

# International Comparison CCQM-K117 – Ammonia in nitrogen

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## Field

Amount of substance

## Subject

Comparison of ammonia in nitrogen (track C)

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## 1 Introduction

This key comparison is a comparison to evaluate specific competences of NMIs (*track C key comparisons*). Ammonia is an important compound in chemical industry. It is widely used and is the basis for producing other compounds containing nitrogen. Ammonia is also very hazardous, and consequently emissions of ammonia need to be controlled and monitored. In the past years, several National Metrology Institutes have developed facilities for the preparation of Primary Standard gas Mixtures (PSMs), dynamically generated ammonia mixtures and facilities for comparing and certifying gas mixtures containing ammonia. This key comparison is a repeat of the CCQM-K46 [1].

For this key comparison, a binary mixture of ammonia in nitrogen has been chosen at an amount-of-substance fraction level of  $14 \mu\text{mol mol}^{-1}$ . The key comparison design follows that of the key comparisons using gas mixtures that are prepared gravimetrically as transfer standards [2][3].

## 2 Design and organisation of the key comparison

### 2.1 Participants

Table 1 lists the participants in this key comparison.

**Table 1: List of participants**

Acronym	Country	Institute
CERI	JP	Chemicals Evaluation and Research Institute, Saitama, Japan
METAS	CH	Federal Institute of Metrology METAS, Bern-Wabern, Switzerland
KRISS	KR	Korea Research Institute of Standards and Science, Daejeon, Republic of Korea
NIST	US	National Institute of Standards and Technology, Gaithersburg MD, United States of America
NIM	CN	National Institute of Metrology, Beijing, China
NPL	GB	National Physical Laboratory, Teddington, United Kingdom
VNIIM	RU	D.I. Mendeleev Institute for Metrology, St Petersburg, Russia
VSL	NL	Van Swinden Laboratorium, Delft, the Netherlands

### 2.2 Measurement standards

A set of mixtures was prepared gravimetrically by an external party in 50 L aluminium cylinders. The filling pressure in the cylinders was approximately 150 bar. The transfer standards were prepared with a nominal amount fraction ammonia of  $14 \mu\text{mol mol}^{-1}$ . The transfer standards were assessed for stability and homogeneity. Prior to shipment to the participating national metrology institutes (NMIs), the set of mixtures was analysed by VSL and then by NIST. After return, the set of mixtures was analysed by NIST and then by VSL. These data were used to:

- 1) Assess the stability of the ammonia amount fraction over time
- 2) Compute the differences in the ammonia amount fraction between the mixtures

The first assessment comprised the evaluation of the slope of a straight line fitted to the four data points and to assess it for significance [4]. After this assessment, the ammonia amount fraction was calculated for each mixture and the differences were calculated using a fixed effects model. These corrections were applied to the reported results prior to calculating a consensus value, which was then used to calculate the key comparison reference values for each of the travelling standards.

### 2.3 Measurement protocol

The cylinders for this comparison were bought by VSL but all NMIs paid for their own cylinder which could be collected from VSL after the final stability measurements. These stability measurements have been performed by VSL-NIST-NIST-VSL. The participants' measurements took place between the two NIST stability measurements. The rationale of having two NMIs to perform stability study is their difference in preparing their measurement standards. VSL used gravimetry and dilution using thermal mass flow controllers [5] and NIST used permeation [6].

The measurement protocol requested each laboratory to perform at least 3 measurements with their own calibrations. The replicates, leading to a measurement, were to be carried out under repeatability conditions. The protocol informed the participants about the nominal amount fraction ranges. The participants were also requested to submit a summary of their uncertainty evaluation used for calculating the uncertainty of their result.

### 2.4 Schedule

The schedule of this key comparison was as follows (table 2).

**Table 2: Key comparison schedule**

<b>Date</b>	<b>Stage</b>
<b>December 2014</b>	Agreement of draft protocol
<b>April 2014</b>	Registration of participants
<b>October 2017</b>	Final protocol available
<b>November 2017</b>	Expected delivery date of mixtures at VSL
<b>Nov 2017 – Sep 2018</b>	Homogeneity and stability study at VSL and NIST
<b>October 2018</b>	Dispatch of mixtures
<b>Nov 2018 – Jun 2019</b>	Measurements by participants
<b>July 2019</b>	Cylinders to be returned to NIST
<b>July 2019</b>	Report received by VSL
<b>Aug 2019 – Dec 2019</b>	Continuation of the stability study by NIST and VSL
<b>October 2019</b>	Preliminary results available
<b>February 2020</b>	Participants can collect their own mixture from VSL
<b>March 2020</b>	Draft A report available
<b>April 2021</b>	Draft B report available

### 2.5 Measurement equation

The evaluation of the data from this key comparison was performed by establishing a consensus value from the results reported by the participants. In this calculation, effects from stability and homogeneity were addressed. As explained in section 2.3, four measurements were taken at different times to enable assessing the stability of the transfer standards. After this assessment, amount fractions were computed for the transfer standards. These amount fractions were subsequently used to calculate the differences due to batch inhomogeneity of the set of transfer standards. Only the gas mixtures that had been used in the key comparison were included. A fixed

effects model was used to calculate these differences [7]. This model is identical to the model used in procedure A (the weighted mean) [8].

The consensus value was calculated after correcting the participants' results for the differences between the transfer standards. The consensus value was calculated using a weighted median [9][10] and procedure B [8], which involves using a Monte Carlo method to propagate the uncertainty. The key comparison reference value for each transfer standard was defined as

$$y_{\text{KCRV},i} = y_{\text{WMed}} + e_i$$

where  $y_{\text{WMed}}$  denotes the weighted median and  $e_i$  the deviation in the amount fraction of transfer standard  $i$ , as computed from the homogeneity study. This approach enables presenting the results, including the KCRV and the degrees-of-equivalence in a fashion that is used in most key comparisons in the gas analysis area.

In detail, the calculations performed were as follows. Given for each component the following data:

1. the amount fraction  $y_{\text{lab},i}$  and associated expanded uncertainty  $U_{\text{lab},i}$  with coverage factor  $k_{\text{lab},i}$  for laboratories  $i = 1 \dots N$
2. the amount fraction  $y_j$  and associated standard uncertainty  $u(y_j)$  for measurements  $j = 1 \dots M$  from the homogeneity and stability study

the following calculations were performed. To assess the stability of the mixtures, for each mixture the following steps were taken:

- A weighted least squares fit using a straight line to the  $t_j, y_j$  for  $j = 1 \dots M$  where  $t_j$  denotes the time and  $y_j$  the amount fraction in the mixture; as weights, the inverse of the variances  $u^2(y_j)$  were used;
- Assess whether  $a_1 \leq u(a_1)$ , where  $a_1$  denotes the slope of the straight line and  $u(a_1)$  the associated standard uncertainty;
- If the slope is significant, check the data and evaluation;
- If the slope is not significant, fit the data using a meta-analysis model to compute a mean amount fraction  $\tilde{y}$  and standard uncertainty  $u(\tilde{y})$ .

The meta-analysis was performed using the DerSimonian-Laird model [11][12]. The calculations were performed in R [13] using the metafor package [14]. The differences  $e_i$  were computed from the  $\tilde{y}_i$  and associated standard uncertainties  $u(\tilde{y}_i)$ . The fixed effects model defines these differences as

$$e_i = \tilde{y}_i - \tilde{y}_{\text{WM}}$$

where  $\tilde{y}_{\text{WM}}$  denotes the weighted mean computed from the  $\tilde{y}_i$  and associated standard uncertainties  $u(\tilde{y}_i)$  [7]. The standard uncertainty associated with  $e_i$  was computed as [8]

$$u^2(e_i) = u^2(\tilde{y}_i) - u^2(\tilde{y}_{\text{WM}})$$

where the minus sign arises due the covariance between  $\tilde{y}_i$  and  $\tilde{y}_{\text{WM}}$ .

The key comparison was based on a weighted median [9][10] as consensus value. Given ordered measured values  $y'_{\text{lab},i}$ , corrected for the differences in ammonia amount fractions between the transfer standards, with weights  $w'_i$ , the weighted median is the element  $\ell$  satisfying

$$\sum_{i'=1}^{\ell-1} w'_{i'} \leq 0.5 \quad \text{and} \quad \sum_{i'=\ell}^N w'_{i'} \leq 0.5$$

where

$$w_i = (U_{\text{lab},i}^2/k_{\text{lab},i}^2 + u^2(e_i))^{-1}$$

and

$$w'_i = w_i \cdot \left[ \sum_{j=1}^N w_j \right]^{-1}$$

to ensure that  $\sum_i w'_i = 1$ .

This estimator is used in the procedure B [8] to obtain the consensus value and degrees-of-equivalence. This approach was required as the reported data did not satisfy the criterion to use procedure A, which requires that the data set passes a consistency test.

The use of the weighted median is a refinement in comparison with the evaluation procedure used for CCQM-K112 (Biogas). Procedure B is implemented using the Monte Carlo method of GUM Supplement 2 (GUM-S2) [16] using  $M_{\text{MCM}} = 10^6$  samples. The steps are as follows:

1. Draw a series of measured values  $z_{\text{lab},i} \sim N(y_{\text{lab},i}, U_{\text{lab},i}/k_{\text{lab},i})$  for  $i = 1 \dots N$
2. Draw a series of measured values  $z_i \sim N(\tilde{y}_i, u(\tilde{y}_i))$  for  $i = 1 \dots N$
3. Compute  $\Delta z_i = z_i - z_{\text{WM}}$ , where  $z_{\text{WM}}$  denotes the weighted mean
4. Compute  $z'_{\text{lab},i} = z_{\text{lab},i} - \Delta z_i$
5. Compute the weighted median  $z_{\text{WMed}}$  using corrected values  $z'_{\text{lab},i}$  and weights  $w'_i$
6. Compute  $z_{\text{KCRV},i} = z_{\text{WMed}} + \Delta z_i$
7. Compute the difference  $\delta_i = z_{\text{lab},i} - z_{\text{KCRV},i}$

The output from this Monte Carlo procedure was used to compute [17]:

- The deviations  $e_i$  as the mean of the  $\Delta z_i$  and its associated standard uncertainty as the standard deviation of the  $\Delta z_i$ ;
- The KCRVs  $y_{\text{KCRV},i}$  as the mean of the  $z_{\text{KCRV},i}$  and its associated standard uncertainty as the standard deviation of the  $z_{\text{KCRV},i}$ ;
- The differences with respect to the KCRV  $d_i$  as the mean of the  $\delta_i$  and the 95 % coverage interval as the probabilistically symmetric interval of the  $\delta_i$ ; the standard uncertainty is obtained by calculating the standard deviation of the  $\delta_i$

This procedure ensures that

- Corrections are made for the differences in composition of the transfer standards through the  $e_i$ ;
- Most weight is given in the formation of the median to the measured values with the smallest uncertainty;
- Effects of covariances between the  $e_i$  are taken into account.

## 2.6 Measurement methods

The measurement methods used by the participants are described in annex A of this report. A summary of these methods, the dates of measurement and reporting, and the way in which metrological traceability has been established is given in Table 3.

**Table 3: Summary of calibration methods and metrological traceability**

Laboratory code	Measurements	Calibration	Traceability	Matrix standards	Measurement technique
VNIIM	4 April – 5 June 2019	Single point calibration	Own standards (ISO 6142)	Nitrogen	Chromatography-mass spectrometry NDIR <sup>1</sup>
NPL	16-17 May 2019	Bracketing	Own standards (ISO 6142)	Nitrogen	
VSL	7-13 March 2019	ISO 6143	Own standards (ISO 6142)	Nitrogen	Photo-Acoustic
CERI	13-March – 4 April 2019	Multipoint calibration	Own standards (ISO 6142)	Nitrogen	NDIR and FTIR <sup>2</sup>
KRISS	28-30 January 2019	Single point	Own standards	Nitrogen	NDIR
NIST	23-25 October 2018	ISO 6143	Own standards	Nitrogen	Chemiluminescence
METAS	11-14 March 2019	Bracketing	Own standards	Nitrogen	CRDS <sup>3</sup>
NIM	23-26 April 2019	Bracketing	Own standards (ISO 6142)	Nitrogen	FTIR

## 2.7 Degrees of equivalence

A unilateral degree of equivalence in key comparisons is defined as

$$d_i = y_{\text{lab},i} - y_{\text{KCRV},i} \quad (1)$$

and the uncertainty associated with the difference  $d_i$  at 95% level of confidence.

Given that procedure B has been used with a weighted median as estimator for the KCRV, there is no closed form for the evaluation of the standard uncertainty associated with the difference  $d_i$ . Instead, the Monte Carlo method of GUM Supplement 2 [16] was used to calculate this performance metric. The approach could readily be extended to calculate bilateral degrees-of-equivalence.

## 3 Results

### 3.1 Stability and homogeneity of the transfer standards

The results of the stability and homogeneity study of the transfer standards are summarised in Figure 1. The measurements taken by the NMIs took place between the second and third data point. VNIIM did not manage to deliver its transfer standard in a timely fashion to the coordinating laboratories, so it was omitted from the third series of analyses.

The results shown in Figure 1 demonstrate the stability of the amount fraction ammonia over the period that the measurements of the NMIs took place. The last measurement result (around 850 d) is for some of the transfer standards somewhat higher than the other results. This is probably attributable to an effect in the calibration or operation of the setup used for these analyses and has no meaning for the stability assessment. The amount fraction ammonia is known to increase

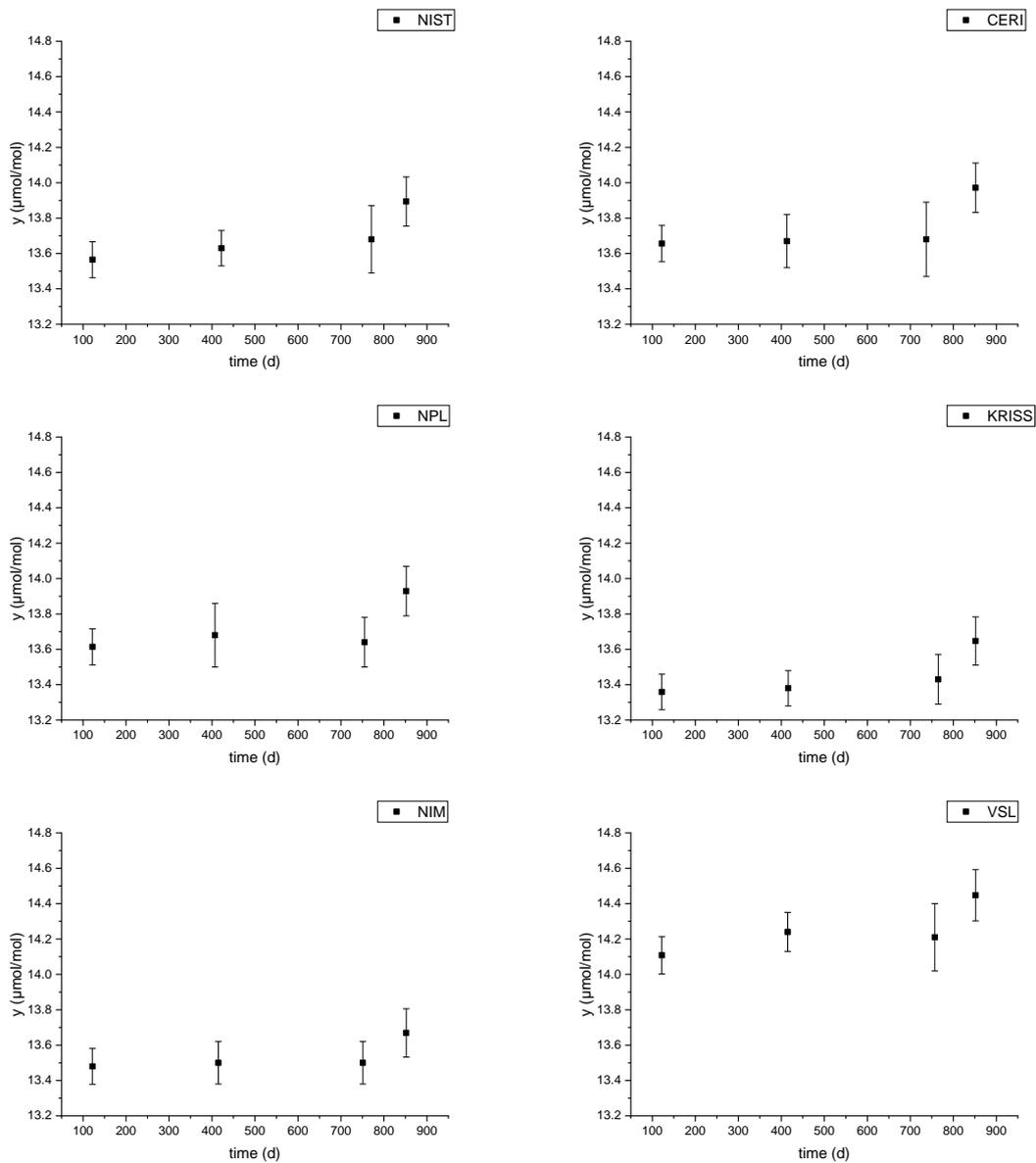
<sup>1</sup> Non-dispersive infrared spectroscopy

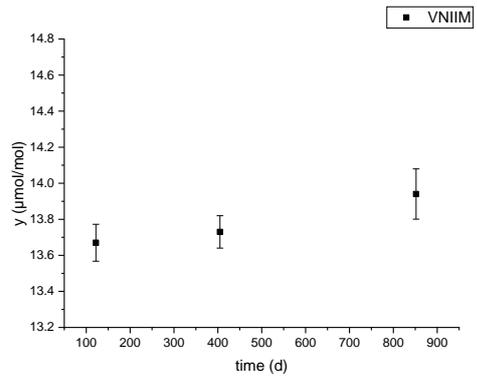
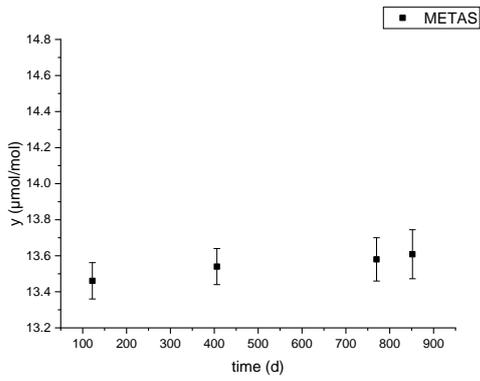
<sup>2</sup> Fourier-transform infrared spectroscopy

<sup>3</sup> Cavity ringdown spectroscopy

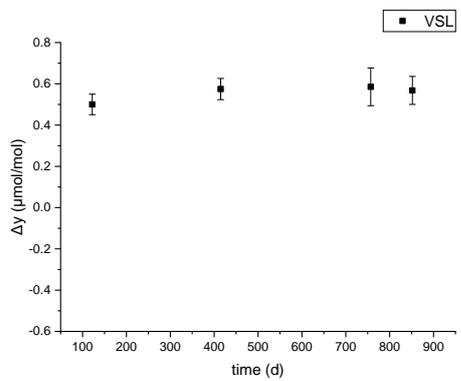
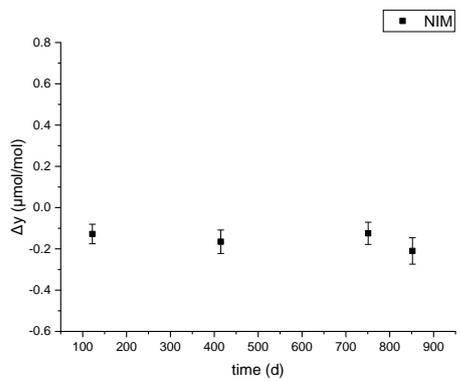
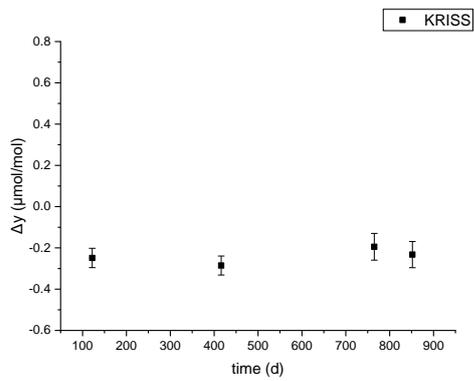
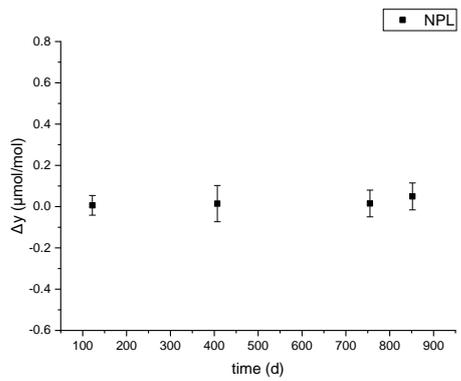
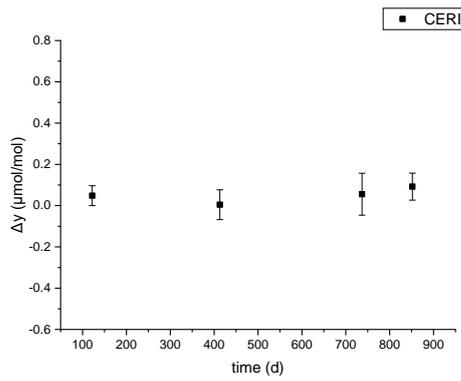
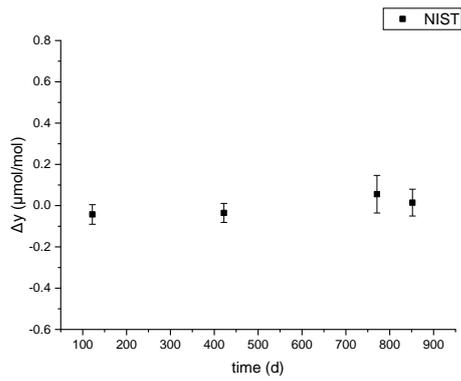
as the pressure of the calibration gas mixture in the cylinder decreases. The pressures in the transfer standards was widely different during the last measurement, and the said effect concerned all mixtures (also the spare ones), so that it can be assumed that the effect is not due to the pressure in the cylinder.

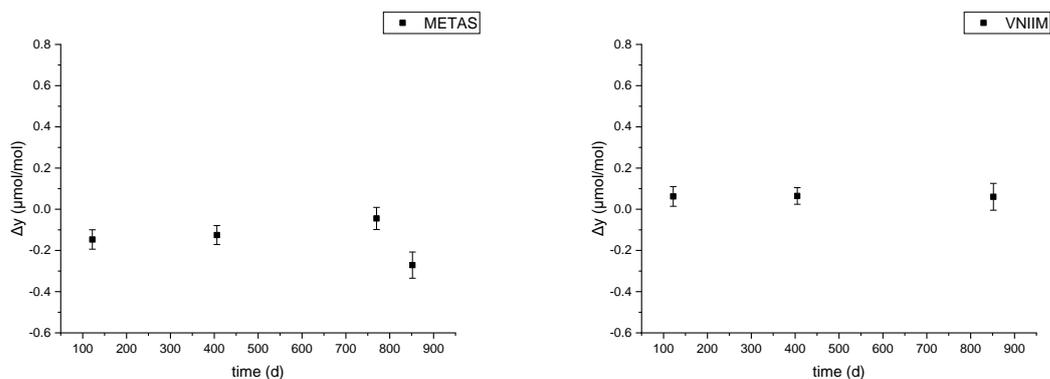
To further process the data, taking into account that the last results may be slightly biased, the differences in amount fraction of the transfer standards have been computed first, before combining these (Figure 2).





**Figure 1: Stability study data of the transfer standards used in CCQM-K117. The uncertainty bars indicate expanded uncertainties**





**Figure 2: Deviations from the weighted mean of the amount fraction ammonia of the transfer standards used in CCQM-K117. The uncertainty bars indicate expanded uncertainties.**

A complication was the missing datum for the transfer standard of VNIIM. The implication of this missing data point is that the weighted mean computed for the third data set would be inconsistent with the others. The missing data point was replaced by a value of  $0.055 \mu\text{mol mol}^{-1}$  which is consistent with the other three data points for this transfer standard and the standard uncertainty was taken as the pooled standard uncertainty from the other cylinders. The aim was to minimise the effect on the outcome of the stability study assessment. The deviations with respect to the weighted mean from the homogeneity and stability study are summarised in Table 4.

**Table 4: Deviations from the weighted mean of the amount fraction ammonia ( $\mu\text{mol mol}^{-1}$ ) as obtained in the stability and homogeneity study**

Mixture	NMI	$\Delta y$	$U(\Delta y)$						
5904173	NIST	-0.04	0.09	-0.04	0.10	0.06	0.18	0.01	0.13
5904216	CERI	0.00	0.14	0.05	0.10	0.06	0.20	0.09	0.13
5904237	NPL	0.01	0.18	0.01	0.10	0.02	0.13	0.05	0.13
5904238	KRISS	-0.29	0.09	-0.25	0.09	-0.19	0.13	-0.23	0.13
5904239	NIM	-0.17	0.11	-0.13	0.09	-0.12	0.11	-0.21	0.13
5904242	VSL	0.57	0.10	0.50	0.10	0.59	0.18	0.57	0.14
5904243	METAS	-0.13	0.09	-0.15	0.09	-0.04	0.11	-0.27	0.13
5904245	VNIIM	0.06	0.08	0.06	0.10	0.05	0.15	0.06	0.13

The results of the stability study assessment are summarised in Table 5. The slope  $a_1$  is given in  $10^{-6} \mu\text{mol mol}^{-1} \text{d}^{-1}$ .  $U_-$  and  $U_+$  denote respectively the lower and upper limit of the 95 % coverage interval of the slope. The regression was performed using the function `lm` in R [13]. All mixtures passed the stability test. Then, using the DerSimonian-Laird model [11][12], followed by a fixed effects model, the deviations  $e_i$  and their standard uncertainties were computed (see also Table 5). Only for one data set, a non-zero value for the excess standard deviation  $\tau$  is obtained. The data set of transfer standard 5904243 was also evaluated using the four amount fractions determined in the stability study. This evaluation revealed that the four data points were much better on a straight line, resulting in a substantially smaller standard uncertainty, and hence also the qualification that there was a significant trend. Looking at the dispersion of the data of the other transfer standards about their straight lines, it was concluded that the small dispersion for this mixture was not representative for the performance in the entire study. Also, the data did not reveal that this transfer standard would behave differently from the others (see also Figure 1 and Figure 2).

**Table 5: Stability assessment and deviations of the amount fraction ammonia for the transfer standards used in CCQM-K117 ( $\mu\text{mol mol}^{-1}$ )**

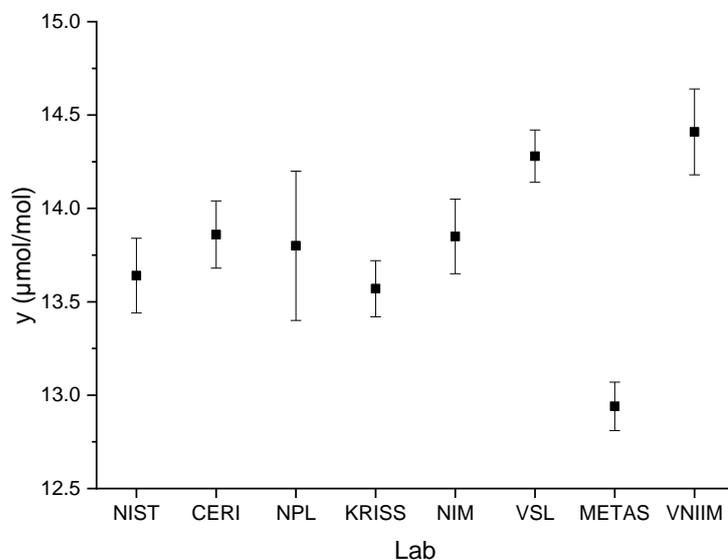
Mixture	Lab	$a_1$	$u(a_1)$	$U_-(a_1)$	$U_+(a_1)$	Stable	$\tau$	$e_i$	$u(e_i)$
5904173	NIST	99	42	-82	280	TRUE	0	-0.020	0.028
5904216	CERI	51	56	-189	291	TRUE	0	0.051	0.032
5904237	NPL	42	23	-55	139	TRUE	0	0.019	0.031
5904238	KRISS	55	68	-238	349	TRUE	0	-0.249	0.027
5904239	NIM	-54	67	-342	234	TRUE	0	-0.151	0.027
5904242	VSL	101	54	-131	334	TRUE	0	0.548	0.030
5904243	METAS	-16	174	-765	733	TRUE	0.064	-0.142	0.041
5904245	VNIIM	-9	10	-54	36	TRUE	0	0.061	0.026

### 3.2 Key comparison reference value and degrees-of-equivalence

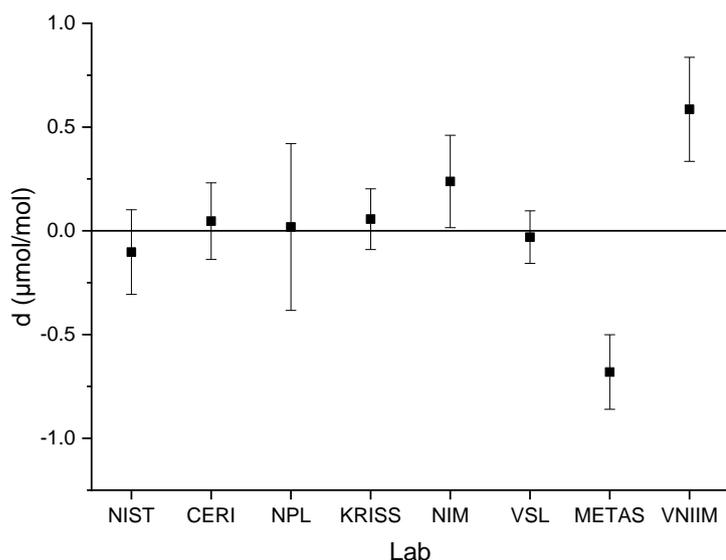
The results reported by the participants are given in Table 6 and Figure 3. The expanded uncertainty associated with the KCRV is generally smaller than that of the results submitted by the participants. There is a small influence of the uncertainty associated with the corrections made for the differences between the amount fractions ammonia of the transfer standards.

**Table 6: Reported results in CCQM-K117 ( $y_{\text{lab}}$ ) and the key comparison reference values, expressed in  $\mu\text{mol mol}^{-1}$ .**

Lab	Mixture	$y_{\text{lab}}$	$U(y_{\text{lab}})$	$k_{\text{lab}}$	$y_{\text{KCRV}}$	$u(y_{\text{KCRV}})$	$U(y_{\text{KCRV}})$
NIST	5904173	13.64	0.2	2	13.743	0.056	0.110
CERI	5904216	13.86	0.18	2	13.814	0.056	0.110
NPL	5904237	13.8	0.4	2	13.782	0.058	0.114
KRISS	5904238	13.57	0.15	2	13.514	0.053	0.104
NIM	5904239	13.85	0.2	2	13.612	0.057	0.111
VSL	5904242	14.28	0.14	2	14.310	0.052	0.102
METAS	5904243	12.94	0.13	2	13.621	0.065	0.127
VNIIM	5904245	14.41	0.23	2	13.824	0.056	0.111



**Figure 3: Reported results in CCQM-K117; the uncertainty bars indicate expanded uncertainties**



**Figure 4: Degrees-of-equivalence**

In Figure 4 and Table 7, the degrees-of-equivalence are shown. Two submitted results are clearly discrepant (METAS and VNIIM), and one result is just inconsistent with the KCRV (NIM). The results in this key comparison do not show the discrepancies between the various methods of realising measurement standards as observed in CCQM-K46 [1].

**Table 7: Degrees of equivalence ( $\mu\text{mol mol}^{-1}$ )**

Lab	Mixture	$d_i$	$u(d_i)$	$U(d_i)$
NIST	5904173	-0.103	0.105	0.204
CERI	5904216	0.046	0.090	0.185
NPL	5904237	0.018	0.203	0.402
KRISS	5904238	0.056	0.073	0.146
NIM	5904239	0.238	0.114	0.223
VSL	5904242	-0.030	0.061	0.127
METAS	5904243	-0.681	0.092	0.180
VNIIM	5904245	0.586	0.128	0.251

## 4 Supported CMC claims

The results of this key comparison can be used to support CMC claims for mixtures in nitrogen and air in the amount of substance fractions between 10  $\mu\text{mol/mol}$  and 1000  $\mu\text{mol/mol}$ .

The way in which this key comparison supports CMC claims is described in more detail in the “GAWG strategy for comparisons and CMC claims” [19]. The extrapolation scheme for CMCs does not apply for this key comparison beyond the amount fraction interval stated.

## 5 Discussion and conclusions

The results in this Track C key comparison on 14  $\mu\text{mol mol}^{-1}$  ammonia in nitrogen are acceptable. Five of the eight NMIs demonstrate equivalence with the KCRV. A discrepancy between static gravimetry on one hand and other methods for realising the national standards for ammonia in nitrogen was not observed in this key comparison. This was one of the features in the data of the previous key comparison (CCQM-K46).

## References

- [1] A.M.H. van der Veen, G. Nieuwenkamp, R.M. Wessel, M. Maruyama, Gwi Suk Heo, Yong-doo Kim, Dong Min Moon, B. Niederhauser, M. Quintilii, M.J.T. Milton, M.G. Cox, P.M. Harris, F.R. Guenther, G.C. Rhoderick, L.A. Konopelko, Y.A. Kustikov, V.V. Pankratov, D.N. Selukov, V.A. Petrov, E.V. Gromova, "International comparison CCQM-K46: Ammonia in nitrogen", *Metrologia* 47 (2010), Tech. Suppl., 08023
- [2] International Organization for Standardization, "ISO 6142-1 Gas analysis - Preparation of calibration gas mixtures - Gravimetric methods", ISO Geneva, 2015
- [3] International Organization for Standardization, "ISO 19229 Gas analysis - Gas analysis — Purity analysis and the treatment of purity data", ISO Geneva, 2019
- [4] ISO Guide 35 Reference materials – Guidance for characterization and assessment of homogeneity and stability. ISO, International Organization for Standardization, Geneva, Switzerland, 2017. Fourth edition.
- [5] International Organization for Standardization, "ISO 6145-7 Gas analysis — Preparation of calibration gas mixtures using dynamic methods — Part 7: Thermal mass-flow controllers", ISO Geneva, 2018
- [6] International Organization for Standardization, "ISO 6145-10 Gas analysis — Preparation of calibration gas mixtures using dynamic volumetric methods — Part 10: Permeation method", ISO Geneva, 2002
- [7] G. Schwarzer, J.R. Carpenter, and G. Rücker, "Meta-Analysis with R (Use R!)", Springer, 2015.
- [8] M.G. Cox. The evaluation of key comparison data. *Metrologia*, 39(6):589–595, dec 2002.
- [9] F. Y. Edgeworth. On observations relating to several quantities. *Hermathena*, 6(13):279–285, 1887.
- [10] F.Y. Edgeworth. XXII. On a new method of reducing observations relating to several quantities. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, 25(154):184–191, mar 1888.
- [11] R. DerSimonian and N. Laird. Meta-analysis in clinical trials. *Controlled Clinical Trials*, 7(3):177–188, 1986.
- [12] R. DerSimonian and R. Kacker. Random-effects model for meta-analysis of clinical trials: An update. *Contemporary Clinical Trials*, 28(2):105–114, feb 2007.
- [13] R Core Team. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria, 2020. Version 4.0.3.
- [14] Wolfgang Viechtbauer. Conducting meta-analyses in R with the metafor package. *Journal of Statistical Software*, 36(3):1–48, 2010.
- [15] A.M.H. van der Veen, E.T. Zalewska, D.R. van Osselen, T.E. Fernández, C. Gómez, J. Beránek, R.J. Oudwater, D.C. Sobrinho, M.C. Brum, C.R. Augusto, J. Fükö, T. Büki, Z. Nagyné Szilágyi, P.J. Brewer, M.L. Downey, R.J.C. Brown, M. Valkova, Z. Durisova, K. Arrhenius, B. Magnusson, H. Yaghooby, T. Tarhan, E. Engin, L.A. Konopelko, T.A. Popova, M.N. Pir, O.V.

Efremova. Final Report international comparison CCQM-K112 Biogas. Metrologia, 57(1A):08011–08011, jan 2020.

- [16] BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP, OIML. Supplement 2 to the ‘Guide to the Expression of Uncertainty in Measurement’ – Extension to any number of output quantities, JCGM 102:2011. BIPM, 2011.
- [17] BIPM, IEC, IFCC, ILAC, ISO, IUPAC, IUPAP, OIML. Supplement 1 to the ‘Guide to the Expression of Uncertainty in Measurement’ – Propagation of distributions using a Monte Carlo method, JCGM 101:2008. BIPM, 2008.
- [18] BIPM, IEC, IFCC, ISO, IUPAC, IUPAP, OIML “Evaluation of measurement data — Guide to the expression of uncertainty in measurement”, first edition, GUM:1995 with minor corrections, JCGM 100:2008. BIPM, 2008.
- [19] P.J. Brewer, A.M.H. van der Veen, “GAWG strategy for comparisons and CMC claims”, CCQM Gas Analysis Working Group, April 2016

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## **Project reference**

CCQM-K117

## **Completion date**

March 2020

## Annex A : Measurement reports

### Measurement report CERI

Cylinder number: 5904216

#### Measurement #1

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (μmol/mol)	number of replicates	Instrument
Ammonia	3/13/2019	13.7598	0.07754	3	NDIR

#### Measurement #2

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (μmol/mol)	number of replicates	Instrument
Ammonia	3/14/2019	13.8916	0.02410	3	NDIR

#### Measurement #3

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (μmol/mol)	number of replicates	Instrument
Ammonia	3/21/2019	13.7468	0.04045	3	NDIR

#### Measurement #4

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (μmol/mol)	number of replicates	Instrument
Ammonia	3/22/2019	13.8174	0.04919	3	NDIR

#### Measurement #5

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (μmol/mol)	number of replicates	Instrument
Ammonia	3/23/2019	13.8747	0.03962	3	NDIR

#### Measurement #6

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (μmol/mol)	number of replicates	Instrument
Ammonia	3/28/2019	13.8619	0.01719	3	FTIR

#### Measurement #7

Component	Date (dd/mm/yy)	Result (μmol/mol)	Standard deviation (μmol/mol)	number of replicates	Instrument
Ammonia	3/29/2019	13.9026	0.03857	3	FTIR

### Measurement #8

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (µmol/mol)	number of replicates	Instrument
Ammonia	3/31/2019	13.9186	0.02403	3	FTIR

### Measurement #9

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (µmol/mol)	number of replicates	Instrument
Ammonia	4/4/2019	13.8399	0.06825	3	NDIR

### Results

Component	Result (µmol/mol)	Expanded uncertainty (µmol/mol)	Coverage factor
Ammonia	13.86	0.18	2

Result was the weighted mean of NDIR data set mean and FTIR data set mean, which was calculated using formula<sup>1)</sup> below.

$$y = \frac{\sum_{i=1}^p W_i X_i}{\sum_{i=1}^p W_i}$$

where:

y= weighted mean

X<sub>i</sub>= each data set mean

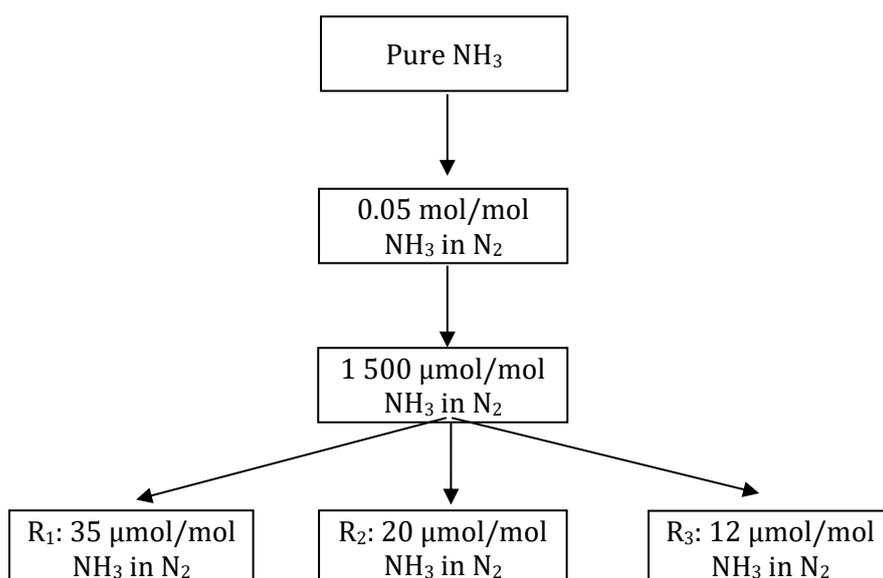
W<sub>i</sub>= 1/u<sub>i</sub><sup>2</sup>

u<sub>i</sub>= standards uncertainty for the value X<sub>i</sub>

p= number of data set mean

### Calibration Standards:

-Method of preparation: ISO 6142-1<sup>2)</sup>



-Weighing data (12  $\mu\text{mol/mol}$   $\text{NH}_3$  in  $\text{N}_2$ )

- 1) Evacuated cylinder - Tare cylinder : 5.678 g
- 2) Cylinder filled with 0.05 mol/mol  $\text{NH}_3$  in  $\text{N}_2$  - Tare cylinder : 16.732 g
- 3) Cylinder filled with nitrogen - Tare cylinder : 1 343.304 g

-Purity tables (composition) of the parent gases ;

Purity table of  $\text{NH}_3$

Component	Analytical value ( $\mu\text{mol/mol}$ )	Distribution	Mole fraction ( $\mu\text{mol/mol}$ )	Standard Uncertainty ( $\mu\text{mol/mol}$ )
$\text{N}_2$	$\leq 100$	Rectangular	50	28.87
$\text{O}_2$	$\leq 100$	Rectangular	50	28.87
$\text{CO}$	$\leq 100$	Rectangular	50	28.87
$\text{CO}_2$	$\leq 100$	Rectangular	50	28.87
$\text{NH}_3$	-	-	999 800	57.74

Purity table of nitrogen

Component	Analytical value ( $\mu\text{mol/mol}$ )	Distribution	Mole fraction ( $\mu\text{mol/mol}$ )	Standard Uncertainty ( $\mu\text{mol/mol}$ )
$\text{CO}$	$\leq 0.003$	Rectangular	0.001 5	0.000 866
$\text{CO}_2$	$\leq 0.003$	Rectangular	0.001 5	0.000 866
Methane	$\leq 0.003$	Rectangular	0.001 5	0.000 866

Non methane hydro carbon (NMHC)	≤ 0.003	Rectangular	0.001 5	0.000 866
SO <sub>2</sub>	≤ 0.002	Rectangular	0.001	0.000 577
NO <sub>x</sub>	≤ 0.002	Rectangular	0.001	0.000 577
N <sub>2</sub>	-	-	999 999.992	0.001 915

Each mole fraction of impurity in nitrogen is adequately low. Therefore, the molar mass of dilution gas wasn't affected from the impurities.

-Verification measure;

We prepared two R<sub>3</sub> Standards. The gas standards were compared by FTIR. Difference between gravimetric value and measurement value is one of the uncertainty sources of the gas standard.

#### **Instrument Calibration:**

We used two instruments for NH<sub>3</sub> measurements.

Non-dispersive Infrared analyser (Type: CGT-7000, Make: Shimadzu corporation) and Fourier Transform Infrared Spectroscopy analyser (Type: MATRIX-MG5, Make: Bruker corporation)

#### **Calibration method and value assignment**

The instruments were calibrated using three gravimetrically prepared standards ranging in concentration from 35 μmol/mol to 12 μmol/mol. Analytical scheme was, R<sub>1</sub> – R<sub>2</sub> – CCQM sample – R<sub>3</sub>. This scheme was repeated 3-times in a day. These measurements were carried out for 9-day. Quadratic calibration model was chosen to the data.

Concentration of standards

Component	Concentration ( μmol/mol )		
	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>
NH <sub>3</sub>	35.37	20.02	12.41

### Uncertainty evaluation:

#### NDIR analysis

Source of uncertainty	Estimate $x_i$	Value +/-	Method of evaluation (type A or typeB)	Assumed probability distribution	Divisor	Standard uncertainty $u(x_i)$	Sensitivity coefficient $ c_i $	Contribution $u_i(y)$
Measurement	13.82 $\mu\text{mol/mol}$	0.086 22 $\mu\text{mol/mol}$	A	—	1	0.086 22 $\mu\text{mol/mol}$	1	0.086 22 $\mu\text{mol/mol}$
Verification	12.41 $\mu\text{mol/mol}$	0.096 39 $\mu\text{mol/mol}$	A	—	1	0.096 39 $\mu\text{mol/mol}$	1.114	0.107 4 $\mu\text{mol/mol}$
R <sub>1</sub>	35.37 $\mu\text{mol/mol}$	0.009 479 $\mu\text{mol/mol}$	A	—	1	0.009 479 $\mu\text{mol/mol}$	0.026 37	0.000 2500 $\mu\text{mol/mol}$
R <sub>2</sub>	20.02 $\mu\text{mol/mol}$	0.006 401 $\mu\text{mol/mol}$	A	—	1	0.006 401 $\mu\text{mol/mol}$	0.267 2	0.001 710 $\mu\text{mol/mol}$
R <sub>3</sub>	12.41 $\mu\text{mol/mol}$	0.004 483 $\mu\text{mol/mol}$	A	—	1	0.004 483 $\mu\text{mol/mol}$	0.758 5	0.003 400 $\mu\text{mol/mol}$
total								0.137 8 $\mu\text{mol/mol}$

#### FTIR analysis

Source of uncertainty	Estimate $x_i$	Value +/-	Method of evaluation (type A or typeB)	Assumed probability distribution	Divisor	Standard uncertainty $u(x_i)$	Sensitivity coefficient $ c_i $	Contribution $u_i(y)$
Measurement	13.89 $\mu\text{mol/mol}$	0.035 07 $\mu\text{mol/mol}$	A	—	1	0.035 07 $\mu\text{mol/mol}$	1	0.035 07 $\mu\text{mol/mol}$
Verification	12.41 $\mu\text{mol/mol}$	0.096 39 $\mu\text{mol/mol}$	A	—	1	0.096 39 $\mu\text{mol/mol}$	1.119	0.107 9 $\mu\text{mol/mol}$
R <sub>1</sub>	35.37 $\mu\text{mol/mol}$	0.009 479 $\mu\text{mol/mol}$	A	—	1	0.009 479 $\mu\text{mol/mol}$	0.023 21	0.000 2200 $\mu\text{mol/mol}$
R <sub>2</sub>	20.02 $\mu\text{mol/mol}$	0.006 401 $\mu\text{mol/mol}$	A	—	1	0.006 401 $\mu\text{mol/mol}$	0.270 3	0.001 730 $\mu\text{mol/mol}$
R <sub>3</sub>	12.41 $\mu\text{mol/mol}$	0.004 483 $\mu\text{mol/mol}$	A	—	1	0.004 483 $\mu\text{mol/mol}$	0.752 9	0.003 375 $\mu\text{mol/mol}$
total								0.113 5 $\mu\text{mol/mol}$

Source of uncertainty	Estimate $x_i$	Standard uncertainty $u(x_i)$	Sensitivity coefficient $ c_i $	Contribution $u_i(y)$
NDIR analysis	13.82 $\mu\text{mol/mol}$	0.137 8 $\mu\text{mol/mol}$	0.4043	0.055 71 $\mu\text{mol/mol}$
FTIR analysis	13.89 $\mu\text{mol/mol}$	0.113 5 $\mu\text{mol/mol}$	0.5957	0.067 61 $\mu\text{mol/mol}$
total				0.087 61 $\mu\text{mol/mol}$

Combined uncertainty: 0.087 61  $\mu\text{mol/mol}$

Coverage factor: 2

Expanded uncertainty: 0.18  $\mu\text{mol/mol}$

**References:**

- 1) International Organization for Standardization, ISO Guide 35:2017 Reference materials -- Guidance for characterization and assessment of homogeneity and stability
- 2) International Organization for Standardization, ISO 6142-1:2015 Gas analysis -- Preparation of calibration gas mixtures -- Part 1: Gravimetric method for Class I mixtures

## Measurement report VNIIM

Cylinder number: 5904245

Measurement #1

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
Ammonia	04/04/2019	14,56	0,8	10

Measurement #2

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
Ammonia	04/04/2019	14,29	1,0	4x10

Measurement #3

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
Ammonia	04/04/2019	14,37	0,6	4x10

Measurement #4

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
Ammonia	21/05/2019	14,42	0,5	4x10

Results

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Expanded uncertainty ( $\mu\text{mol/mol}$ )	Coverage factor
Ammonia	05/06/2019	14,41	0.23	2

Calibration standards

Calibration gas mixtures were prepared in accordance with [1]. Preparation was carried out from pure substances in 3 dilution stages :

1-st stage – 3 mixtures  $\text{NH}_3/\text{N}_2$  –level 3,3 %;

2-nd stage – 3 mixtures  $\text{NH}_3/\text{N}_2$  –level 570  $\mu\text{mol/mol}$ ;

3-rd stage – 4 mixtures  $\text{NH}_3/\text{N}_2$  – level 12-15  $\mu\text{mol/mol}$ .

All the mixtures were prepared in Luxfer cylinders ( $V=5 \text{ dm}^3$ ) with Aculife4+Aculife3 coating.

Characteristics of pure substances used for preparation of the calibration standards are shown in the tables 1 and 2.

**Table 1:** Purity table for N<sub>2</sub>

Monoblock		
Main component N <sub>2</sub>		Mole fraction 99.9998572 %
Component	Mole fraction, μmol/mol	Standard uncertainty, μmol/mol
Ar	0.916	0.011
O <sub>2</sub>	0.0015	0.0009
CO <sub>2</sub>	0.0025	0.0014
H <sub>2</sub>	0.0025	0.0014
CH <sub>4</sub>	0.0025	0.0014
CO	0.0025	0.0014
H <sub>2</sub> O	0.50	0.05

**Table 2:** Purity table for NH<sub>3</sub>

Cylinder № 666		
Main component NH <sub>3</sub>		Mole fraction 99.9963 %
Component	Mole fraction, μmol/mol	Standard uncertainty, μmol/mol
C <sub>2</sub> H <sub>5</sub> OH	0.160	0.020
C <sub>2</sub> H <sub>7</sub> N	0.18	0.06
C <sub>3</sub> H <sub>9</sub> N	12	3
C <sub>4</sub> H <sub>8</sub> [1-butene]	0.26	0.03
C <sub>6</sub> H <sub>6</sub>	0.0062	0.0016
C <sub>7</sub> H <sub>8</sub> (toluene)]	0.40	0.05
C <sub>8</sub> H <sub>10</sub> (ethylbenzene)	0.0018	0.0002
CH <sub>3</sub> OH	0.140	0.020
CO	7.2	1.2
CO <sub>2</sub>	0.0190	0.0020
H <sub>2</sub> O	15.0	2.0
N <sub>2</sub>	1.80	0.20
O <sub>2</sub>	0.0200	0.0020
o-C <sub>8</sub> H <sub>10</sub> (o- xylene)	0.00120	0.00015
m-C <sub>8</sub> H <sub>10</sub> (m- xylene) +p-C <sub>8</sub> H <sub>10</sub> (p- xylene )	0.0056	0.0007

Verification measurements for the 1-st stage premixtures (3.3 %) were carried out by means of FTIR spectrometer FSM 1201 (Russia).  $u_{\text{ver}} \approx 0.1$  % rel.

Measurement for the 2-st stage premixtures (570 μmol/mol) were carried out by means of UV-Vis-NIR spectrophotometer Cary 5000 (Agilent).  $u_{\text{ver}} \approx 0.3$  % rel.

Verification measurements for the final mixtures were carried out by Chromato-mass-spect-rometry,  $u_{\text{ver}} \approx 0,7$  % rel.

All verification measurements consisted of checking consistency between the batch of similar prepared mixtures.

The values of ammonia amount of substance fraction in the calibration gas mixtures and their standard uncertainties are shown in the table 3.

Table 3

Cylinder number	Component	Mole fraction ( $\mu\text{mol/mol}$ )	Standard uncertainty due to weighing and purity ( $\mu\text{mol/mol}$ )
D648608	NH <sub>3</sub>	12.073	0.011
D648609	NH <sub>3</sub>	13.098	0.012
D648610	NH <sub>3</sub>	14.072	0.013
D648618	NH <sub>3</sub>	14.491	0.015

#### Instrumentation

The instrument used for the measurements of the ammonia content in the comparison mixture (cylinder № 5904245) is Chromato-mass-spectrometer «Chromatec-Crystal 5000» (Russia).

#### Operating mode

Chromatographic column	Rxi -1ms (Restek), Cat.№ 43802 (20 m x 0,15 mmID x 2.0 $\mu\text{m}$ )
Carrier gas	High purity Helium 99,9999%
Pressure at the inlet of the column	360 kPa
Carrier gas flow rate	1.1 ml/min
Split	1:50
Column oven temperature	160°C
SIM	m/z=17
Ionization mode	EI
Ionization energy	70 eV
Sample volume	0.25 ml

#### Calibration method and value assignment

Single point calibration method was used to determine ammonia mole fraction in the comparison gas mixture.

Measurement sequence was in the order: standard<sub>i</sub> - sample — standard<sub>i</sub>.

Each of the 4 measurement results was received under repeatability conditions with the different calibration standards (table 3). Each of these 4 results is the mean from 4 series and each series consisted of 10 sub-measurements.

The amount of substance fraction for a sub-measurement was calculated according to the

$$C_x = C_{st} \frac{A_x}{(A'_{st} + A''_{st})/2}$$

where  $C_x$  and  $C_{st}$  – amount of substance fractions of ammonia in the comparison and calibration mixtures;

$A_x$  – analytical signal of ammonia in the comparison gas mixture

$A'_{st}$  and  $A''_{st}$  analytical signals of ammonia in the calibration standard before and after measurement of the comparison mixture.

Temperature corrections were not applied due to use of above-mentioned measurement sequence.

Uncertainty evaluation

### Uncertainty table:

Uncertainty source Xi	Estimate xi, μmol/mol	Assumed distribution	Standard uncertainty u(xi) μmol/mol	Sensitivity coefficient ci	Contribution to standard uncertainty ui(y), μmol/mol
Calibration standards	14.491	Normal	0.015	0.995	0.015
Scatter of the results	14.41	Normal	0.116	1	0.116

Combined standard uncertainty: 0.117 μmol/mol

Coverage factor: k=2

Expanded uncertainty: 0.234 μmol/mol

Relative expanded uncertainty: 1,6 %

### References

[1] International Organization for Standardization, ISO 6142:2001 Gas analysis – Preparation of calibration gas mixtures - Gravimetric methods, 2<sup>nd</sup> edition.

## Measurement report VSL

Cylinder number: 5904242

### Measurement #1

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
Ammonia	07-03-2019	14.271	0.96	1

### Measurement #2

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
Ammonia	12-03-2019	14.336	0.62	1

### Measurement #3<sup>4</sup>

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
Ammonia	13-03-2019	14.226	0.96	1

## Results

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Expanded uncertainty ( $\mu\text{mol/mol}$ )	Coverage factor
Ammonia	13-03-2019	14.28	0.14	2

## Calibration standards

The standards used by VSL are prepared gravimetrically but the gravimetric value is only used for amount fractions above 1000  $\mu\text{mol/mol}$ . These mixtures are measured against each other to confirm internal consistency. Mixture with a lower amount fraction are certified against PSMs in the range between 1000 and 5000  $\mu\text{mol/mol}$ . A calibration curve is made using dynamic dilution with Thermal Mass Flow controllers and a certified value is assigned using ISO6143. The rationale behind this scheme are the results from the European research project MetNH<sub>3</sub> which showed that adsorption of ammonia on the internal cylinder surface was cylinder dependent and could be quantified [1]. To eliminate stability effects the mixtures used in the assignment of the K117 cylinder were certified in a period of 2 months before or after the measurements of the K117 mixture.

The gasses used for the preparation of the mixtures are Nitrogen 6.0 quality and Ammonia 4.0 quality. For the purity table of the Ammonia manufacturer specifications are used except for the water impurity. As it was not possible to assign a value to water in the pure Ammonia due to interference the water amount in a 5% ammonia in nitrogen mixture was measured and recalculated for the pure ammonia. This amount is probably excessive but the difference between

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<sup>4</sup> If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary

no water and the assigned value gives a change in composition of only 0.06% rel. The gravimetric preparation itself has an uncertainty of 0.026% rel.

**Purity table of cylinder : APN26B**

Supplier : Air Products  
Component : N2

Component		Mass fraction	Mol fraction	Uncertainty	Rel. Unc. [%]
Argon	Ar	0.0000071300650999	0.0000050000000000	0.0000030000000000	60
Methane	CH4	0.0000000005726648	0.0000000100000000	0.0000000060000000	60
Carbon monoxide	CO	0.000000009998654	0.0000000100000000	0.0000000060000000	60
Carbon dioxide	CO2	0.0000000157099172	0.0000000100000000	0.0000000060000000	60
hydrogen	H2	0.000000017990706	0.0000000250000000	0.0000000150000000	60
water	H2O	0.0000000064308911	0.0000000100000000	0.0000000060000000	60
Nitrogen	N2	0.9999927301972344	0.9999948530000000	0.0000060000000000	0.0006
Oxygen	O2	0.0000001142252564	0.0000001000000000	0.0000000300000000	30

**Purity table of cylinder : AL5453**

Supplier : Air Liquide  
Component : Ammonia  
Quality : 4.0

Component :		Mass fraction :	Mol fraction :	Uncertainty :	% :
Methaan	CH4	0.0000004709679645	0.0000005000000000	0.0000003000000000	60
Koolstofmonoxide	CO	0.0000008223040477	0.0000005000000000	0.0000003000000000	60
Koolstofdioxide	CO2	0.0000012920067032	0.0000005000000000	0.0000003000000000	60
Water	H2O	0.0006346631299746	0.0006000000000000	0.0001000000000000	17
Stikstof	N2	0.0000024672388922	0.0000015000000000	0.0000009000000000	60
Zuurstof	O2	0.0000009394053110	0.0000005000000000	0.0000003000000000	60
Ammonia	NH3	0.9993593449471068	0.9993965000000000	0.0001000000000000	0.010

Number of components : 7

Mixture cylinder : **VSL403665** Date : 2017-11-08  
 Raw data-file : M:\312\F-CHEMIE\CS\DATA\WEEG\MC403665 By : LM/RB  
 Output data-file : M:\312\F-CHEMIE\CS\DATA\WEEG\stand\SL403665

Calibration mass (mg) : 0.000

**Weighing data-1**

Pressure (mbar) : 000.00 mass (g) : 257.7134  
 Temperature (°C) : 00.00  
 Humidity (%) : 00.0 sd weighing (mg) : 0.78  
 Mass W0 (g) : 0.0 1 scalevalue (mg) : 0.0000  
 M0 (g) : 0.0 Mean (g) : 0.000

T+W+Q : 7579.592 g  
 T+W : 7321.878 g  
 C+M : 7579.590 g  
 T+W : 7321.879 g  
 C+M : 7579.593 g  
 T+W : 7321.878 g  
 C+M : 7579.593 g  
 T+W : 7321.880 g  
 T+W+Q : 7579.593 g

**Weighing data0**

Pressure (mbar) : 000.00 mass (g) : 278.4201  
 Temperature (°C) : 00.00 Added mass (g) : 20.70675  
 Humidity (%) : 00.0 sd weighing (mg) : 0.36  
 Mass W1 (g) : 0.0 1 scalevalue (mg) : 0.0000  
 M1 (g) : 0.0 Mean (g) : 0.000

T+W+Q : 7600.297 g  
 T+W : 7321.876 g  
 C+M : 7600.297 g  
 T+W : 7321.876 g  
 C+M : 7600.296 g  
 T+W : 7321.877 g  
 C+M : 7600.296 g  
 T+W : 7321.876 g  
 T+W+Q : 7600.296 g

**Weighing data1**

Pressure (mbar) : 000.00 mass (g) : 925.3827  
 Temperature (°C) : 00.00 Added mass (g) : 646.96263  
 Humidity (%) : 00.0 sd weighing (mg) : 0.64  
 Mass W2 (g) : 0.0 1 scalevalue (mg) : 0.0000  
 M2 (g) : 0.0 Mean (g) : 0.000

T+W+Q : 8247.252 g  
 T+W : 7321.871 g  
 C+M : 8247.254 g  
 T+W : 7321.871 g  
 C+M : 8247.255 g  
 T+W : 7321.872 g  
 C+M : 8247.255 g  
 T+W : 7321.872 g  
 T+W+Q : 8247.254 g

## Purity table of cylinder : VSL403665

By : LM/RB raw data : m:\312\chemie\cs\data\weeg\mc403665  
 Date : 2017-11-08 output data : m:\312\chemie\cs\data\weeg\stand\sl403665

Component :	Cylinder :	Supplier :	Mass fraction :	Mol fraction :	Uncertainty :	(%) :
1 ammonia	AL5453	Air Liquide				
2 stikstof	APN26B	Air Products				
Component :			Mass fraction :	Mol fraction :	Uncertainty :	(%) :
Argon	Ar		0.0000069089369772	0.0000047499413619	0.0000028499638017	60
Methaan	CH4		0.0000000151612594	0.0000000259558521	0.0000000150143365	58
Koolstofmonoxide	CO		0.0000000264713652	0.0000000259558520	0.0000000150143315	58
Koolstofdioxide	CO2		0.0000000552923205	0.0000000345057465	0.0000000160497435	47
Waterstof	H2		0.0000000017432752	0.0000000237497064	0.0000000142498241	60
Water	H2O		0.0000196893429668	0.0000300165364509	0.0000049981667828	17
Stikstof	N2		0.9689795533872114	0.9499834578143523	0.0000149078262937	0.002
Zuurstof	O2		0.0000001398169605	0.0000001200046911	0.0000000322076894	27
Ammonia	NH3		0.0309936098476638	0.0499815455359868	0.0000130493504085	0.026

## Instrumentation

### Purity table of cylinder : APN26B

Supplier : Air Products  
 Component : N2

Component		Mass fraction	Mol fraction	Uncertainty	Rel. Unc. [%]
Argon	Ar	0.0000071300650999	0.0000050000000000	0.0000030000000000	60
Methane	CH4	0.0000000005726648	0.0000000100000000	0.0000000060000000	60
Carbon monoxide	CO	0.000000000998654	0.0000000010000000	0.0000000060000000	60
Carbon dioxide	CO2	0.0000000157099172	0.0000000100000000	0.0000000060000000	60
hydrogen	H2	0.0000000017990706	0.0000000250000000	0.0000000150000000	60
water	H2O	0.0000000064308911	0.0000000100000000	0.0000000060000000	60
Nitrogen	N2	0.9999927301972344	0.9999948530000000	0.0000060000000000	0.0006
Oxygen	O2	0.0000001142252564	0.0000001000000000	0.0000000300000000	30

The instrument used to perform the measurements is an Innova 1412 Photo Acoustic analyser. The mixtures were connected to the analyser using the method given in fig.1. This ensures that there is no influence of individual pressure reducing valves as only on reducer is used in connection with 1 MFC. The mixtures are connected over night and all lines as checked for leakage. The cylinders to which to assign a value are not diluted (N<sub>2</sub> flow zero) while the calibration standards are diluted to create the response curve. The total flow is 1500 ml and the individual dilution flows are measured with a BIOS Drycal flowmeter.

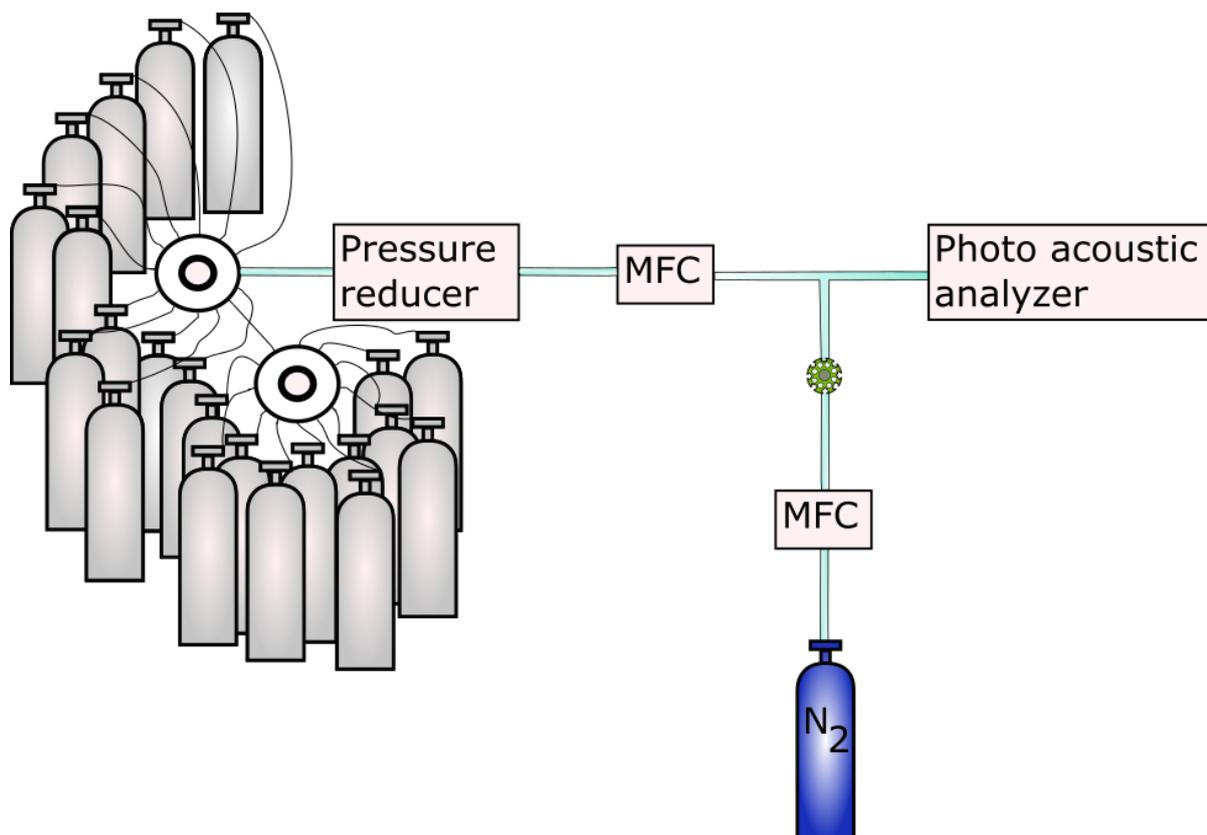


Fig 1- applying 2 multi position valves to connect multiple cylinders using 1 reducer and MFC

#### Calibration method and value assignment

Ten individual responses of the mixtures are collected and the average taken after 30 minutes flushing of the analyser. The calibration curve and the assigned value are determined using ISO6143. To ensure that the mixing of the gas flows was not affected by the use of two MFCs the same dilutions were also measured using mol% mixtures of O<sub>2</sub> in N<sub>2</sub> and measured against Oxygen PSMs on a Servomex paramagnetic analyzer.

#### Uncertainty evaluation

Uncertainty component	U	U
Purity of ammonia	0.03%	
Gravimetric Preparation (first dilution)	0.026%	
Gravimetric preparation (second dilution)	0.026%	
Assignment certified values to calibration standards	0.20% <sup>1</sup>	
Dilution of calibration standards to range 10-17 µmol/mol	0.20% <sup>1</sup>	
Value assignment according to ISO6143	0.30%	
Assigned value	0.50%	1%

<sup>1</sup>These values are added together because the dilution is a systematic effect and cannot be averaged out

## References

[1] Janneke I.T. van Wijk et.al.; Primary ammonia reference materials fulfilling EU quality data; Gas Analysis 2017

## Measurement report METAS

Cylinder number: 5904243

### Measurement #1

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
Ammonia	11/03/2019	12.93	0.48	2
	14/03/2019			

### Measurement #2

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
Ammonia	12/03/2019	13.00	0.49	1

### Measurement #3

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
Ammonia	12/03/2019	12.93	0.48	2
	14/03/2019			

### Measurement #4

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
Ammonia	12/03/2019	12.93	0.48	2
	14/03/2019			

### Measurement #5

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
Ammonia	12/03/2019	12.89	0.49	2
	13/03/2019			

## Results

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Expanded uncertainty ( $\mu\text{mol/mol}$ )	Coverage factor
Ammonia	14/03/19	12.94	0.13	2

### Calibration standards

We generated dynamically the calibration standards (permeation method [1]) using one of the METAS primary magnetic suspension balances (MSB; Rubotherm GmbH, Germany), a  $\text{NH}_3$  permeation unit of 99.98% purity (Fine Metrology S.r.l.s., Italy) and nitrogen 6.0 as matrix and dilution gas (Fig.1). Total matrix and dilution gas flows were measured by calibrated flow meters placed before and after the MSB permeation chamber (Red-y GSC-B9TT-BB23, Vögtlin Instruments, Switzerland).

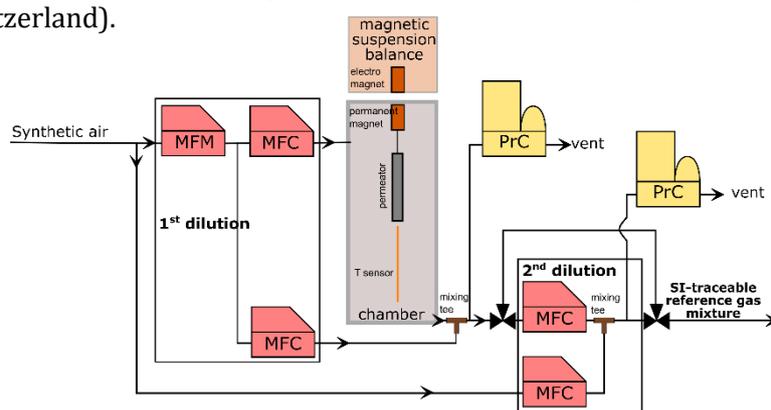


Fig. 1: Permeation system to generate the  $\text{NH}_3$  reference gas mixtures used to calibrate the analysers.

The permeation rate –  $(311.3 \pm 2.7) \text{ ng/min}$  ( $k = 2$ ) at  $48^\circ\text{C}$  and  $2600 \text{ hPa}$  – was estimated as the mass loss of the permeation unit during a period of 137 hours after a 3-day stabilization period within the MSB. Calibration standards were produced using the first dilution system of the magnetic suspension balance (Fig. 1). Different flow rates within the range between  $1.0 \text{ L}$  and  $5.2 \text{ L}$  were led to the mixing tee as shown in Fig. 1. Calibration standard values were estimated using Eq. 1.

$$X_{\text{NH}_3} = ((q_{\text{mC}} * \text{PU} * (V_{\text{M}_{\text{N}_2}}/M_{\text{NH}_3})) / q_{\text{v}}) + X_{\text{res NH}_3} \quad [\text{Eq. 1}]$$

where,

$X_{\text{NH}_3}$ :  $\text{NH}_3$  calibration standard (nmol/mol);

$q_{\text{mC}}$ : permeation rate (g/min);

PU: purity of the permeation unit (0.9998);

$V_{\text{M}}$ : molar volume of the matrix/dilution gas (mL/mol);

$M_{\text{NH}_3}$ : molar mass of  $\text{NH}_3$  (g/mol);

$q_{\text{v}}$ : total gas flow (matrix + dilution, mL/min);

$X_{\text{res NH}_3}$ : residual amount fraction of  $\text{NH}_3$  in the matrix/dilution gas (nmol/mol).

Each calibration standard was generated for 90 minutes: the first 60 minutes were considered the stabilization time of the system and the last 30 minutes the measuring period.

### Instrumentation

We used two calibrated NH<sub>3</sub> analysers based on cavity ring-down spectrometry for this key comparison: G2103 (S/N 1283-AEDS-2035) and G1103t (S/N 127-CPVU-AF004) (Picarro Inc., CA, USA). Cavity and sampling handling of the analyser G2103 are coated with SilcoNert 2000. The minimum sample flow rates of the analysers were 0.8 slm (G1103t) and 1.8 slm (G2103). We placed a distribution tee at the supply inlet of the analysers to ensure overflow. The gas mixtures were fed to one end of the distribution tee through a coated tube (SilcoNert 2000, 1/8") and a particle filter. The particle filter in G2103 analyser was a coated in-line-filter with nominal pore dimension of 0.5 µm (SS-4F-05, Swagelok). The particle filter in G1103t analyser was a PTFE membrane filter with nominal pore dimension of 5 µm within a PFA filter holder (TE 47, supporting fabric PES, Whatman, Switzerland). We connected the other end of the distribution tee to a flowmeter (serie 1350, Wisag AG, Switzerland); the overflow was then fed to the exhaust tube. G2103 and G1103t analysers recorded reading values every 1 and 3 seconds respectively.

#### Calibration method and value assignment

We let the two NH<sub>3</sub> analysers running for 24 hours with nitrogen 6.0 for stabilization purposes before calibrating them. For both analysers, nitrogen 6.0 was concentration zero. We produced 5 calibration standards between 79 and 212 nmol/mol to calibrate G2103 and 4 calibration standards between 81 and 404 nmol/mol to calibrate G1103t. For each calibration standard, the amount fraction value read by the analyser was the average reading of the last-30 minutes of generation.

We obtained one calibration curve per analyser [Eq. 2] by linear regression using the least square method [2]. Table 1 includes values of the calibration curve parameters for each analyser.

$$X_{\text{read}} = a + b * X_{\text{gen}} \quad [\text{Eq. 2}]$$

where,

$X_{\text{read}}$ : average analyser readings of the last 30 minutes of generation (nmol/mol)

a: intercept of the linear regression (nmol/mol)

b: slope of the linear regression

$X_{\text{gen}}$ : average of the amount fraction generated by the permeation method during the last 30 minutes of generation (nmol/mol).

Table 1: Calibration curve parameters of the used NH<sub>3</sub>-analysers

Analyser	Intercept (a) (nmol/mol)	Slope (b)	Number of observations
G2103	0.714	1.0056	518
G1103t	0.057	0.9996	1988

In order to assign the transfer standard value, we generated several gas mixtures within the calibration range of the analysers by diluting the transfer standard. We used a dilution system (Fig. 2) formed by a compact pressure regulator (KCP1GRM2D1P20000, Swagelok Company, OH, USA), two critical orifices (LNI Swissgas SA, Switzerland), two pressure controllers (Bronkhorst High-Tech B.V., the Netherlands), one mass flow controller (GSC Red-y, Vötglin Instruments GmbH, Switzerland). All the listed elements as well as the tubing of the dilution system were coated (SilcoNert 2000, SilcoTek Corporation, PA, USA). All the flows of the dilution system (i.e. critical orifices, MFC) were calibrated with the primary volumetric standard of METAS.

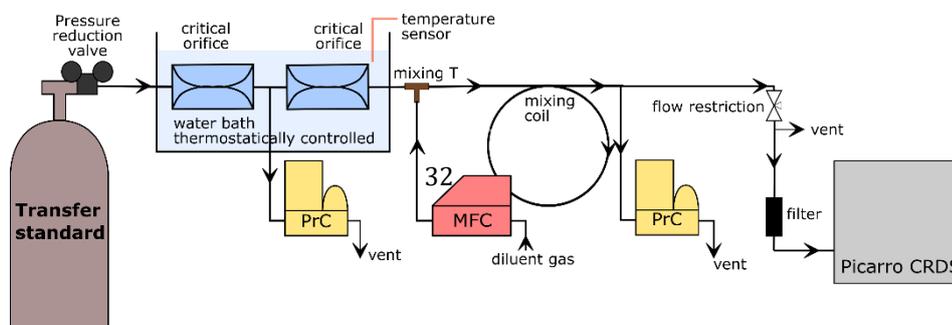


Fig. 2: Dilution system for the transfer standard using a cascade of critical orifices.

We used a lab water bath to keep the critical orifices at 22.0°C. We monitored the water temperature with a calibrated NTC thermistor connected to a multimeter (Almemo 2390-5, Ahlborn Mess- und Regelungstechnik GmbH, Germany). Pressure before the critical orifices was kept at 9.00 bar with the pressure reduction valve. After the first critical orifice, we regulated the pressure at 4.00 bar using one of the pressure controllers. The dilution gas (N<sub>2</sub> 6.0) was led at different flow rates to the mixing tee, located after the cascade of critical orifices, through the mass flow controller. We regulated the pressure after the mixing coil at 1.00 bar.

We generated each gas mixture for 120 minutes: 80 minutes of system stabilization (including analysers) and 40 minutes of measurement. For the first gas mixture generated, we increased the time up to 360 minutes, to account for stabilization time of the critical orifices (240 minutes). We performed 5 measurements with two replicates each, except for the second measurement (one replicate). The first replicate of each measurement took place before the homogenization of the transfer standard, which happened on 13/03/2019 for 4 hours. The temperature in the lab during the measurements was (20.0 ± 1.0)°C.

The amount fractions read by the analysers were corrected using the calibration equation to estimate the amount fraction generated by the dilution system (Eq. 3):

$$X_{\text{NH}_3} = (X_{\text{read}} - a) / b \quad [\text{Eq. 3}]$$

where,

$X_{\text{NH}_3}$ : amount fraction generated by the dilution system (nmol/mol)

$X_{\text{read}}$ : amount fraction read by the analysers (nmol/mol)

a: intercept of the linear regression (nmol/mol) (Table 1)

b: slope of the linear regression (Table 1)

We estimated the amount fraction of NH<sub>3</sub> in the transfer standard for each replicate (Eq. 4):

$$X_{\text{cyl}i} = (X_{\text{NH}_3} * (q_{\text{VMFC}} + q_{\text{Vco}}) / q_{\text{Vco}}) + X_{\text{resNH}_3} \quad [\text{Eq. 4}]$$

where,

$X_{\text{cyl}ij}$ : NH<sub>3</sub> amount fraction in transfer standard estimated during measurement i (i = 1, ..., 5) replicate j (j = 1, 2) (nmol/mol)

$X_{\text{NH}_3}$ : NH<sub>3</sub> amount fraction generated by the dilution system (nmol/mol)

$q_{\text{VMFC}}$ : diluting gas flow (mL/min)

$q_{\text{Vco}}$ : transfer standard flow through the critical orifices (mL/min)

$X_{\text{resNH}_3}$ : residual NH<sub>3</sub> amount fraction in the diluting gas (nmol/mol)

The resulting amount fraction values of each pair of replicates were average to get a single value per measurement.

The final amount fraction value assigned to the transfer standard was the average of the five measurements (Eq. 5):

$$X_{cyl5904243} = ((X_{cyl_{m1}} + X_{cyl_{m2}} + X_{cyl_{m3}} + X_{cyl_{m4}} + X_{cyl_{m5}}) / 5) * 10^{-3} \text{ [Eq. 5]}$$

where,

$X_{cyl5904243}$ : NH<sub>3</sub> amount fraction assigned to the transfer standard #5904243 (μmol/mol)

$X_{cyl_{m1}}$ : NH<sub>3</sub> amount fraction estimated in measurement 1 (average 2 replicates) (nmol/mol)

$X_{cyl_{m2}}$ : NH<sub>3</sub> amount fraction estimated in measurement 2 (nmol/mol)

$X_{cyl_{m3}}$ : NH<sub>3</sub> amount fraction estimated in measurement 3 (average 2 replicates) (nmol/mol)

$X_{cyl_{m4}}$ : NH<sub>3</sub> amount fraction estimated in measurement 4 (average 2 replicates) (nmol/mol)

$X_{cyl_{m5}}$ : NH<sub>3</sub> amount fraction estimated in measurement 5 (average 2 replicates) (nmol/mol)

Uncertainty evaluation

We evaluated the measurement uncertainty for this key comparison using the software GUM Workbench Pro (version 2.4.1., Metrodata GmbH, Germany, s/n 05-2.4-00002020-0). The uncertainty propagation through the calculation followed the GUM rules [3]. The main contributions to the combined standard uncertainty were the slope dispersion of the temporal mass loss of the permeation unit and the standard uncertainties of the flow measurements of the critical orifices used in the dilution system.

## Model equations

Uncertainty contribution of the magnetic suspension balance

$$f_{qm}(m1,m2,t1,t2,SC) = (((m1 - NP1) / K_{kalread1}) - ((m2 - NP2) / K_{kalread2})) * K_{kal} / (t2 - t1) * SC * 10^9;$$

$$K_{kal} = K_{kalhigh} - K_{kalow};$$

$$K_{kalread1} = K_{kalhighread1} - K_{kalowread1};$$

$$K_{kalread2} = K_{kalhighread2} - K_{kalowread2};$$

Uncertainty contribution of the permeation unit used to generate reference gas mixtures to calibrate the analysers

$$qmC = f_{qm}(m1C,m2C,t1C,t2C,SC);$$

Uncertainty contribution of the reference gas mixtures

$$VM_{N2} = 1000 * (2 * M_N) / d_{N2};$$

$$M_{NH3} = M_N + 3 * M_H;$$

$$f_{X_{MSB}}(qmC, PU, VM_{N2}, M_{NH3}, qV, X_{resNH3}) = ((qmC * PU * (VM_{N2} / M_{NH3})) / qV) + X_{resNH3};$$

Example for G1103t analyser

$$X_{0_{MSBe}} = 0 + X_{resNH3}; \{0 \text{ ppb}\}$$

$$X_{1_{MSBe}} = f_{X_{MSB}}(qmC, PU, VM_{N2}, M_{NH3}, qV_{1e}, X_{resNH3});$$

[...]

$$X_{4_{MSBe}} = f_{X_{MSB}}(qmC, PU, VM_{N2}, M_{NH3}, qV_{4e}, X_{resNH3});$$

$$X_{gen_{emean}} = (X_{0_{MSBe}} + X_{1_{MSBe}} + X_{2_{MSBe}} + X_{3_{MSBe}} + X_{4_{MSBe}}) / 5;$$

$$X_{read_{emean}} = (X_{0_{eread}} + X_{1_{eread}} + X_{2_{eread}} + X_{3_{eread}} + X_{4_{eread}}) / 5;$$

Linear regression of the calibration; least square method;  $X_{read} = a + b * X_{gen}$

Example for G1103t analyser

$$b_e = p_e / q_e;$$

$$p_e = (X_{0_{MSBe}} - X_{gen_{emean}}) * (X_{0_{eread}} - X_{read_{emean}}) + (X_{1_{MSBe}} - X_{gen_{emean}}) * (X_{1_{eread}} - X_{read_{emean}}) +$$

$$(X_{2_{MSBe}} - X_{gen_{emean}}) * (X_{2_{eread}} - X_{read_{emean}}) + (X_{3_{MSBe}} - X_{gen_{emean}}) * (X_{3_{eread}} - X_{read_{emean}}) +$$

$$(X_{4_{MSBe}} - X_{gen_{emean}}) * (X_{4_{eread}} - X_{read_{emean}});$$

$$q_e = (X_{0_{MSBe}} - X_{gen_{emean}})^2 + (X_{1_{MSBe}} - X_{gen_{emean}})^2 + (X_{2_{MSBe}} - X_{gen_{emean}})^2 + (X_{3_{MSBe}} - X_{gen_{emean}})^2 +$$

$$(X_{4_{MSBe}} - X_{gen_{emean}})^2;$$

$$a_e = X_{read_{emean}} - b_e * X_{gen_{emean}};$$

Uncertainty contribution of the dilution system used to generate the calibration standards.

$$fX_{NH_3}(X_{read}, a, b) = (X_{read} - a) / b;$$

Measurement 1

$$X11_{NH_3} = fX_{NH_3}(X_{read11}, a_e, b_e);$$

$$X12_{NH_3} = fX_{NH_3}(X_{read12}, a_e, b_e);$$

[...]

Measurement 5

$$X51_{NH_3} = fX_{NH_3}(X_{read51}, a_m, b_m);$$

$$X52_{NH_3} = fX_{NH_3}(X_{read52}, a_m, b_m);$$

$$fX_{cyl}(X_{NH_3}, qV_{MFC}, qV_{co}, X_{residualNH_3}) = (X_{NH_3} * (qV_{MFC} + qV_{co}) / qV_{co}) + X_{resNH_3};$$

Example Measurement 1

$$X_{cyl_{m11}} = fX_{cyl}(X11_{NH_3}, qV_{MFC_{dil11}}, qV_{co}, X_{resNH_3});$$

$$X_{cyl_{m12}} = fX_{cyl}(X12_{NH_3}, qV_{MFC_{dil12}}, qV_{co}, X_{resNH_3});$$

$$X_{cyl_{m1}} = ((X_{cyl_{m11}} + X_{cyl_{m12}}) / 2) / 1000;$$

Amount fraction NH<sub>3</sub> in gas cylinder to calibrate

$$X_{cyl_{5904243}} = ((X_{cyl_{m1}} + X_{cyl_{m2}} + X_{cyl_{m3}} + X_{cyl_{m4}} + X_{cyl_{m5}}) / 5);$$

Quantity	Unit	Definition
NP1	g	uncertainty contribution of the zero point correction; correction of lift change at time 1 due to atmospheric pressure variation
K <sub>kal</sub> read1	g	differences between the readings of the calibration masses during time 1
NP2	g	uncertainty contribution of the zero point correction; correction of lift change at time 2 due to atmospheric pressure variation
K <sub>kal</sub> read2	g	differences between the readings of the calibration masses during time 2
K <sub>kal</sub>	g	mass difference between the calibration masses according to certificate
K <sub>al</sub> high	g	heavy calibration mass
K <sub>al</sub> low	g	light calibration mass
K <sub>al</sub> highrea	g	balance reading of heavy calibration mass at time 1
K <sub>al</sub> lowread	g	balance reading of light calibration mass at time 1
K <sub>al</sub> highrea	g	balance reading of heavy calibration mass at time 2
K <sub>al</sub> lowread	g	balance reading of light calibration mass at time 2
qmC	ng/min	permeation rate at 48°C and 2600 hPa
m1C	g	permeator mass at time 1
m2C	g	permeator mass at time 2
t1C	min	time1
t2C	min	time2
SC		uncertainty contribution of the slope dispersion (relative standard deviation of single
VM <sub>N2</sub>	mL/mo	molar volume N <sub>2</sub> (dilution gas)
M <sub>N</sub>	g/mol	N atomic mass
d <sub>N2</sub>	g/L	density N <sub>2</sub> (dilution gas)
M <sub>NH3</sub>	g/mol	NH <sub>3</sub> molar mass
M <sub>H</sub>	g/mol	H atomic mass
X <sub>0MSBe</sub>	ppb	calibration amount fraction (0 ppb) (G1103t analyser)
X <sub>resNH3</sub>	ppb	residual NH <sub>3</sub> in dilution gas
X <sub>iMSBe</sub>	ppb	calibration amount fraction i (i = 1, ..., 4) (G1103t analyser)
PU		purity of the permeator (from 0 to 1)
q <sub>vie</sub>	mL/mi	flow MFM (dil1) calibration point i (i = 1, ..., 4) (G1103t analyser)
X <sub>genemean</sub>	ppb	average amount fraction NH <sub>3</sub> generated for calibration G1103t analyser
X <sub>reademean</sub>	ppb	average amount fraction NH <sub>3</sub> read by G1103t analyser

Quantity	Unit	Definition
X <sub>i</sub> eread	ppb	read amount fraction i (i = 0, ..., 4) (G1103t analyser)
X <sub>read</sub> mmea	ppb	average amount fraction NH <sub>3</sub> read by G2103 analyser
X <sub>i</sub> mread	ppb	read amount fraction i (i = 0, ..., 5) (G2103 analyser)
b <sub>e</sub>		slope of the linear regression (G1103t analyser)
a <sub>e</sub>	ppb	intercept of the linear regression (G1103t analyser)
X <sub>ij</sub> NH <sub>3</sub>	ppb	amount fraction ij (i = 1, ..., 5; j = 1, 2) generated for calibration gas cylinder
X <sub>read</sub> ij	ppb	amount fraction read by the analyser during the generation of X <sub>ij</sub> NH <sub>3</sub>
X <sub>cyl</sub> mi	ppb	amount fraction estimated in measurement i (i = 1,...,5) replicate j (j = 1, 2).
q <sub>v</sub> MFCdij	mL/mi	average flow MFC measurement 1 i (i = 1,...,5) replicate j (j = 1, 2).
q <sub>v</sub> co	mL/mi	flow critical orifices dilution system
X <sub>cyl</sub> mi	ppm	average amount fraction NH <sub>3</sub> measurement i (replicates 1 and 2)
X <sub>cyl</sub> 5904243	ppm	amount fraction NH <sub>3</sub> in cylinder intercomparison CCQM-K117 (average 5 measurements)

### Uncertainty budget of the amount fraction NH<sub>3</sub> in cylinder #5904243

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
NP1	0.0 g	289·10 <sup>-9</sup> g	rectangular	-5000	-1.5·10 <sup>-3</sup> ppm	0.0 %
NP2	0.0 g	289·10 <sup>-9</sup> g	rectangular	5000	1.5·10 <sup>-3</sup> ppm	0.0 %
Kal <sub>high</sub>	29.9923070 g	25.0·10 <sup>-6</sup> g	normal	0.59	15·10 <sup>-6</sup> ppm	0.0 %
Kal <sub>low</sub>	7.9516970 g	20.0·10 <sup>-6</sup> g	normal	-0.59	-12·10 <sup>-6</sup> ppm	0.0 %
m1C	22.667813150 g	289·10 <sup>-9</sup> g	rectangular	5000	1.5·10 <sup>-3</sup> ppm	0.0 %
m2C	22.665248260 g	289·10 <sup>-9</sup> g	rectangular	-5000	-1.5·10 <sup>-3</sup> ppm	0.0 %
t1C	4299.0500 min	0.0250 min	normal	1.6·10 <sup>-3</sup>	39·10 <sup>-6</sup> ppm	0.0 %
t2C	12539.3200 min	0.0250 min	normal	-1.6·10 <sup>-3</sup>	-39·10 <sup>-6</sup> ppm	0.0 %
<b>SC</b>	<b>1.00000</b>	<b>4.40·10<sup>-3</sup></b>	<b>normal</b>	<b>13</b>	<b>0.057 ppm</b>	<b>84.4 %</b>
M <sub>N</sub>	14.006855 g/mol	174·10 <sup>-6</sup> g/mol	triangular	0.16	28·10 <sup>-6</sup> ppm	0.0 %
d <sub>N2</sub>	1.250100 g/L	150·10 <sup>-6</sup> g/L	normal	-10	-1.5·10 <sup>-3</sup> ppm	0.0 %
M <sub>H</sub>	1.0079750 g/mol	55.1·10 <sup>-6</sup> g/mol	triangular	-2.3	-130·10 <sup>-6</sup> ppm	0.0 %
X <sub>res</sub> NH <sub>3</sub>	0.300 ppb	0.122 ppb	triangular	0.10	0.013 ppm	4.2 %
PU	0.9998000	81.6·10 <sup>-6</sup>	triangular	13	1.1·10 <sup>-3</sup> ppm	0.0 %
q <sub>v</sub> 1e	5054.12 mL/min	5.05 mL/min	normal	-210·10 <sup>-6</sup>	-1.1·10 <sup>-3</sup> ppm	0.0 %
q <sub>v</sub> 2e	2833.49 mL/min	2.83 mL/min	normal	-610·10 <sup>-6</sup>	-1.7·10 <sup>-3</sup> ppm	0.0 %
q <sub>v</sub> 3e	1827.34 mL/min	1.83 mL/min	normal	-1.3·10 <sup>-3</sup>	-2.3·10 <sup>-3</sup> ppm	0.1 %
q <sub>v</sub> 4e	1013.34 mL/min	1.01 mL/min	normal	-2.6·10 <sup>-3</sup>	-2.6·10 <sup>-3</sup> ppm	0.2 %
q <sub>v</sub> 1m	5176.12 mL/min	5.18 mL/min	normal	-120·10 <sup>-6</sup>	-600·10 <sup>-6</sup> ppm	0.0 %
q <sub>v</sub> 2m	4323.71 mL/min	4.32 mL/min	normal	-170·10 <sup>-6</sup>	-720·10 <sup>-6</sup> ppm	0.0 %
q <sub>v</sub> 3m	3342.64 mL/min	3.34 mL/min	normal	-280·10 <sup>-6</sup>	-930·10 <sup>-6</sup> ppm	0.0 %
q <sub>v</sub> 4m	2333.09 mL/min	2.33 mL/min	normal	-560·10 <sup>-6</sup>	-1.3·10 <sup>-3</sup> ppm	0.0 %
q <sub>v</sub> 5m	1929.60 mL/min	1.93 mL/min	normal	-820·10 <sup>-6</sup>	-1.6·10 <sup>-3</sup> ppm	0.0 %
X <sub>0</sub> eread	0.4070 ppb	0.0148 ppb	normal	-0.015	-220·10 <sup>-6</sup> ppm	0.0 %
X <sub>1</sub> eread	83.1070 ppb	0.0203 ppb	normal	-0.013	-270·10 <sup>-6</sup> ppm	0.0 %
X <sub>2</sub> eread	146.8460 ppb	0.0192 ppb	normal	-0.012	-230·10 <sup>-6</sup> ppm	0.0 %
X <sub>3</sub> eread	225.8690 ppb	0.0496 ppb	normal	-0.010	-510·10 <sup>-6</sup> ppm	0.0 %
X <sub>4</sub> eread	407.316 ppb	0.120 ppb	normal	-6.5·10 <sup>-3</sup>	-780·10 <sup>-6</sup> ppm	0.0 %
X <sub>0</sub> mread	0.29100 ppb	7.94·10 <sup>-3</sup> ppb	normal	-7.7·10 <sup>-3</sup>	-61·10 <sup>-6</sup> ppm	0.0 %

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
X1 <sub>mread</sub>	79.2370 ppb	0.0108 ppb	normal	-7.6·10 <sup>-3</sup>	-82·10 <sup>-6</sup> ppm	0.0 %
X2 <sub>mread</sub>	95.1300 ppb	0.0126 ppb	normal	-7.6·10 <sup>-3</sup>	-96·10 <sup>-6</sup> ppm	0.0 %
X3 <sub>mread</sub>	123.11600 ppb	9.11·10 <sup>-3</sup> ppb	normal	-7.6·10 <sup>-3</sup>	-69·10 <sup>-6</sup> ppm	0.0 %
X4 <sub>mread</sub>	175.8460 ppb	0.0230 ppb	normal	-7.5·10 <sup>-3</sup>	-170·10 <sup>-6</sup> ppm	0.0 %
X5 <sub>mread</sub>	212.3110 ppb	0.0223 ppb	normal	-7.5·10 <sup>-3</sup>	-170·10 <sup>-6</sup> ppm	0.0 %
X <sub>read11</sub>	123.4340 ppb	0.0118 ppb	normal	0.011	120·10 <sup>-6</sup> ppm	0.0 %
X <sub>read12</sub>	122.1120 ppb	0.0119 ppb	normal	0.011	130·10 <sup>-6</sup> ppm	0.0 %
X <sub>read21</sub>	108.8070 ppb	0.0122 ppb	normal	0.024	290·10 <sup>-6</sup> ppm	0.0 %
X <sub>read31</sub>	223.2720 ppb	0.0132 ppb	normal	5.8·10 <sup>-3</sup>	77·10 <sup>-6</sup> ppm	0.0 %
X <sub>read32</sub>	222.4780 ppb	0.0139 ppb	normal	5.8·10 <sup>-3</sup>	81·10 <sup>-6</sup> ppm	0.0 %
X <sub>read41</sub>	121.20000 ppb	4.16·10 <sup>-3</sup> ppb	normal	0.011	44·10 <sup>-6</sup> ppm	0.0 %
X <sub>read42</sub>	121.49700 ppb	4.08·10 <sup>-3</sup> ppb	normal	0.011	43·10 <sup>-6</sup> ppm	0.0 %
X <sub>read51</sub>	106.90500 ppb	3.98·10 <sup>-3</sup> ppb	normal	0.012	48·10 <sup>-6</sup> ppm	0.0 %
X <sub>read52</sub>	106.37900 ppb	4.29·10 <sup>-3</sup> ppb	normal	0.012	52·10 <sup>-6</sup> ppm	0.0 %
qVMFCdil11	2201.38 mL/min	2.20 mL/min	normal	590·10 <sup>-6</sup>	1.3·10 <sup>-3</sup> ppm	0.0 %
<b>q<sub>vc</sub></b>	<b>20.8600 mL/min</b>	<b>0.0313 mL/min</b>	<b>normal</b>	<b>-0.61</b>	<b>-0.019 ppm</b>	<b>9.7 %</b>
qVMFCdil12	2201.40 mL/min	2.20 mL/min	normal	580·10 <sup>-6</sup>	1.3·10 <sup>-3</sup> ppm	0.0 %
qVMFCdil21	2501.73 mL/min	2.50 mL/min	normal	1.0·10 <sup>-3</sup>	2.6·10 <sup>-3</sup> ppm	0.2 %
qVMFCdil31	1200.28 mL/min	1.20 mL/min	normal	1.1·10 <sup>-3</sup>	1.3·10 <sup>-3</sup> ppm	0.0 %
qVMFCdil32	1200.28 mL/min	1.20 mL/min	normal	1.1·10 <sup>-3</sup>	1.3·10 <sup>-3</sup> ppm	0.0 %
qVMFCdil41	2201.39 mL/min	2.20 mL/min	normal	580·10 <sup>-6</sup>	1.3·10 <sup>-3</sup> ppm	0.0 %
qVMFCdil42	2201.38 mL/min	2.20 mL/min	normal	580·10 <sup>-6</sup>	1.3·10 <sup>-3</sup> ppm	0.0 %
qVMFCdil51	2501.72 mL/min	2.50 mL/min	normal	510·10 <sup>-6</sup>	1.3·10 <sup>-3</sup> ppm	0.0 %
qVMFCdil52	2501.71 mL/min	2.50 mL/min	normal	510·10 <sup>-6</sup>	1.3·10 <sup>-3</sup> ppm	0.0 %
<b>Xcyl5904243</b>	<b>12.9369 ppm</b>	<b>0.0618 ppm</b>				

## References

- [1] ISO 6145-10:2002: Gas analysis – Preparation of calibration gas mixtures using dynamic volumetric methods – Part 10: Permeation method
- [2] Cantrell, C.A. (2008). Technical Note: Review of methods for linear least-squares fitting of data and application to atmospheric chemistry problems, Atmospheric Chemistry and Physics, 8, 5477 – 5487.
- [3] Joint Committee for Guides in Metrology. Evaluation of measurement data – Guide to the expression of uncertainty in measurement (GUM). JCGM 100:2008.  
[https://www.bipm.org/utis/common/documents/jcgm/JCGM\\_100\\_2008\\_E.pdf](https://www.bipm.org/utis/common/documents/jcgm/JCGM_100_2008_E.pdf)

## Measurement report KRISS

Cylinder number: D597002

### Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Ammonia	28/01/19	13.55	0.3	3

### Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Ammonia	29/01/19	13.60	0.4	3

### Measurement #3<sup>5</sup>

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Ammonia	30/01/19	13.56	0.1	3

### Results

Component	Date (dd/mm/yy)	Result (µmol/mol)	Expanded uncertainty (µmol/mol)	Coverage factor
Ammonia		13.57	0.15	2

### Calibration standards

- Method of preparation

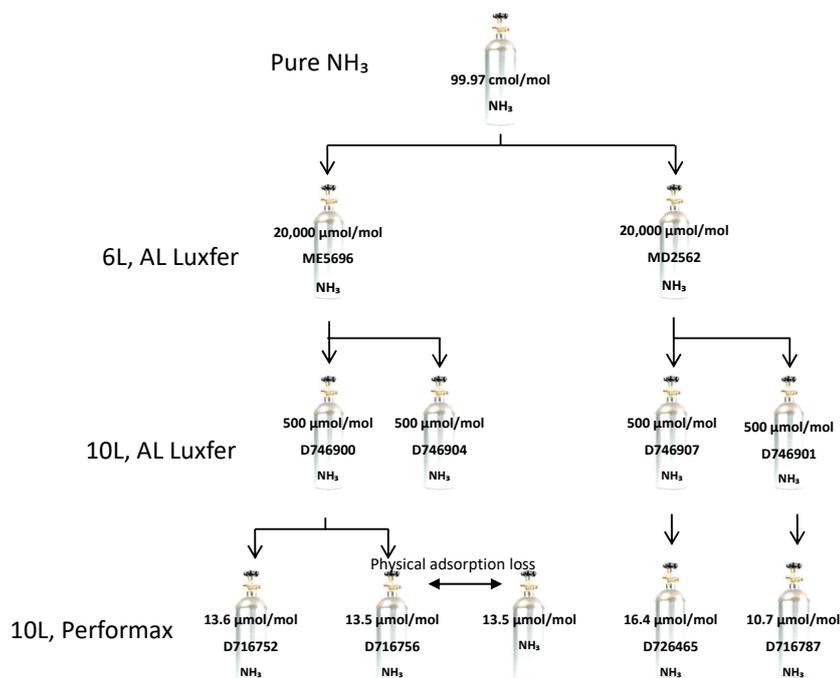
Gas mixtures were prepared gravimetrically and their masses were determined using an automated top-pan balance (XP26003L, Mettler Toledo) with 26 kg capacity and 1 mg resolution.

- Weighing data

Primary reference gas mixtures, which were used to analyse a key comparison sample, were prepared with 3-step dilutions from a pure material to a range of from about 10 µmol/mol to about 17 µmol/mol.

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<sup>5</sup> If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary



### Gravimetric preparation hierarchy

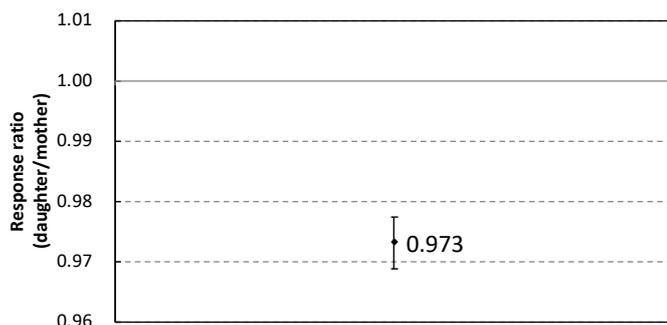
- Purity tables (composition) of the parent gases

Components	Amount fraction (μmol/mol)	Distribution	Standard uncertainty (μmol/mol)	Analytical methods
He	0.5	Rectangular	0.29	MS
Ar	0.5	Rectangular	0.29	MS
N <sub>2</sub>	5.87	Normal	1.17	GC/DID
H <sub>2</sub>	0.5	Rectangular	0.29	GC/DID
O <sub>2</sub>	0.5	Rectangular	0.29	GC/DID
CO <sub>2</sub>	3.42	Normal	0.68	GC/DID
CO	0.5	Rectangular	0.29	GC/DID & FTIR
H <sub>2</sub> O	272	Normal	81.5	FTIR
CH <sub>4</sub>	0.5	Rectangular	0.29	GC/DID & FTIR
THC	4.69	Normal	0.94	GC/FID
NO	2.5	Rectangular	1.44	FTIR
NO <sub>2</sub>	2.5	Rectangular	1.44	FTIR
N <sub>2</sub> O	2.5	Rectangular	1.44	FTIR
<b>NH<sub>3</sub></b>	<b>999704</b>		<b>90.31</b>	

- Physical adsorption loss

In order to estimate physical adsorption loss onto the internal surface of a sample cylinder at about 13 μmol/mol using cylinder-to-cylinder division method (Lee et al., 2017), a newly prepared primary reference gas mixture (Performax, D716756) was divided into another new cylinder (Performax, D716790) and then analysed against each other. Results from multiple analysis show that a response ratio (daughter to mother) is significantly less than 1, which indicates physical adsorption loss occurred during or a short time after the preparation. Therefore, gravimetrically determined amount fractions

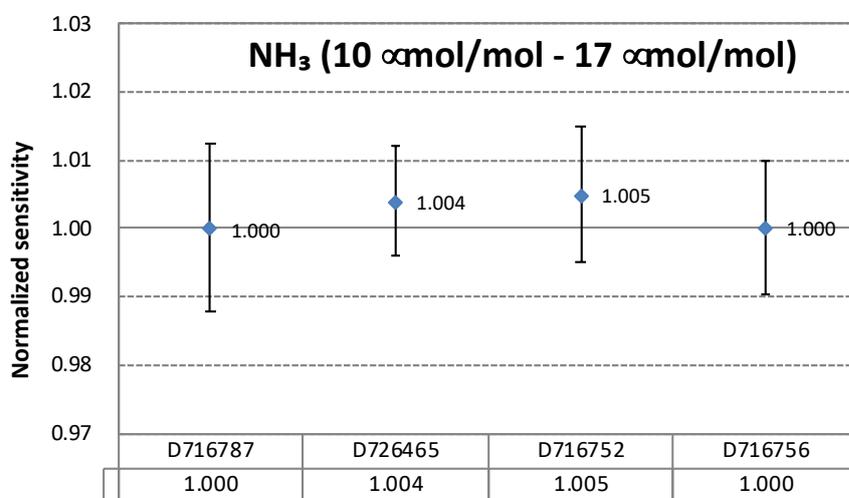
and their uncertainties are recalculated to account the physical adsorption loss on the cylinder internal surface.



**Results from Cylinder-to-cylinder division**

– Verification measures

Primary reference gas mixtures were analysed to verify their gravimetric preparation using NDIR analyser (ULTRAMAT 6, Siemens). Results show that primary reference gas mixtures agree well within their associated uncertainties of about 1 % ( $k = 2$ ).



**Results from verification measurement**

Instrumentation

A NDIR gas analyser was used to verify primary reference gas mixtures and analyse a sample for this key comparison.

Calibration method and value assignment, uncertainty evaluation

A sample for this comparison was analysed against a KRISS primary reference gas mixture (D716752) using a NDIR gas analyser. The sample analysis has done by alternating between the gas mixtures (i.e.,  $PRM_{KRISS} - PRM_{KC} - PRM_{KRISS} - PRM_{KC} - PRM_{KRISS} - PRM_{KC} - PRM_{KRISS}$ ) at three different days. The amount fraction of the KC sample cylinder is determined by the following equation for each measurement.

$$x_{KC,i,j} = x_{KRISS} \times R_{i,j}$$

$$u(x_{KC,i,j}) = x_{KC,i,j} \times \sqrt{\left(\frac{u(x_{KRiSS})}{x_{KRiSS}}\right)^2 + \left(\frac{u(R_{i,j})}{R_{i,j}}\right)^2}$$

where  $x_{KC,i,j}$  is the amount fraction of KC gas mixture,  $x_{KRiSS}$  is the amount fraction of KRiSS PRM, and  $R_{i,j}$  is the analyser's response ratio of 15 repeated measurements (i.e., response of PRM<sub>KC</sub> to response of PRM<sub>KRiSS</sub>). At three different days ( $i=1, 2, 3$ ), three repeated measurements ( $j= 1, 2, 3$ ) have been conducted. The total number of measurements are 9 for three days.

	average	1 <sup>st</sup> analysis	2 <sup>nd</sup> analysis	3 <sup>rd</sup> analysis
1 <sup>st</sup> day measurement	$x_{KC,1,avg}$	$x_{KC,1,1}$	$x_{KC,1,2}$	$x_{KC,1,3}$
2 <sup>nd</sup> day measurement	$x_{KC,1,avg}$	$x_{KC,2,1}$	$x_{KC,2,2}$	$x_{KC,2,3}$
3 <sup>rd</sup> day measurement	$x_{KC,1,avg}$	$x_{KC,3,1}$	$x_{KC,3,2}$	$x_{KC,3,3}$
<b>Reported final results</b>	$x_{KC,f}$	$u(x_{KC,f})$		

$$x_{KC,i,avg} = \frac{x_{KC,i,1} + x_{KC,i,2} + x_{KC,i,3}}{3}$$

$$x_{KC,f} = \frac{x_{KC,1,avg} + x_{KC,2,avg} + x_{KC,3,avg}}{3}$$

#### Uncertainty budget of reported final results ( $x_{KC,f}$ )

Uncertainty component	Standard uncertainty, $\mu\text{mol/mol}$	Contribution to uncertainty, %
Analytical repeatability	0.033	18.7
Analytical reproducibility	0.014	3.6
KRiSS PRM	0.067	77.7
Combined	0.076	

#### Important note

The pressure of the key comparison sample cylinder was checked as about 250 psig prior its analysis. The residual pressure was checked as 200 psig after the analysis and returned to NIST.

#### References

Lee *et al.* 2017 Determination of physical adsorption loss of primary standard gas mixtures in cylinders using cylinder-to-cylinder division *Metrologia* 54 L26

## Measurement report NIM

Cylinder number: 5904239

### Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Ammonia	23/04/2019	13.94	0.52%	4

### Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Ammonia	24/04/2019	13.85	0.26%	4

### Measurement #3<sup>6</sup>

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Ammonia	25/04/2019	13.89	0.81%	4

### Measurement #4

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Ammonia	26/04/2019	13.74	0.33%	4

## Results

Component	Date (dd/mm/yy)	Result (µmol/mol)	Expanded uncertainty (µmol/mol)	Coverage factor
Ammonia	26/04/2019	13.85	0.20	2

### 1. Calibration standards

#### 1.1 Preparation method and cylinder treatment

The standards were prepared by gravimetric method, all the cylinders used were pumped to lower than  $1 \times 10^{-4}$  Pa, a 65°C heating temperature was set and lasted for more than 8 hours to remove moisture in cylinders at the same time.

#### 1.2 Filling and weighing

Three steps were selected to fill gas to targeted concentration from pure ammonia and pure nitrogen.

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<sup>6</sup> If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary

The first step: pure NH<sub>3</sub> and pure N<sub>2</sub> were added into cylinder to gain mole fraction of 2% mol·mol<sup>-1</sup>;

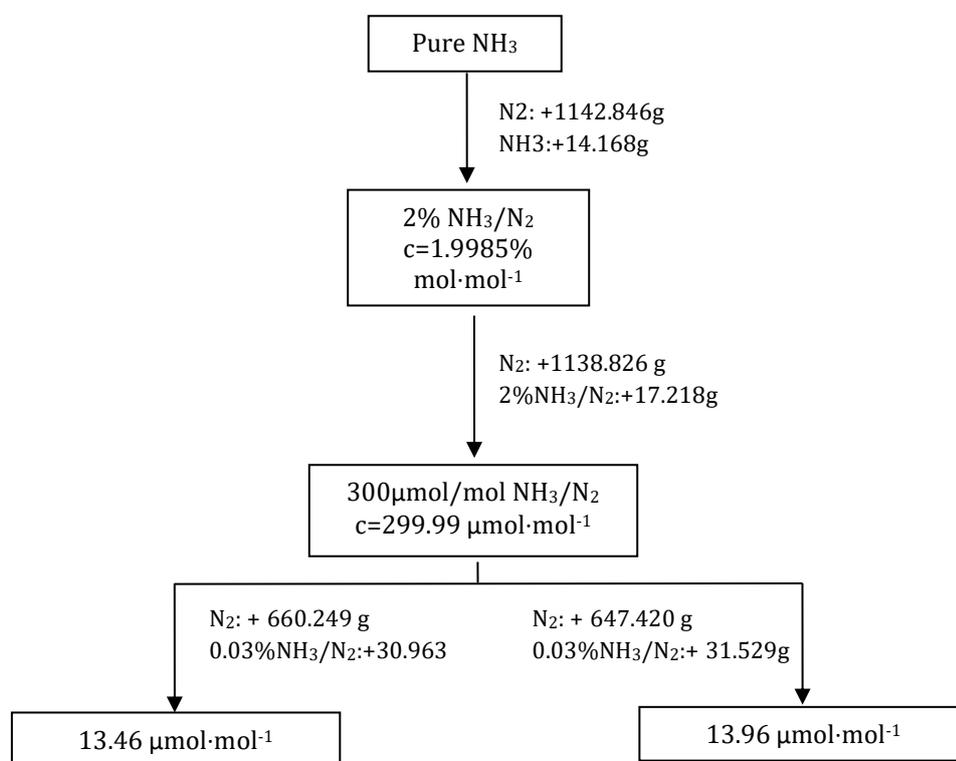
The second step: 2% mol·mol<sup>-1</sup> NH<sub>3</sub>/N<sub>2</sub> was further diluted by nitrogen to reach a more lower concentration of 300 μmol·mol<sup>-1</sup>.

The third step : the two standards were finally prepared by diluting 300 μmol·mol<sup>-1</sup> NH<sub>3</sub>/N<sub>2</sub>.

The typical amount of gas filled in each step is presented in Fig. 1. The balance used is Metter XP26003L, capacity 26 kg, Readability 1 mg. A substitution method (A-B-A) was selected when weighing, here A represents reference cylinder, B represents sample cylinder.

Concentration's calculation equation is according to ISO 6142:

$$x_i = \frac{\sum_{A=1}^P \left( \frac{x_{i,A} \cdot m_A}{\sum_{i=1}^n (x_{i,A} \cdot M_i)} \right)}{\sum_{A=1}^P \left( \frac{m_A}{\sum_{i=1}^n (x_{i,A} \cdot M_i)} \right)}$$



**Figure 1. Three filling steps with added gas weight each**

### 1.3 Purity data of parent gases

Purity data of parent gases N<sub>2</sub> and NH<sub>3</sub> are shown in Table 1 and Table 2 with the analysis method for common impurity components.

**Table 1. Purity of N<sub>2</sub>**

Component	Method	Mole fraction ( $\mu\text{mol}\cdot\text{mol}^{-1}$ )	Distribution	Uncertainty ( $\mu\text{mol}\cdot\text{mol}^{-1}$ )
O <sub>2</sub>	Oxygen Analyzer	0.030	Rectangular	0.014
Ar	GC-PDHID	50.0	Normal	2.9
H <sub>2</sub>	GC-PDHID	0.05	Rectangular	0.03
H <sub>2</sub> O	CRDs	0.10	Rectangular	0.06
CO	GC-PDHID	0.030	Rectangular	0.014
CO <sub>2</sub>	GC-PDHID	0.010	Rectangular	0.006
CH <sub>4</sub>	GC-PDHID	0.030	Rectangular	0.014
N <sub>2</sub>	-	999949.7	-	2.9

**Table 2. Purity of NH<sub>3</sub>**

Component	Method	Mole fraction ( $\mu\text{mol}\cdot\text{mol}^{-1}$ )	Distribution	Uncertainty ( $\mu\text{mol}\cdot\text{mol}^{-1}$ )
Ar	GC-PDHID	0.350	Normal	0.035
O <sub>2</sub>	GC-PDHID	0.79	Normal	0.08
THC (CH <sub>4</sub> )	GC-PDHID	0.010	Rectangular	0.006
H <sub>2</sub> O	-	1.0	Rectangular	0.6
N <sub>2</sub>	GC-PDHID	1.7	Normal	0.5
NH <sub>3</sub>	-	999996.2	-	0.8

#### 1.4 Verification of standards

In the verification measurements, the two intermediate mixed gases of  $300\mu\text{mol}\cdot\text{mol}^{-1}$  NH<sub>3</sub>/N<sub>2</sub> obtained from two different filling route were verified through FTIR, one cylinder was chose as standard, with which the other cylinder was calibrated, the results showed the these two cylinders have good consistency, their difference between gravimetric mole fraction and the calibrated mole fraction was smaller than 0.1%. Similarly, for the final standards, each concentration point ( $13.5\mu\text{mol}\cdot\text{mol}^{-1}$  and  $13.9\mu\text{mol}\cdot\text{mol}^{-1}$ ) was prepared two cylinders, the differences between each two cylinders were both smaller than 0.2%.

#### 2. Instrumentation

The main instrument used in this comparison is FT-IR Spectrometer with the trade name MultiGas™ analyzer (Models 2032, MKS company), which equipped with necessary components for this kind of instrument. The detector is mercury-cadmium-telluride (MCT), which is cooled by a thermo-electrically mode. The sample cell has a path length of 5.11m. The resolution is  $1\text{ cm}^{-1}$ , the scan number for each spectrum was set at 120 with a total scan time of 1 minute. To obtain a

clean background, the whole system was purged by high-purity nitrogen, of which the flow was set at 200 mL·min<sup>-1</sup> for sample cell and 800 mL·min<sup>-1</sup> for other parts of the spectrometer. Besides, the temperature for the sample cell was kept at 35.7°C, and its inner pressure was equal to the ambient atmospheric pressure. Two absorption regions (3166~3285) cm<sup>-1</sup> and (3409~3475) cm<sup>-1</sup> were selected to determinate the targeted analyte, while the reading was obtained through automatically integrating by the instrument itself.

### 3. Calibration method and value assignment

As for the calibration of the comparison sample, two-points calibration method was used. As shown in Figure 2, standard 1 represents the lower concentration point 13.46 μmol·mol<sup>-1</sup> NH<sub>3</sub>/N<sub>2</sub> and standard 2 represents the higher concentration point 13.96 μmol·mol<sup>-1</sup> NH<sub>3</sub>/N<sub>2</sub>. When sampling, the flow was kept at 200 mL·min<sup>-1</sup> and lasted for at least 1 hour to make reading stabilization. The assigned value was calculated in the following formulae.

$$C_0 = C_1 + \frac{(C_2 - C_1)}{(R_2 - R_1)}(R_0 - R_1)$$

Here,

$C_0$  represents the mole fraction of the comparison sample;

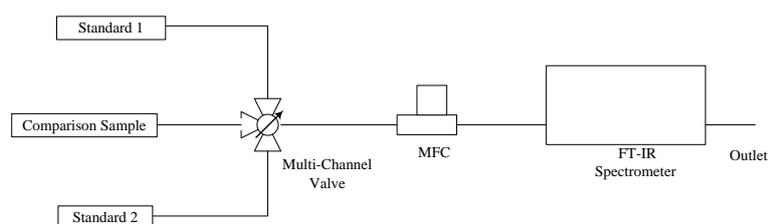
$C_1$  represents the mole fraction of the standard 1 at lower concentration point;

$C_2$  represents the mole fraction of the standard 2 at higher concentration point;

$R_0$  represents the instrument reading from the comparison sample;

$R_1$  represents the instrument reading from the standard 1 at lower concentration point;

$R_2$  represents the instrument reading from the standard 2 at higher concentration point;



**Figure 2. Measurement setup**

#### Uncertainty evaluation

The contributions to combined standard uncertainty were from preparation of gravimetric method, repeatability of verification in one day and in different days.

$$u_c = \sqrt{u_{prep}^2 + u_{ver,1}^2 + u_{ver,2}^2}$$

Here,  $u$  means relative standard uncertainty.

$u_c$ : Combined uncertainty of assigned concentration value of NH<sub>3</sub> in the comparison cylinder;

$u_{prep}$ : Uncertainty from gravimetric preparation;

$u_{ver,1}$ : Uncertainty from repeatability of verification in one day;

$u_{ver,2}$ : Uncertainty from repeatability of verification in different 4 days;

**Table 3. Uncertainty budget**

Source of uncertainty	$u_{\text{prep}}$	$u_{\text{ver},1}$	$u_{\text{ver},2}$
Relative standard uncertainty	0.3%	0.5%	0.4%
Relative expanded uncertainty	1.5% ( $k=2$ )		

## Measurement report NIST

Cylinder number: 5904173

### Measurement #1

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard uncertainty ( $\mu\text{mol/mol}$ )	number of replicates
Ammonia	23/10/18	13.60	0.21	6

### Measurement #2

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard uncertainty ( $\mu\text{mol/mol}$ )	number of replicates
Ammonia	23/10/18	13.60	0.32	6

### Measurement #3

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard uncertainty ( $\mu\text{mol/mol}$ )	number of replicates
Ammonia	23/10/18	13.62	0.19	6

### Measurement #4

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard uncertainty ( $\mu\text{mol/mol}$ )	number of replicates
Ammonia	24/10/18	13.70	0.24	6

### Measurement #5

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard uncertainty ( $\mu\text{mol/mol}$ )	number of replicates
Ammonia	24/10/18	13.67	0.25	6

### Measurement #6

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard uncertainty ( $\mu\text{mol/mol}$ )	number of replicates
Ammonia	24/10/18	13.70	0.42	6

## Results

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Expanded uncertainty ( $\mu\text{mol/mol}$ )	Coverage factor
Ammonia	25/10/18	13.64	0.20	k=2

## Calibration standards

Since NIST does not house primary standard mixtures (PSMs) of  $\text{NH}_3$  in the amount-of-substance fraction range of  $10 \mu\text{mol/mol}$  –  $30 \mu\text{mol/mol}$ , standards were prepared by use of a permeation device system (PDS). Permeation tubes were purchased that were 6.5 cm in length with a nominal permeation rate of  $2860 \text{ ng/min} \pm 15\%$  at  $34^\circ \text{C}$ . Four permeation tubes were inserted into the

permeation device system (PDS), which was setup in continuous-weighing-mode in compliance with ISO 6145 Part 10 [1] and internal procedures. The mass of the four NH<sub>3</sub> permeation tubes was measured every fifteen minutes using a Rubotherm magnetic suspension balance. The mass resolution of the balance is 0.001 mg. The total gas flow from the PDS was measured by a DH Instruments (DHI) MolBloc (1E3 Series) flow meter to an uncertainty of 0.1% relative. The MolBoc had been previously calibrated by flowing known masses of nitrogen across the flow meter following internal procedures. See figure 1 for permeation schematic setup. The gas flow over the permeation tubes was kept constant at 800 ml/min. By varying the dilution gas flow, a suite of NH<sub>3</sub> standards could be produced on demand. A permeation rate in μg min<sup>-1</sup> was determined for the mean amount-of-substance fraction to be analyzed using equation 1 and was converted to μmol min<sup>-1</sup> using equation 2.

**Permeation Rate (μg min<sup>-1</sup>)**

$$q_m = slope \left| \frac{\Delta m}{\Delta t} \right| \cdot 10^6 \quad (\text{Eq. 1})$$

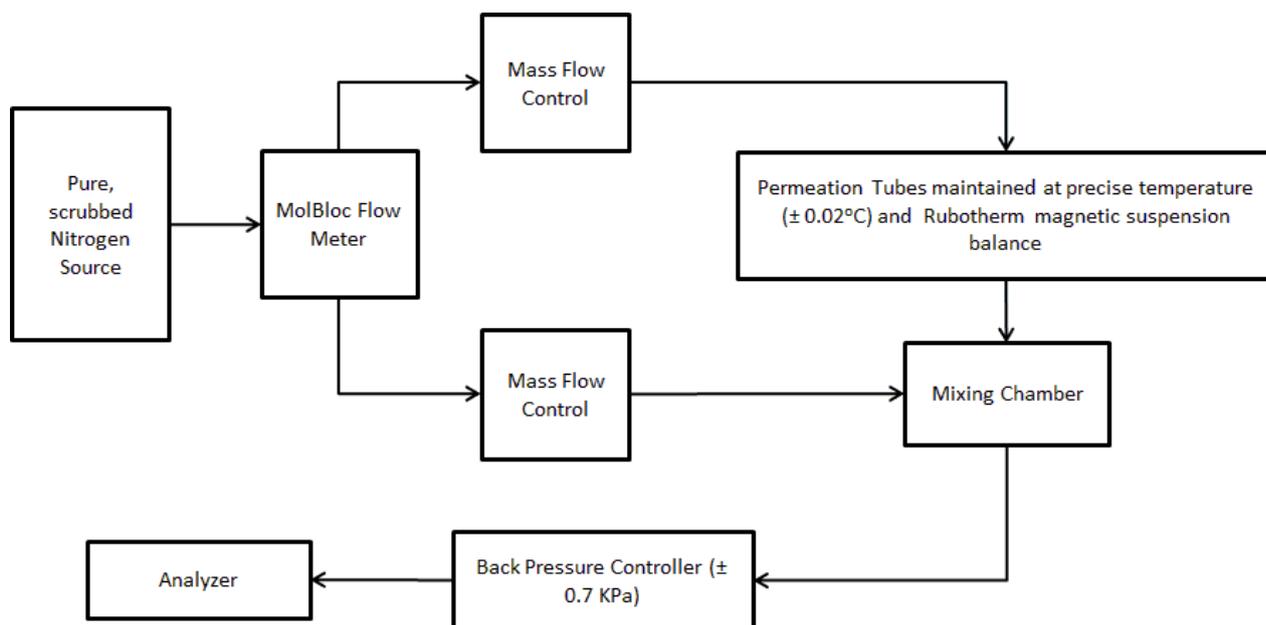
q <sub>m</sub>	Permeation Rate (μg min <sup>-1</sup> )
m	Mass (g)
t	time (min)

**Permeation Rate (μmol min<sup>-1</sup>)**

$$q_m = \frac{q_m}{M} \quad (\text{Eq. 2})$$

q <sub>m</sub>	Perm Rate (μg min <sup>-1</sup> )
M	Molar Mass of Ammonia (g)

**Figure 2:** Schematic of the basic elements of the Permeation Device System.

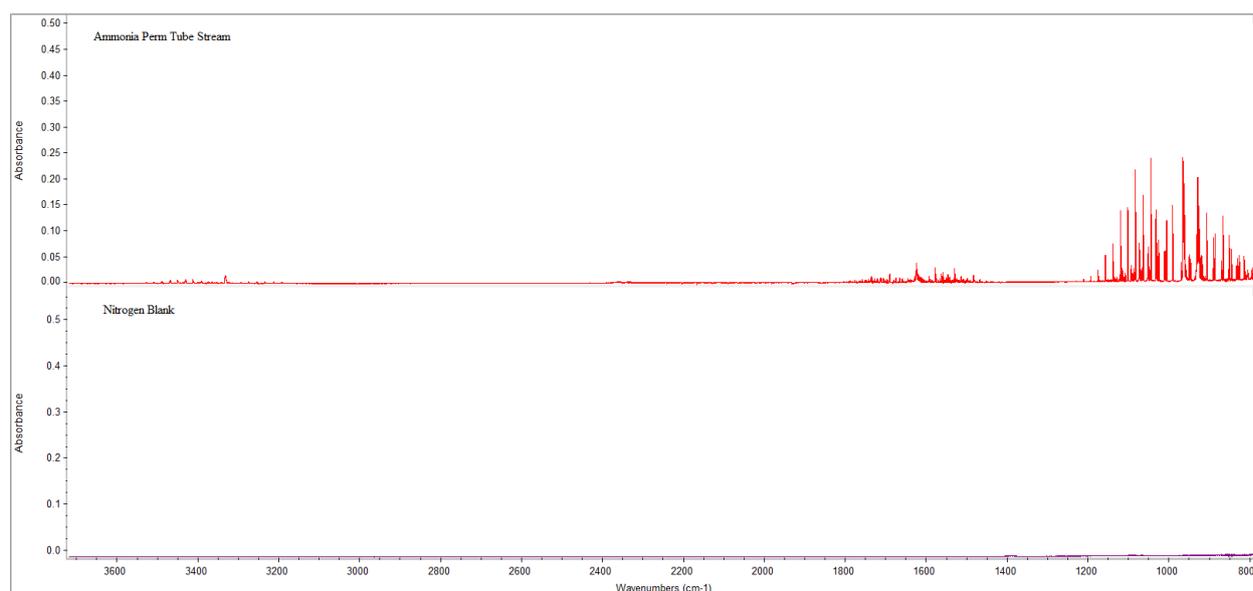


*Impurity Analysis:* The purchased tubes were stated to be  $\geq 99.999\%$  pure from the manufacturer. The dilution gas used for generating the standard was  $N_2$  nominal purity was  $\geq 99.999\%$ . Impurity data was obtained for the permeation tubes from the manufacturer, and were stated to be:

Component		Amount-of-substance fraction
Carbon Dioxide	<	1 $\mu\text{mol/mol}$
Carbon Monoxide	<	0.1 $\mu\text{mol/mol}$
Methane	<	0.1 $\mu\text{mol/mol}$
Water	<	2 $\mu\text{mol/mol}$

Impurity data for the gas generated by the permeation tubes was obtained by diverting the gas flow stream from the permeation device system to a Nicolet Nexus 670 fourier-transform infrared spectroscopy (FTIR) instrument with a mercury cadmium telluride (MCT) detector. The FTIR was also equipped with a 1.5L Specac 10 meter fixed path length Cyclone gas cell. The gas cell was filled with dilution gas, in this case nitrogen, and a background was obtained. A second analysis of the nitrogen was obtained to verify that a background subtraction was occurring and that there was no ammonia present in the matrix gas. The gas cell was then filled with the unknown gas sample to 800 torr and vacuum evacuated. This purge cycle was repeated six times. After the sixth evacuation cycle the gas was set to continuously flow while maintaining a cell pressure of 760 torr. Six spectra were then collected at 256 scans with a resolution of  $0.5\text{ cm}^{-1}$  and averaged together. See Figure 2 for comparative spectra of the matrix gas and perm tube flow. Impurities were evaluated from the resulting spectra with nothing measurable being detected above baseline, therefore, the purity of the permeation tubes is the stated  $\geq 99.999\%$ .

**Figure 2:** Nitrogen background and perm tube gas spectra.



## Instrumentation

The ammonia ( $\text{NH}_3$ ) component of the unknown sample (Cylinder#: 5904173) was analyzed by chemiluminescence (Eco Physics, Model CLD 844). Delivery pressure (10 psig) to the analyzer was controlled by a high purity, stainless steel, two stage regulator dedicated to ammonia service (DIN14). The regulator was purged for one hour, at a sample gas flow rate of approximately 300 mL/min, before data analysis was conducted. From this sample flow an analysis range was established based on the nominal amount-of-substance fraction from the cylinder. The analyzer was purged (at a flow of approximately 300 mL/min) for five minutes before sample data was collected.

## Calibration method and value assignment

Six calibration curves were produced (see table 1), from the standards that were prepared by use of the PDS for the submitted CCQM-K117 sample in the range of 10-15  $\mu\text{mol/mol}$ . The CCQM-K117 submitted sample was used as the analytical control for the curves. The ammonia amount-of-substance fraction for the submitted CCQM-K117 sample was predicted from the calibration curves.

Sample selection of control or the on-demand standard (from the PDS) was achieved by using a Computer Operated Gas Analysis System (COGAS). This COGAS was configured so that the control was always flowing as either 300 mL/min to the analyzer (when the standard from the PDS flowed to vent) or 100 mL/min to vent (when the standard from the PDS was flowing to the analyzer). The analytical sequence was control, standard 1, standard 2, control, standard 3, et cetera until all six standards had been bracketed by the control. Each data point is an average of 60 readings taken at 1s intervals with 6 replicate measurements recorded for each.

The sequence was repeated six times with the order of the standards being randomized in each set collected in the same manner to give six independent curves from which the amount-of-substance fraction could be determined.

Each analytical sequence of control, standard, standard, control was corrected for linear instrument drift by using equation 3. The corrected instrument response for each control in the sequence was then ratioed to each sample response in the sequence (Eq. 4).

$$A = C_{R1} + \frac{(C_{R2} - C_{R1})}{(N - 1)} \cdot (n - 1) \quad (\text{Eq. 3})$$

A	Control Drift Correction ( $\mu\text{mol/mol}$ )
$C_{R1}$	Average of repeat responses Control Response 1 ( $\mu\text{mol/mol}$ )
$C_{R2}$	Average of repeat responses Control Response 2 ( $\mu\text{mol/mol}$ )
N	Number of Samples in sequence
n	Sample number in sequence

$$r = \frac{S_{Ri}}{A} \quad (\text{Eq. 4})$$

r	Ratio
$S_{Ri}$	Average $i^{\text{th}}$ Sample Response ( $\mu\text{mol/mol}$ )
A	Control Drift Correction ( $\mu\text{mol/mol}$ )

The average flow was also calculated for each sample response and was then converted to a molar flow volume using equation 5.

$$\dot{n}_n = \frac{Q}{v_m} \quad (\text{Eq. 5})$$

$\dot{n}_n$	Molar Flow for associated sample number in sequence ( $\text{mmol min}^{-1}$ )
Q	Average Flow ( $\text{mL min}^{-1}$ )
$V_m$	Molar Volume ( $\text{L mol}^{-1}$ )

The amount-of-substance fraction for each on demand standard was then calculated utilizing equation 6.

$$C = \left( \frac{q_m}{\dot{n}_n} \right) \cdot 1000 \quad (\text{Eq. 6})$$

C	Amount-of-substance fraction ( $\mu\text{mol/mol}$ )
$q_m$	Perm Rate ( $\mu\text{mol min}^{-1}$ )
$\dot{n}$	Molar Flow ( $\mu\text{mol min}^{-1}$ )
n	Sample number in sequence

The resulting data was then analyzed using the NIST GenLine program, which is an ISO 6143-compliant generalized least squares regression. The average ratio and standard error were plotted on the x-axis and the gravimetric amount-of-substance fraction and uncertainty were

plotted on the y-axis for each on demand standard amount-of-substance fraction. In each case, all PSMs passed the u-test.

The ammonia amount-of-substance fraction for the submitted CCQM-K117 sample was determined for a response ratio of 1.0000 in equation 7, using the A and B values from each set of curve data from table 1. The NIST assigned value for the CCQM-K117 sample was then calculated by generating one amount-of-substance fraction response from a linear fit curve by combining all curve data points in one final curve giving a combined value assignment (table 2).

$$f(r) = A * r + B \quad (\text{Eq. 7})$$

f(r)	Predicted Concentration ( $\mu\text{mol/mol}$ )
r	Response ratio
A	Slope
B	y-intercept

**Table 1:** Individual Ammonia Calibration Curves. The stated uncertainties are not expanded ( $k=1$ )

(range: 10.0 to 15.0  $\mu\text{mol/mol}$  in increments of 1.0  $\mu\text{mol/mol}$ ).  
Permeation tubes at 34°C and a permeation rate of 12  $\mu\text{g/min}$ .

Measurement	Slope (A)	Intercept (B)	Predicted Control ( $\mu\text{mol/mol}$ ) ( $k=1$ )
1	12.2455 $\pm$ 1.5408	1.3569 $\pm$ 1.4097	13.60 $\pm$ 0.21
2	12.2519 $\pm$ 1.4630	1.3524 $\pm$ 1.1885	13.60 $\pm$ 0.32
3	12.3157 $\pm$ 1.2953	1.3073 $\pm$ 1.1870	13.62 $\pm$ 0.19
4	12.4359 $\pm$ 1.0768	1.2611 $\pm$ 0.8787	13.70 $\pm$ 0.24
5	12.4096 $\pm$ 1.4992	1.2617 $\pm$ 1.3165	13.67 $\pm$ 0.25
6	12.4333 $\pm$ 1.9089	1.2715 $\pm$ 1.5777	13.70 $\pm$ 0.42

**Table 2:** Combined Ammonia Calibration Curve. The stated uncertainties are expanded ( $k=2$ )

(range: 10.0 to 15.0  $\mu\text{mol/mol}$  in increments of 1.0  $\mu\text{mol/mol}$ ).  
Permeation tubes at 34 °C and a permeation rate of 12  $\mu\text{g/min}$ .

CCQM - K117	Slope (A)	Intercept (B)	Predicted Amount of Substance Fraction ( $\mu\text{mol/mol}$ ) ( $k=2$ )
5904173	12.2783 $\pm$ 0.5433	1.3621 $\pm$ 0.4723	13.64 $\pm$ 0.20

## Uncertainty evaluation

All measured data and calculations for the final amount-of-substance fraction of ammonia have been reviewed for sources of systematic and random errors. The following uncertainties were considered contributors to the overall uncertainty of the assigned value of the sample.

The uncertainty in the permeation rate was determined using the LINEST function in excel (Eq. 8). Excel calculated this as the uncertainty of the slope of the line from the calculation of the permeation rate.

$$u(q_m) = \text{LINEST function slope uncertainty} \quad (\text{Eq. 8})$$

$q_m$	Perm Rate ( $\mu\text{g min}^{-1}$ )
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The uncertainty in the instrument response for the controls and samples of each analysis sequence was determined by taking the standard deviation of the total number of responses and dividing by the square root of the number of responses in the standard deviation (Eq. 9).

$$u(R) = \frac{s}{\sqrt{N}} \quad (\text{Eq. 9})$$

R	Instrument response
s	Standard Deviation
N	Number of responses in standard deviation

The uncertainty in the calculated ratio of the sample to control was also calculated. The uncertainty was found by taking the square root of the sum of the squares of the two bracketing controls and sample for which the ratio was being calculated (Eq. 10).

$$u_r = \sqrt{u^2(C_{R1}) + u^2(S_{Rn}) + u^2(C_{R2})} \quad (\text{Eq. 10})$$

$u_{C_{R1}}$	Uncertainty of repeat responses for control 1
$u_{C_{R2}}$	Uncertainty of repeat responses for control 2
$u_{S_{Rn}}$	Uncertainty of repeat responses for sample in the $n^{\text{th}}$ position

The uncertainty of the flow rates for each set of responses was also calculated in the same manner as the instrument response uncertainty, by taking the standard deviation of the total number of responses and dividing by the square root of the number of responses in the standard deviation (Eq. 11).

$$u(Q_n) = \frac{s}{\sqrt{N}} \quad (\text{Eq. 11})$$

$Q_n$	Average flow for response
s	Standard Deviation
N	Number of responses in standard deviation

As in the previous calculations the average flow uncertainty was then calculated as a molar flow uncertainty and was found by using equation 12.

$$u(\dot{n}_n) = \sqrt{u^2(Q) + u^2(v_m^{(\text{Eq. 12})})}$$

$\dot{n}_n$	Molar Flow for associated sample number in sequence ( $\mu\text{mol min}^{-1}$ )
Q	Average Flow ( $\text{mL min}^{-1}$ )
$V_m$	Molar Volume ( $\text{L mol}^{-1}$ )

The uncertainty of the predicted concentration for each of the on-demand standards generated by the permeation system was also calculated. This was done by taking the square root of the sum of the squares of the calculated molar flow rate uncertainty and the permeation rate uncertainty that was found with the LINEST function (Eq. 13).

$$u(C)_{\text{(Eq. 13)}} = \sqrt{u^2(\dot{n}_n) + u^2(q_m)}$$

$q_m$	Perm Rate ( $\mu\text{mol min}^{-1}$ )
$\dot{n}$	Molar Flow ( $\text{mmol min}^{-1}$ )
n	Sample number in sequence

Finally, the combined relative uncertainty was calculated from the ratio uncertainty and the uncertainty of the standard concentrations were put into the NIST Genline software with their respective values and the overall uncertainty was calculated when the linear least squares regression was run.

The relative expanded uncertainty,  $U$  is given by:

$$U = k * u$$

where  $k$  is the coverage factor and is equal to 2. The true value of the ammonia amount-of-substance fraction is asserted to lie in the intervals defined in Table 2, with a level of confidence of approximately 95 %. [2].

## References

- [1] International Organization for Standardization. International Standard ISO 6145-10:2002(E), Geneva.
- [2] *Guide to Expression of Uncertainty in Measurement*, ISBN 92-67-10188-9, 1st Ed. ISO, Geneva, Switzerland, 1993.

## Measurement report NPL

Cylinder number: 5904237

### Measurement #1

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
Ammonia	16/5/2019	14.04	3.01	4

### Measurement #2

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
Ammonia	17/5/2019	13.72	2.15	2

### Measurement #3<sup>7</sup>

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Standard deviation (% relative)	number of replicates
Ammonia	17/5/2019	13.73	2.14	2

## Results

Component	Date (dd/mm/yy)	Result ( $\mu\text{mol/mol}$ )	Expanded uncertainty ( $\mu\text{mol/mol}$ )	Coverage factor
Ammonia	17/05/2019	13.80	0.40	2

## Calibration standards

Two NPL primary reference materials (NPL PRMs) of nominally  $14 \mu\text{mol mol}^{-1}$  ammonia in nitrogen were prepared in accordance with ISO 6142-1 from one source of pure ammonia. The purity of the source of ammonia (gas phase) was analysed and determined to be  $> 99.999 \%$ . The NPL PRMs were prepared in BOC-supplied 10 litre cylinders that had undergone BOCs SPECTRA-SEAL passivation. Additionally, each cylinder was conditioned prior to use using an NPL proprietary treatment. Mixtures were prepared in one stage by dilution of nominally  $100 \mu\text{mol mol}^{-1}$  ammonia in nitrogen mixtures either by direct filling (NPL 2626) or by exchange dilution (NPL 2555) [Brewer et al., 2019], followed by the addition of nitrogen (direct filling). The nominally  $100 \mu\text{mol mol}^{-1}$  ammonia in nitrogen mixtures were prepared by dilution of nominally  $2000 \mu\text{mol mol}^{-1}$  ammonia in nitrogen mixtures, which were in turn prepared by dilution of a nominally  $20 \text{mmol mol}^{-1}$  ammonia in nitrogen mixture. Both mixtures were used in determining the amount fraction of the CCQM K117 mixture. The amount fractions of the two NPL PRMs (NPL 2626 and NPL 2555) are  $13.98 \pm 0.04$  and  $13.95 \pm 0.08 \mu\text{mol mol}^{-1}$  respectively (uncertainties from gravimetry only are stated as expanded ( $k=2$ ) uncertainties).

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<sup>7</sup> If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary

Purity tables for the ammonia and nitrogen used are provided below:

Table 1 – Ammonia purity table

<b>Component</b>	<b>Amount Fraction (<math>\mu\text{mol/mol}</math>)</b>	<b>Expanded Uncertainty (<math>\mu\text{mol/mol}</math>)</b>
NH <sub>3</sub>	999996.0	2.2
N <sub>2</sub>	1.5	1.8
H <sub>2</sub> O	0.5	0.6
C <sub>x</sub> H <sub>y</sub>	0.5	0.6
O <sub>2</sub>	0.5	0.6
CO	0.5	0.6
CO <sub>2</sub>	0.5	0.6

Table 2 – Nitrogen purity table

<b>Component</b>	<b>Amount Fraction (<math>\mu\text{mol/mol}</math>)</b>	<b>Expanded Uncertainty (<math>\mu\text{mol/mol}</math>)</b>
N <sub>2</sub>	999999.5	1.7
Ar	0.50	0.10
O <sub>2</sub>	0.005	0.005
H <sub>2</sub> O	0.0050	0.0040
C <sub>x</sub> H <sub>y</sub>	0.0050	0.010
CH <sub>4</sub>	0.0010	0.0020
H <sub>2</sub>	0.0010	0.0020
NO	0.0005	0.0005
SO <sub>2</sub>	0.0005	0.0005
CO	0.00030	0.00030

### Instrumentation

The amount fraction of ammonia was measured using an ABB AO2020 non-dispersive infrared spectrometer (NDIR) set to a measurement range of 0 – 100  $\mu\text{mol mol}^{-1}$ .

### Calibration method and value assignment

Before measuring any gas mixtures, the analyser response to the balance gas (nitrogen) was recorded. The analyser response to an NPL in house calibration standard (NPL 2626 or NPL 2555) was recorded for at least ten minutes followed by the CCQM-K117 mixture (cylinder 5904237) for a ten-minute period. This sequence was repeated between two and four times. Finally, the analyser response to the balance gas was recorded at the end of the sequence. To minimise the

effects of analyser drift, the mean analyser response to the balance gas before and after the comparison was used to apply a balance gas correction. The amount fraction of ammonia in the CCQM-K117 mixture was then determined by multiplying the ratio of the analyser response of the CCQM-K117 mixture and the calibration standard (both were corrected for the analyser response to the balance gas) by the gravimetric amount fraction of ammonia within the calibration standard used. Samples were introduced into the analyser at atmospheric pressure using a low volume gas regulator (excess flow was passed to a vent). Cylinders were maintained at a laboratory temperature of  $20 \pm 3^\circ\text{C}$ .

### Uncertainty evaluation

The ratio of the NDIR instrument response from the CCQM-K117 mixture ( $V_{unk} - V_{zero}$ ) and the NPL PRM ( $V_{std} - V_{zero}$ ) is calculated by:

$$r = \left( \frac{V_{unk} - V_{zero}}{V_{std} - V_{zero}} \right)$$

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

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

Where  $n$  is the number of ratios. The amount fraction of the ammonia in the CCQM-K117 mixture,  $x_u$ , is calculated by:

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

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

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

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

	<b>unit</b>	<b>example value</b>	<b>standard unc</b>	<b>Sensitivity coefficient</b>	<b>unc contribution</b>	<b>unc type</b>	<b>distribution</b>
$x_s$	umol/mol	14.00	0.24	0.98	0.23	A	normal
$\bar{r}$	-	0.98	0.01	14.00	0.18	A	normal
$x_u$	umol/mol	13.72					
$u(x_u)$	umol/mol	0.29					
$U(x_u)$	umol/mol	0.59					

The standard uncertainty of  $x_s$  includes both the uncertainties of the gravimetric preparation and of the subsequent analytical validation. The analytical validation dominates this uncertainty. For NPL 2626 this also includes an additional uncertainty associated with adsorptive loss of ammonia

to the cylinder wall during preparation. Our best estimate of this effect imposes a measurement uncertainty of 0.3  $\mu\text{mol/mol}$  (absolute) consistent with our previous work in CCQM-K46.

To obtain the final result for the comparison, a weighted average taking into account the associated uncertainties was determined from the three measurement results. The following table shows the calculation of the final results and its uncertainty.

	<b>unit</b>	<b>value</b>	<b>standard unc</b>	<b>Sensitivity coefficient</b>	<b>unc contribution</b>	<b>unc type</b>	<b>distribution</b>
$x_1$	umol/mol	14.04	0.42	0.33	0.12	A	normal
$x_2$	umol/mol	13.72	0.29	0.33	0.10	A	normal
$x_3$	umol/mol	13.73	0.29	0.33	0.10	A	normal
$x_f$	umol/mol	13.8					
$u(x_f)$	umol/mol	0.20					
$U(x_f)$	umol/mol	0.40					

Where  $x_1$ - $x_3$  is the measurement number and  $x_f$  is the final value of the amount fraction of ammonia in the CCQM-K117 mixture.

#### Reference

Brewer, P. J.; Brown, R. J. C.; Mussell Webber, E. B.; van Aswegen, S.; Ward, M. K. M.; Hill-Pearce, R. E.; Worton, D. R. Breakthrough in Negating the Impact of Adsorption in Gas Reference Materials. *Analytical Chemistry* **2019**, *91*, (8), 5310-5315. doi:10.1021/acs.analchem.9b00175.