Euromet Consultation 764 Ammonia in Nitrogen

Final Report

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Field

Metrology in Chemistry (amount-of-substance)

Subject

Comparison of measurements of ammonia in nitrogen (Consultation project)

Participants

NL (NMi VSL), RU (VNIIM), UK (NPL)

Organising body

EUROMET

Introduction

NMi Van Swinden Laboratorium acted as pilot laboratory in this consultation. A set of 3 primary standard gas mixtures were individually prepared using gravimetry and thoroughly checked for their chemical composition and stability. Each participating laboratory received one cylinder for analysis. The nominal amount-of-substance fraction level was 100 µmol/mol.

The participants measured the composition using their own primary standard gas mixtures of ammonia in nitrogen. After completion, participants returned the cylinders to NMi-VSL for re-analysis. No significant change in ammonia amount of substance fraction was observed within the estimated uncertainty for the gravimetric reference value.

The data analysis in this report follows the structure used in previous key-comparisons.

Schedule

The cylinders were shipped November 2003. A formal deadline for submission of results was not set. The measurements were carried out in the period December 2003 till June 2004. Reports were received until October 2004. Cylinders were returned beginning of 2004 (NPL) and end of 2004 (VNIIM)

Measurement equation

The evaluation of measurement uncertainty of the preparation procedure have been described elsewhere [1].

Four groups of uncertainty components have been considered for the preparation process:

1. gravimetric preparation (weighing process)
2. purity of the parent gases
3. stability of the gas mixture
4. correction due to partial recovery of a component

There has been no evidence that there would be any relevant effect of adsorption, so that only the first three groups of uncertainty components appear in the model for evaluating the uncertainty from gravimetry

$$u^2(x_{grav}) = u^2(x_{weighing}) + u^2(\Delta x_{purity}) + u^2(\Delta x_{stab}) \quad (1)$$

The data from purity verification and weighing are combined as described in ISO 6142. The pure NH_3 has been purchased from Scott Specialty Gases USA. Purity was claimed to be 99,999% or better. No specific purity analysis was performed. Nitrogen was purchased from Air Products (>99,9999 with Built-in-Purifier) [Was the BIP analysed ?]

The uncertainty due to instability is estimated from the long-term behaviour of similar mixtures at NMi VSL.

From the stability data, a mean relative deviation of 0.7% has been obtained, with a standard deviation of 0.3%. This standard deviation accounts for both the instability, as well as for the uncertainty from verification. No drift was observed.

For a typical mixture, the following results have been obtained, whereby for u_{ver} the standard deviation from the stability study is used (table 1).

Table 1: Uncertainty components

	u_{grav} (%,rel.)	u_{ver} (%,rel.)
NH_3	0,7	0,5

The results from table 1 have been used to compute the expanded uncertainty in the assigned (reference) value

$$U_{gravR} = ku_R \quad (2)$$

where

$$u_R = \sqrt{u_{grav}^2 + u_{ver}^2} \quad (3)$$

and k = 2. The relative uncertainty u_R has been used to compute the combined standard uncertainty of the reference value for all mixtures.

Measurement methods

The following measurement and calibration methods have been employed (table 2).

Table 2: Measurement and calibration methods

Laboratory	Measurement method	Calibration method	Traceability
NMi VSL	Non dispersive IR; photoacoustic detector	linear regression (6 points), weighted	NMi Gravimetric PSMs
VNIIM	UV absorption	Single point analysis	VNIIM Gravimetric PSM
NPL	Non dispersive IR; photoacoustic detector	Bracketing with 3 cylinders	NPL Primary gravimetric Standards

Results

In this comparison, measurements were performed on individually prepared gas mixtures with (slightly) different concentrations. Since the coordinating laboratory prepared these mixtures using the same methods and materials, the individual gravimetric values can be adopted as reference values, despite the small differences that exist. This was done because these small differences are of the same order as the differences found between the national metrological institutes, and thus would influence the outcome of the key comparison if it were operated with a single reference value.

In order to evaluate the differences between the participating national metrology institutes, the difference between the gravimetric and analysed values has been taken as starting point. The results are expressed as the degree of equivalence, defined as

$$D_i = x_{lab} - x_{grav} \tag{4}$$

where on the right-hand side the index *i* has been dropped. The combined standard uncertainty of the degree of equivalence can be expressed as

$$u(D_i) = \sqrt{u_{lab}^2 + u_R^2} \tag{5}$$

and the expanded uncertainty, at a 95% confidence level

$$U(D_i) = k\sqrt{u_{lab}^2 + u_R^2} \tag{6}$$

where *k* denotes the coverage factors. For all degrees of equivalence, *k* = 2 (normal distribution, approximately 95% level of confidence).

The results of this comparison are presented in Table 3. The procedure normally used for a formal key comparison has been followed. The table contains the following information

Cylinder	Identification code of cylinder
x_{grav}	Assigned amount of substance fraction of a component
U_R	Expanded uncertainty of the assigned value x_{grav}
x_{lab}	Result as reported by the participant
k_{lab}	Coverage factor as reported by participant
U_{lab}	Expanded uncertainty as reported by participant
D_i	Degree of equivalence, difference between laboratory value and the gravimetric value
$U(D_i)$	Uncertainty of the degree of equivalence

The differences between gravimetric and reported values are given as degree of equivalence, that is the difference between the value measured by the laboratory and the gravimetric value.

The uncertainty of the degrees are given with k = 2 for all laboratories, taking into consideration both the uncertainty reported from the laboratory as well as the uncertainty from gravimetry (and validation). The combined standard uncertainty of a laboratory has been computed from U_{lab} and k_{lab}.

Table 3: Results and degrees of equivalence for NH_3 (µmol/mol)

Lab	Cylinder	x_{grav}	U_R	x_{lab}	k_{lab}	U_{lab}	D_i	$U(D_i)$
NPL	ML6825	100.10	1.8	100.50	2	1.85	0.40	2.6
VNIIM	ML6823	100.02	1.8	96.3	2	0.8	-3.72	2.0
NMi VSL	ML6822	99.77	1.8	100.5	2	2.0	0.85	2.7

The unilateral degrees of equivalence are visualised in figure 1.

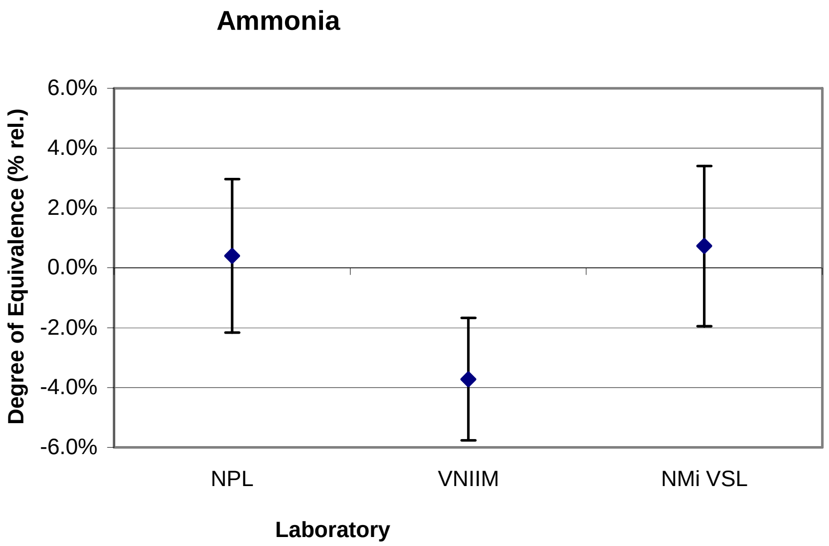

Figure 1: Degrees of equivalence for ammonia

After return to NMi all three cylinders were analysed to observe for possible changes in composition. The results are presented in Table 4. In this table x_{return} is the analysed mole fraction after return of the cylinder and u_{return} is the standard uncertainty in this analysis.

Table 4: Results of analyses after return NH_3 (µmol/mol)

Code	Cylinder	x_{grav}	U_R	x_{return}	u_{return}	$x_{grav} - x_{return}$	$k\sqrt{(u^2_{grav.} + u^2_{return})}$
NPL	ML6825	100.10	1.8	99.8	1.0	-0.30	2.8
VNIIM	ML6823	100.02	1.8	99.7	1.0	-0.32	2.8
NMi VSL	ML6822	99.77	1.8	99.5	1.0	-0.27	2.8

Discussion and ”how far the light shines”

The results of NPL and NMi overlap the reference value. VNIIM’s result shows a larger deviation from the reference value, which is also not covered by this reported uncertainty.

Results from this comparison can be used to review CMCs (calibration and measurement capabilities). As the stability of ammonia becomes more critical at lower concentrations it is wise to limit extrapolation downwards. It is therefore proposed that the range to which this comparison gives a suitable demonstration of measurement capabilities is 80 – 300 μmol/mol.

References

[1] Alink A., Van der Veen A.M.H., “Uncertainty calculations for the preparation of primary gas mixtures. 1. Gravimetry”, Metrologia **37** (2000), pp 641-650

Completion date

December 2004