

# International Pilot Study CCQM-P193: 10 $\mu\text{mol mol}^{-1}$ water vapour in nitrogen

P J Brewer<sup>1</sup>, B Giesekeing<sup>1</sup>, V F Ferracci<sup>1</sup>, M Ward<sup>1</sup>, S Bell<sup>1</sup>, P Carroll<sup>1</sup> and B Hall<sup>2</sup>

<sup>1</sup>National Physical Laboratory, Hampton Road, Teddington, TW11 0LW, UK.

<sup>2</sup>National Oceanic and Atmospheric Administration (NOAA), 325 Broadway, Mail Stop R.GMD1, Boulder, CO 80305 USA.

## Abstract

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 pilot study aims to assess the analytical capabilities of laboratories for measuring the composition of 10  $\mu\text{mol mol}^{-1}$  water vapour in nitrogen.

## Field

Amount of substance

## Subject

Comparison of the composition of water vapour in nitrogen

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## 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 pilot study aims to assess the analytical capabilities of laboratories for measuring the composition of  $10 \mu\text{mol mol}^{-1}$  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

### 2.1 List of participants

Table 1 provides a list of the participating laboratories.

Acronym	Country	Full Institute Name and address
NPL	UK	National Physical Laboratory, Hampton Road, Teddington, Middlesex, TW11 0LW, United Kingdom
NOAA-GMD	US	National Oceanic and Atmospheric Administration, Global Monitoring Division, 325 Broadway, Mail Stop R.GMD1, Boulder, CO 80305 USA

Table 1 Participating laboratories

### 2.2 Schedule

The schedule for the pilot study 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 Pilot study schedule

### 2.3 Measurement standards

A batch of 15 gas mixtures with a nominal composition of  $10 \mu\text{mol mol}^{-1}$  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 CCQM-K116 and a further two used for this parallel pilot study. This was based on selecting an ensemble with the lowest drift rates 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 ( $> 5 \text{ MPa}$ ) 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).

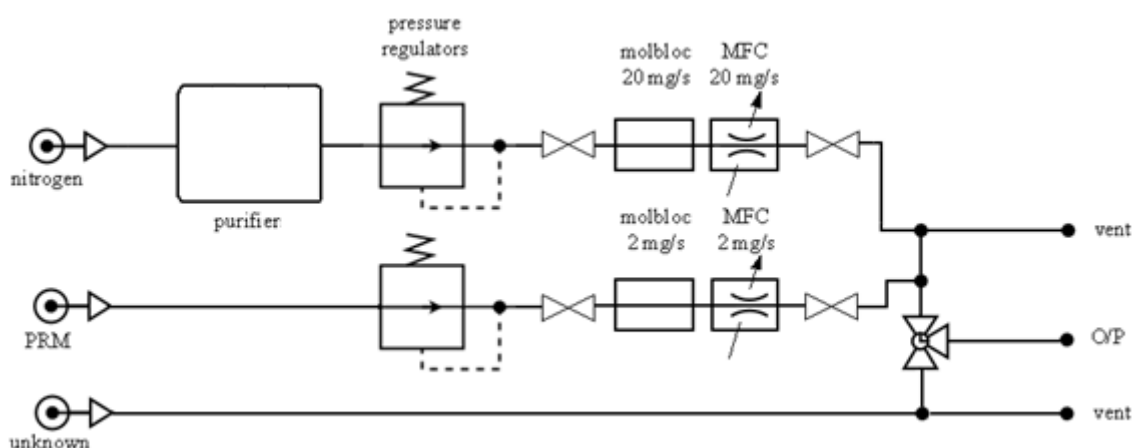
### 2.4 Molbloc dilution facility

The dynamic gas mixture used for validating the travelling standards was produced by blending a  $100.8 \mu\text{mol mol}^{-1}$  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  $20 \text{ mg/s}$  full-scale Viton seal (Brooks SLA5850-SE1AB1B2A1) and a  $2 \text{ mg/s}$  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 Molblobs (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 Molblobs 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:



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  $\mu\text{mol mol}^{-1}$  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  $\mu\text{mol mol}^{-1}$  H<sub>2</sub> in N<sub>2</sub> and 232643SGR2 9.9839  $\mu\text{mol mol}^{-1}$  H<sub>2</sub> in N<sub>2</sub>) were prepared gravimetrically in accordance with ISO 6142 <sup>[1]</sup> using high purity hydrogen (BIP<sup>+</sup> grade, > 99.9999 %, Air Products) and nitrogen (BIP<sup>+</sup> 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.

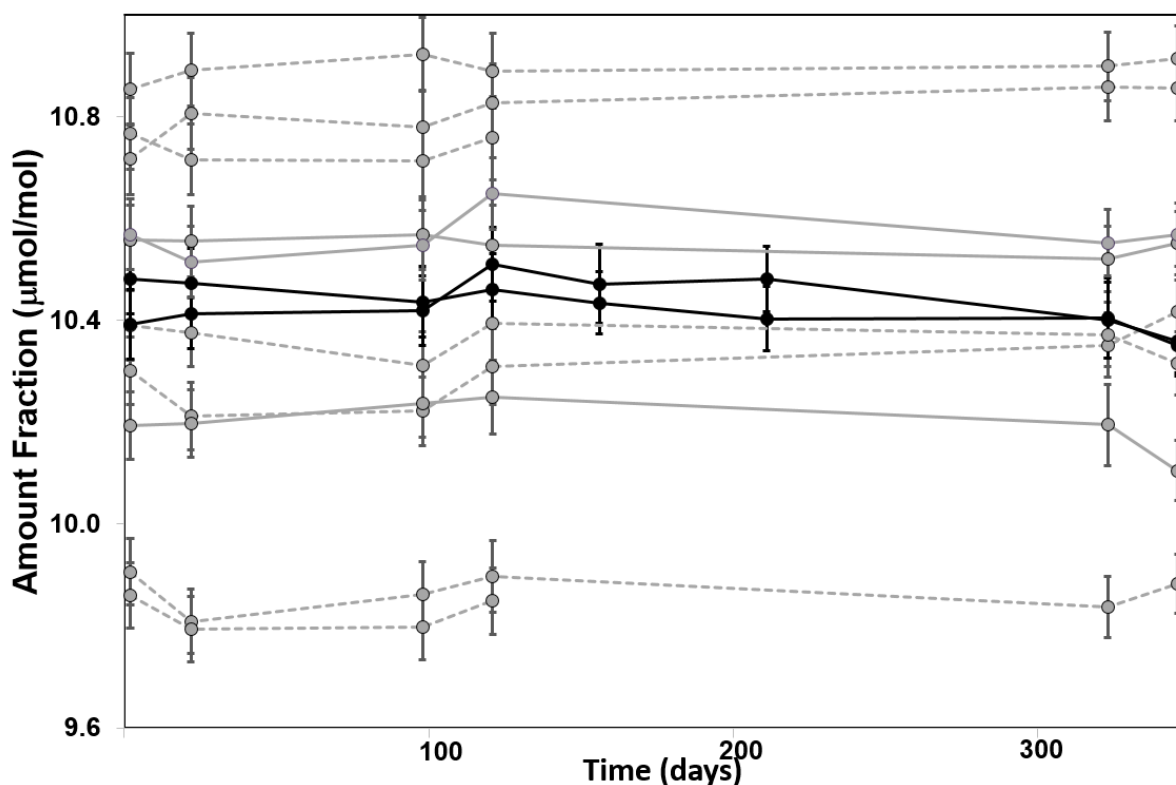
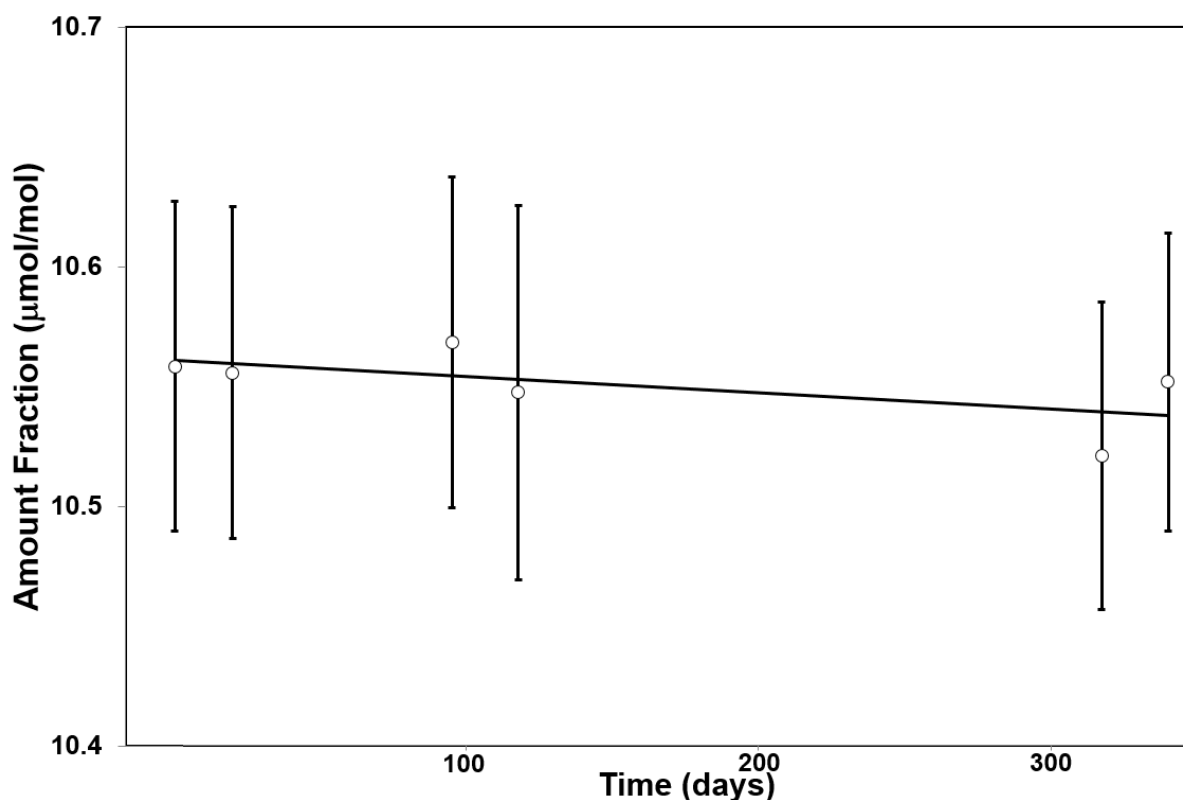


Figure 2 Stability data for all eight travelling standards in CCQM-K116 (grey dotted lines), the three used in this parallel pilot study (solid grey lines) and two control mixtures (black solid lines) held at NPL during the comparison. Bars show the standard uncertainties.

The results of these analyses were plotted as a function of time and a linear squares fit in accordance with 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.

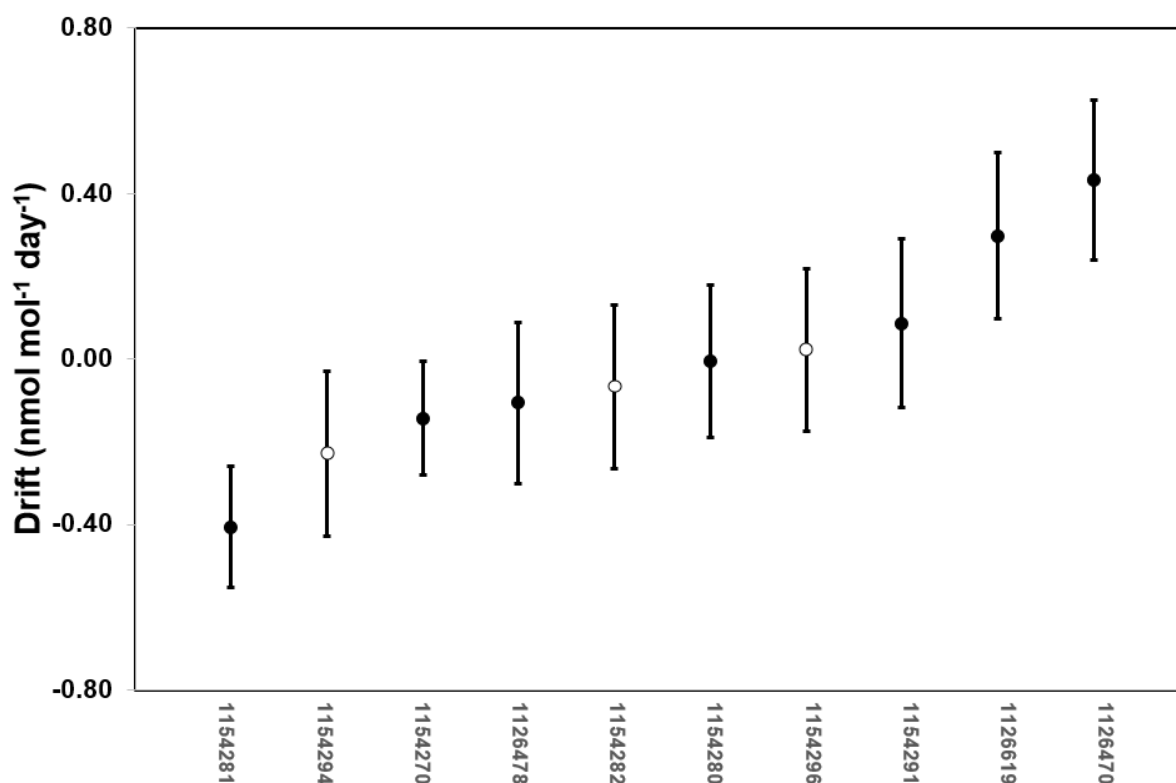
In all cases it was found that a straight line was a good fit to the data. The use of a straight line fit is further justified because it is consistent with typical chemical decay or absorption processes over a small range of amount fractions.<sup>[2]</sup> The reference value for each travelling standard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

Laboratory	identifier	cylinder	$x_a$	$u(x_a)$	$x_{stab}$	$u_{stab}$	$x_b$	$x$	$u(x)$	$d_f$	$U(d_f)$
NPL-1	Q	1154294	10.25	0.03	-0.01	0.01	10.24	10.17	0.04	-0.07	0.10
NOAA-GMD	J	1154282	10.55	0.04	-0.012	0.035	10.54	10.58	0.20	0.04	0.42
NPL-2	P	1154296	10.65	0.04	0.004	0.039	10.65	10.53	0.07	-0.12	0.17

**Table 3** Assigned values to travelling standards in CCQM-P193, values are expressed in  $\mu\text{mol mol}^{-1}$



**Figure 4** The estimated drift of each travelling standard and the standard error for all mixtures used in CCQM-K116 and this parallel pilot study (open circles).

Figure 4 shows that the population has no significant outliers and that the estimated drifts are distributed around a median value of  $-0.037 \text{ nmol mol}^{-1} \text{ day}^{-1}$ . The maximum drift  $0.43 \text{ nmol mol}^{-1} \text{ day}^{-1}$  corresponds to a drift of 0.8% over 6 months calculated at the nominal amount fraction of  $10 \mu\text{mol mol}^{-1}$ .

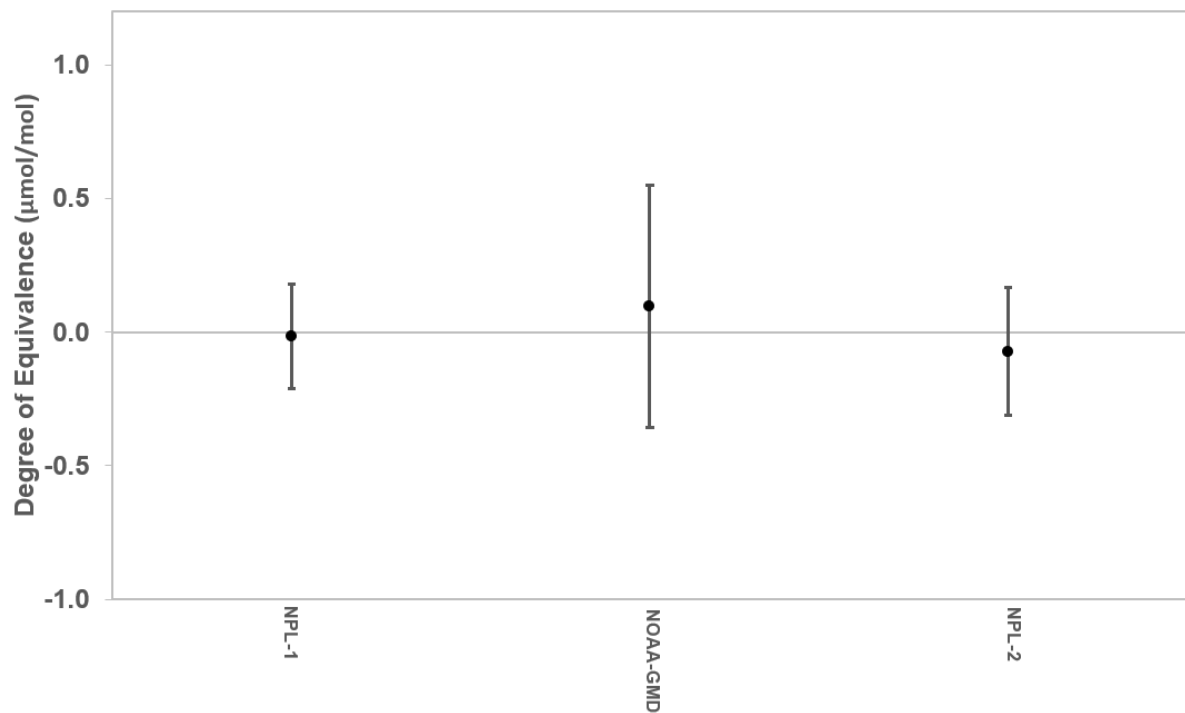
### 3. Results

Table 4 presents the results from the pilot study. Two results are reported for NPL. The first (NPL-1) is the value reported in CCQM-K116 and was determined using a permeation system for generating dynamic water vapour reference standards and analysis by Cavity Ring Down Spectroscopy. The second (NPL-2) was determined by measurements with traceability to NPL's Low Frost Point primary standard humidity generator. The reference values have been determined using a mean of the participants' results weighted by the submitted uncertainties. An 'excess-variance' approach<sup>[3]</sup> has been used to allow for unexplained laboratory effects as described in the report for CCQM-K116.

Laboratory	identifier	cylinder	$x_a$	$u(x_a)$	$m$	$u(m)$	date	$x_{stab}$	$u_{stab}$	$x_{ref}$	$x$	$u(x)$	$d_i$	$U(d_i)$
NPL-1	Q	1154294	10.25	0.03	-2.30E-04	2.00E-04	25/09/15	-0.01	0.01	10.24	10.17	0.04	-0.02	0.20
NOAA-GMD	J	1154282	10.55	0.04	-6.69E-05	1.97E-04	14/02/16	-0.012	0.035	10.54	10.58	0.20	0.09	0.45
NPL-2	P	1154296	10.65	0.04	2.16E-05	1.97E-04	06/03/16	0.004	0.039	10.65	10.53	0.07	-0.07	0.24

**Table 4** Results of CCQM-P193 with values are expressed in  $\mu\text{mol mol}^{-1}$

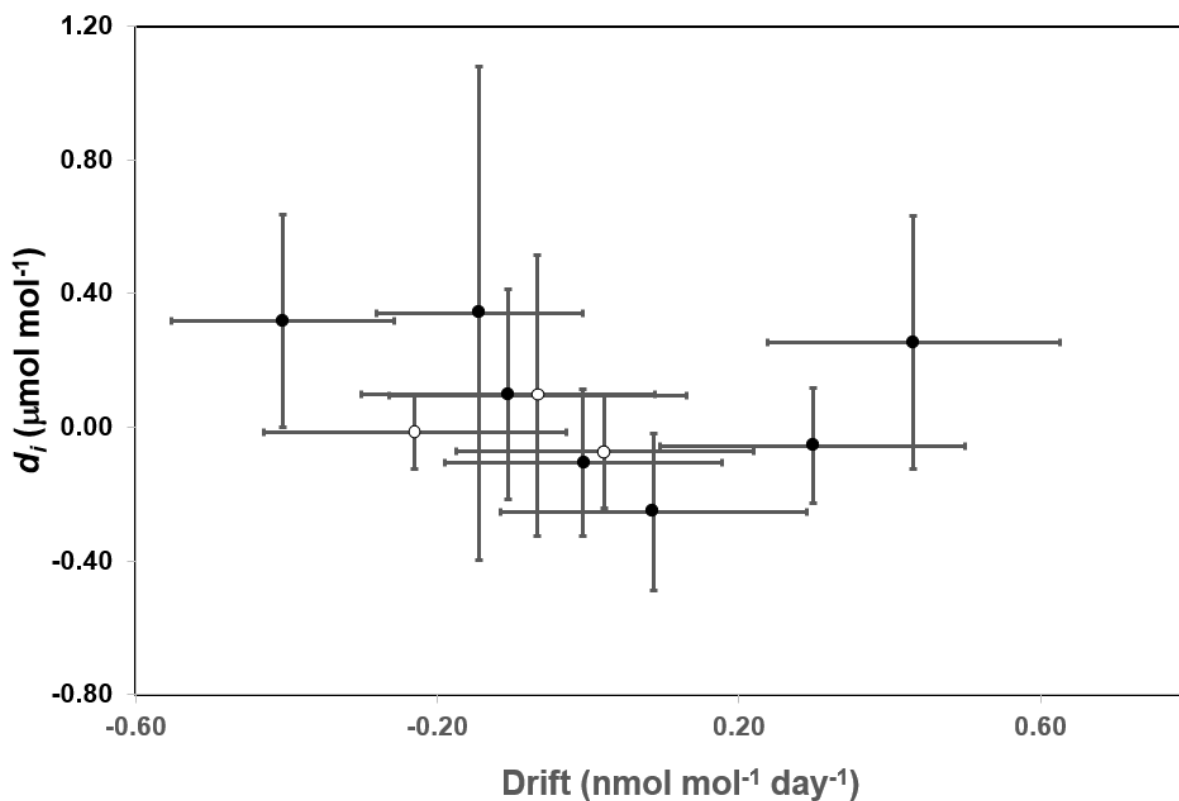
Figure 5 shows the degree of equivalence of the participating laboratories. The error bars are the expanded uncertainties obtained from the uncertainty of the results reported by each participant and the uncertainty in the KCRV.



**Figure 5** Degrees of equivalence for the participants

The degree of equivalence of each laboratory was plotted against the drift of its assigned cylinder. Figure 6 shows 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 for all travelling standards in CCQM-K116 and the parallel pilot study (open circles). 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 all 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 References

- [1] International Organization for Standardization, ISO 6142:2015 Gas analysis -- Preparation of calibration gas mixtures -- Part 1: Gravimetric method for Class I mixtures
- [2] International Key Comparison CCQM-K26a and Pilot Study CCQM-P50a (NO). Final Report. [http://kcdb.bipm.org/appendixB/appbresults/ccqm-k26.a/ccqm-k26.a\\_final\\_report.pdf](http://kcdb.bipm.org/appendixB/appbresults/ccqm-k26.a/ccqm-k26.a_final_report.pdf)
- [3] M Cox, P Harris, S Ellison, CCQM/11-18, Use of an 'excess-variance' approach for the estimation of a key comparison reference value, associated standard uncertainty and degrees of equivalence for CCQM key comparison data, CCQM.
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- [5] CCQM-10-03. CCQM guidance note: estimation of a consensus KCRV and associated degrees of equivalence. CCQM, 2010.
- [6] R. DerSimonian and R. Kacker, Random-effects model for meta-analysis of clinical trials: An update, *Contemporary Clinical Trials*, 2007, 28, 105–114.
- [7] R. DerSimonian and N. Laird, Meta-analysis in clinical trials, *Controlled Clinical Trials*, 1986, 7, 177–188.
- [8] H. K. Iyer, C. M. J. Wang and T. Mathew, Models and confidence intervals for true values in interlaboratory trials, *J. Amer. Statist. Assoc.*, 2004, 99, 1060–1071.

## Annex A: Measurement reports

### NPL MEASUREMENT REPORT

Cylinder number: **1154294**

Measurements made at NPL: **September 2015**

#### Analytical comparison methods

The nominal 10  $\mu\text{mol/mol}$  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  $(20 \pm 3) ^\circ\text{C}$  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 =  $1392.5 \pm 0.5 \text{ nm}$ ), 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  $1 \text{ L min}^{-1}$ .

#### 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  $100.8 \mu\text{mol/mol}$  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<sub>2</sub>O 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
$x_1$	$\mu\text{mol/mol}$	10.19	0.05	0.5	6.6E-04
$x_2$	$\mu\text{mol/mol}$	10.16	0.06	0.5	7.6E-04
$x_a$	$\mu\text{mol/mol}$	10.17			
$u(x_a)$	$\mu\text{mol/mol}$	0.038			
$U(x_a)$	$\mu\text{mol/mol}$	0.08			

**Table 1 Assigned value of the comparison mixture and uncertainties**

## Measurement Report: NOAA Global Monitoring Division

Cylinder number: 1154282

### Measurement Result

Mean H<sub>2</sub>O mole fraction: 10.58 μmol/mol

Standard uncertainty: 0.20 μmol/mol

Expanded uncertainty ( $k=3.16$ ): 0.64 μmol/mol

### Calibration standards

Primary standards were prepared gravimetrically in 34-L electropolished stainless steel cylinders (Essex Cryogenics, St. Louis, Missouri). Four primary standards were prepared in 2007-2010 and have been analyzed several times by different methods since preparation.

To prepare a primary standard, an aliquot of HPLC-grade H<sub>2</sub>O is drawn into a 1-3 cm length of glass capillary tubing, sealed at one end, and weighed previously. After adding water, the capillary is placed in a centrifuge to transfer the H<sub>2</sub>O to the sealed end, cooled to ~-70 deg C to reduce the H<sub>2</sub>O vapor pressure, and sealed in a propane/oxygen flame. After sealing and warming to room temperature, the capillary is weighed. All weighings are performed relative to a control piece of similar mass and density. Then the H<sub>2</sub>O aliquot is transferred to an evacuated cylinder that has also been weighed. The mass of H<sub>2</sub>O is calculated based on weighing results, corrected for buoyancy.

To transfer, we load the capillary into a 10-cm section of 1/4" o.d. PFA Teflon tubing, with small amounts of steel wool and glass wool placed in the downstream end. The Teflon tube is connected to the evacuated cylinder and purged with dry air for several minutes. Then we open the cylinder valve, break the glass capillary, and apply modest heat with dry gas overflow. After about 5 minutes we remove the Teflon tube and fill the cylinder with dry air (additional drying is achieved using Mg(ClO<sub>4</sub>)<sub>2</sub>). We used a frost-point hygrometer to estimate the H<sub>2</sub>O content of the dilution gas (typically < 0.3 μmol/mol).

Purity table (composition) of the dilution gas (synthetic air)(

O <sub>2</sub>	0.2105 (measured)
N <sub>2</sub>	0.7895 (inferred)
Ar	not measured (assumed zero)
CO <sub>2</sub>	< 3 μmol/mol (typical)
CH <sub>4</sub>	< 5 nmol/mol (typical)
H <sub>2</sub> O	< 0.3 μmol/mol

### Instrumentation

Sample # 1154282 was compared to gravimetrically-prepared primary standards using a frost-point hygrometer (RH Systems model 373LX; Wettingen, Switzerland).

## Analysis method

Prior to analysis, the 373LX hygrometer was purged with dry air (0.3  $\mu\text{mol/mol}$ ) overnight. In parallel, a Veriflo model 959 pressure-reducing regulator was purged with 20 cc/min dry nitrogen for 12 hours. Stainless steel tubing (1/16" o.d.) was used to connect the samples (gas cylinders) to the regulator and from the regulator to the hygrometer inlet. Because the regulator and sample lines represent a small volume, we were able to change gas cylinders quickly with minimal disturbance.

We performed analyses on two separate days. On each day, we ran sample 1154282 for 1 hour, followed by analysis of the primary standards in order of increasing water vapor mole fraction (30 min each). In March 2016, we analyzed the same 4 primary standards and an additional 8.7  $\mu\text{mol/mol}$  standard to verify the response of the hygrometer at nominal 10  $\mu\text{mol/mol}$ .

Samples were analyzed at a flowrate of 750 cc/min. Because we observed a slow increase in the response for sample 1154282, we used an exponential function to estimate the asymptotic response of this sample. For example, after 1 hour, the hygrometer signal was 10.50  $\mu\text{mol/mol}$ , but the asymptotic response was 10.57  $\mu\text{mol/mol}$ . Because the hygrometer response is a slight function of flowrate (or pressure), we also applied a pressure correction to account for minor flow-rate instability. The hygrometer reaches equilibrium more rapidly at higher mole fractions and when small gas volumes are present upstream of the regulator, as is the case for the primary standards.

We used the results of 5 primary standards (10-200  $\mu\text{mol/mol}$ ) to define a linear response function, and assigned a value to sample 1154282 based on this response function. The hygrometer response for four primary standards was consistent between analyses performed in January and March, 2016, so we included the nominal 10  $\mu\text{mol/mol}$  primary standard in our response function even though it was prepared after the NPL sample was analyzed.

### Uncertainty at 10 $\mu\text{mol/mol}$

Primary stds (N=5)	0.19 $\mu\text{mol/mol}$
Inst. repeatability	0.05 $\mu\text{mol/mol}$
Total: standard unc.	0.20 $\mu\text{mol/mol}$
<b>Total: expanded unc.</b>	<b>0.64 <math>\mu\text{mol/mol}</math></b>
Coverage factor, $k$	3.16

Note: Trade names and vendors are provided as a matter of record, and do not constitute an endorsement.

## CCQM P-193 Water in Nitrogen reporting from NPL humidity group.

Paul Carroll, Stephanie Bell

13/5/2016 and May 2018

### Measurement method

The comparison gas of nominally  $10 \mu\text{mol mol}^{-1}$  of water vapour in nitrogen was measured in terms of frost-point temperature using a transfer-standard chilled-mirror hygrometer (MBW model 373-LX). The hygrometer had been calibrated against the NPL primary Low Frost-point Generator (LFG) [1]. Pressure measurements were made using digital pressure indicators (Druck model DPI 501 and hygrometer's integral pressure sensor) with calibrations traceable to NPL pressure standards.

The chilled-mirror hygrometer was used to measure the frost-point temperature of the gas regulated at a pressure of nominally 105 kPa. The sampling system was pre-conditioned using air supplied from the LFG with a water vapour amount fraction just below  $10 \mu\text{mol mol}^{-1}$ . This gas was supplied continuously to the hygrometer before the initial measurement of cylinder gas and between repeated measurements.

The measurement set-up is shown in the schematic diagram in Figure 1 below. The gas supply to the hygrometer was switched between the LFG air and the cylinder nitrogen using a three-way valve. A Swagelok high-purity gas regulator was used in conjunction with a needle valve to ensure the pressure of gas from the cylinder when used was nominally 105 kPa also. All tubing used was 1/4" outer diameter internally electropolished stainless steel and connections were made using Swagelok compression fittings. The chilled-mirror hygrometer had an integral pressure sensor which was calibrated by comparison against the Druck model DPI 501. A flow rate of 0.5 litres per minute was used for all measurements.

The measurements from the hygrometer were logged at one-minute intervals and over periods of between 35 minutes and 149 minutes. The frost-point temperature values were used to calculate the water vapour partial pressure in the measured gas. The measurements of total pressure at the hygrometer head were then used for calculation of amount fraction of water vapour in the measured gas. The vapour pressure equation used was that due to Sonntag (1990) [2], and the water vapour enhancement factor equation used was that due to Hardy (1998) [3].

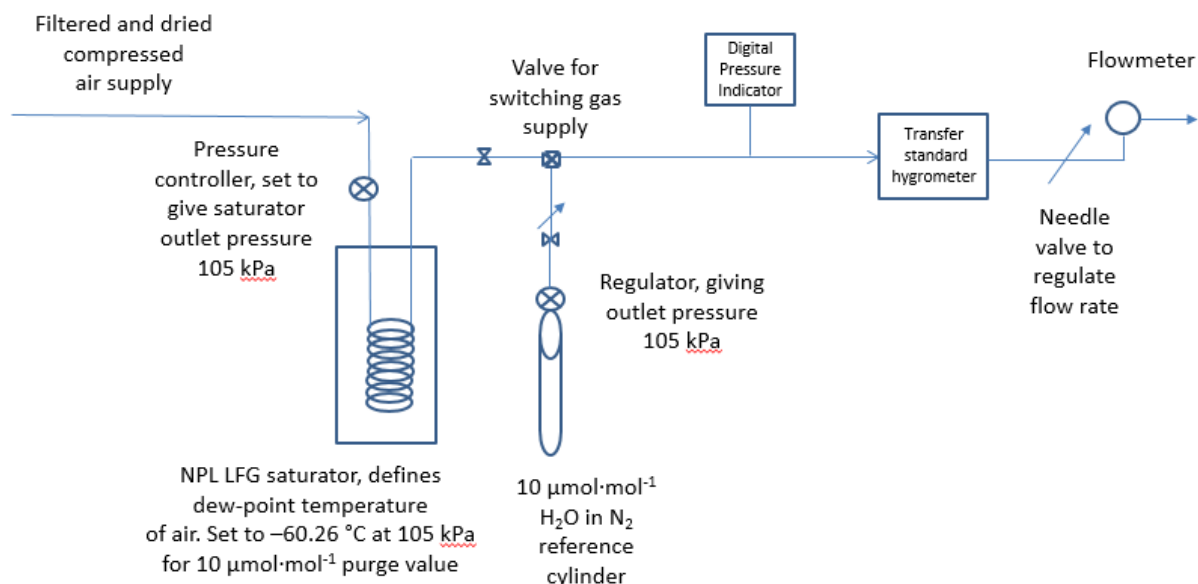
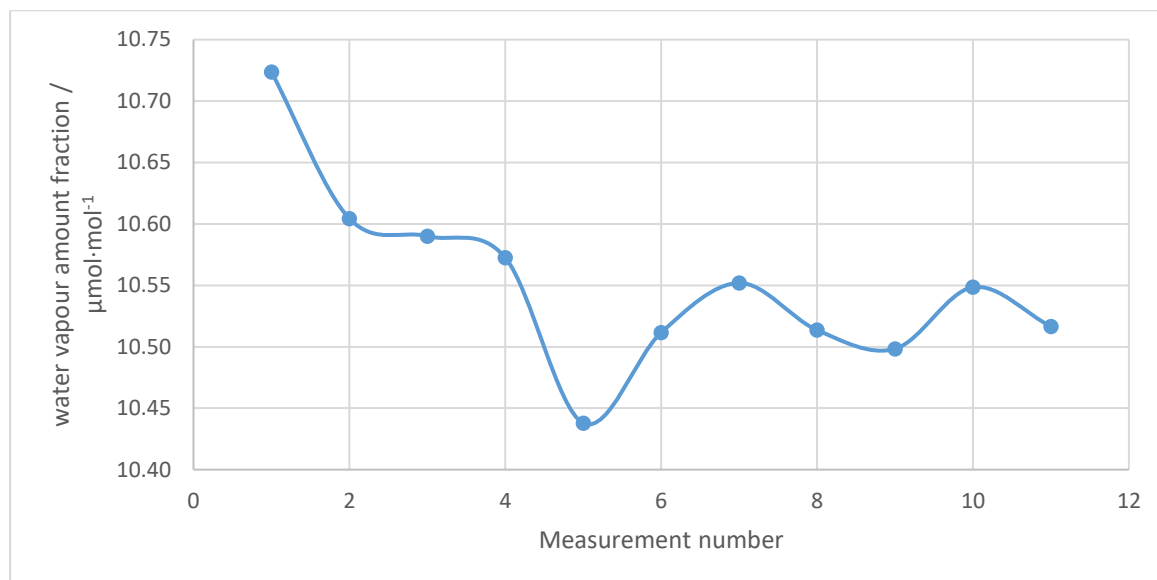


Figure 1: Schematic diagram of NPL humidity group measurement set-up

## Results:

In total, 11 cylinder measurements were made on four separate dates. The graph below shows the variation in measured cylinder value with sequential cylinder measurements. It was decided that only measurements 6 to 11 would be reported as the results prior to these seemed to show incomplete equilibration of the sampling and measurement system.



**Figure 2:** Graph of measured cylinder water vapour amount fraction against measurement number

In the reporting of results in Table 1 below, the “number of readings” is the number of data points logged at one-minute intervals once the measured value of the hygrometer had been observed to have stabilised for that particular cylinder measurement.

**Table 1:** Water vapour amount fraction values from NPL humidity group reference cylinder measurements

Cylinder measurement number	Date	Result / mol/mol	Standard deviation /mol/mol	Standard deviation / % relative	Number of readings	Measurement uncertainty $k = 2$ / mol/mol
1 (6)	03/03/2016	$1.051 \times 10^{-5}$	$0.0082 \times 10^{-5}$	0.78	66	$0.013 \times 10^{-5}$
2 (7)	04/03/2016	$1.055 \times 10^{-5}$	$0.0067 \times 10^{-5}$	0.64	61	$0.013 \times 10^{-5}$
3 (8)	04/03/2016	$1.051 \times 10^{-5}$	$0.0083 \times 10^{-5}$	0.79	65	$0.013 \times 10^{-5}$
4 (9)	04/03/2016	$1.050 \times 10^{-5}$	$0.0064 \times 10^{-5}$	0.61	67	$0.013 \times 10^{-5}$
5 (10)	08/03/2016	$1.055 \times 10^{-5}$	$0.0065 \times 10^{-5}$	0.62	149	$0.013 \times 10^{-5}$
6 (11)	08/03/2016	$1.052 \times 10^{-5}$	$0.0084 \times 10^{-5}$	0.80	118	$0.013 \times 10^{-5}$

The reported result for the cylinder measurements made shown below in Table 2 uses the mean of all data (526 measurements) from the 6 measurements selected for submission.

**Table 2:** Reported mean measured water vapour amount fraction value for NPL humidity group reference cylinder

	Result / mol/mol	Standard deviation /mol/mol	Standard deviation / % relative	Number of readings	Measurement uncertainty $k = 2$ / mol/mol
Mean value	$1.053 \times 10^{-5}$	$0.0076 \times 10^{-5}$	0.72	526	$0.013 \times 10^{-5}$



### Uncertainty evaluation:

The standard uncertainty of the measured value represents a combination of the uncertainties arising from the calibration, estimated stability and resolution of the reference standard hygrometer and pressure measurements, from the standard deviation of the measurements, from the method of sampling, and from the formulae used for conversion from values of frost point into amount fraction of water vapour.

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

A summary uncertainty budget is shown below in Table 3.

**Table 3.** Summary uncertainty budget for measurements of nominally  $10 \mu\text{mol mol}^{-1}$  of water vapour in nitrogen

Source of uncertainty	Value $\pm$	Unit	Probability distribution	Divisor	Sensitivity coefficient	Sensitivity coefficient unit	Standard uncertainty $u$ / ppmv
Dew-point temperature measurement	0.079	°C	Normal	2	1.374	ppmv / °C	0.054
Pressure measurement	232.36	Pa	Normal	2	$9.77 \times 10^{-5}$	ppmv / Pa	0.011
Water vapour pressure calculation	0.051	ppmv	Rectangular	$\sqrt{3}$	1		0.029
Water vapour enhancement factor pressure calculation	0.034	ppmv	Rectangular	$\sqrt{3}$	1		0.020
Combined standard uncertainty $u$			Normal				0.065
Expanded uncertainty $U$			Normal ( $k=2$ )				0.130

### References:

1. Stevens, M. "The new NPL low frost-point Generator" in Proceedings of TEMPMEKO '99, 7th International Symposium on Temperature and Thermal Measurements in Industry and Science, ed. by JF Dubbeldam, MJ de Groot (Edauw Johannissen bv, Delft, 1999), pp191-196.
2. Sonntag, D. "Important new values of the physical constants of 1986, vapour pressure formulations based on the ITS-90, and psychrometer formulae." *Z. Meteorol.* 70.5 (1990): 340-344.
3. Hardy, Bob. "ITS-90 formulations for vapor pressure, frostpoint temperature, dewpoint temperature, and enhancement factors in the range  $-100$  to  $+100$  C." *Proceedings of the Third International Symposium on Humidity and Moisture, Teddington, London, England.* 1998.