International Comparison CCQM K46 – Ammonia in Nitrogen

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Field

Amount of substance

Subject

Ammonia in nitrogen

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Introduction

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 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 report describes the results of a key comparison for ammonia in nitrogen. The amount–of–substance fraction level of ammonia chosen for this key comparison is 30-50 µmol/mol. This key comparison aims to support CMC-claims for ammonia from 30 µmol/mol onwards.

Participants

Table 1 lists the participants in this key comparison.

Acronym	Country	Institute
CERI	JP	Chemicals Evaluation and Research Institute, Saitama, Japan
KRISS	KR	Korea Research Institute of Standards and Science, Daejeon,
		Republic of Korea
METAS	СН	Federal Office of Metrology, Wabern, Switzerland
VSL	NL	Van Swinden Laboratorium B.V., Delft, the Netherlands
NPL	UK	National Physical Laboratory, Teddington, Middlesex, United
		Kingdom
NIST	US	National Institute of Standards and Technology, Gaithersburg
		MD, United States of America
VNIIM	RU	D.I. Mendeleyev Institute for Metrology, St. Petersburg,
		Russia

Table 1: List of participants

Measurement standards

A set of mixtures was prepared gravimetrically by VSL. The mixtures were verified against a set of VSL PSMs and in addition validated by a dynamic method.

The pressure in the cylinders was approximately 80 bar; cylinders of 5 dm³ nominal were used. The amount-of-substance fractions as obtained from gravimetry and purity verification of the parent gases were supposed to be used as reference values. In due course of the key comparison, it turned out that the assigned amount fractions could not be regarded as the best realisation of SI, so that a consensus-based approach was developed, taking into consideration the small differences in the amount fractions as obtained from the preparation data.

The nominal amount-of-substance fraction was 30-50 μ mol/mol.

Measurement protocol

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

Schedule

The schedule of this key comparison was as follows:

February 2006	Draft protocol to participants
October 2006	Registration of participants
October 2006	Preparation of gravimetric mixtures + first verification measurement
November 2006	Second verification
December 2006	Third verification
January 2007	Shipment of cylinders to participating laboratories
May 15, 2007	Reports due to pilot laboratory
May 31, 2007	Cylinders due to pilot laboratory
June 2007	Final verification measurement

Mixture preparation

The intention was to use as reference values the ones based on gravimetry, and the purity verification of the parent gases. All mixtures underwent verification prior to shipping them to the participants. After return of the cylinders, they have been verified once more to reconfirm the stability of the mixtures.

In the preparation, the following four groups of uncertainty components have been considered:

- 1. gravimetric preparation (weighing process) $(x_{i,grav})$
- 2. purity of the parent gases ($\Delta x_{i,purity}$)
- 3. stability of the gas mixture ($\Delta x_{i,stab}$)
- 4. correction due to partial recovery of a component $(\Delta x_{i,nr})$

The amount of substance fraction $x_{i,prep}$ of a particular component in mixture *i*, as it appears during use of the cylinder, can now be expressed as

$$x_{i,prep} = x_{i,grav} + \Delta x_{i,purity} + \Delta x_{i,stab} + \Delta x_{i,nr}, \qquad (1)$$

The value obtained from equation (1) is sometimes referred to as "gravimetric value". Assuming independence of the terms in equation (1), the expression for the combined standard uncertainty becomes

$$u_{i,prep}^{2} = u_{i,grav}^{2} + u_{i,purity}^{2} + u_{i,stab}^{2} + u_{i,nr}^{2}$$
(2)

For the mixtures used in this key comparison, the following statements hold (for all components involved). First of all, the preparation method has been designed in such a way that

$$\Delta x_{i,nr} = 0, \tag{3}$$

and its standard uncertainty as well. Furthermore, long-term stability study data has shown that

$$\Delta x_{i,stab} = 0, \tag{4}$$

and its standard uncertainty is estimated from the validation measurements.

Validation measurements

After preparation the mixtures have been validated four times over a period of four months to evaluate the mixture stability. After return the mixtures have again been analysed to control the stability. Mixtures were analysed by a calibrated photo-acoustic analyzer. Calibration was performed in the range from 30-40 μ mol/mol using 2 PSMs of 30 μ mol/mol and 2 PSMs of 40 μ mol/mol. In Table 2 the results of the 4 measurements are summarized. In figure 1, the results are visualized calculated as recovery being the results of analysis divided by the gravimetric value.

Figure 2 shows the mean value of the 4th validation measurements.

cylinder number	Preparation	October analysis	November analysis	December analysis	January analysis
D751992	33.929	33.9	33.8	33.9	33.6
D752114	33.983	34.2	34.2	34.2	34.1
D751916	34.028	34.2	34.1	34.0	34.0
D751986	34.057	34.0	33.8	33.6	33.6
D751946	34.091	34.0	33.8	33.7	33.9
D751929	34.104	34.2	34.1	33.7	34.2
D751936	34.113	34.0	34.1	33.6	34.0

Table 2: Validation results (µmol mol⁻¹)



Figure 1: Results of 4 validation measurements



Figure 2: Mean values of 4 validation measurements

As an independent extra validation step, a dynamic preparation method was set-up to validate the gravimetric values of the 10 mixtures. For this dynamic method (ISO 6145-4 [13]) a gas tight syringe was filled with a 50 mmol/mol NH₃ in N₂ mixture and injected in a calibrated flow of nitrogen. The injection was controlled by a motor driven injector. The injection volume per time was calibrated with a stable gas component (carbon monoxide). By repeated filling of the syringe 6 mixtures were



prepared in the calibrated range of the photo-acoustic analyser. The results of the 4th analysis are given in figure 3.

Figure 3: Results of 4th analysis including 6 dynamically prepared mixtures

After return of the cylinders a final analysis was performed to check the stability. The results were compared to the initial validation analysis and visualised in figure 4.



Figure 4: Results before and after shipment of the cylinders

Measurement methods

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

Laboratory	Calibration	Traceability	Measurement technique
CERI	ISO 6143	3 CERI PSMs	ND-IR
KRISS	Single point	KRISS CRM	ND-IR
METAS	ISO 6143	Permeation system; dilution of KC mixture to 550 nmol/mol	Photo acoustic IR
VSL	ISO 6143	9 VSL PSMs	Photo acoustic IR
NPL	Bracketing	2 NPL PSMs	Photo acoustic IR
NIST	ISO 6143	Permeation system; multiple permeation tubes	Chemiluminescence
VNIIM	OLS ¹	Own standards	UV absorption

Table 3: Summary of calibration methods and metrological traceability

Results

This comparison involves N = 7 participant laboratories using three methods of measurement, static gravimetry (method 1), dynamic gravimetry (method 2) and static gravimetry with pre-bleaching (method 3). The laboratories that apply method *j* are termed laboratory group *j*.

The results are given in table 4.

Table 4: Results submitted in this key comparison

Mixture	Laboratory	x_i^{prep}	$u(x_i^{\text{prep}})$	x_i^{lab}	$U(x_i^{\text{lab}})$	k _{lab}	Method
		µmol mol ⁻¹	µmol mol ⁻¹	µmol mol ⁻¹	µmol mol ⁻¹		
D751916	VSL	34.028	0.201	33.8	0.7	2	1
D751929	NPL	34.104	0.201	34.52	0.99	2	1
D752114	VNIIM	33.983	0.201	33.7	0.5	2	1
D751986	METAS	34.057	0.201	32.27	0.36	2	2
D751992	NIST	33.929	0.201	32.37	0.28	2	2
D751936	KRISS	34.113	0.201	32.91	0.62	2	3
D751946	CERI	34.091	0.201	32.81	0.38	2	3

where

 x_i^{prep} amount of substance fraction, from gravimetric preparation

 u_i^{prep} standard uncertainty associated with x_i^{prep} accounting for stability $(u_i^{\text{stab}} = 0.2 \ \mu\text{mol mol}^{-1})$

 x_i^{lab} measured value for laboratory *i*

 $U(x_i^{\text{lab}})$ expanded uncertainty associated with x_i^{lab}

Ordinary least squares

1



Figure 5: Results and key comparison reference value

The data can be specified as follows

$$(x_i, u(x_i)), i = 1, ..., N$$
, where $x_i = x_i^{\text{lab}} - x_i^{\text{prep}}$ and $u^2(x_i) = u^2(x_i^{\text{lab}}) + u^2(x_i^{\text{prep}})$

The standard uncertainty associated with x_i^{lab} is obtained in the usual way by dividing the expanded uncertainty by the coverage factor *k*.

The data are shown in figure 5. On the *y*-axis, the differences with respect to the assigned amount–of–substance fraction on the basis of mixture preparation are given.

Model for the key comparison

Each x_i relating to a particular method estimates the sum of the KCRV and a method-related bias quantity. There are four parameters in the model: the quantity of which the KCRV is a best estimate and three method bias quantities.

There are only three independent parameters since an arbitrary constant can be added to the KCRV and subtracted from the bias quantities without essentially changing the solution. This lack of independence can be resolved by introducing a constraint. Here the sum of the biases is chosen to be zero.

The value component of the i^{th} degree–of–equivalence is taken as x_i minus the calculated KCRV. Correlations are taken into account when evaluating the uncertainty components of the degrees–of–equivalence.

The procedure can be summarised as follows. Given are measured values x_i and associated standard uncertainties $u(x_i)$, i = 1, ..., 7, and the knowledge that laboratories in group 1 (i = 1, 2, 3), group 2 (i = 4, 5) and group 3 (i = 6, 7) have different biases.

1. Form weights

$$w_i = u^{-2}(x_i), \quad i = 1, ..., 7.$$

2. Calculate weighted means of the three groups:

$$v_{1} = (w_{1}x_{1} + w_{2}x_{2} + w_{3}x_{3})/(w_{1} + w_{2} + w_{3}),$$

$$v_{2} = (w_{4}x_{4} + w_{5}x_{5})/(w_{4} + w_{5}),$$

$$v_{3} = (w_{6}x_{6} + w_{7}x_{7})/(w_{6} + w_{7}).$$

and evaluate the associated standard uncertainties $u(v_1)$, $u(v_2)$, $u(v_3)$ using

$$\frac{1}{u^{2}(v_{1})} = w_{1} + w_{2} + w_{3},$$

$$\frac{1}{u^{2}(v_{2})} = w_{4} + w_{5},$$

$$\frac{1}{u^{2}(v_{3})} = w_{6} + w_{7}.$$

- 3. Test the consistency of the measured values with respect to the relevant weighted means [14].
- 4. Calculate the (overall) KCRV and evaluate the associated standard uncertainty $u(x_{ref})$ using

$$x_{\rm ref} = (v_1 + v_2 + v_3)/3$$
,

and

$$u^{2}(x_{\rm ref}) = \left[u^{2}(v_{1}) + u^{2}(v_{2}) + u^{2}(v_{3})\right]/9.$$

5. Calculate biases for the three groups:

$$s_1 = v_1 - x_{\text{ref}}$$
, $s_2 = v_2 - x_{\text{ref}}$, $s_3 = v_3 - x_{\text{ref}}$,

and evaluate the associated standard uncertainties $u(s_1)$, $u(s_2)$, $u(s_3)$ using

$$u^{2}(s_{1}) = \left[4u^{2}(v_{1}) + u^{2}(v_{2}) + u^{2}(v_{3})\right]/9,$$

$$u^{2}(s_{2}) = \left[u^{2}(v_{1}) + 4u^{2}(v_{2}) + u^{2}(v_{3})\right]/9,$$

$$u^{2}(s_{1}) = \left[u^{2}(v_{1}) + u^{2}(v_{2}) + 4u^{2}(v_{3})\right]/9.$$

6. Form the degrees–of–equivalence $(d_i, 2u(d_i)), i = 1, ..., 7$, using

$$d_{i} = x_{i} - x_{ref}, \ u^{2}(d_{i}) = u^{2}(x_{i}) + \left[-5u^{2}(v_{1}) + u^{2}(v_{2}) + u^{2}(v_{3})\right]/9,$$

for i = 1, 2, 3,

$$d_i = x_i - x_{ref}, \ u^2(d_i) = u^2(x_i) + [u^2(v_1) + -5u^2(v_2) + u^2(v_3)]/9,$$

for i = 4, 5, and

$$d_i = x_i - x_{ref}, u^2(d_i) = u^2(x_i) + [u^2(v_1) + u^2(v_2) - 5u^2(v_3)]/9,$$

for i = 6, 7.

The results from applying the above procedure are given below. The data and weights are given in table 5.

Mixture	Lab	x	u(x)	w	Method
		µmol mol ⁻¹	µmol mol ⁻¹	µmol ⁻² mol ²	
D751916	VSL	-0.228	0.40	6.14	1
D751929	NPL	0.416	0.53	3.50	1
D752114	VNIIM	-0.283	0.32	9.72	1
D751986	METAS	-1.787	0.27	13.74	2
D751992	NIST	-1.559	0.24	16.68	2
D751936	KRISS	-1.203	0.37	7.33	3
D751946	CERI	-1.281	0.28	13.08	3

Table 5: Key comparison data and assigned weights

The method means (v_i) and biases (s_i) are given in table 6.

 Table 6: Method means and biases

Method		v_j	$u(v_j)$	S_j	$u(s_j)$	χ^2
		µmol mol ⁻¹	µmol mol ⁻¹	µmol mol ⁻¹	µmol mol ⁻¹	
	1	-0.14	0.23	0.88	0.18	1.33
	2	-1.66	0.18	-0.64	0.16	0.39
	3	-1.25	0.22	-0.23	0.18	0.03

The values for χ^2 are in all cases smaller than the critical values with a probability of 0.05 and 2 (method 1) respectively 1 degree of freedom (methods 2 and 3). The results are consistent with the method means.

The reference value is $-1.018 \ \mu\text{mol mol}^{-1}$. The associated standard uncertainty is 0.122 $\mu\text{mol mol}^{-1}$. The χ^2 value for the method means is 28.7 and exceeds by far the critical value with a probability of 0.05 and 2 degrees of freedom ($\chi^2_{\text{crit}} = 5.99$).

The degrees-of-equivalence are given in table 7 and shown in figure 6.

Table '	7:	Degrees-of-equivalence	
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Mixture	Lab	d_i	$u(d_i)$	$U(d_i)$
		µmol mol ⁻¹	µmol mol ⁻¹	µmol mol ⁻¹
D751916	VSL	0.790	0.38	0.757
D751929	NPL	1.434	0.52	1.031
D752114	VNIIM	0.735	0.29	0.577
D751986	METAS	-0.769	0.26	0.513
D751992	NIST	-0.541	0.23	0.460
D751936	KRISS	-0.185	0.34	0.689
D751946	CERI	-0.263	0.24	0.484



Figure 6: Degrees-of-equivalence relative to the KCRV

Discussion

The evaluation of the data in this key comparison had to be revisited. In the protocol of this key comparison, it was envisaged to use the data from static gravimetric preparation as key comparison reference value (KCRV), which had been successful in a preceding comparison between NPL, VNIIM and VSL. The experimental work undertaken prior to releasing the gas mixtures for this key comparison, including the independent validation through the syringe injection method, seemed to confirm the amount fractions assigned by the procedures described in ISO 6142 [7]. In retrospect, it can only be concluded that these experiments were not sufficiently accurate to take away all doubts concerning the validity of the preparation data.

The stratification of the data along the lines of the three different methods and subsequent data evaluation highlights that the three methods used provide different results. Within a stratum, the data submitted are nicely consistent, but between strata the differences are substantial.

The biggest differences are observed between the static gravimetric preparation with and without prebleaching of the cylinder. In a supplementary report [10], the passivation process is described to be carried out with 500 μ mol mol⁻¹ ammonia in nitrogen. After evacuation with a pressure below 5 Pa, the cylinders are used for preparing mixtures of ammonia in the range 100 μ mol mol⁻¹ down to 20 μ mol mol⁻¹. The quantity of residual gas is so small, that it cannot explain the difference between the results of method 1 (gravimetric preparation without pre-bleaching) and method 3.

Adsorption effects of ammonia can have a more profound effect on the amount fraction of gas as sampled from the cylinder. These effects impact method 1, where an apparent loss can occur as well as method 3, where ammonia adsorbed to the wall can be released. Additional work by CERI [11] confirms the difference between methods 1 and 3 (table 8). It is important to note that the cylinders without treatment are not of the same type as the ones used in this key comparison.

	Pre-	x_i^{prep}	x_i^{anal}	x_i^{anal}	x_i^{anal}
	treatment	µmol mol ⁻¹	µmol mol ⁻¹	µmol mol ⁻¹	µmol mol ⁻¹
time			0 days	3 days	3 weeks
CPB-18498	none	34.85	32.04	30.9	30.68
			-8.06%	-11.33%	-11.97%
CPB-18499	none	34.85	30.28	28.75	28.41
			-13.11%	-17.50%	-18.48%
		x_i^{prep}	x_i^{anal}	x_i^{anal}	x_i^{anal}
time			2 days	1 week	3 weeks
CPB-18498	passivated	35.26	35.08	34.95	34.99
	_		-0.51%	-0.88%	-0.77%
CPB-18499	passivated	34.89	34.7	34.53	34.59
	_		-0.54%	-1.03%	-0.86%

 Table 8: Supplementary results static gravimetric preparation [11]

The results of CERI do not provide independent proof of its validity; the PSMs used for calibration are likely to be affected in the same manner as the mixtures prepared in the passivated cylinders. The losses observed in the untreated cylinders are larger than the discrepancy between methods 1 and 3 in this key comparison, which may be due to the different cylinder wall treatments performed by the cylinder manufacturers.

Further work by the coordinating laboratory has demonstrated equivalence, within the respective uncertainties, of method 1 with the continuous injection method (ISO 6145-4 [13]) [12]. The implementation of the syringe method was validated using carbon monoxide (figures 7 and 8) [12].



Figure 7: Comparison of syringe injection with gravimetry at 80 µmol/mol CO in N₂ mixtures [12]



Figure 8: Comparison of syringe injection with gravimetry at 40 µmol/mol CO in N₂ mixtures [12]

The results show the validity of the results of the syringe method with an expanded uncertainty of 1% relative. The comparisons between gravimetry and the syringe method for ammonia are shown in figures 9 and 10.



Figure 9: Comparison of syringe injection with method 1 at 300 µmol/mol NH₃ in N₂ [12]





The setup of the validation experiments precludes that effects of, e.g., wall adsorption are fully propagated. Therefore, it can be said that method 1 is supported by the continuous injection method (ISO 6145-4 [13]). This conclusion was the basis for the proposal of CCQM-K46 in the first place.

After the first presentation of the results of this key comparison, NIST stated that the cylinder has a side connection (DIN-1) that is different than their usual size. This means that the pressure regulator used for this comparison was not of the preferred type. VSL has sent one of their regulators to NIST.

With this pressure regulator NIST observed a smaller discrepancy (-3% relative instead of -4.6% relative, see table 4) with respect to the value from preparation for the key comparison mixture.

The results of the syringe method and method 1 are however not consistent with methods 2 and 3. All four methods are designed in a way that they should be able to deliver metrologically traceable results. This key comparison demonstrates that notwithstanding the strong belief about the validity of the results and methods with the participants, there are serious discrepancies in the measurement data. This discrepancy is clearly reflected in the value of χ^2 computed at the level of the KCRV. The value of χ^2 exceeds by far the critical value at the 5% level. Hence, the consistency criterion as defined for a weighted mean is violated [14].

HFTLS

This key comparison aims to support CMC claims for ammonia in nitrogen or air in the range from 30 μ mol/mol to 100 μ mol/mol.

Conclusions

The results in this key comparison do not show true consensus. Three different methods have been used, which give results that are discrepant. When grouped in accordance with the employed methods, the data are consistent. This key comparison cannot resolve the observed differences between the laboratories. Further experimental work is needed.

As KCRV the mean of the three methods is used. In its uncertainty, no allowance is made for the observed biases. With respect to the KCRV, only two laboratories report consistent results: CERI and KRISS.

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Annex A: Justification of procedure for evaluating this key comparison

The model is given by

$$\begin{split} X_i &= X_{\rm ref} + S_1, \quad i = 1, 2, 3 \quad ({\rm Group \ 1}), \\ X_i &= X_{\rm ref} + S_2, \quad i = 4, 5 \quad ({\rm Group \ 2}), \\ X_i &= X_{\rm ref} + S_3, \quad i = 6, 7 \quad ({\rm Group \ 3}), \end{split}$$

with

 X_i quantity for which x_i is the measured value and $u(x_i)$ the associated standard
uncertainty provided by laboratory i, X_{ref} quantity for which the KCRV is the best estimate,
bias quantities for methods 1, 2 and 3.

Reference value(s) and bias quantities

Make the changes of variables

$$V_1 = X_{\text{ref}} + S_1, V_2 = X_{\text{ref}} + S_2, V_3 = X_{\text{ref}} + S_3.$$
(5)

The model becomes

$$X_i = V_1$$
, (Group 1),
 $X_i = V_2$, (Group 2),
 $X_i = V_3$, (Group 3).

Because each of these three sub-models has the same structure as a model for a key comparison in which each laboratory measures a single, stable artefact, each V_k can be regarded as a reference value for the *k*th group of laboratories.

A best estimate v_k of V_k is the weighted mean of the values x_i in group k. The standard uncertainty $u(v_k)$ associated with v_k can be established as described in reference [14]. As the groups are mutually independent there is no correlation associated with the v_k .

Summing expressions (5),

$$V_1 + V_2 + V_3 = 3X_{\text{ref}} + S_1 + S_2 + S_3.$$
(6)

As a result of the resolving constraint, which can be written as

$$S_1 + S_2 + S_3 = 0,$$

expression (6) gives

$$X_{\rm ref} = (V_1 + V_2 + V_3)/3.$$
⁽⁷⁾

Hence the KCRV x_{ref} and its associated standard uncertainty $u(x_{ref})$ are given by

$$x_{\text{ref}} = (v_1 + v_2 + v_3)/3, \ u^2(x_{\text{ref}}) = [u^2(v_1) + u^2(v_2) + u^2(v_3)]/9.$$

Bias quantities

Using expressions (5) and (7), the bias quantity for method 1, with similar expressions for methods 2 and 3, is

$$S_1 = V_1 - X_{\text{ref}} = (2V_1 - V_2 - V_3)/3,$$

and so the method biases s_1 , s_2 and s_3 and the associated standard uncertainties $u^2(s_1)$, $u^2(s_2)$ and $u^2(s_3)$ are given by

$$s_{1} = v_{1} - x_{ref}, \ u^{2}(s_{1}) = \left[4u^{2}(v_{1}) + u^{2}(v_{2}) + u^{2}(v_{3})\right]/9,$$

$$s_{2} = v_{2} - x_{ref}, \ u^{2}(s_{2}) = \left[u^{2}(v_{1}) + 4u^{2}(v_{2}) + u^{2}(v_{3})\right]/9,$$

$$s_{3} = v_{3} - x_{ref}, \ u^{2}(s_{1}) = \left[u^{2}(v_{1}) + u^{2}(v_{2}) + 4u^{2}(v_{3})\right]/9.$$

Degrees of equivalence

Take the degrees-of-equivalence with respect to the overall KCRV:

$$D_i = X_i - X_{\text{ref}}$$

Accordingly, the degrees-of-equivalence can be expressed as

$$(d_i, 2u(d_i)), \ d_i = x_i - x_{ref}, \ u^2(d_i) = u^2(x_i - x_{ref}).$$
 (8)

Now, using expression (7),

$$X_{i} - X_{\text{ref}} = X_{i} - (V_{1} + V_{2} + V_{3})/3.$$
⁽⁹⁾

The quantities on the right-hand side of expression (9) are mutually independent apart from X_i and V_k , where k = 1, 2 or 3 as appropriate. Accordingly, for group 1,

$$u^{2}(x_{i} - x_{ref}) = u^{2}(x_{i} - v_{1}/3) + u^{2}(v_{2})/9 + u^{2}(v_{3})/9.$$
(10)

The first term on the right-hand side of expression (10) can be written as $u^2(x_i - \theta v_1)$ with $\theta = 1/3$. When $\theta = 1$, this term is identical in form to that in expression (8), used in evaluating the uncertainty component of the degree–of–equivalence for laboratory *i*. By a similar analysis to that in appendix C of reference [1], a modest generalization of that expression is

$$u^{2}(x_{i} - \theta v_{1}) = u^{2}(x_{i}) - \theta(2 - \theta)u^{2}(v_{1}).$$

For the case in hand ($\theta = 1/3$),

$$u^{2}(x_{i}-v_{1}/3) = u^{2}(x_{i})-5u^{2}(v_{1})/9$$

So, applying this result to expression (10) and extending to all groups,

$$u^{2}(d_{i}) = u^{2}(x_{i}) - 5u^{2}(v_{1})/9 + u^{2}(v_{2})/9 + u^{2}(v_{3})/9 \text{ (Group 1),}$$

$$u^{2}(d_{i}) = u^{2}(x_{i}) + u^{2}(v_{1})/9 - 5u^{2}(v_{2})/9 + u^{2}(v_{3})/9 \text{ (Group 2),}$$

$$u^{2}(d_{i}) = u^{2}(x_{i}) + u^{2}(v_{1})/9 + u^{2}(v_{2})/9 - 5u^{2}(v_{3})/9 \text{ (Group 3).}$$

Annex B: Measurement report NPL

Report from the National Physical Laboratory CCQM-K46 (Ammonia in nitrogen)

Reference Method

The CCQM-K46 standard (D751929) was compared with two NPL gravimetric standard using an Innova 1301 Gas Analyser based on photoacoustic absorption.

Sample Handling

Cylinders were connected directly to a gas sampling system (with no regulators) and purged prior to connection to the gas analyser via 1/8" 316L stainless steel tubing. The configuration of the sampling system and analyser are shown below:



Data Processing

Comparisons were made by completing the following sequence:

$$A_1 - B_1 - A_2 - B_2 - A_3 - B_3 - A_4$$

Where 'A_n' is the measurement of the amount fraction of NH_3 in the NPL standard and 'B_n' is the measurement of the amount fraction of NH_3 in the CCQM-K46 standard and 'n' is the number of repeats of each measurement made of an individual standard. The result of each of these measurements (A_n and B_n) was derived from the average of four individual measurements.

A value for the amount fraction of NH_3 in the CCQM-K46 standard was then calculated as follows:

$$\frac{\sum_{1}^{3} x. \frac{2B_{n}^{r}}{A_{n}^{r} + A_{n+1}^{r}}}{3}$$

Where A_n^r is the result from measurement A_n of the amount fraction of NH₃ in the NPL standard and B_n^r is the result from measurement B_n of the amount fraction of NH₃ in the CCQM-K46 standard and x is the reference amount fraction of NH₃ in the NPL standard (from gravimetry).

NPL Standards

The two standards used for this inter-comparison are listed below. In each case Air Products VLSI NH3 was used. The principal impurities specified by the manufacturer are (in μ mol/mol): N2(3), H20 (2), CO (1), CO2 (1), O2 (0.5) and Ar (0.5).

NPL No 30636

Component	Supplier	Grade	Amount fraction (µmol/mol)
NH ₃	Air Products	VLSI	34.37
N_2	Air Products	BIP+	Balance

The standard was prepared in a 10 litre aluminium cylinder supplied by Scott Gases, which had been treated using the Aculife III process. The standard was produced by the dilution of an appropriate quantity of a standard (#30588), which had itself been prepared from a standard at approximately 5 % prepared using "traditional" cascade dilution techniques.

30588	X	U(x)
'Ar'	4.991	14.401
'CO'	0.027	0.010
'CO2'	0.027	0.010
'H2O'	0.024	0.010
'CxHy'	0.050	0.030
'N2'	997925.822	14.495
'CH4'	0.076	0.009
'O2'	0.001	0.000
'NH3'	2000.172	1.879

30636	X	<i>U</i> (<i>x</i>)
'Ar'	5.000	14.184
'CO'	0.025	0.010
'CO2'	0.025	0.010
'H2O'	0.020	0.010
'CxHy'	0.050	0.029
'N2'	999891.499	14.184
'CH4'	0.075	0.009
'O2'	0.000	0.000
'NH3'	34.363	0.060

NPL No 30575

Component	Supplier	Grade	Amount fraction
			(µmol/mol)
NH ₃	Air Products	VLSI	39.98
N2	Air Products	BIP+	Balance

The standard was prepared in a 10-litre aluminium cylinder supplied by Scott Gases, which had been treated using the Aculife III process. The standard was produced using a single step "loop injection" method (of 38.02g + 0.1g). The cylinder was rolled for 1 hour after preparation and prior to analysis in order to ensure the homogeneity of the standard.

30575	X	$U(\mathbf{x})$
'Ar'	5.000	14.429
'CO'	0.025	0.010
'CO2'	0.025	0.010
'H2O'	0.020	0.010
'CxHy'	0.050	0.030
'N2'	999885.888	14.429
'CH4'	0.075	0.009
'02'	0.000	0.000
'NH3'	39.975	0.105

The single-step loop injection method used to prepare this standard was a departure from the traditional cascade dilution methods that have been employed at NPL and were used previously for the preparation of sub 100 μ mol/mol NH₃ standards. NPL 30575 was compared with NPL 30577 (39.97 μ mol/mol), a standard prepared using traditional dilution methods, in order to validate the new approach. The two standards were compared and found to agree within the estimated uncertainties of their gravimetric values (see section entitled 'Results').

Uncertainty in the Reference Values

The dominant uncertainty in the reference values of the gravimetric NH3 standards is that due to loss of material to the walls of the cylinder. Our best estimate of this effect imposes a measurement uncertainty of 1% (relative).

Results

Validation of single-step preparative method (NPL 30577 vs NPL 30575)

	Cylinder number									
Measurement number	30577	30575	30577	30575	30577	30575	30577			
1	250.4	245.6	237.6	230.1	220.4	258.4	246.0			
2	242.8	224.4	232.7	241.6	219.0	239.5	247.7			
3	234.8	224.5	229.8	241.3	228.9	237.8	242.7			
4	238.7	227.4	238.2	240.0	228.3	241.8	238.2			
5	248.1	227.2	233.1	235.6	230.0	237.5	233.3			
1	248.1	258.8	236.1	235.4	244.0	250.0	235.9			
2	244.2	243.5	235.0	235.9	237.0	236.8	232.8			
3	244.2	237.6	232.8	231.6	235.7	238.8	233.3			
4	244.0	238.9	237.8	230.7	231.1	233.6	230.9			
5	243.2	234.5	237.0	229.2	232.5	236.4	230.1			
Mean	243.90	238.63	235.65	231.85	234.08	236.40	231.78			
Std dev	0.476	3.738	2.235	2.876	2.740	2.142	1.522			
% std dev	0.195	1.566	0.949	1.240	1.171	0.906	0.657			
								AVG	STDEV	% RSD
Concentrations calculated		39.78		39.46		40.57		39.93	0.47	1.17
by backeting										
Measured amount fraction 30575	39.93									
Gravimetric amount fraction 30575	39.98									
% difference	-0.13									
Dicarded data (instrument purge)										

Results of analyses NPL 30575 vs D751929(CCQM)

	Cylinder number									
Measurement number	NPL	CCQM	NPL	CCQM	NPL	CCQM	NPL			
1	181.5	233.6	184.1	177.3	180.2	147.0	200.8			
2	181.5	204.5	207.3	177.2	195.5	153.8	220.1			
3	184.9	191.6	205.5	163.5	209.4	158.1	223.9			
4	184.3	185.2	199.3	168.1	216.4	175.2	210.1			
5	183.6	193.6	210.5	181.3	203.4	181.5	205.1			
1	210.8	172.8	237.8	215.4	231.1	166.1	213.4			
2	204.3	183.7	224.4	223.8	198.4	192.8	214.5			
3	210.6	186.1	217.7	200.0	212.5	180.9	209.0			
4	211.8	178.7	214.8	184.1	209.1	171.8	211.7			
5	211.9	183.7	218.6	181.3	197.4	166.1	203.8			
Mean	209.65	183.05	218.88	182.70	204.35	177.90	209.75			
Std dev	3.615	3.113	4.024	10.086	7.587	11.654	4.558			
% std dev	1.724	1.701	1.839	5.520	3.713	6.551	2.173			
								AVG	STDEV	% RSD
Concentrations calculated		34.16		34.52		34.35		34.34	0.15	0.430
by backeting										
Start pressure D751929 (bar)	71.36									
Finish pressure D751929 (bar)	48.58									
Dicarded data (instrument purge)										

Results of analyses NPL 30636 vs D751929(CCQM)

	Cylinder number									
Measurement number	NPL	CCQM	NPL	CCQM	NPL	CCQM	NPL			
1	174.2	194.5	176.0	170.4	182.7	158.8	197.2			
2	186.5	184.0	188.6	186.6	174.2	163.5	193.5			
3	193.8	184.9	178.0	185.2	176.2	171.5	191.9			
4	189.9	184.2	172.6	184.5	179.3	175.9	192.4			
5	186.5	183.4	176.3	184.7	173.7	173.6	189.6			
1	165.1	195.1	154.2	182.0	191.1	161.1	198.0			
2	181.8	181.6	172.3	184.4	179.7	178.9	192.0			
3	185.6	178.2	173.9	182.4	177.8	184.7	186.5			
4	180.1	184.5	178.2	173.5	178.9	186.6	183.9			
5	176.6	184.7	183.5	174.4	180.0	186.5	183.9			
Mean	181.03	182.25	176.98	178.68	179.10	184.18	186.58			
Std dev	3.740	3.049	5.013	4.899	0.983	3.623	3.819			
% std de∨	2.066	1.673	2.833	2.742	0.549	1.967	2.047			
								AVG	STDEV	% RSD
Concentrations calculated		34.99		34.49		34.62		34.70	0.21	0.612
by backeting										
Start pressure D751929 (bar)	48.58									
Finish pressure D751929 (bar)	31.31									
Dicarded data (instrument purge)										

Summary of results

Measurement	Measured mole
	fraction
	[µmol/mol]
1	34.16
2	34.52
3	34.35
4	34.99
5	34.49
6	34.62
Mean	34.52
Standard deviation	0.28

Estimation of Measurement Uncertainty

Source of uncertainty	
Analytical repeatability	$\left(\frac{1}{\sqrt{6}} \cdot 0.28\right)^2$
Non-linearity of analyser	0.2^{2}
Uncertainty in reference values due to gravimetry and stability	0.3 ²
Standard uncertainty (<i>k</i> =1)	$\sqrt{\left(\frac{0.28}{\sqrt{6}}\right)^2 + 0.2^2 + 0.3^2} = 0.49$
Expanded uncertainty (<i>k</i> =2)	0.99

Final result for D751929

34.52 μ mol/mol ± 0.99 μ mol/mol (k=2)

Annex C: Measurement report KRISS

Report Form CCQM-K46 Ammonia in nitrogen

Laboratory name: KRISS (written by Gwi Suk Heo) Cylinder number: D751936 Initial inner pressure of Cylinder as received : 1100 PSIG Date of reception : March 1, 2007 Name of the contact person : Gwi Suk Heo (e-mail address : heo@kriss.re.kr)

Measurement #1

Component	Date (dd/mm/yy)	Result (umol/mol)	Standard deviation (% relative)	number of replicates
Ammonia	04/05/07	32.92	0.01	10

Measurement #2

Component	Date (dd/mm/yy)	Result (umol/mol)	Standard deviation (% relative)	number of replicates
Ammonia	04/05/07	32.91	0.03	10

Measurement #3

Component	Date (dd/mm/yy)	Result (umol/mol)	Standard deviation (% relative)	number of replicates
Ammonia	04/05/07	32.92	0.01	10

Results

Component	Result (umol/mol)	Expanded Uncertainty (umol/mol)	Coverage factor
Ammonia	32.91	0.62	2.0

KRISS NDIR raw data in analysis of K-46 sample

*conc in excel below not corrected for adsorption loss of NH3. The adsorption loss was corrected and recalculated during the uncertainty evaluation of the K-46 sample analysis.

A 1 1	070514 1				
Analy.data	0/0514-1				
	KRISS CRM	K-46 cyl			
Cyl. No	D518955	D751936	D518955	D751936	D518955
File No	70001	70001	80001	80001	90001
nc.(<i>m</i> mol/m	34.154	33.241	34.154	33.245	34.154
1	33.87	32.93	33.86	32.94	33.82
2	33.87	32.93	33.86	32.94	33.82
3	33.87	32.93	33.84	32.94	33.82
4	33.87	32.99	33.84	32.92	33.81
5	33.87	32.99	33.84	32.92	33.81
Mean area	33.870	32.954	33.848	32.932	33.816
u	0.9917		0.99104		0.9901
S.T.D	0.00	0.03	0.01	0.01	0.01
R.S.D(%)	0.00	0.10	0.03	0.03	0.02
R.U(%)	0.00	0.07	0.02	0.02	0.01

Analy.data	070514-2				
Cyl. No	D518955	D751936	D518955	D751936	D518955
File No	60001	60001	70001	70001	80001
nc.(<i>m</i> mol/m	34.154	33.224	34.154	33.238	34.154
1	34.39	33.46	34.38	33.45	34.36
2	34.40	33.46	34.38	33.45	34.36
3	34.40	33.43	34.35	33.45	34.36
4	34.40	33.43	34.35	33.42	34.35
5	34.38	33.43	34.35	33.42	34.35
Mean area	34.394	33.442	34.362	33.438	34.356
u	1.0070		1.0061		1.0059
S.T.D	0.01	0.02	0.02	0.02	0.01
R.S.D(%)	0.03	0.05	0.05	0.05	0.02
R.U (%)	0.02	0.03	0.03	0.03	0.01

Analy.data	070514-3					
Cyl. No	D518955	D751936	D518955	D751936	D518955	
File No	50001	50001	60001	60001	70001	
nc.(<i>m</i> mol/m	34.154	33.244	34.154	33.241	34.154	
1	34.27	33.35	34.22	33.34	34.32	
2	34.27	33.35	34.22	33.34	34.32	
3	34.27	33.34	34.22	33.36	34.32	
4	34.28	33.34	34.27	33.36	34.26	
5	34.28	33.34	34.27	33.36	34.26	
Mean area	34.274	33.344	34.240	33.352	34.296	
u	1.0035		1.0025		1.0042	
S.T.D	0.01	0.01	0.03	0.01	0.03	
R.S.D(%)	0.02	0.02	0.08	0.03	0.10	
R.U(%)	0.01	0.01	0.06	0.02	0.07	

Uncertainty evaluation for preparation of KRISS NH3 CRM and analysis of K-46 NH3 sample

Model equation:

 $C_{K46} = (C_a + C_b + C_c) / 3;$

 $\begin{array}{l} C_a = \left((Ra_1 / ((Ra_{x1} + Ra_{x2})/2) * x_A \right) + (Ra_2 / ((Ra_{x2} + Ra_{x3})/2) * x_A) \right) / 2 * f_{press} ; \\ C_b = \left((Rb_1 / ((Rb_{x1} + Rb_{x2})/2) * x_A \right) + (Rb_2 / ((Rb_{x2} + Rb_{x3})/2) * x_A) \right) / 2 * f_{press} ; \\ C_c = \left((Rc_1 / ((Rc_{x1} + Rc_{x2})/2) * x_A \right) + (Rc_2 / ((Rc_{x2} + Rc_{x3})/2) * x_A) \right) / 2 * f_{press} ; \end{array}$

 $\begin{aligned} x_A &= (n_{A2} / n_T) * 1000000 * (f_{ads} * f_{homo2} * f_{stab2}); \\ n_T &= n_{A2} + n_{Nofm} + n_{N2}; \\ n_{A2} &= (m_{A2} / M_{T2}) * (x_{A1} / 100); \\ n_{Nofm} &= (m_{A2} / M_{T2}) * (x_{N1} / 100); \\ M_{T2} &= M_A * (x_{A1} / 100) + M_N * (x_{N1} / 100); \\ n_{N2} &= m_{N2} / M_N; \\ m_{A2} &= (W_{balA2} + \delta W_{ug} / 1000000 + \delta W_{hadug} / 1000000); \\ m_{N2} &= (W_{balN2} + \delta W_g / 1000 + \delta W_{had} / 1000); \end{aligned}$

 $\begin{aligned} x_{A1} &= (n_{A1} / n_{T1} * 100) * f_{purity} * f_{homo1} * f_{stab1}; \\ x_{NI} &= n_{NI} / n_{T1} * 100; \\ n_{TI} &= n_{A1} + n_{N1}; \\ n_{A1} &= m_{A1} / M_A; \\ n_{NI} &= m_{NI} / M_N; \\ m_{A1} &= (W_{balA1} + \delta W_g / 1000 + \delta W_{had} / 1000); \\ m_{NI} &= (W_{balN1} + \delta W_g / 1000 + \delta W_{had} / 1000); \end{aligned}$

List of quantities:

Quantity	Unit	Definition
C _{K46}	ppm	conc of K-46 from analysis (mean value)
Ca	ppm	conc of K-46 from analysis
C _b	ppm	conc of K-46 from analysis
Cc	ppm	conc of K-46 from analysis
Ra ₁		peak area of sample from analysis
Ra _{x1}		peak area of std from analysis
Ra _{x2}		peak area of std from analysis
X _A	ppm	conc of KRISS NH3 std gas
Ra ₂		peak area of sample from analysis
Ra _{x3}		peak area of std from analysis
f _{press}		factor for pressure difference in sample introduction
Rb ₁		peak area of sample from analysis
Rb _{x1}		peak area of std from analysis
Rb _{x2}		peak area of std from analysis
Rb ₂		peak area of sample from analysis
Rb _{x3}		peak area of std from analysis

Quantity	Unit	Definition		
Rc ₁		peak area of sample from analysis		
Rc _{x1}		peak area of std from analysis		
Rc _{x2}		peak area of std from analysis		
Rc ₂		peak area of sample from analysis		
Rc _{x3}		peak area of std from analysis		
n _{A2}	mole	mole of NH3 in 30 ppm std gas (kriss)		
n _T		total mole of gases in 30 ppm NH3 std gas		
f _{ads}		factor related to loss of NH3 by adsorption in 30 ppm std gas		
f _{homo2}		uncertainty related to homogeneity of 30 ppm std gas		
f _{stab2}		uncertainty related to stability of 30 ppm NH3 std gas		
n _{Nofm}	mole	mole of N2 contained 2% NH3 used in preparation of 30 ppm NH3		
n _{N2}	mole	mole of N2 used for preparation of 30 ppm NH3(as dilution gas)		
m _{A2}	g	wt(g) of 2% NH3 gas taken for prep of 30 ppm gas		
M _{T2}	g/mol	MW of 2% NH3 gas taken for prep of 30 ppm gas		
X _{A1}	%	conc of NH3 at 2% NH3 gas		
x _{N1}	%	conc of N2 at 2% NH3 gas		
M _A	g/mol	MW of NH3		
M _N	g/mol	MW of N2		
m _{N2}	g	wt of N2 dil gas in prep of 10 ppm gas		
W _{balA2}	g	wt of 2% NH3 std gas taken for prep of 30 ppm gas		
δW_{ug}	ug	uncertainty related to chemical balance measurement		
δW_{hadug}	ug	uncertainty related to handling of cylinder in balance measurement		
W _{balN2}	g	wt of N2 taken for prep of 30 ppm gas		
δWg	mg	uncertainty related to chemical balance measurement		
δW_{had}	mg	uncertainty related to handling of cylinder in balance measurement		
n _{A1}	mole	mole of NH3 in 2% NH3 std gas		
n _{T1}	mole	total mole of gases in 2% std gas		
f _{purity}		uncertainty of NH3 purity		
f _{homo1}		uncertainty related to homogeneity of 2 % std gas		
f _{stab1}		uncertainty related to stability of 2% H2S std gas		
n _{N1}	mole	mole of N2 used in prep of 2% std gas		
m _{A1}	g	wt of NH3 in prep of 2% std gas		
m _{N1}	g	wt of N2 used in prep of 2% std gas		
W _{balA1}	g	wt of NH3 in prep of 2% std gas		

Quantity	Unit	Definition
W_{balN1}	g	wt of N2 used in prep of 2% std gas

С_{к46}: Result

C_a: Interim result

C_b: Interim result

C_c: Interim result

Ra₁: Type B t-distribution Value: 32.954 Standard uncertainty: 0.0147 Degrees of freedom: 4

Ra_{x1}: Type B t-distribution Value: 33.870 Standard uncertainty: 0.0000 Degrees of freedom: 4

Ra_{x2}: Type B t-distribution Value: 33.848 Standard uncertainty: 0.0049 Degrees of freedom: 4

x_A: Interim result

Ra₂: Type B t-distribution Value: 32.932 Standard uncertainty: 0.0049 Degrees of freedom: 4

Ra_{x3}: Type B t-distribution Value: 33.816 Standard uncertainty: 0.0024 Degrees of freedom: 4

f_{press}: Type B normal distribution Value: 1 Expanded uncertainty: 0.002 Coverage factor: 2

Rb₁: Type B t-distribution Value: 33.442 Standard uncertainty: 0.0073 Degrees of freedom: 4

Rb_{x1}: Type B t-distribution Value: 34.394 Standard uncertainty: 0.0040 Degrees of freedom: 4

Rb_{x2}: Type B t-distribution Value: 34.362 Standard uncertainty: 0.0073 Degrees of freedom: 4

Rb₂: Type B t-distribution Value: 33.438 Standard uncertainty: 0.0073 Degrees of freedom: 4

Rb_{x3}: Type B t-distribution Value: 34.356 Standard uncertainty: 0.0024 Degrees of freedom: 4

Rc₁: Type B t-distribution Value: 33.344 Standard uncertainty: 0.0024 Degrees of freedom: 4

Rc_{x1}: Type B t-distribution Value: 34.274 Standard uncertainty: 0.0024 Degrees of freedom: 4

Rc_{x2}: Type B t-distribution Value: 34.240 Standard uncertainty: 0.0122 Degrees of freedom: 4

Rc₂:

Type B t-distribution Value: 33.352 Standard uncertainty: 0.00489898 Degrees of freedom: 4

Rc_{x3}: Type B t-distribution Value: 34.296 Standard uncertainty: 0.0147 Degrees of freedom: 4

n_{A2}: Interim result

n_T: Interim result

f_{ads}: Type B normal distribution Value: 1 Expanded uncertainty: 0.022 Coverage factor: 2

f_{homo2}: Type B normal distribution Value: 1 Expanded uncertainty: 0.0068 Coverage factor: 2

f_{stab2}: Type B normal distribution Value: 1 Expanded uncertainty: 0.0002 Coverage factor: 2

n_{Nofm}: Interim result

n_{N2}: Interim result

m_{A2}: Interim result

M_{T2}: Interim result

x_{A1}: Interim result

x_{N1}: Interim result M_A: Type B normal distribution Value: 17.03056 g/mol Expanded uncertainty: 0.000255604 g/mol Coverage factor: 2

M_N:

Type B normal distribution Value: 28.01348 g/mol Expanded uncertainty: 0.000161658 g/mol Coverage factor: 2

m_{N2}: Interim result

W_{balA2}: Type B t-distribution Value: 1.04436 g Standard uncertainty: 0.000012603 g Degrees of freedom: 82

δW_{ug}: Type B normal distribution Value: 0 ug Expanded uncertainty: 100 ug Coverage factor: 2

δW_{hadug}: Type B normal distribution Value: 0 ug Expanded uncertainty: 1000 ug Coverage factor: 2

W_{balN2}: Type B t-distribution Value: 616.33531 g Standard uncertainty: 0.00013254 g Degrees of freedom: 74

δW_g: Type B normal distribution Value: 0 mg Expanded uncertainty: 20 mg Coverage factor: 2

δW_{had}: Type B normal distribution Value: 0 mg Expanded uncertainty: 10 mg Coverage factor: 2 n_{A1}: Interim result

n_{T1}: Interim result

f_{purity}: Type B normal distribution Value: 0.9997 Expanded uncertainty: 0.000133 Coverage factor: 2

f_{homol}: Type B normal distribution Value: 1 Expanded uncertainty: 0.0018 Coverage factor: 2

f_{stab1}: Type B normal distribution Value: 1 Expanded uncertainty: 0.002 Coverage factor: 2

n_{N1}: Interim result

m_{A1}: Interim result

m_{N1}: Interim result

W_{balA1}: Type B t-distribution Value: 8.0074 g Standard uncertainty: 0.000205 g Degrees of freedom: 91

W_{balN1}: Type B t-distribution Value: 644.0219 g Standard uncertainty: 0.00000023 g Degrees of freedom: 98

Uncertainty budget: red color uncertainty factors are major factors.

Quantity	Value	Standard uncertainty	Degrees of freedom	Sensitivity coefficient	Uncertainty contribution	Corr coeff.	Index
Ca	32.917 ppm	0.309 ppm					
C _b	32.905 ppm	0.309 ppm					

Quantity	Value	Standard uncertainty	Degrees of freedom	Sensitivity coefficient	Uncertainty contribution	Corr coeff.	Index
Cc	32.916 ppm	0.309 ppm	0.309 ppm				
Ra ₁	32.9540	0.0147	4	0.166	2.45·10 ⁻³ ppm	0.01	0.000
Ra _{x1}	33.87	0.0	4	0.0	0.0 ppm	0.0	0.0
Ra _{x2}	33.84800	4.90·10 ⁻³	4	-0.162	-794·10 ⁻⁶ ppm	0.00	0.000
XA	33.819 ppm	0.316 ppm					
Ra ₂	32.93200	4.90·10 ⁻³	4	0.167	816·10 ⁻⁶ ppm	0.00	0.000
Ra _{x3}	33.81600	2.40.10-3	4	-0.0811	-195·10 ⁻⁶ ppm	0.00	0.000
f _{press}	1.00000	$1.00 \cdot 10^{-3}$	50	32.9	0.0329 ppm	0.11	0.011
Rb ₁	33.44200	7.30·10 ⁻³	4	0.164	1.20·10 ⁻³ ppm	0.00	0.000
Rb _{x1}	34.39400	$4.00 \cdot 10^{-3}$	4	-0.0797	-319·10 ⁻⁶ ppm	0.00	0.000
Rb _{x2}	34.36200	7.30·10 ⁻³	4	-0.160	-1.16·10 ⁻³ ppm	0.00	0.000
Rb ₂	33.43800	7.30·10 ⁻³	4	0.164	1.20·10 ⁻³ ppm	0.00	0.000
Rb _{x3}	34.35600	2.40.10-3	4	-0.0798	-192·10 ⁻⁶ ppm	0.00	0.000
Rc ₁	33.34400	2.40·10 ⁻³	4	0.165	395·10 ⁻⁶ ppm	0.00	0.000
Rc _{x1}	34.27400	2.40.10-3	4	-0.0801	-192·10 ⁻⁶ ppm	0.00	0.000
Rc _{x2}	34.2400	0.0122	4	-0.160	-1.95·10 ⁻³ ppm	-0.01	0.000
Rc ₂	33.35200	4.90·10 ⁻³	4	0.164	806·10 ⁻⁶ ppm	0.00	0.000
Rc _{x3}	34.2960	0.0147	4	-0.0800	-1.18·10 ⁻³ ppm	0.00	0.000
n _{A2}	752.86·10 ⁻⁶	1.48·10 ⁻⁶					
	mole	mole					
n _T	22.038959	405.10-6					
f _{ads}	0.99000	5.00 ·10 ⁻³	50	33.2	0.166 ppm	0.54	0.289
f _{homo2}	1.00000	7.00·10 ⁻³	50	32.9	0.230 ppm	0.74	0.555
f _{stab2}	1.00000	3.00·10 ⁻³	50	32.9	0.0987 ppm	0.32	0.102
n _{Nofm}	0.0368229 mole	17.7·10 ⁻⁶ mole					

Quantity	Value	Standard uncertainty	Degrees of freedom	Sensitivity coefficient	Uncertainty contribution	Corr coeff.	Index
n _{N2}	22.001383	404.10^{-6}					
		mole					
m _{A2}	1.044360 g	503·10 ° g					
M _{T2}	27.793260 g/mol	553·10 ⁻⁶ g/mol					
X _{A1}	2.00358 %	3.82·10 ⁻³ %					
x _{N1}	97.99582 %	2.71·10 ⁻³ %					
M _A	17.030560 g/mol	128·10 ⁻⁶ g/mol	50	-1.93	-247·10 ⁻⁶ ppm	0.00	0.000
M _N	28.0134800	80.8·10 ⁻⁶	50	1.17	95.0·10 ⁻⁶	0.00	0.000
	g/mol	g/mol			ppm		
m _{N2}	616.3353 g	0.0112 g					
W _{balA2}	1.0443600 g	12.6·10 ⁻⁶ g	82	31.5	397·10 ⁻⁶ ppm	0.00	0.000
δW_{ug}	0.0 ug	50.0 ug	50	31.5.10-6	1.57·10 ⁻³ ppm	0.01	0.000
δW_{hadug}	0.0 ug	500 ug	50	31.5·10 ⁻⁶	0.0157 ppm	0.05	0.003
W _{balN2}	616.335310 g	133·10 ⁻⁶ g	74	-0.0533	-7.07·10 ⁻⁶ ppm	0.00	0.000
δW_g	0.0 mg	10.0 mg	50	3.96·10 ⁻³	0.0396 ppm	0.13	0.016
δW_{had}	0.0 mg	5.00 mg	50	3.96·10 ⁻³	0.0198 ppm	0.06	0.004
n _{A1}	0.470178 mole	657·10 ⁻⁶ mole					
n _{T1}	23.45989 mole	1.06·10 ⁻³ mole					
f _{purity}	0.9997000	66.5·10 ⁻⁶	50	32.5	2.16·10 ⁻³ ppm	0.01	0.000
f _{homo1}	1.000000	900·10 ⁻⁶	50	32.5	0.0293 ppm	0.09	0.009
f _{stab1}	1.00000	$1.00 \cdot 10^{-3}$	50	32.5	0.0325 ppm	0.11	0.011
n _{N1}	22.989714 mole	405·10 ⁻⁶ mole					
m _{A1}	8.0074 g	0.0112 g					
m _{N1}	644.0219 g	0.0112 g					
W _{balA1}	8.007400 g	205·10 ⁻⁶ g	91	4.06	832·10 ⁻⁶ ppm	0.00	0.000
W _{balN1}	644.0219000 00 g	230·10 ⁻⁹ g	98	0.0	0.0 ppm	0.0	0.0
C _{K46}	32.913 ppm	0.309 ppm	124				

Result: Quantity: C_{K46} Value: 32.91 ppm Expanded uncertainty: ± 0.62 ppm Coverage factor: 2.0 Coverage probability: 95.45%

Annex D: Measurement report CERI

Report Form CCQM-K46 Ammonia in nitrogen

Laboratory name: Chemicals Evaluation and Research Institute, Japan

Cylinder number: D751964

Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
NH3	3/3/2007	32.679	0.069	3

Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
NH3	4/3/2007	32.740	0.059	3

Measurement #3

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
NH3	5/3/2007	32.907	0.076	3

Measurement #4

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
NH3	5/3/2007	32.882	0.1132	3

Measurement #5

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
NH3	6/3/2007	32.840	0.064	3

Results

Component	Result (µmol/mol)	Expanded Uncertainty	Coverage factor
NH3	32.81	0.38	2

Reference Method:

Instruments for NH3 measurement Principles : NDIR (Type:CGT-7000, Make : Shimadzu corporation)

Data collection : output of integrator of data

Calibration Standards:

Preparation : Gravimetric method

Purity analysis ;

NH3, N2: The impurities in NH3 and N2 are determined by analyses and the amount of the major component is conventionally determined by,

$$X_{pure} = 1 - \sum_{i=1}^{N} x_i$$

where:

 x_1 = mole fraction of impurity i , determined by analysis

N = number of impurities likely in the final mixture

 X_{pure} = mole fraction 'purity' of the 'pure' parent gas

Instrument Calibration:

Table 1	concentration of PSMs

Component	Concentration (µmol/mol)			
Component	R ₁	R ₁	R ₃	
NH3	50.47	34.83	20.29	

This procedure is for the determination of NH3 in a sample using NDIR.

- 1) Inject the calibration standard (R_1) into NDIR. Record the output.
- 2) Inject the calibration standard (R₂). Record the output.
- 2) Inject the sample to be tested in same manner as the calibration standard. Record the output.
- 3) Inject the calibration standard (R₃). Record the output.
- 4) Calculate the concentration of NH3.

Following above procedure, 3 measurements are repeated subsequently in a day and iterated for 5 days.

Uncertainty:

Uncertainty source	Estimate	Assumed distribution	Standard uncertainty $u(x_i)$	Sensitivit y coefficien t c ₁	Contributio n to standard uncertainty $u_1(y)$
Repeatability of analysis	32.81	Normal (A)	0.185	1	0.185
Reference gas R1 preparation	50.47	normal (A)	0.025	1	0.025
Reference gas R2 preparation	34.83	Normal (A)	0.017	1	0.017
Reference gas R3 preparation	20.29	Normal (A)	0.010	1	0.010
total					0.188

Coverage factor: 2 Expanded uncertainty: 0.38 µmol/mol

Annex E: Measurement report METAS

Report Form CCQM-K46 Ammonia in nitrogen

Laboratory name:	METAS
Cylinder number:	D751986
Nominal composition: ammonia in nitrogen	30 to 40.10^{-6} mol·mol ⁻¹

Measurement #1

Component	Date	Result	Combined standard	number of
	(dd/mm/yy)	(µmol∙mol ⁻¹)	uncertainty (µmol·mol ⁻¹)	replicates
Ammonia	05.03.07	32.30	0.19	100

Measurement #2

Component	Date	Result	Combined standard	number of
	(dd/mm/yy)	(µmol∙mol ⁻¹)	uncertainty (µmol·mol ⁻¹)	replicates
Ammonia	06.03.07	32.49	0.19	100

Measurement #3²

Component	Date	Result	Combined standard	number of
	(dd/mm/yy)	(µmol·mol ⁻¹)	uncertainty (µmol·mol ⁻¹)	replicates
Ammonia	07.03.07	32.04	0.19	100

Result

Component	Amount of substance fraction in the test mixture (µmol·mol ⁻¹)	Expanded uncertainty (µmol·mol ⁻¹)	Coverage factor ³
Ammonia	32.27	0.36	2.0

Uncertainty budget

The uncertainty budget has been calculated using GUM Workbench Pro software (version 2.3.2.36 beta).⁴ The main contributions to the combined standard uncertainty are:

- the standard uncertainty of the ammonia mass flow from the permeation unit with 42 %,
- the standard uncertainties of the purities of the two dilution gases with 26 %,
- the estimated standard uncertainties resulting from the interaction of the test mixture with the surface of the sampling line, consisting of the pressure regulator of the cylinder, the absolute pressure regulator and the sonic nozzle, with 21%
- and the standard uncertainties of the flow measurements with 11 %.

The standard uncertainty of the purity of the permeated ammonia contributes less than 0.1 % to the combined standard uncertainty.

² If more than three measurements are taken, please copy and insert a table of the appropriate format as necessary

³ The coverage factor shall be based on approximately 95% confidence.

⁴ The complete budget is available on request

Also negligible are the standard deviations of the readings of the ammonia analyzer. With a 100 replicates the relative standard deviation of the mean of the readings is only 0.02 %.

Analysis Method

A commercial photo-acoustic NH₃-analyzer was calibrated with NH₃ calibration standards in the range from 510 to 594 nmol·mol⁻¹ NH₃ in N₂ for measurements 1 and 2 and with NH₃ calibration standards in the range from 529 to 571 nmol·mol⁻¹ NH₃ in N₂ for measurement 3.

The VSL-test mixture D751986 was dynamically diluted with nitrogen BIP Plus (Air Products) by a factor of about 0.017 such that the expected amount of substance fraction of the sample lies within the validated and calibrated range of the analyzer and of the METAS Primary micro-gravimetric Standard. The flow of the test mixture was set using a sonic nozzle. The upstream pressure at the sonic nozzle was kept constant by an absolute pressure regulator. The flow of the dilution gas was regulated with a mass flow controller and measured using a molbox-molbloc system. The resulting gas mixture was measured with the photo-acoustic NH_3 -analyzer and the amount of substance fraction calculated by linear interpolation in agreement with ISO 6143:2001(E).

Calibration Standards

The calibration standards were produced by the METAS primary micro gravimetric standard and a NH_3 permeation unit with purity \ge 99.99 %. The total N_2 dilution gas flow was measured by a molbox-molbloc system. The nominal N_2 purity was \ge 99.999 %. The ammonia mass flow of the permeation unit was approx. 550 ng·min⁻¹ at 30 °C.

The two molbox-molbloc systems and the sonic nozzle were calibrated with the METAS Primary Standard for low gas flows.

Sample Handling

An electro polished stainless steal pressure regulator with a flushing system was used for dispensing the VSL test mixture. Several flushing cycles with N_2 and the NH_3 test mixture were carried out.

After stable readings by the NH₃ analyzer, data were sampled for at least 25 minutes.

Purity analysis of the dilution and permeation gases

Method

An ion-molecule-reaction mass spectrometer was used for analysing the residual amount of substance fraction of ammonia in the used N_2 qualities and to identify and quantify possible impurities in ammonia permeators. The ionising gases with the corresponding ionisation energies were: Hg (10.4 eV), Xe (12.13 eV) and Kr (14 eV) and Hg with high acceleration voltage (Ue high) for the unspecific ionisation of most analytes.

The calibration of the MS for ammonia in N₂ was performed with a calibrated permeation unit with a mass flow of 100.4 ng·min⁻¹ at 30 °C in a temperature controlled oven. The amount of substance fraction was set at three points in the lowest accessible range of 49 to 100 nmol·mol⁻¹ by two calibrated mass flow controllers for the N₂ carrier and dilution gas flows of the permeation oven, respectively. The MS parameters with Xe ionisation were optimized for maximum signal and minimal drift for the mass of ¹⁴NH₃ at m/z=17.027 m_u/e. The mass scale and mass resolution of the quadrupol MS were optimised with the signal from ¹⁴NH₃ with the least contribution from the ubiquitous neighbouring H₂¹⁶O (m/z=18.011 m_u/e). The conditioning times derived from the NH₃ signal were at least 30 min.

Residual ammonia in dilution gases

The limit of detection calculated from the intercept of measurement function at $X_{NH3} = 0$ and the 3 σ criteria from the measurement of the N₂ BIP Plus (Air Products) with a specified purity \geq 99.9999 % was 1.9 nmol·mol⁻¹ with typical sampling times of 6 min. The residual NH₃ amount of substance fractions in the dilution gases were calculated with the B_LEAST program (Vs. 1.11, 1999, in agreement with ISO 6143:2001(E)) by linear regression and with the limit of detection being the least detectable amount. For both nitrogen gases N₂ 99.999 % and N₂ BIP Plus the residual NH₃ amounts were below the limit of detection.

Permeation gases

Survey mass spectra with the three available ionisation energies and with Hg (Ue high) were recorded within a mass range of 10 to 195 m_u/e . The sample was a NH₃ permeation unit in the permeation oven with an N₂ carrier flow of 300 ml·min⁻¹. The model permeation unit used for these investigations had a permeation rate of about 997 ng·min⁻¹ at 30 °C resulting in a NH₃ amount of substance fraction of about 3070 nmol·mol⁻¹. It was from the same producer and from the same production batch with identical geometry as the unit used for the calibration of the photo-acoustic NH₃-analyzer. The high permeation rate was intentionally chosen to enhance the sensitivity of the method for detecting trace impurities. Before storing of the spectra the long conditioning times for NH₃ were taken into account. Time scan spectra of the major suspected impurities of gas flows through the oven with and without the permeation unit and of the dilution gases alone were recorded.

Results

In addition to NH₃ H₂O, O₂ and CO₂ were detected in the reference gas mixture from the oven. Because H₂O, O₂, and CO₂ were about equally present in N₂ after flowing only through PFA (Copolymer of Perfluoralkoxy and Tetrafluorethylene) tubes, it is concluded that the observed substances are not impurities from the permeation unit. The increase of the O₂ amount of substance fraction in an N₂ flow of 485 ml·min⁻¹ in a model PFA tubing with comparable dimensions as the tubes in the oven was estimated to be 4 µmol·mol⁻¹. With O₂ having the highest permeation rate of the 3 substances through PFA, the amount of the other traces is supposed to be lower. Since NH₃ exists in ambient air in combination with H₂O, O₂, CO₂ they are unlikely to react with NH₃ within the few seconds between the mixing and the detection. Therefore no significant loss of NH₃ due to the detected trace amounts of impurities in the dilution gases from the used PFA tubes is expected.

Annex F: Measurement report VNIIM

RESEARCH DEPARTMENT FOR THE STATE MEASUREMENT STANDARDS IN THE FIELD OF PHYSICO-CHEMICAL MEASUREMENTS

Key Comparison CCQM-K46 Ammonia in Nitrogen

REPORT Date: 26.06.07 Authors: L.A. Konopelko, Y.A. Kustikov, V.V. Pankratov, D.N. Selukov, V.A. Petrov, E.V. Gromova

Reference method: UV absorption Instrument: Spectrophotometer Lambda 900 ("Perkin Elmer", USA) Length of the cell – 14 cm.

Calibration standards

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

Table 1 – Description of pure components

Component	Mole fraction 10 ⁻⁶ mol/mol	Standard uncertainty 10 ⁻⁶ mol/mol
NH ₃	999900	60
N ₂	999990,0	0,5

All standard gas mixtures were prepared in aluminium cylinders with Aculife IV treatment,

V= 5 L.

Weighing was performed on the balances 81-V-HCE-20kg (hnu-Voland, USA). Experimental standard deviation for 5 L cylinders: 8 mg.

Preparation of standard gas mixtures was carried out in 3 stages

1 stage:

Preparation of the first stage gas pre-mixtures NH_3/N_2 with ammonia mole fraction on the level of 4 %.

Verification of mole fraction was carried out by UV absorption gas analyzer "OAC-3600" ("Monitoring Ltd", Russia). Standard deviation for each measurement series was not more than 0.1 %.

2 stage:

Preparation of the second stage gas pre-mixtures NH_3/N_2 with ammonia mole fraction on the level of 0,2 %.

Verification of mole fraction was carried out by UV absorption gas analyzer "OAG" ("Monitoring Ltd", Russia). Standard deviation for each measurement series was not more than 0,1 %.

3 stage:

Preparation of standard gas mixtures NH_3/N_2 with ammonia mole fraction of 32-34 ppm.

There were prepared 4 standard gas mixtures.

Verification of mole fraction was carried out by UV absorption analyzer "Lambda" ("Perkin Elmer", USA). Standard deviation for each measurement series was not more than 0,2 %.

The characteristics of calibration standards are shown in table 2.

Standard gas mixture N	Component	Assigned value, 10 ⁻⁶ mol/mol	Standard uncertainty, 10 ⁻⁶ mol/mol
1	NH ₃	32,73	0,18
	N ₂	balance	-
2	NH ₃	33,23	0,18
	N ₂	balance	-
3	NH ₃	34,62	0,18
	N ₂	balance	-
4	NH ₃	33,15	0,18
	N ₂	balance	-

Table 2 –	Character	istics	of	calibration	standards
	Character	ISUICS	01	canoration	standarus

Instrument calibration

Linear regression by 4 calibration points (4 standard gas mixtures with similar concentrations) was used for instrument calibration.

There were made 4 independent measurements under repeatability conditions with 4 independent calibrations. One single measurement consisted of 4 sub-measurements.

Sample handling

Prior to measurements the cylinder was stabilized to room temperature.

Results of measurements

Results of measurements of ammonia mole fraction in cylinder No D7521114 are shown in the table 3

Table 3 - Results of measurements of ammonia mole fraction in cylinder № D752114

Measurement #1

Component	Date (dd/mm/yy)	Result (10 ⁻⁶ mol/mol)	Standard deviation (% relative)	number of replicates
NH ₃	21/05/07	33,72	0,3	4

Measurement #2

Component	Date (dd/mm/yy)	Result (10 ⁻⁶ mol/mol)	Standard deviation (% relative)	number of replicates
NH ₃	25/05/07	33,65	0,3	4

Measurement #3

Component	Date (dd/mm/yy)	Result (10 ⁻⁶ mol/mol)	Standard deviation (% relative)	number of replicates
NH ₃	31/05/07	33,65	0,3	4

Measurement #4

Component	Date (dd/mm/yy)	Result (10 ⁻⁶ mol/mol)	Standard deviation (% relative)	number of replicates
NH ₃	08/06/07	33,68	0,3	4

Evaluation of uncertainty of measurements

Total standard uncertainty of ammonia mole fraction was calculated on the base of the following constituents:

- total standard uncertainty of ammonia mole fraction in standard gas mixture (including uncertainty of weighing of parent gases and pre-mixtures, uncertainty in the purity of the parent gases);

- standard deviation of linear regression;

- standard deviation of the measurement result of ammonia mole fraction in investigated gas mixture in cylinder No D752114

Uncertainty budget for ammonia mole fraction in gas mixture in the cylinder \mathbb{N}_{2} D752114 is shown in the table 4.

Table 4– Uncertainty budget for ammonia mole fraction in gas mixture in cylinder N_{2} D752114

N⁰		Source of uncertainty	Type of evaluation	Standard uncertainty, % relative
1	PreparationPreparationof standardof the first pre-mixtures		А	0,055
	gas mixtures	mixtures Preparation of the second pre-mixtures		0,044
		Preparation of the final mixtures	А	0,55
		Impurities in N ₂	A;B	0,000045
		Impurities in NH ₃	A;B	0,0058
2	Standard uncer	rtainty of calibration	A	0,4
3	Standard devia	tion of the measurement result	A	0,3
Combined standard uncertainty				0,75
Expanded uncertainty 1,4			1,5	

Final result of measurements

Final result of measurements of ammonia mole fraction in investigated gas mixture is shown in the table 5

Table 5

Component	Result (10 ⁻⁶ mol/mol)	Expanded Uncertainty (10 ⁻⁶ mol/mol)	Relative Expanded Uncertainty (%)	Coverage factor
NH ₃	33,7	0,5	1,5	2

Annex G: Measurement report VSL

Report Form CCQM-K46 Ammonia in nitrogen

Laboratory name: VSL

Cylinder number: D751916

Measurement #1

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (µmol/mol)	number of replicates
Ammonia	2007-04-25	33,77	0,30	5

Measurement #2

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (µmol/mol)	number of replicates
Ammonia	2007-06-01	33,80	0,34	2 x 5

Measurement #3

Component	Date (dd/mm/yy)	Result (µmol/mol)	Standard deviation (µmol/mol)	number of replicates
Ammonia	2007-06-06	33,84	0,35	2 x 5

Results

Component	Result (µmol/mol)	Expanded Uncertainty (µmol/mol)	Coverage factor
Ammonia	33,8	0,7	2

Reference Method:

The CCQM-K46 mixture is compared to gravimetric standards using an Innova 1312 Multigas Analyzer based on Photo Acoustic Spectroscopy (PAS).

Instrument Calibration:

The following VSL PSMs were used to calibrate the PAS analyser. All PSMs contained NH_3 in a matrix of nitrogen, similar to the sample mixture.

Cylinder No	Gravimetric composition	standard uncertainty
	(µmol/mol)	(µmol/mol)
VSL118876	29,99	0,18
VSL328516	30,01	0,18
VSL328518	40,00	0,24
VSL118880	40,04	0,24
VSL328515	60,03	0,30
VSL238433	79,19	0,40

Cylinder No	Gravimetric composition	standard uncertainty
	(µmol/mol)	(µmol/mol)
VSL206351	80,13	0,40
VSL309544	100,01	0,45
VSL328438	200,09	0,60
VSL118863	200,72	0,60
VSL118862	299,10	0,75
VSL206346	301,18	0,75

Sample handling:

Each cylinder was equipped with a stainless steel pressure regulator that was adequately purged.

A flow of approx. 1,0 L/min was flushed for fifteen minutes, through FEP tubing, to the PAS analyser before the readings were taken.

Calibration Standards:

The PSMs used for calibration are prepared from pre-mixtures in accordance with ISO 6142: 2001

(Gas analysis - Preparation of calibration gas mixtures - Gravimetric method). After preparation the composition was verified.

The concentration of the PSMs has been validated with a continuous syringe injection technique according to ISO 6145:2004 (Gas analysis - Preparation of calibration gas mixtures using dynamic volumetric methods - Part 4: Continuous syringe injection method).

Evaluation of measurement uncertainty:

The listed gravimetric uncertainty is a combined standard uncertainty and includes:

- The uncertainty in the weighings
- The uncertainty on the purity analysis
- Stability issues; the dominant source of uncertainty in these type of mixtures

The listed standard deviations in the three measurements come from Generalized Distance Regression (GDR), already taking into account the uncertainties of the PSMs and the standard deviation in the responses.

The expanded uncertainty in the result is calculated by taking the square root of the average variance of the individual measurements, multiplied with a coverage factor of 2.

Annex H: Measurement report NIST

U.S. Department of Commerce National Institute of Standards and Technology Chemical Science and Technology Laboratory Analytical Chemistry Division Gaithersburg, MD 20899

REPORT OF ANALYSIS

May 18, 2007

Analysis of One Compressed Gas Mixture for CCQM-K46, Ammonia in Nitrogen

Submitted to:

Stephen A. Wise, Chief Analytical Chemistry Division

The Gas Analysis Working Group of the CCQM initiated a Key Comparison (CCQM-K46) on the analysis of ammonia in nitrogen. VSL, the Dutch Metrology Institute, was selected as the coordinating laboratory, which produced the gas mixtures, prepared the protocol, and conducted the comparison. VSL produced a batch of cylinders containing nominally the same concentration of ammonia. One each of these gas mixtures, contained in an aluminum cylinder, was sent to each participant for analysis. The gas mixture was to be between 30 μ mol/mol and 40 μ mol/mol ammonia in a balance of nitrogen. NIST analyzed this gas mixture, using a system utilizing permeation tubes, as the primary reference, and then returned the cylinder to VSL for reanalysis.

Permeation System

A permeation system was used to produce dynamic primary reference gas mixtures to calibrate the instrument used in this comparison. The permeation system consisted of a magnetic suspension microbalance (NIST #624294), a water bath (NIST #622824) to control the temperature of the permeation environment, a pressure controller to maintain a stable pressure in the permeation environment, and molbloc flow elements to measure the flow from mass flow meters.

The microbalance had a resolution of 1 μ g, with a repeatability of approximately 3 μ g. This microbalance is capable of engaging and disengaging the load (the permeation tubes) through a magnetic suspension mechanism. This allows the balance to be recalibrated and the zero read at any time during the experiment. For this work the balance was recalibrated, and the zero determined, every 30 minutes. The mass of the permeation tubes were determined prior to each recalibration. The reading from the balance was averaged until 10 consecutive points resulted in a standard deviation of less than 6 μ g.

The permeation environment was water jacketed and over wrapped with insulation to stabilize temperature in the permeation space. The water bath set point was 40 °C, and the internal environment temperature was determined to be (39.56 ± 0.02) °C. Long term drift of the temperature was measured to be less than 0.08 °C. The pressure in the permeation environment was also pressure stabilized, in order to eliminate buoyancy effects.

Two controlled flows, both nitrogen, were directed into the permeation system. The first flow of 500 sccm was directed to the top of the permeation environment, and flowed over the permeation tubes. The second flow was varied to produce the differing concentrations required to produce the calibration curve. This flow varied between 1000 sccm and 1300 sccm, depending on the concentration of ammonia required. The total flow into the permeation system (Flow 1 plus Flow 2) was measured by a calibrated 5000 sccm molbloc. This molbloc was calibrated using a piston prover primary calibrator and gravimetric calibration. The nitrogen gas was supplied from boil off from a liquid nitrogen container.

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A total of 4 permeation tubes, each 10 cm long and rated at 3100 ng/min ammonia at 30 °C, were used. These tubes were inserted into the permeation environment and allowed to permeate for one week at 25 °C prior to use. An identical permeation tube, purchased at the same time and from the same lot was used to determine the purity of the ammonia permeating from the device. A RGA-200 was used to determine the purity of the ammonia. The permeation tube was inserted into a glass container which was subsequently evacuated to < 0.05 torr. The tube was kept under this vacuum for 1 week in order to eliminate ambient water, and to remove the natural nitrogen and oxygen in the permeation tube which is in normal equilibrium with the atmosphere. After a one week purge, the following mass spectra was obtained.



This mass spectra shows the primary peaks associated with ammonia along with peaks associated with hydrogen and nitrogen. It is believed that the ammonia was disassociated within the RGA into hydrogen and nitrogen, and that these peaks do not indicate impurities. The purity of the ammonia gas was determined to be 99.4 %, with 0.1 % argon, 0.1 % oxygen, and 0.4 % carbon dioxide. Since these contaminants would not result from permeation, they were determined to be artifacts, perhaps from some leaks in the system, and the purity was taken at 100 %. However, since there is some uncertainty associated with this determination, a standard uncertainty of 0.35 % was assigned (0.6 %, rectangular distribution).

FTIR was also used to assess the purity of the ammonia by directing the flow from the permeation system through a 10 m cell, and scanning for 4 hours. This spectra, shown below, shows some water contamination which was not above the background levels. There was no evidence of carbon dioxide contamination.



Calibration

From a quick analysis of the comparison cylinder, it was determined that the concentration of the mixture was at the lower range of the 30 μ mol/mol to 40 μ mol/mol spread. Therefore, the permeation system was setup to provide mixture concentrations of nominally 28 μ mol/mol, 30 μ mol/mol, 32 μ mol/mol,

 $34 \mu mol/mol$ and $36 \mu mol/mol$ ammonia in nitrogen. The uncertainty of the gas mixture concentrations from the permeation system were assessed to be 0.2 % relative. This uncertainty is dominated by the flow calibration, and flow stability uncertainty.

A total of three analytical runs were conducted over three days. Each analytical run consisted of analyzing the calibration gas mixtures a minimum of three times, and sampling the comparison cylinder before and after each calibration series. The uncertainty associated with the reproducibility of the analytical measurement was approximately 0.05 % relative. The data from each analytical run was processed using the GENLINE algorithm.

Results

The results of the three independent analytical runs are given in Table 1. The uncertainty in this table are results only from the GENLINE algorithm, and thus are from the instrument reproducibility and calibration gas mixture uncertainty only.

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Analytical	Value	Uncertainty		
Run	(µmol/mol)	(k=1)		
1	32.46	0.02		
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Average	32.37			

Table 1; Analytical Results

The uncertainty of this analysis is dominated by the purity uncertainty of 0.35 % relative. The standard error of the mean of the three values is 0.08 μ mol/mol. Combining the three sources, where k=2, yields a final expanded uncertainty of 0.28 μ mol/mol (0.9 % relative). The final submitted value for CCQM-K46, cylinder D751992, is (32.37 ± 0.28) μ mol/mol.

Prepared by:

Franklin R. Guenther, Ph.D. Supervisory Research Chemist

Reviewed by:

George C. Rhoderick Research Chemist

Dec.2008

Passivation processes for ammonia gas standards in CERI Masaaki Maruyama Shinji Uehara (CERI)

1. Introduction

We prepare ammonia gas standards by diluting from pure material every 6 months. A passivation process depends on whether a cylinder is new or has been used already.

I explain how to maintain primary ammonia gas standards, before I describe passivation processes for ammonia gas standards.

2. How to maintain primary ammonia gas standards

CERI has primary ammonia gas standards the nominal concentrations of which are 100, 75, 50, 35, and 20µmol/mol. We have 2 sets (Group A and Group B) of 5 cylinders. At first, five primary gas standards are prepared in cylinders of Group A (I).

6 months later, new gas standards prepared in the other cylinders of Group B (II).

Concentration of old gases is checked with new gas standards. Results of old 35 µmol/mol mixtures are usually less than 0.5% difference. And then new gas standards of Group B become primary gas standards (III). Old gases of Group A become non-primary gas standards and are kept without exhausting gases until next preparation.

Another 6 months later, we reprepare new gas standards in cylinder of Group A (IV). Those nominal concentrations are the same as the last.



3. A passivation process for used cylinders (It is used in many cases)

For this maintaining, we don't use for a special passivation but it has the same effect as doping with same concentration for a year.

4. A passivation process for new cylinders

A pressure proof test must be carried out every 5 years for Japanese regulation. A passivation of tested cylinder's inner surface is initialized. When we use new or tested cylinders, we have to execute a below passivation process.

Cylinders are doped with 500 $\mu mol/mol~NH_3$ in N_2 for over a week followed by evacuation (< 5 Pa) .

An additional study of NH₃ gas standards

Maruyama masaaki, Uehara shinji, CERI

1. Introduction

CERI's result was approximately 5% lower than preparation value on CCQM-K46 (NH₃ in N_2). Each participant used Scott cylinders or Luxfer cylinders or Permeation system. CERI used Luxfer cylinders. Therefore we planned an additional study to check the difference between treatment by Luxfer and Scott.

We had already verified that NH₃ concentration was stable in passivated Luxfer cylinders treated by Luxfer. (The stability in 6 month is less than 1%.) We need to show the stability of NH₃ gas standards in Scott cylinders treated by Scott. But Scott cylinders are not allowed to fill gases because of Japanese regulation. So, we used Luxfer cylinders treated by Air Liquide instead of Scott cylinders treated by Scott in this study. Treatment by Air Liquide is the same as that by Scott. These cylinders aren't commercial. But we could get them in collaboration with K. K. Air Liquide Laboratories and Air Liquide America Specialty Gases LLC. (Scott Specialty Gases is now Air Liquide America Specialty Gases LLC.)

- 2. Experiment
- 2.1 Stability on non-passivated Luxfer cylinders treated by Air Liquide
 - (1) Cylinders were filled with N_2 after treatment.
 - (2) Evacuated the cylinders (below 5 Pa).
 - (3) Transferred NH_3 gas standard into the cylinder.

Parent gas was one single approximately 35µmol/mol.

(4) Calibrated the samples by PSMs Right after transfer, 3 days later and 3 weeks later

2.2 Stability on passivated Luxfer cylinders treated by Air Liquide

(1) Passivation

Experiment 2.2 was done after the Experiment 2.1

- (2) Evacuated the cylinders (below 5 Pa).
- (3) Prepared 35µmol/mol NH₃ gas standards (7MPa) into the cylinders by gravimetric.

Parent gas was one single 1500µmol/mol

(4) Calibrated samples by PSMs.

 $2~\mathrm{days}$ later, a week later and $3~\mathrm{weeks}$ later

3. Results

- 3.1 Non-passivated cylinders
 - Table 1 shows the result of Experiment 2.1

All of the calibrated values were lower than the concentration of parent gas The calibrated values of '3 days later' and 3 weeks later' were close.

Cylinder	Parent gas	Calibrated values (µmol/mol)			
Numbers	(um ol/m ol)	(Relative deviation(%))			
	(µmoi/moi)	Right after transfer	3 days later	3 weeks later	

Table 1 Results of non-passivated cylinders

CPB-18498	34.85	32.04 (-8.77)	30.90 (-12.78)	30.68 (-13.59)
CPB-18499	34.85	30.28 (-15.09)	28.75 (-21.22)	28.41 (-22.67)

3.2 Passivated cylinders

Table 1 shows the results of Experiment 2.2

All of the calibrated values were almost consist with gravimetric value.

Cylinder	Gravimetric	Calibrated values (µmol/mol)		
Numbors		(Relative deviation(%))		
Numbers	(µmol/mol)	2 days later	A week later	3 weeks later
CDD-19409	25.90	35.08	34.95	34.99
CFD-16496	59.20	(-0.51)	(-0.89)	(-0.77)
CDD-19400	24.80	34.70	34.53	34.59
CFD-16499	34.89	(-0.55)	(-1.04)	(-0.87)

Table 2 Results of passivated cylinders

4. Discussion

4.1 Non-passivated cylinders

 $NH_{\rm 3}$ concentration was decreased even when 'the right after transfer'.

But after '3 days later', concentration was considered to become stable since calibrated values of '3 days later' and '3 weeks later' were close.

From those results, on cylinders treated by Air Liquide without passivation, NH_3 concentration was considered to be decreased within 3 days after filling NH_3 gas standards.

4.2 Passivated cylinders

 NH_3 concentration was considered to be stable since all of the calibrated values were almost consistent with gravimetric values.

5. Conclusion

If the concentration of passivation is more appropriate, prepared concentration will be more stable in Luxfer cylinder treated by Air Liquide.

These results are consistent with the result of Luxfer cylinder treated by Luxfer.

Consequently, these results suggest that there are few differences about stability between treatment by Luxfer and Scott.



CCQM K46 – Ammonia in nitrogen

Overview of the results and report of additional actions carried out at VSL

Gerard Nieuwenkamp, Rob Wessel VSL B.V., Department of Chemistry, Thijsseweg 11, 2629 JA Delft, the Netherlands Report number S-CH.09.07 Delft, 14 April 2009

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1 Introduction

The results of the CCQM K-46 have not led to a clear consensus between the participants. This document summarises the analytical results so far, including the validation of the cylinders prior to shipment and the additional actions that have been performed by some of the participants. This overview may be of help in the discussion how to proceed with the results of K-46.

2 Validation prior to shipment

A total number of 7 mixtures with a nominal amount of substance fraction of $34 \cdot 10^{-6}$ mol/mol NH₃ in N₂ has been prepared gravimetrically by VSL (ISO6142). These mixtures have been analyzed against a set of VSL PSMs and in addition by use of continuous syringe injection (ISO6145-part 4).

2.1 Validation with Primary Standard gas Mixtures in cylinders

The new mixtures for K-46 have been prepared in October 2006. The verification is performed by a bracketing method using two PSMs of $30 \cdot 10^{-6}$ mol/mol NH₃ in N₂ and two PSMs of $40 \cdot 10^{-6}$ mol/mol NH₃ in N₂. The PSMs used in this measurement have been prepared in 2005 and 2006. VSL has an annual maintenance schedule, in which new mixtures are prepared every year and compared to the existing standards. No significant issues of long-term instability have been observed.

Table 1: verification results for the K-46 mixtures in comparison to Primary Standard gas Mixtures

cylinder number	gravimetry µmol/mol	October analysis	November analysis	December analysis	January analysis
D751992	33.929	33.9	33.8	33.9	33.6
D752114	33.983	34.2	34.2	34.2	34.1
D751916	34.028	34.2	34.1	34.0	34.0
D751986	34.057	34.0	33.8	33.6	33.6
D751946	34.091	34.0	33.8	33.7	33.9
D751929	34.104	34.2	34.1	33.7	34.2
D751936	34.113	34.0	34.1	33.6	34.0

Figure 1: verification results for the K-46 mixtures in comparison to Primary Standard gas Mixtures, expressed as recovery related to the gravimetric value



Conclusions:

- The analytical results for the new mixtures for K-46 overlap within the uncertainty with their gravimetric values.
- By using older PSMs, this also proofs that there is no significant sign of long term instability of this type of mixtures in this type of cylinders.
- However, these results do not yet prove that there is no initial loss in the preparation of this type of mixtures.

2.2 Validation by use of a continuous syringe injection method

In order to detect the presence of systematic errors (e.g. initial loss caused by absorption) in the gravimetrically prepared mixtures, the new set of mixtures has been verified by calibration with an independent method. A gas-tight syringe is initially filled with pure NH₃ and injected in a flow of nitrogen. The flow is adjusted to make a dilution with a nominal concentration of $300 \cdot 10^{-6}$ mol/mol NH₃ in N₂. The flow is measured by using a calibrated mercury piston sealed flow meter. The monitor response of the dynamically prepared mixture is compared to the response of two gravimetrically prepared cylinders of comparable concentration. Figure 2 shows these results, expressed as monitor response / ppm NH₃.

Figure 2: Comparison of syringe injection with gravimetrically prepared $300 \cdot 10-6$ mol/mol NH3 in N2 mixtures



After the comparison at the 300 \cdot 10⁻⁶ mol/mol NH₃ in N₂ level, the syringe is filled with a gravimetrically prepared 5 \cdot 10⁻² mol/mol NH₃ in N₂ mixture. The flow is adjusted to make a 30 \cdot 10⁻⁶ mol/mol NH₃ in N₂ mixture by dilution. The dynamic mixture is compared to two gravimetric mixtures; one of them prepared in 2005, and the other already in 2001.

Figure 3: Comparison of syringe injection with gravimetrically prepared 30 \cdot 10 $^{-6}$ mol/mol NH_3 in N_2 mixtures



Conclusions:

- The results of the dynamically prepared mixtures overlap with the gravimetric values, both at the $300 \cdot 10^{-6}$ mol/mol NH₃ in N₂ and the $30 \cdot 10^{-6}$ mol/mol NH₃ in N₂ level.
- This confirms the overall consistency of the different NH_3 concentrations (pure, 5%, 300 ppm, 30 ppm) that have been used in this comparison.
- However, there may have been an unidentified systematic error in the performance of the dynamic method.

2.3 Validation of the continuous syringe injection method

To validate the method, all individual parts of the method can be calibrated, but that is still no 100% guarantee that the system works as expected. To overcome any doubt, the continuous syringe injection method has been validated as a whole.

The syringe has been filled with a gravimetrically prepared $5 \cdot 10^{-2}$ mol/mol CO in N₂ mixture. The flow is adjusted to generate dilutions of respectively 80 and $40 \cdot 10^{-6}$ mol/mol CO in N₂ mixture. These dynamically generated mixtures have been compared to PSMs of CO in N₂ of similar concentration.

Figure 4: Comparison of syringe injection with gravimetrically prepared 80 \cdot 10 6 mol/mol CO in N_{2} mixtures



Figure 5: Comparison of syringe injection with gravimetrically prepared 40 \cdot 10 6 mol/mol CO in N_{2} mixtures



Conclusions:

- The results for the dynamically generated CO mixtures overlap with the gravimetric value of CO mixtures in cylinders (these values are beyond any doubt, based on previous Key comparisons)
- The dynamic generation of gas mixtures by this continuous syringe method appears to be OK, with an expanded uncertainty of 1% relative.
- The combined set of validation results (2.1, 2.2. and 2.3) gave enough evidence and confidence to proceed with the shipment of the cylinders to the participating laboratories.

3 Results of participating NMI's

Figure 6 shows the result of the key-comparison.





The participating institutes used different methods of calibration. Roughly the methods can be divided in three groups:

- Calibration with NH₃ mixtures in cylinders
 - o VNIIM, NMi and NPL
- Calibration with NH₃ mixtures in "doped" cylinders
 - o CERI and KRISS
- Calibration with permeation standards
 - o NIST and Metas

The results of the participants using the same type of calibration are in good agreement with each other.

For the discussion about the different results with the different calibration methods it may help to give an overview with the obvious advantages vs. disadvantages of the selected methods.

Calibration by:	Advantage	Disadvantage
NH ₃ mixtures in cylinders	Sample and calibration gas are sampled under the same conditions	Possible absorption to the cylinder surface
NH ₃ mixtures in pre-filled cylinders	Minimized possibility for absorption	Possible increased concentration by desorption of NH_3 from the surface
Permeation	No stability/absorption issues related to cylinder surface	Use of a well conditioned calibration compared to a less conditioned sample

Table 2: Advantages and disadvantages of the different calibration methods

4 Discussion:

4.1 Permeation

- After the presentation of the K46 results, NIST stated that the cylinder has a side connection (DIN-1) that is different than their usual size. This means that the pressure regulator used for this comparison was not of the preferred type. VSL has sent one of their regulators to NIST. With this pressure regulator NIST had a smaller discrepancy (-3% rel) for the K46 mixture.
- Metas send a report of their permeation set-up. They did not find any source in their measurements that could cause the observed discrepancy between the K46 mixture and their calibration

From our personal point-of-view there is no reason to question the quality of the permeation system as used by the two institutes. The dynamic generation system will provide a constant and well-defined calibration gas in a good conditioned sampling system. However, the gas sample from a relatively small cylinder is taken under significant different conditions. A (non-conditioned) pressure regulator, new tubing and a mass flow controller are required to take a representative sample from the cylinder. Due to the limited amount of gas in the cylinder, the flushing time is limited. It seems possible that the discrepancy is caused by the comparison of two different systems (comparing apples to pears).

4.2 Calibration standards in cylinders: Doping vs not doping

One of the uncertainty sources in the preparation of reactive gas mixtures by gravimetry is the initial loss caused by absorption of component to the cylinder surface. Much work is performed by the commercial gas suppliers to treat the internal cylinder surface in order to avoid absorption. Treatments with the names of Aculife, Brillanté, Spectra Seal, Quantum, AlphaTech, etc., are available. VSL has worked in many co-operation studies with the suppliers to find a suitable treatment for every component in the scope of VSL's activities. Apart from that, experiments have been performed by doping the cylinder with an elevated concentration of the component prior to the gravimetrically preparation of a mixture (e.g. NO₂, ethanol). Also doping with other components has been tried (doping with SO₂ for NO₂ mixtures and vice versa).

From a principal point-of-view VSL chooses not to use doped cylinders for their reference materials. Mixtures are prepared very accurate with gravimetry, so "what goes in" is very well-defined. By selecting an appropriate cylinder treatment this should be equal to "what comes out". This is demonstrated by comparison with independent dynamic methods, or by comparison to mixtures from sister NMI's.

In case that significant absorption is expected to take place, the cylinders can be doped to occupy active sites at the surface. However, this opens the possibility of desorption, because of changing equilibrium conditions in the cylinder. This can be very complex to integrate in the uncertainty budget of the mixture. In relation to a changing pressure during the gas mixture's lifetime the desorption behaviour becomes even more complex.

For VSL, the annual repetition of mixture preparation gives confidence in the absence of significant absorption, considering that the amount of absorption will be cylinder dependant and therefore random spread over a certain interval. Discrepancies as found in K46 between the participants have not been observed in the results of VSL mixtures.

VSL performed an experiment with doping of NH_3 cylinders. Mixtures prepared in doped cylinders have been compared to mixtures in "normal" cylinders. At the 35 ppm level, a difference of 2% relative was observed in the results, which is in the same order of magnitude as the uncetainty of this comparison. So, this experiment does not confirm the results of KRISS and CERI being at approx. - 4%, but it also doesn't confirm that no absorption at the cylinder surface takes place.

In addition, an ordinary VSL cylinder filled with $300 \cdot 10^{-6}$ mol/mol NH₃ in N₂ has been evacuated and filled with pure nitrogen. After two weeks the NH₃ concentration is analysed by CRDS to be less than $10 \cdot 10^{-9}$ mol/mol. This means that no desorption has taken place. Does this also proof that no absorption has taken place in the initial cylinder?

In an additional report of CERI, the results of using doped cylinders are described. From the new mixtures that are prepared every 6-months, they obtain the same kind of confidence in their values as was described for VSL before. The presence of a significant effect of desorption is even unlikely as was the absorption in the VSL figures. So both methods look solid.

CERI also reported additional research on a commercially passivated cylinder similar to that used by VSL, NPL and VNIIM. Using this passivated cylinder without doping caused a drop in concentration of more the 20%. This is not comparable to the differences seen in this key comparison.

5 Conclusions

The spread in results as found in K46 indicate that the 3 different methods used give similar results for similar methods but do not overlap with each others within the given uncertainties. It is clear that all three methods have advantages as well as disadvantages were the size of the effect is summarized in table 3.

Calibration by:	Advantage	Disadvantage	Size of effect
NH₃ mixtures in cylinders	Sample and calibration gas are sampled under the same conditions	Possible absorption to the cylinder surface	0-2 %
NH ₃ mixtures in pre-filled cylinders	Minimized possibility for absorption	Possible increased concentration by desorption of NH ₃ from the surface	2-4 %
Permeation	No stability/absorption issues related to cylinder surface	Use of a well conditioned calibration compared to a less conditioned sample	3-4 %

Table 3: Advantages and disadvantages and size of effect of the different calibration methods

U.S. Department of Commerce National Institute of Standards and Technology Chemical Science and Technology Laboratory Analytical Chemistry Division Gaithersburg, MD 20899

REPORT OF ANALYSIS

October 11, 2007

Analysis of One Compressed Gas Mixture for CCQM-K46, Ammonia in Nitrogen

Submitted to:

Stephen A. Wise, Chief Analytical Chemistry Division

The Gas Analysis Working Group of the CCQM initiated a Key Comparison (CCQM-K46) on the analysis of ammonia in nitrogen. The Netherlands Measurement Institute (NMi) was selected as the coordinating laboratory, which produced the gas mixtures, prepared the protocol, and conducted the comparison. NMi produced a batch of cylinders containing nominally the same concentration of ammonia. One each of these gas mixtures, contained in an aluminum cylinder, was sent to each participant for analysis. The gas mixture was to be between 30 μ mol/mol and 40 μ mol/mol ammonia in a balance of nitrogen. NIST analyzed this gas mixture, using a system utilizing permeation tubes, as the primary reference, and then returned the cylinder to NMi for reanalysis.

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leaks in the system, and the purity was taken at 100 %. However, since there is some uncertainty associated with this determination, a standard uncertainty of 0.35 % was assigned (0.6 %, rectangular distribution).

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Calibration

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A total of three analytical runs were conducted over three days. Each analytical run consisted of analyzing the calibration gas mixtures a minimum of three times, and sampling the comparison cylinder before and after each calibration series. The uncertainty associated with the reproducibility of the analytical measurement was approximately 0.05 % relative. The data from each analytical run was processed using the GENLINE algorithm.

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Table 1: Analytical Results

The uncertainty of this analysis is dominated by the purity uncertainty of 0.35 % relative. The standard error of the mean of the three values is 0.08 μ mol/mol. Combining the three sources, where k=2, yields a final expanded uncertainty of 0.28 μ mol/mol (0.9 % relative). The final submitted value for CCQM-K46, cylinder D751992, is (32.37 ± 0.28) μ mol/mol. The gravimetric value reported by the coordinating laboratory (NMi) was (33.93 ± 0.20) μ mol/mol. NIST is biased from this value by -4.6%.

In September 2007 NMi sent NIST a new ammonia standard to be analyzed along with a regulator which they have used to analyze the cylinder. The regulator was sent because the regulator used by NIST in the Key comparison was identified as a potential source of bias. NIST used a new set of ammonia permeation tubes and analyzed the new cylinder using the Rubotherm permeation system. The analysis gave a value of $(29.08 \pm 0.30) \mu mol/mol$ ammonia in nitrogen. The gravimetric value NMi assigned to the cylinder was 30.006 $\mu mol/mol$, which results in a -3.1 % relative bias. The 1.5 % improvement can be attributed to the regulator. This result will be reported to the CCQM Gas Analysis working group.

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