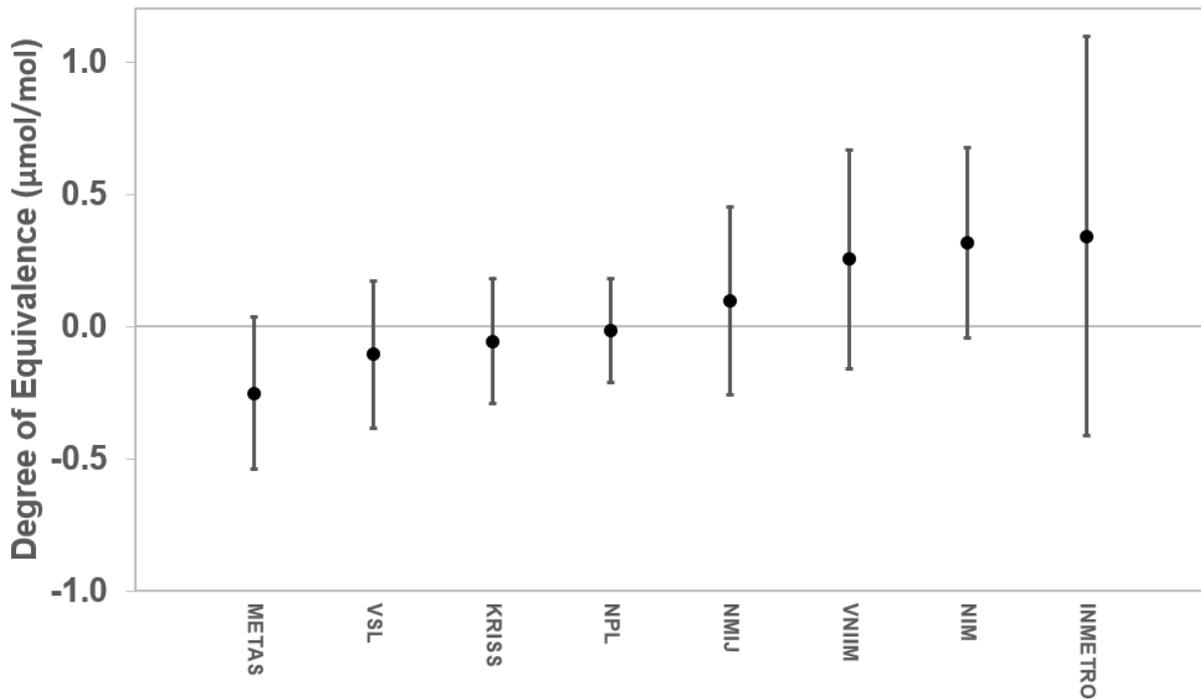

Figure 5 Degrees of equivalence for CCQM-K116.

The degree of equivalence of each laboratory was plotted against the drift of its assigned cylinder. Figure 6 shows that there is no correlation between the degree of equivalence and the drift rate of

the cylinder. Therefore, no participants had any advantage from receiving cylinders that were more stable.
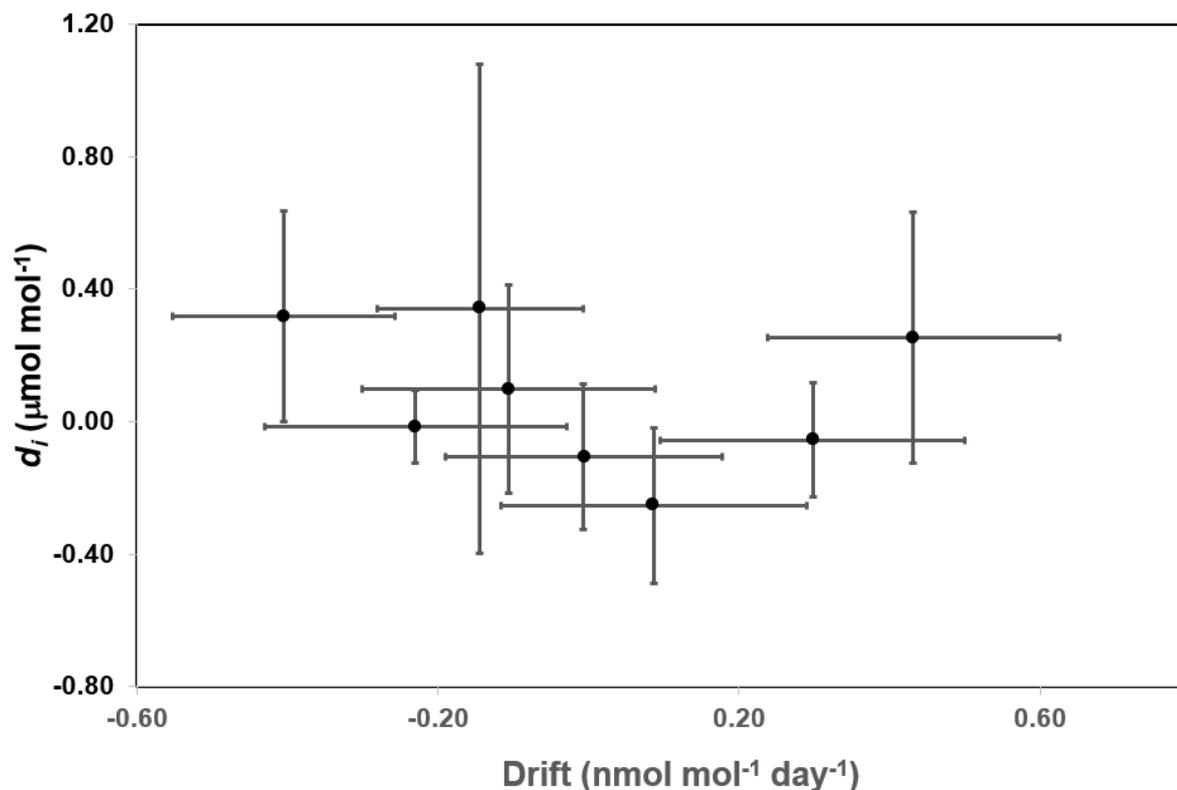
Figure 6 Degree of equivalence vs drift rate. Vertical error bars are the expanded uncertainties of the degree of equivalence. The horizontal error bars are the standard errors of the drift rates.

4 Conclusions

The results for the 8 participants are presented. Degrees of equivalence have been calculated based on a reference value derived from the analysis of each travelling standard by the coordinating laboratory and a weighted mean with consideration of excess variance. All laboratories demonstrate equivalence with the reference value to within their estimated uncertainty (k=2).

5 Supported CMC claims

The results of this key comparison can be used to support CMC claims for water vapour in air and nitrogen as a track C key comparison. The support of CMC claims is described in more detail in the "GAWG strategy for comparisons and CMC claims".[9]

Laboratories that demonstrate equivalence with the KCRV without the inclusion of the excess variance computed from the submitted data can use their stated uncertainty as basis for supporting CMCs. Laboratories that can only demonstrate equivalence including the excess variance computed for the dataset, should combine their stated uncertainty with the excess variance as basis for supporting CMCs.

6   References

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[8] F. A. Graybill and R. B. Deal, Combining unbiased estimates. *Biometrics*, 1959, **15**, 543–550.

[9] Brewer PJ, van der Veen AMH, GAWG strategy for comparisons and CMC claims, CCQM Gas Analysis Working Group, (2016).

Annex A: Measurement reports

Report CCQM-K116 "Water in Nitrogen"

Laboratory: VNIIM, Research Department for the State Measurement Standards in the field of Physico-Chemical Measurements.

Cylinder number: 1126470
Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
water	14/10/2015	10.36	-	1

Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
water	16/10/2015	10.50	-	1

Measurement #3

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
water	19/10/2015	10.51	-	1

Measurement #4

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
water	21/10/2015	10.72	-	1

Measurement #5

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
water	22/10/2015	10.48	-	1

Measurement #6

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	Number of replicates
water	27/10/2015	10.69	-	1

Result

Component	Result (µmol/mol)	Expanded uncertainty (µmol/mol)	Coverage factor
water	10.54	0.37	2

Preparation of calibration standards

Calibration gas mixtures were prepared with the help of standard Low Frost Point Generator (LFPG) «Polus», which is a part of State secondary standard of humidity units (VNIIM). The VNIIM secondary standard is used for measurement of water in pure gases in certification of pure gases.

Standard LFPG «Polus» provides generating of humidified gases with dew/frost temperature in the range from -100 °C to 20 °C. Operating principle of LFPG is based on equilibrium isothermal saturation of a gas with water vapour by flowing the gas over surface of water/ice at known temperature and pressure. The value of generated frost point is determined by platinum resistance thermometer. Traceability of measurements is provided by calibration of the thermometer to ITS-90 through VNIIFTRI (Russia) temperature standards.

Values of frost point of generated humidified gas were converted to values of vapour pressure in accordance with Sonntag formula [1]. The water amount fraction x_w (μmol/mol) in the generated humidified gas was calculated from partial pressure of water in accordance with (1):

$$x_w = \frac{e_w(T_s)}{P_s} \cdot f(T_s, P_s) \qquad (1),$$

where
$e_w(T_s)$ − water vapour pressure (in Pa) over ice at absolute temperature T_s and total pressure P_s, Pa;
$f(T_s, P_s)$- enhancement factor at P_s and T_s, which accounts for departures of water amount fraction in real gas from water amount fraction for ideal gas model.

Values of frost point, water mole fraction and its standard uncertainty in calibration gas mixtures

Date	Frost point (range*),°C	Water mole fraction (range*), μmol/mol	Standard uncertainty of water mole fraction in the calibration gas mixtures, μmol/mol
(16-27)/10/2015	(-60.30) − (-60.04)	10.17 -10.52	0.13

*- one point calibration approach was used; the range includes the values in different days.

2 Description of measurements

Measurements were carried out by direct measurements of frost point with the help of high precision chilled mirror hygrometer S8000RS (by "Michell Instruments Ltd.", Great Britain) and
subsequent recalculation to mole fraction of water in accordance with [1] и (1).

There were carried out 6 measurements in 6 days. Each measurement was preceded by one-

point calibration.

Pressure in the cylinder before measurements was 15 MPa, after measurements – 8.5 MPa.

Sequence of measurements was:

Calibration mixture $\rightarrow$ comparison mixture.

Calibration mixture (from LFPG) was delivered to hygrometer with flow rate – 500±10 cm^3/min.

Stabilization time – 5 hours.

Comparison mixture from the cylinder № 1126470 was delivered to hygrometer with the same flow rate. Stabilization time – 3 hours.

A schematic of measurements is shown in fig. 1
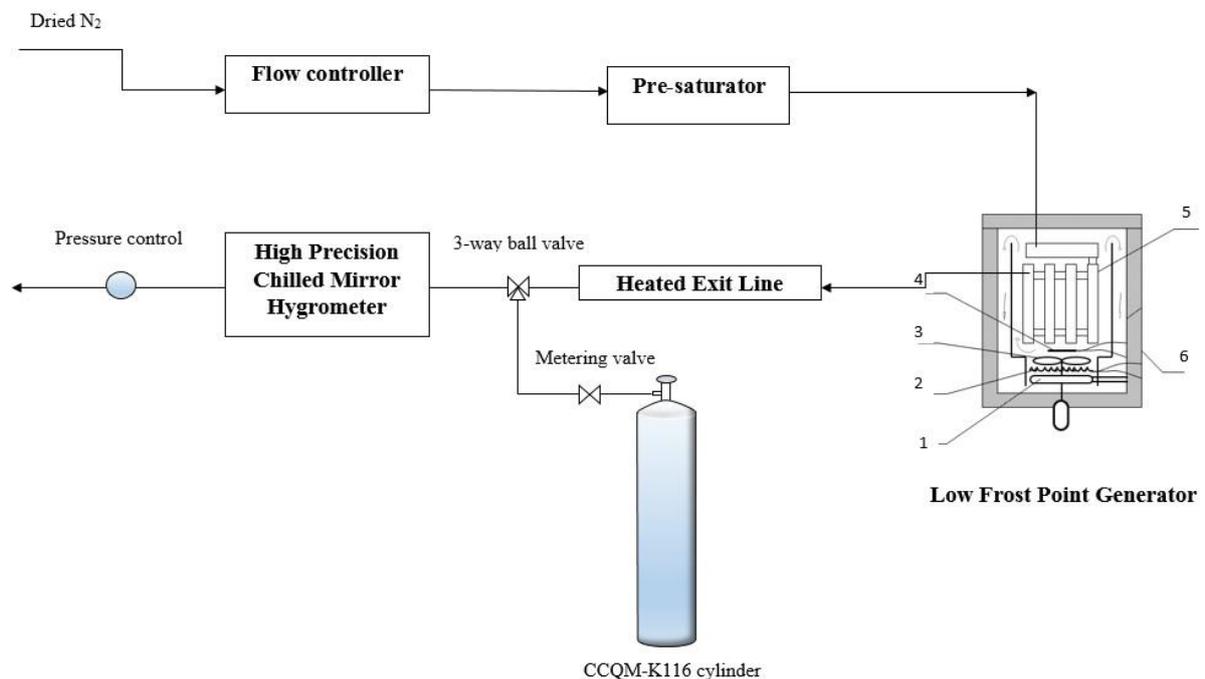
Figure 1 Schematic of measurements of water amount fraction in CCQM-K116

1-nitrogen heat exchange unit; 2- heating device, 3- fan, 4- Pt resistance thermometer, 5 – heat-mass-exchange device, 6- insulating case.

3 Uncertainty budget

Uncertainty source			Estimate x_i	Units	Standard uncertainty $u(x_i)$	Sensitivity coefficient c_i	Contribution $u_i(y)$ μmol/mol
Water amount fraction in calibration gas mixture	Partial pressure of water vapour in calibration gas mixture	Measurment of frost point temperature	213.02 (-60.13)	K (°C)	0.075	1.47	0.107
		Calculation of water partial pressure in accordance with [1]	1.0677	Pa	0.0050*	10.6	0.053
	Measurement of pressure, P_s		101845	Pa	177	0.0001017	0.018
	Enhancement factor at P_s and T_s		1.0061	-	0.0027**	10.4	0.028
Scatter of the measurement results			10.54	μmol/mol	0.137	1	0.137
Combined standard uncertainty							0.185
Expanded uncertainty k=2							0.37

*Standard uncertainty of calculation of partial pressure of water vapour according to Sonntag D. (1990) [1] is taken from [2];

** Standard uncertainty of enhancement factor is taken from [2].

References

[1] D. Sonntag Advancements in the field of hygrometry. Meteorologische Zeitschrift, N.F., 3, pp. 51-66, 1994

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Authors: L.A.Konopelko, A.V. Malginov, G.M. Mamontov, O.V. Efremova, A.A. Orshanskaya

Report CCQM-K116 Water

Laboratory name: METAS, Swiss Federal Institute of Metrology, Gas analysis laboratory

Cylinder number: 1154291

The water content in test cylinder n. 1154291 was injected and measured by a CRDS laser instrument calibrated by reference mixtures dynamically prepared at METAS. The preparation of the reference mixture is presented in section 1, the calibration of the comparator in section 2, the measurements of the test cylinder in section 3 and its associated uncertainty budget in section 4. The results are summarised in Section 5.

1. Calibration standards

The reference gas mixtures are produced with the permeation method according to ISO 6145-10. This experimental setup is presented in Figure 1. The permeation unit was filled by the manufacturer Fine-Metrology in Italy with millipore-filtered tap-water. This permeator is weighed with a magnetic suspension balance (Rubotherm) made of Silconert2000 coated stainless steel. The flows of carrier and dilution gas are regulated by Silconert2000 coated mass flow controllers (MFC) from Vögtlin and the total flow is measured with a coated mass flow meter (MFM) from Vögtlin. The MFM calibration is made using the secondary standard for low gas flows of METAS (molbloc-molbox system). The pressure in the permeation chamber is maintained constant at 1800 hPa with a pressure controller from Bronkhorst. The temperature is constant and measured in the permeation chamber with a calibrated Pt-100 temperature sensor.
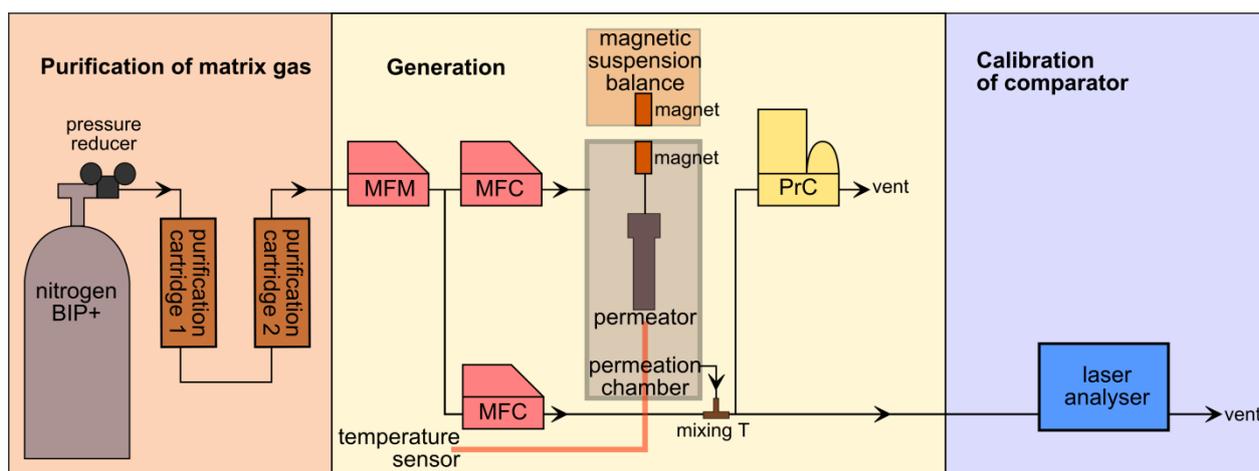
Figure 1: Schematic of the generation system to produce the primary reference mixture.

As matrix gas nitrogen BIP+ from Multigas was used, purified with two purification cartridges in series, a Monotorr cartridge (model PS3MT3N2) and a Microtorr cartridge (model MC400-203V) from SAES Getter. The residual water amount of fraction in the matrix gas going through the entire system was estimated by removing the permeation unit and measuring the water amount fraction at the exit of the generation system with the CRDS comparator. This residual water is taken into account in the uncertainty budget.

The reference gas mixtures were produced in the range 9-11 µmol/mol by changing the flow of the dilution MFC.

2. Instrumentation

To be used as a comparator, a cavity ring-down analyser (model LaserTrace OP 1505 from Tiger Optics, S/N 3426-3-21) was connected at the exit of the magnetic suspension balance. The inlet pressure is regulated by the pressure controller from the generation system (Figure 1), at 1800 hPa for all the measurements (calibration of the comparator as well as cylinder analyses).

To connect the cylinder to the analyser, we used a Silconert-coated pressure reducer, set at 1800 hPa, with a Wika WU-20 pressure indicator. The lines to the analyser were all 1/8" Silconert-coated stainless steel, as short as possible (less than 1 m). The flux of gas through the comparator was approx. 1 L/min (proportional to the comparator inlet pressure, which was stable).

The temperature in the laboratory was constant at 20 +/- 0.1 °C.

3. Description of the procedure

Two calibrations of the comparator were made according to section 1, one before and one after the measurement of the cylinder to confirm the stability of the comparator through the entire time period. One calibration consists of 3 calibration points generated between 9 and 11 µmol/mol.

Before measuring the cylinder, a purge-vacuum cycle of all lines including the pressure reducer between the cylinder and the analyzer was made 3 times. Four independent measurements of the test mixture were done, each one during 2 hours from which the last 30 minutes were taken into account. The first measurement was excluded as some residual water was probably still present in the pipes.

4. Uncertainty evaluation

The software GUM Workbench 2.4 was used to calculate the uncertainty. The uncertainty on the cylinder value was also confirmed with the software B_least according to ISO 6143.

The uncertainty evaluation was made following the recommendation from GUM. The model equation was as follow, with each variable presented in Table 1.

Model Equation:

Generation of reference gas mixtures, with i={1;2;3}:

$VM_{null}=M_{Null}/(d_{Null}*1000/1000000)$;

$X_{ppbAi}=(qmC*VM_{null}/M_{Substanziso}/qvi_{null})+X_N$;

$M_{Substanziso}=(M_{VSMOW}+M_{1H1H16O})/2$;

$halfdistance=(M_{VSMOW}-M_{1H1H16O})/2$;

Note that in a conservative way we take for $M_{Substanziso}$ a rectangular distribution with the half-distance of limit such as half the distance in between VSMOW and the light isotopologue $^{1}H_2^{16}O$.

Linear regression

$b=p/q$;

$p=(X_{ppbA1}-X_{ppb}meanA)*(Anz_{ppbA1}-Anz_{meanA})+(X_{ppbA2}-X_{ppb}meanA)*(Anz_{ppbA2}-Anz_{meanA})+(X_{ppbA3}-X_{ppb}meanA)*(Anz_{ppbA3}-Anz_{meanA})$;

$q=(X_{ppbA1}-X_{ppb}meanA)^2+(X_{ppbA2}-X_{ppb}meanA)^2+(X_{ppbA3}-X_{ppb}meanA)^2$;

$a=Anz_{meanA}-b*X_{ppb}meanA$;

Assigned value to the test cylinder:

Resi=(AnzResi-a)/b;

Res_{final}=(Res1+Res2+Res3)/3;

Table 1: List of variables contributing to the uncertainty budget of the amount of substance fraction in the test cylinder. 1st column: name of the variable. 2nd column: unit. 3rd column: description of the variable.

Quantity	Unit	Description
X_{ppbA1}	nmol/mol	H2O in final mixture for first calibration point
qmC	ng/min	Permeation rate
VM_{null}	L	Molar volume
$M_{Substanziso}$	g/mol	Molar mass of water
$qv1_{null}$	ml/min	Flow for first calibration point
X_N	nmol/mol	Residual H2O in carrier gas
X_{ppbA2}	nmol/mol	H2O in final mixture for second calibration point
$qv2_{null}$	ml/min	Flow for second calibration point
X_{ppbA3}	nmol/mol	H2O in final mixture for third calibration point
$qv3_{null}$	ml/min	Flow for third calibration point
M_{Null}	g/mol	Molar mass of nitrogen (N2)
d_{Null}	kg/m^3	carrier gas (N2) density
$X_{ppb}meanA$	nmol/mol	Average of generated H2O mixtures
Anz_{meanA}	nmol/mol	Average of H2O mixtures display
Anz_{ppbA1}	nmol/mol	Display for first calibration point
Anz_{ppbA2}	nmol/mol	Display for second calibration point
Anz_{ppbA3}	nmol/mol	Display for third calibration point
b	no units	Slope of calibration curve
p	(nmol/mol)^2	Slope numerator
q	(nmol/mol)^2	Slope denominator
a	nmol/mol	y-intercept of calibration curve
Res1	nmol/mol	Result of first measurement
AnzRes1	nmol/mol	Display of first measurement
Res2	nmol/mol	Result of second measurement
AnzRes2	nmol/mol	Display of second measurement
Res3	nmol/mol	Result of third measurement

Quantity	Unit	Description
AnzRes3	nmol/mol	Display of third measurement
Res$_{final}$	nmol/mol	Amount of substance fraction of cylinder

Uncertainty budget

The uncertainty budget for the amount substance fraction in the test cylinder is reported in Table 2.

Table 2: uncertainty budget for the measured amount substance fraction in the test cylinder.

Quantity	unit	Value	Standard Uncertainty	Degrees of freedom	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index, %
M_Null	nmol/mol	28.013	0.000577	infinity	rectangular	370	0.22	0
d_Null	kg/m^3	1.25053	0.0000577	infinity	rectangular	-8400	-0.48	0
qmC	ng/min	10894	22.9	100	normal	0.96	22	3.8
M_Substanziso	g/mol	18.01292	0.00136	infinity	rectangular	-580	-0.79	0
qv1_null	ml/min	1321.87	1.98	100	normal	-2.6	-5.1	0.2
X_N	nmol/mol	100	40.8	infinity	triangular	1	41	13
qv2_null	ml/min	1219.47	1.83	100	normal	-4.2	-7.7	0.5
qv3_null	ml/min	1424.98	2.14	100	normal	-1.4	-2.9	0
Anz_ppbA1	nmol/mol	9188	71	240	normal	-0.45	-32	8.1
Anz_ppbA2	nmol/mol	9855	100	240	normal		-65	33.1
Anz_ppbA3	nmol/mol	8705	96	240	normal		-28	6.1
p	(nmol/mol)^2	9.25E+005	1.12E+005	490				
q	(nmol/mol)^2	1.29E+006	3.57E+004	200				
AnzRes1	nmol/mol	9427.7	56	240	normal	0.46	26	5.2
AnzRes2	nmol/mol	9359.6	78	240	normal	0.46	36	10.2
AnzRes3	nmol/mol	9405	109	240	normal	0.46	50	19.8
Res_final	nmol/mol	10590	113	1400				

5. Results

The three individual measurement points are reported in the following tables and in Figure 2, together with the generated water amount of substance fractions used to calibrate the

comparator (in nmol/mol). Each measurement (#1, #2, #3,) is the average of 120 single points ; the LaserTrace measures every 15 seconds and we measured during 30 minutes.

Measurement #1

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	number of replicates
water	23/09/15	10640	2.3%	1

Measurement #2

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	number of replicates
water	24/09/15	10540	2.7%	1

Measurement #3

Component	Date (dd/mm/yy)	Result (nmol/mol)	Standard deviation (% relative)	number of replicates
water	25/09/15	10610	3.3%	1

Results:

Component	Date (dd/mm/yy)	Result (nmol/mol)	Expanded uncertainty (k=2)	number of replicates
water	N/A	10590	2.1% rel	3
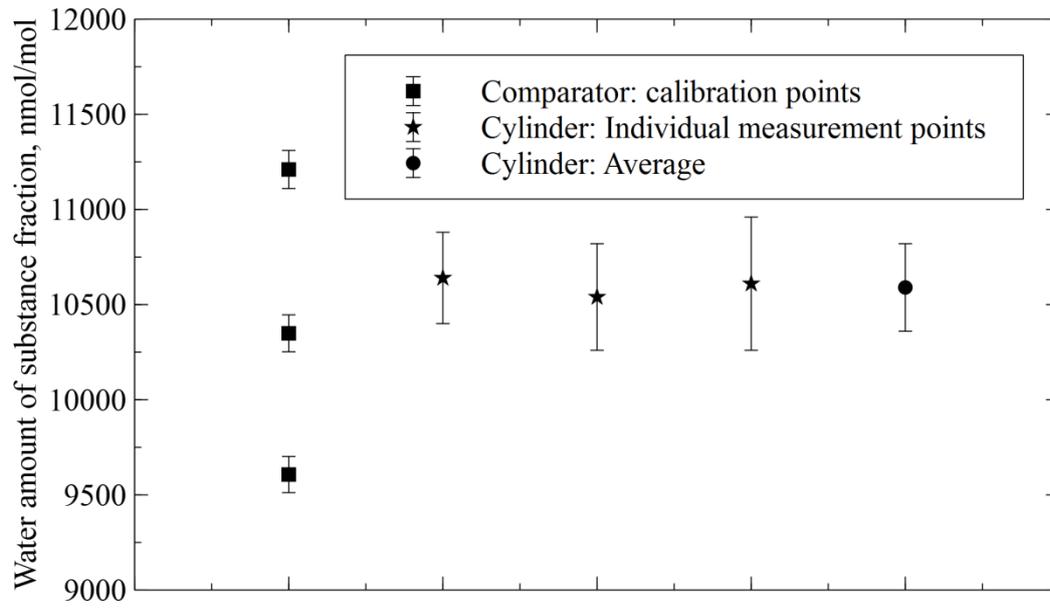
Figure 2: Comparator calibration and cylinder measurements. The water amount of substance fraction is in nmol/mol.

Report Form : CCQM-K116 Water

Laboratory name : National Metrology Institute of Japan (NMIJ)

Cylinder number : 1126478

Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Water	17/12/2015	10.44×10^{-6}	1.4	50

Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Water	18/12/2015	10.40×10^{-6}	1.4	50

Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Water	21/12/2015	10.44×10^{-6}	1.4	50

Result

Component	Result (mol/mol)	Expanded uncertainty (mol/mol)	Coverage factor
Water	10.43×10^{-6}	0.36×10^{-6}	2.4

The coverage factor (k) of 2.4 gives a level of confidence of approximately 95 %.

Calibration standards

Calibration standard is a humidity generator of NMIJ's humidity standard group. Calibration standard gases were nitrogen saturated with water under controlled pressure at the selected temperature which was measured by a platinum resistance thermometer traceable to ITS-90 through NMIJ temperature standards. The uncertainty of the frost points is calculated by combining the uncertainties from the temperature, pressure, Sonntag equation, and Greenspan equation, and the expanded uncertainties (k = 2.4, 95% confidence level) of the calibration at -50 °C, -60 °C, -70 °C are 0.096 °C, 0.24 °C, and 0.86 °C, respectively.

Instrumentation

Frost point of the CCQM-K116 sample was determined by a chilling-mirror-typed hygrometer (Michell Instruments, S4000-TRS) calibrated at -50 °C, -60 °C and -70 °C by NMIJ humidity standard group. An absolute pressure transmitter (MKS-628B) was set at the outlet of the hygrometer to monitor the pressure of the sample. Sample flow rate was controlled by a needle valve on upstream to the hygrometer. We used a small pressure regulator without pressure gauges to reduce contamination from the gauge. Temperature of the sample cylinder was 25 °C during the measurement.

Description of the procedure

Temperature of a refrigerator of the hygrometer was set at -40 °C which is the same condition on the calibration of the hygrometer. Before the determination, the sample was flowed about 50 ml/min in several hours to achieve equilibrium of adsorption-desorption between the sample gas and the inner surface of pipes, regulators and so on. Frost point of the sample was measured by the hygrometer at least two hours with 500 ml/min flow rate. Drift of the monitored frost point in the last one hour was much less than the uncertainty of the calibration at -60 °C frost point.

The result of each measurement was average of the frost point of the CCQM-116 sample during the last nine minutes (50 data). The molar fraction was calculated from Sonntag's and Greenspan's equations with the averaged frost point and sample pressure monitored by the absolute pressure transmitter at the outlet of the hygrometer. The sample was measured three times. The value to be reported was an arithmetic average of the three results.

Uncertainty evaluation

Uncertainty of the reported value was calculated by combining the uncertainties of the calibration of the hygrometer, pressure at the outlet, repeatability and the equations of Sonntag and Greenspan. The uncertainties of the Sonntag's and Greenspan's equation are evaluated by the equations given as

$(0.01 - 0.005TT) \times 0.01$, and (1)

$(1.68 \times 10^{-9} PP - 1 \times 10^{-5}) \times \exp\{[2.2 \times 10^{-5} \log_e(PP) - 0.0139]TT\}$, (2)

respectively, where T is temperature of the frost point in °C, P is pressure of the sample in Pa [1]. Table 1 shows the uncertainty budget table. The expanded uncertainty (k = 2.4, 95 confidence level) of the reported value is 0.36 µmol/mol.

Table 1 Uncertainty budget table for the determination.

	Uncertainty	Sensitivity	Contribution (nmol/mol)
Frost Point	0.1 °C	1414 nmol/mol/ °C	141
Pressure	60 Pa	-0.102 nmol/mol / Pa	9.18
Repeatability	11.7 nmol/mol	1	27.7
Sontag's eq.	0.00311 (relative)	1	32.5
Greenspans's eq.	3.63×10^{-4} (relative)	1	3.76
		Combined standard uncertainty	148
		Expanded uncertainty ($k = 2.4$)*)	355

*) The coverage factor (k) of 2.4 gives a level of confidence of approximately 95 %.

Reference

[1] J. Lovell-Smith, *Metrologia*, **46**, 607 (2009).

Report Form CCQM-K116 water in nitrogen

Laboratory name: VSL

Cylinder number: APE1154280

Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
H_2O	12-01-16	$9.73 \cdot 10^{-6}$	0.81	1

Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
H_2O	13-01-16	$9.76 \cdot 10^{-6}$	1.08	1

Measurement #3[1]

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
H_2O	19-01-16	$9.72 \cdot 10^{-6}$	0.95	1

Measurement #4[1]

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
H_2O	21-01-16	$9.76 \cdot 10^{-6}$	1.96	1

Results

Component	Result (mol/mol)	Expanded Uncertainty	Coverage factor[2]

---

[1] If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary

[2] The coverage factor shall be based on approximately 95% confidence.

H_2O	$9.74 \ 10^{-6}$	$0.20 \ 10^{-6}$	2

Measurement procedure and value assignment

Calibration standards

All standards used are commercially bought mixtures of water in nitrogen. All mixtures are certified by against the primary humidity standard at VSL. Stability is demonstrated by recertification of the majority of the mixtures after 3 years time. Mixtures with an amount fraction between 1.5 and 107 µmol/mol H_2O in N_2 were used.

Standard Certifcate date	Amount fraction (mol/mol) 30-11-2015	Uncertainty (k=2)	Amount fraction (mol/mol) 14-09-2012	Uncertainty (k=2)
D392662	$149.4 \cdot 10^{-6}$	$1.9 \cdot 10^{-6}$	$148.75 \cdot 10^{-6}$	$2.7 \cdot 10^{-6}$
188280	$107.9 \cdot 10^{-6}$	$1.4 \cdot 10^{-6}$	$107.13 \cdot 10^{-6}$	$2.1 \cdot 10^{-6}$
D392669	$74.14 \cdot 10^{-6}$	$0.94 \cdot 10^{-6}$	$74.06 \cdot 10^{-6}$	$1.5 \cdot 10^{-6}$
D392665	$49.95 \cdot 10^{-6}$	$0.65 \cdot 10^{-6}$	$50.04 \cdot 10^{-6}$	$0.9 \cdot 10^{-6}$
D392660	$24.91 \cdot 10^{-6}$	$0.32 \cdot 10^{-6}$	$25.03 \cdot 10^{-6}$	$0.4 \cdot 10^{-6}$
D392663	$10.54 \cdot 10^{-6}$	$0.17 \cdot 10^{-6}$	$10.38 \cdot 10^{-6}$	$0.2 \cdot 10^{-6}$
D392668	$1.486 \cdot 10^{-6}$	$0.066 \cdot 10^{-6}$		
5902153	$25.05 \cdot 10^{-6}$	$0.33 \cdot 10^{-6}$		
D412523	$8.3 \cdot 10^{-6}$	$0.2 \cdot 10^{-6}$		

Analytical method

The TigerOptics MTO1000 CRDS analyzer was used for all measurements. VSL has a non-standard version of this instrument whereby an absorption line can be chosen by setting the temperature of the laser. In this manner the optimal absorption line can be chosen for the amount fraction to be analysed. The tau-zero (τ_0) value which is necessary to perform the calculations was determined by scanning over a large part of the absorption spectrum (see figure 1) and applying a baseline to determine the value at the laser temperature used for the measurements.
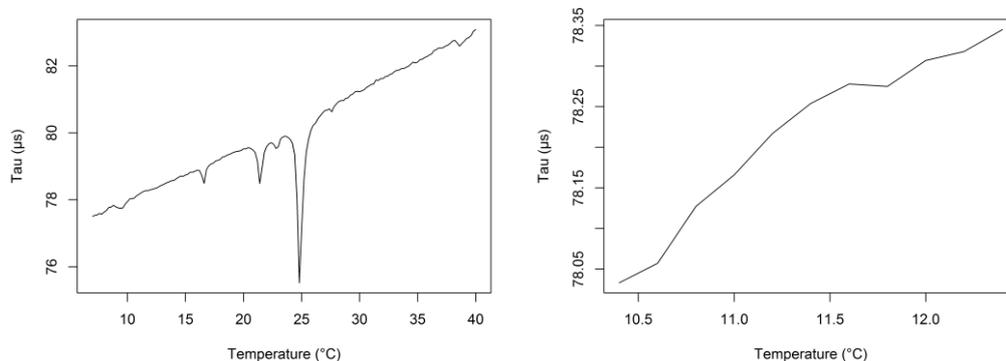
Figure 3: Ringdown time as a function of the laser temperature (left: full range; right: range in the neighbourhood of the absorption line used for the measurements)

Before analysis, all tubing between the analyzer and the cylinder was evacuated for 30 minutes using an oil free turbo molecular pump. Thereafter the analyzer was flushed with a flow of approximately 1 litre per minute for 45 minutes and the responses of the last 15 minutes were averaged to give a the decay response value tau (τ_x) with a standard uncertainty.

Calibration method and value assignment

The analyser was calibrated before each measurement using a suite of 8 calibration standards. The ringdown time of the empty cell was determined as described previously to e $\tau_0 = 78.250$ µs with a standard uncertainty of 0.064 µs. The fraction water (X_i) was determined by comparison with a single calibration standard using the following formula:

$$X_i = X_s \times \left(\frac{1}{\tau_x} - \frac{1}{\tau_0}\right) \bigg/ \left(\frac{1}{\tau_s} - \frac{1}{\tau_0}\right) \tag{1}$$

where X_s denotes the water fraction of the calibration standard, τ the ringdown time of the mixture being analysed, and τ_s the ringdown time of the calibration standard. Only in the first measurement, 5 calibration standards were used, otherwise the complete suite. The data of a typical calibration are shown in table 1.

Table 3: Calibration data (second measurement)

x	U(x)	τ	u(τ)
µmol/mol	µmol/mol	µs	µ
25.05	0.33	55.92	0.09
24.91	0.32	56.44	0.17
10.54	0.17	67.05	0.05
8.30	0.20	69.20	0.06
107.9	1.4	29.28	0.25
74.14	0.94	36.40	0.20

49.95	0.65	44.01	0.07
1.486	0.066	76.46	0.06

The results for the four measurements have been summarised in table 2. The standard uncertainty is computed in R [1] with the help of the package numDeriv [2] for calculating the sensitivity coefficients arising from equation (1). The law of propagation of uncertainty of the GUM-S2 [3] was used to perform these calculations.

Table 4: Values and standard uncertainties for the amount fraction water in cylinder APE1154280 for all 4 measurements

Standard	Measurement 1		Measurement 2		Measurement 3		Measurement 4	
1	9.63	0.30	9.61	0.30	9.63	0.29	9.79	0.29
2	9.84	0.30	9.88	0.31	9.74	0.29	9.77	0.28
3	9.78	0.20	9.67	0.19	9.62	0.20	9.56	0.19
4	9.73	0.28	9.73	0.27	9.72	0.27	9.84	0.26
5			9.89	0.43	9.87	0.42	10.12	0.40
6			9.88	0.40	9.82	0.39	9.80	0.39
7			9.84	0.37	9.73	0.36	9.75	0.35
8	9.70	2.29	9.76	2.33	9.64	2.25	9.48	2.13

The arithmetic mean of the results in table 2 is x = 9.75 µmol mol^{-1} with standard uncertainty 0.16 µmol mol^{-1}. This standard uncertainty is obtained by using the law of propagation of uncertainty for multivariate measurement models and the covariance matrix calculated for the water fractions. The resulting standard uncertainty does account for most correlations between the measurement results, except for those arising between the standards, for which no data was at hand.

Calculation of an uncertainty-weighted mean from the results in table 2 gives x = 9.74 µmol mol^{-1} with a standard uncertainty of 0.03 µmol mol^{-1}.

Finally, from each of the 4 measurements a data evaluation was performed based on ISO 6143 [4], which gives for the standard uncertainty of each of the four measurements about 0.10 µmol mol^{-1}. Considering the not entirely known degree of correlation between the measurements, this standard uncertainty has been adopted for the result in this key comparison, as a cautious value.

References

[1]   R Core Team. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria, 2016.

[2]   Paul Gilbert and Ravi Varadhan. numDeriv: Accurate Numerical Derivatives, 2015. R package version 2014.2-1.

[3]   BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP, OIML. Evaluation of measurement data – Supplement 2 to the "Guide to the expression of uncertainty in measurement" – Extension to any number of output quantities, JCGM 102:2011. BIPM, 2011.

[4]   ISO 6143. Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures, 2001. Second edition.

Authorship

J.I.T. van Wijk and A.M.H. van der Veen

Report Form CCQM-K116 Water

Laboratory name: Inmetro / Lanag

Cylinder number: 1154270

Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Water	07/03/2016	$10{,}88 \times 10^{-6}$	2,85	13

Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Water	10/03/2016	$11{,}23 \times 10^{-6}$	3,74	13

Measurement #3[3]

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	number of replicates
Water	11/03/2016	$10{,}96 \times 10^{-6}$	2,92	13

Results

Component		Result (mol/mol)	Coverage factor	Assigned expanded uncertainty (mol/mol)
Water		$11{,}02 \times 10^{-6}$	2	$0{,}73 \times 10^{-6}$

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[3] If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary

Calibration standards

NPL primary gas standards in the range: from 9,6 – 10,8 (x 10^{-6} mol/mol) water in nitrogen (table 1).

Table 5. Calibration standards

Mixture code	x (mol/mol) $\times 10^{-6}$	u_x (mol/mol) $\times 10^{-6}$
NPL1797	9,58	0,24
NPL1793	10,0	0,25
NPL1805	10,8	0,25

Instrumentation

The measurements were performed using a CRDS (Prismatic, Tiger Optics), with 30 minutes of sample purge and 60 minutes of sample running analysis.

The sample and calibration standards were connected to a dedicated reducer previously flushed. Every line was flushed for 30 minutes with nitrogen before sampling, and with 30 minutes with sample, and the flow for each mixture was set equally. For the 2nd and 3rd day of analyses the reducers were disconnected and connected to a different cylinder. The flushing and setting of the flow was done equal to the first measurement.

Calibration method and value assignment

The calibration was done according to ISO 6143. The calibration curve was made using the software XLgenline, the curve model for the data resulted in a linear curve, which was used for the value assignment. The goodness of fit for all 3 measurements was lower than 1.

Uncertainty evaluation

The uncertainty was calculated according to ISO 6143, using the software XLgenline. The combined uncertainty was multiplied by a coverage factor of 2 with a confidence interval of 95%. Three sources of uncertainty were considered:
- Uncertainty of the standards (certificate – type B)
- Uncertainty of the repeatability (analysis – type A)
- Uncertainty of the area (analysis – type A)

Authorship

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National Institute of Metrology (NIM), China

Transmission of International Comparison Results

The title of international comparison: Water in Nitrogen

Serial number for international comparison: CCQM-K116

Comparison experiment period: June, 2016

Experiment reporter: HAN Qiao, HU Shuguo and Zhang Peizhuang

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International Key Comparison(CCQM-K116) Report

Water in Nitrogen

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Date of Receiving the Comparison Cylinder: May, 2016

Cylinder No.: D254105

Measurement and Result

Measurement #1

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	Instrument
Water	19/05/16	10.02×10^{-6}	1.0%	Tiger Optics Halo CRDS

Measurement #2

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	Instrument
Water	20/05/16	9.952×10^{-6}	1.0%	Tiger Optics Halo CRDS

Measurement #3

Component	Date (dd/mm/yy)	Result (mol/mol)	Standard deviation (% relative)	Instrument
Water	21/06/16	10.04×10^{-6}	1.0%	Tiger Optics Halo CRDS

Results

Component	Result (mol/mol)	Expanded Uncertainty (% relative)	Coverage factor**
Water	10.00×10⁻⁶	3.0%	2

**The coverage factor *k*=2(95% confidence level)

Method Description

1. Calibration Standard

The low frost-point humidity generator (two-temperature and two-pressure method) of National Institute of Metrology（NIM）provides the primary humidity standard of frost/dew-point in the range from -75℃ to +20℃. The uncertainty in the generated frost point is calculated by combining the estimated uncertainties including the temperature control and measurement, the pressure control and measurement ,the bias of the temperature and pressure sensors from calibration, the saturation efficiency, the temperature variations in the generator bath, the pressure differences in the system, the fluctuation of temperature and pressure. The uncertainty of frost/dew-point is 0.05°C (at a coverage factor of *k* =2).

2. Instrument

A Tiger Optics Halo CRDS calibrated by Calibration Standard was used to analyze the comparison sample.

3. Description of the procedure

Comparison sample cylinder was connected to the single stage pressure regulator without gauge. By using the stainless steel internal polishing tube(1/8"), pressure regulator, analyzer and high purity nitrogen was connected to a three-way valve respectively. Before analysis of comparison sample high purity nitrogen was used to purge the tube untill the reading of the analyzer was lower than 10ppm, then the comparison sample was introduced to the analyzer by turning the three-way valve The flow rate of sample was controlled about 1L/min.

Evaluation of measurement uncertainty

The contributions of measurement uncertainty were from standard device, signal readings of the sample gas, reproducibility in different days or groups.

$$u(c_{CCQM}) = \sqrt{u^2(C_S) + u^2(S_{CCQM}) + u^2(f_{inter})}$$

Here, *u* means relative standard uncertainty.

$u(c_{CCQM})$: Measurement uncertainty of concentration of the target component in the comparison sample gas cylinder.

1. $u(C_S)$: Uncertainty of analyzer calibration from the standard device.

2. $u(S_{CCQM})$: Uncertainty of signal reading of the comparison sample from analyzer.

3. $u(f_{inter})$: Uncertainty of reproducibility in different days. It was calculated from the relative standard deviation (RSD) of repeating test in different days. $u(f_{inter})$ =RSD/sqrt(n), where n=3 is the number of the repeating test.

Source of uncertainty	$u(C_S)$	$u(S_{CCQM})$	$u(f_{inter})$
Relative standard uncertainty	1.0%	1.0%	0.5%
Relative expanded uncertainty**	3.0%		

**The coverage factor *k*=2(95% confidence level)

Report Form CCQM-K116 Water

Laboratory name: KRISS
Participants: Sang Hub OH, Byung Moon KIM, Sangil LEE
Cylinder number: 1126619

Measurement #1

Component	Date (dd/mm/yy)	Result (μmol mol^{-1})	Standard deviation (% relative))	Number of replicates
Water vapor	30/11/15	10.771	0.26	3

Measurement #2

Component	Date (dd/mm/yy)	Result (μmol mol^{-1})	Standard deviation (% relative))	Number of replicates
Water vapor	01/12/15	10.724	0.18	3

Measurement #3

Component	Date (dd/mm/yy)	Result (μmol mol^{-1})	Standard deviation (% relative))	Number of replicates
Water vapor	02/12/15	10.719	0.16	3

Measurement #4

Component	Date (dd/mm/yy)	Result (μmol mol^{-1})	Standard deviation (% relative))	Number of replicates
Water vapor	03/12/15	10.793	0.08	3

Results

Component	Date (dd/mm/yy)	Result (μmol mol^{-1})	Expanded uncertainty (k=2)	
Water vapor		10.752	0.146	

Calibration standards

- Method of preparation

A dynamic gravimetric system for generating primary standard gas mixtures of water vapor has been developed in KRISS. A schematic diagram of the system is shown in Figure 1. The nitrogen gas from the liquid nitrogen tank (LN2) is dried by a purifier (SAES Getters, Monotorr), and is controlled by two mass flow controllers (one for the diffusion chamber, the other for dilution). The pressure in the diffusion chamber is maintained at 0.9 kPa (absolute) by a pressure controller. The chamber contains a diffusion bottle that is attached to a magnetic suspension balance.
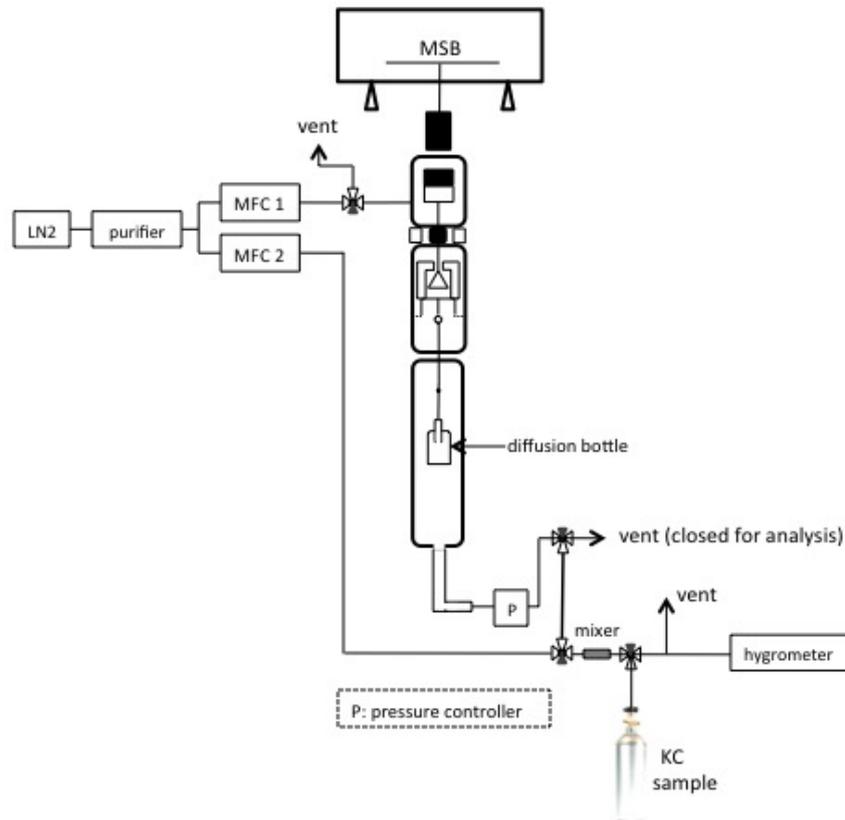
**Figure 4. Schematic Diagram of KRISS dynamic gravimetric system (DGS)**

- Gravimetric data

The gravimetric data for the mass loss of the diffusion bottle is shown in Figure 2. The mass loss data was recorded at an interval of 2 minutes continuously for 19 days (from November 26 to December 15, 2015). The diffusion rate was determined for a period of 24 h using a linear least squares fit (Table 1).
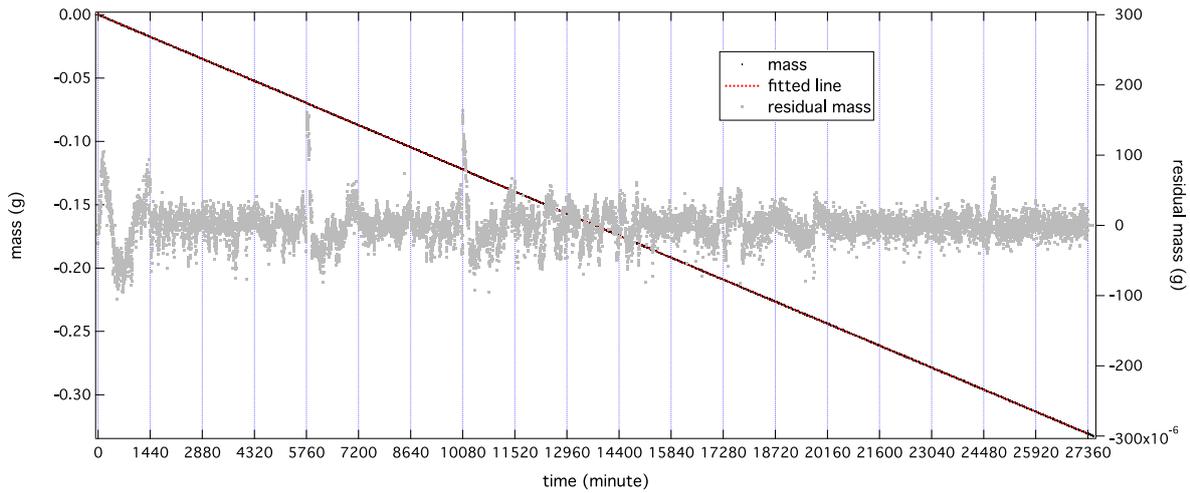
Figure 5. Mass loss of a diffusion bottle measured by a magnetic suspension balance

Table 6. Estimated diffusion rates and their standard deviations

	Diffusion rate, μg/min	Standard deviation of diffusion rate, μg/min
Day 1	12.232	0.004
Day 2	12.068	0.002
Day 3	12.046	0.002
Day 4	12.064	0.001
Day 5	12.135	0.004
Day 6	12.059	0.001
Day 7	12.091	0.002
Day 8	12.133	0.004
Day 9	12.083	0.002
Day 10	12.081	0.002
Day 11	12.020	0.002
Day 12	12.078	0.002
Day 13	12.107	0.002
Day 14	12.029	0.002
Day 15	12.057	0.001
Day 16	12.070	0.001
Day 17	12.087	0.001
Day 18	12.095	0.001
Day 19	12.084	0.001
Average*	**12.077**	**0.030**

- Note that the data from the day 1 is not used for estimating the average value
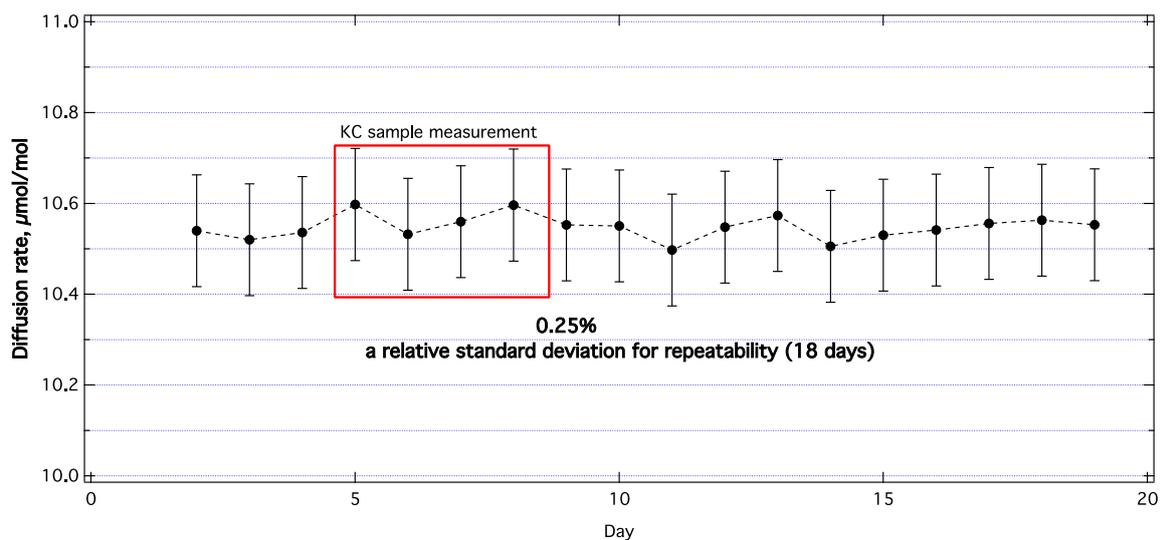
Figure 6. Diffusion rates for continuous 18 days

- Purity tables of the parent gases

Ultrapure water generated by a Labpure (ELGA, PureLab Ultra) was used for the diffusion bottle. Total organic carbon of the ultrapure water was maintained at less than 4 nmol/mol that is negligible. Therefore, the purity of water in the diffusion bottle was assumed as 100%.

Instrumentation

The amount mole fraction of a mixture generated by the dynamic gravimetric system (DGS) and a sample cylinder are analyzed using a hygrometer, a dew point meter equipped with a chilled mirror (K-1806/DP30, MBW Elektronik AG, Switzerland). Two cavity ring-down spectroscopy (CRDS) instruments (one with a low inlet pressure, the other with a high pressure inlet equipped with a vacuum pump) were tested for analyzing water vapor sample cylinders (about 10 μmol mol^{-1}) prepared by KRISS before the final analysis with the hygrometer. Results showed that both CRDS has an issue either for repeatability or time to be stabilized. Therefore, the hygrometer was used for the sample analysis because of the limited sample volume for analysis.

Description of the procedure

As shown in Figure 1, the NPL cylinder and the KRISS dynamic gravimetric system (DGS) were connected to a hygrometer. The analysis was conducted by alternating the NPL cylinder and the KRISS DGS (i.e., KRISS DGS– NPL – KRISS DGS – NPL – KRISS DGS).

Uncertainty evaluation

- Model equation for KRISS DGS

The model equation for estimating the amount mole fraction of water vapor is expressed as

$$x_w = \frac{D \times V_m}{M_w \times Q_T} + x_0 \tag{1}$$

where x_w is the amount mole fraction of water vapor, D is the diffusion rate, V_m is the molar volume of an ideal gas at 25 °C and 101.325 kPa, M_w is the molecular weight of water vapor, Q_T is the total flow rate, and x_0 is the background water vapor in the system.

The combined standard uncertainty is estimated as

$$u(x_w) = \sqrt{x_w^2 \left[\left(\frac{u(D)}{D}\right)^2 + \left(\frac{u(V_m)}{V_m}\right)^2 + \left(\frac{u(M_w)}{M_w}\right)^2 + \left(\frac{u(Q_T)}{Q_T}\right)^2\right] + u^2(x_0)} \qquad (2)$$

$$u(x_w) \cong \sqrt{x_w^2 \left[\left(\frac{u(D)}{D}\right)^2 + \left(\frac{u(Q_T)}{Q_T}\right)^2\right] + u^2(x_0)} \qquad (3)$$

Table 7. Uncertainty budget for estimating the diffusion rate of water vapor

Component (y)	Uncertainty $u(y)$			Sensitivity $c_i = \partial x_w / \partial y$	Contribution to $u(x_w), |c_i| \cdot u(y)$, μmol mol^{-1}
	Source	Standard uncertainty	Combined standard uncertainty		
Diffusion rate (D)	Regression	1.56×10^{-9} g/min	1.56×10^{-9} g/min	x_w/D	$3.19 \times 10^{-4} x_w$
Total flow rate (Q_T)	Calibration	1.63×10^{-3} L/min	2.04×10^{-3} L/min	$-x_w/Q_T$	$1.31 \times 10^{-3} x_w$
	Reproducibility	1.22×10^{-3} L/min			
Background water vapor			6.00×10^{-2} μmol/mol	1	6.00×10^{-2}

- Uncertainty budgets for the reported result

$$x_{NPL} = x_{KRISS} \times R_{avg}$$

(4)

where x_{NPL} is the amount mole fraction of NPL PSM, x_{KRISS} is the amount mole fraction of KRISS DGS, and R_{avg} is the average of the hygrometer response ratios (i.e., response of NPL PSM to response of KRISS DGS) for twelve measurements during four days.

Table 8. Uncertainty budget for the reported result

Component	Relative uncertainty (%)			
	Gravimetric $(k=1)$	Analytical $(k=1)$	Combined $(k=1)$	Expanded $(k=2)$

Water vapor	0.58	0.35	0.68	1.36

NPL MEASUREMENT REPORT

Cylinder number: **1154294**

Measurements made at NPL: **September 2015**

Analytical comparison methods

The nominal 10 µmol/mol water in nitrogen mixture was analysed by means of comparison with to NPL Primary Reference Materials (PRMs) using a commercial water vapour analyser based on cavity ring-down spectroscopy. Gas samples were delivered to the analyser *via* a manifold comprising stainless steel Swagelok fittings, which was purged before analysis using a gas of the same nominal composition. The analyser response to the matrix gas was recorded. The analyser response to a PRM was then recorded for at least a 10 minute period followed by the travelling standard for the same time. This sequence was repeated four times. At the end of the experiment the analyser response to the matrix gas was recorded a second time. To minimise the effects from zero drift, a mean of the analyser response to the matrix gas before and after the experiment was used. The amount fractions of the travelling standard was then determined by multiplying the ratio of the analyser response to the travelling standard and the PRM (both were corrected for the analyser response to matrix gas) with the amount fraction of the PRM. Cylinders were maintained at a laboratory temperature of (20 ± 3) °C throughout the period of analysis. Samples were introduced into the analyser at approximately 0.5 bar above atmospheric pressure using a low volume gas regulator.

Water vapour Analyser

Water vapour detection was afforded by a LaserTrace™ 3 water vapour trace gas analyser (F6000, Tiger Optics, LLC, Warrington, USA) based on continuous wave cavity ring-down spectroscopy (Laser

wavelength = 1392.5 ± 0.5 nm), having a sensitivity of 0.1 ppbv and detection limit of 0.2 ppbv. Sample gases flowed through the gas cell at a rate of approximately 1 L min^{-1}.

Calibration standards

The travelling standard was certified against two systems maintained at NPL (the Molbloc dilution facility and the chemical looping combustor. With the first, a dynamic reference mixture was validating produced by blending a 100.8 µmol/mol PRM of water in nitrogen (NPL 1346) with nitrogen (Air products, BIP). The diluent gas was passed through a purifier system (SAES Getter Monotorr) to ensure it was free from the target gas. The flows of the diluent and the PRM were regulated by a 20 mg/s full-scale Viton seal (Brooks SLA5850-SE1AB1B2A1) and a 2 mg/s full scale metal seal (Brooks SLA7950-S1EGG1B2A1) thermal mass flow controllers respectively. The mass flow of each gas was measured accurately with 'Molbloc-L' laminar mass flow elements (DHI, models 1E3-VCR-V-Q and 1E2-VCR-V-Q for the target and balance gases, respectively), located upstream, and matched to the full scale setting of the mass flow controllers. The travelling standard was also certified using NPL PRMs of hydrogen in nitrogen after conversion with a Chemical Looping Combustor (CLC) containing a bed of copper oxide (Gas Recovery and Recycle Ltd).

Final Results and Expanded Uncertainties

Table 1 shows the final certified values with uncertainties of the NPL travelling standard using the Mobloc facility (x_1) and the chemical looping combustor (x_2). Measurements made using each method were given equal weighting. The evaluation of measurement uncertainties is based on the statistical analysis of the repeated measurements of the comparison mixture from the response H_2O analyser. For each measurement of the comparison mixture, the standard deviation was calculated from the average comprising each analysis.

Quantity	Units	Value	Unc	Sensitivity	Sum of Sq
x_1	µmol/mol	10.19	0.05	0.5	6.6E-04
x_2	µmol/mol	10.16	0.06	0.5	7.6E-04
x_a	µmol/mol	10.17			
$u(x_a)$	µmol/mol	0.038			
$U(x_a)$	µmol/mol	0.08			

Table 1 Assigned value of the comparison mixture and uncertainties

Annex B: Measurement data

Table 5 Results of CCQM-K116, values expressed in μmol mol^{-1} using NPL reference (*not used as KCRV*)

NMI	identifier	cylinder	x_a	$u(x_a)$	m	$u(m)$	date	x_{stab}	u_{stab}	x_b	x	$u(x)$	df	$U(df)$
INMETRO	D	1154270	10.76	0.04	-1.44E-04	1.37E-04	09/03/16	-0.029	0.028	10.73	11.02	0.37	0.29	0.74
VSL	F	1154280	9.90	0.04	-6.37E-06	1.84E-04	16/01/16	-0.001	0.027	9.90	9.74	0.10	-0.16	0.22
VNIIM	G	1126470	10.31	0.04	4.31E-04	1.94E-04	22/10/15	0.027	0.012	10.34	10.54	0.19	0.20	0.38
NMIJ	I	1126478	10.39	0.04	-1.06E-04	1.94E-04	19/12/15	-0.013	0.024	10.38	10.43	0.15	0.05	0.31
METAS	K	1154291	10.89	0.04	8.71E-05	2.03E-04	24/09/15	0.003	0.007	10.89	10.59	0.11	-0.30	0.23
KRISS	N	1126619	10.83	0.03	2.98E-04	2.02E-04	01/12/15	0.031	0.021	10.86	10.75	0.07	-0.11	0.17
NIM	O	1154281	9.85	0.03	-4.05E-04	1.47E-04	30/05/16	-0.115	0.042	9.73	10.00	0.15	0.27	0.32
NPL	Q	1154294	10.25	0.03	-2.30E-04	2.00E-04	25/09/15	-0.008	0.007	10.24	10.17	0.04	-0.07	0.10

Table 6 Measurement results used to assign values to the travelling standards

	INMETRO		VSL		VNIIM		NMIJ		METAS		KRISS		NIM		NPL	
	x	$u(x)$	x	$u(x)$	x	$u(x)$	x	$u(x)$	x	$u(x)$	x	$u(x)$	x	$u(x)$	x	$u(x)$
1	10.75	0.07	9.89	0.06	10.30	0.07	10.39	0.07	10.85	0.06	10.79	0.06	9.81	0.05	10.21	0.06
2	10.79	0.09	9.93	0.08	10.34	0.08	10.43	0.08	10.89	0.08	10.83	0.08	9.85	0.07	10.25	0.07
3	10.72	0.07	9.86	0.06	10.27	0.07	10.36	0.07	10.88	0.07	10.82	0.06	9.84	0.05	10.24	0.06
4	10.76	0.08	9.90	0.08	10.31	0.08	10.40	0.08	10.93	0.08	10.87	0.08	9.88	0.07	10.29	0.07
x_a	10.76	0.039	9.90	0.036	10.31	0.038	10.39	0.037	10.89	0.037	10.83	0.035	9.85	0.029	10.25	0.033

Table 7 Measurements of stability correction for the travelling standards (date of t = 0 is 20-08-2015)

day	VSL x	$u(x)$	VNIIM x	$u(x)$	NMIJ x	$u(x)$	METAS x	$u(x)$	KRISS x	$u(x)$	NPL x	$u(x)$
0	9.91	0.06	10.30	0.07	10.39	0.07	10.85	0.07	10.72	0.07	10.19	0.07
20	9.81	0.06	10.21	0.07	10.38	0.07	10.89	0.07	10.81	0.07	10.20	0.07
96	9.86	0.06	10.22	0.07	10.31	0.07	10.92	0.07	10.78	0.07	10.24	0.07
119	9.90	0.07	10.31	0.07	10.40	0.07	10.89	0.07	10.83	0.08	10.25	0.07
321	9.84	0.06	10.35	0.06	10.37	0.06	10.90	0.07	10.86	0.07	10.19	0.08
344	9.88	0.06	10.42	0.06	10.32	0.06	10.91	0.06	10.86	0.06	10.11	0.06

day	INMETRO x	$u(x)$	NIM x	$u(x)$
0	10.77	0.07	9.86	0.06
20	10.72	0.07	9.79	0.06
96	10.71	0.07	9.80	0.06
119	10.76	0.08	9.85	0.07
448	10.75	0.07	-	-
532	10.61	0.07	9.62	0.06