International Comparison EUROMET.QM-K1c

Final Report

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Field

Metrology in Chemistry (amount of substance)

Subject

Comparison of measurements of nitrogen monoxide in nitrogen.

Participants

CH (Metas), CZ (CMI-CHMI), FI (FMI), FR (LNE), NL (NMi VSL), PO (GUM), PT (IPQ), RU (VNIIM), SP (CEM), UK (NPL)

Organising body

EUROMET

Rationale

Following-up the CCQM-K1c key comparison [1], EUROMET accepted the project proposal for the organisation of a regional key comparison. The objectives of this EUROMET key comparison are essentially the same as for the CCQM-K1c comparison: to compare the measurement capabilities of national metrological institutes (NMIs) in measuring amount of substance fractions of nitrogen monoxide in nitrogen.

Introduction

NMi Van Swinden Laboratorium operated as pilot laboratory both in CCQM-K1c and in this comparison. The selected PSMs for this comparison were individually prepared using gravimetry and thoroughly studied for their chemical composition and stability. A long-term experience in the behaviour of these mixtures and the technical challenges in preparing batches of very similar mixtures is available at the pilot laboratory.

The uncertainty calculations used during this comparison are based on the experience gained in EUROMET.QM-K3 (Automotives). All calculations made are fully compliant to the principles of the "Guide to the expression of uncertainty in measurement" (GUM), and represent state of the art in gas analysis.

Measurement standards

The design of the comparison was adopted from CCQM-K1c [1]. The gas mixtures were prepared by means of primary methods (gravimetry) at the pilot laboratory NMi VSL and in order to do the whole comparison in a limited time frame, a batch of 10 mixtures was produced. There are small differences in the actual property values of these mixtures, which makes working with a single reference value undesirable. The differences in the compositions are of the same order of magnitude as the (expected) differences between laboratories, so that these two aspects are interfering.

In this key comparison, the nominal amount of substance fraction nitrogen monoxide in nitrogen is 100 μmol/mol.

Schedule

The cylinders were shipped June 2002. A formal deadline for submission of results was not set. The cylinder to GUM was returned to NMi and sent again due to problems with shipping documents. The measurements were carried out in the period July 2002-January 2003. Reports were received until January 2003.

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.

Measurement equation

The measurement model has been taken from the CCQM-K1 [1] with the modifications as made for CCQM-K3 [2] and EUROMET.QM-K3 [3]. The mixtures are prepared by means of gravimetry [1,4]; the evaluation of measurement uncertainty of the preparation procedure have been described elsewhere [5].

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

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

The data from purity verification and weighing are combined as described in ISO 6142 [4]. The pure NO was purchased from L'Air Liquide S.A. and was freshly prepared before shipment to NMi. In order to safeguard its stability the cylinder was filled up to 20 bar.

The uncertainty due to instability is estimated from the long-term behaviour of similar mixtures at NMi VSL. The data are given in figure 1. Each data point indicates the relative deviation from the gravimetric value of the stability cylinder when calibrated against a suite of newly prepared Primary Standard Gas Mixtures. Using the same methodology as in the CCQM-K3 [2] and EUROMET.QM-K3 [3], the standard uncertainty due to instability has been assessed. The principles of this approach have been outlined elsewhere [6,7].

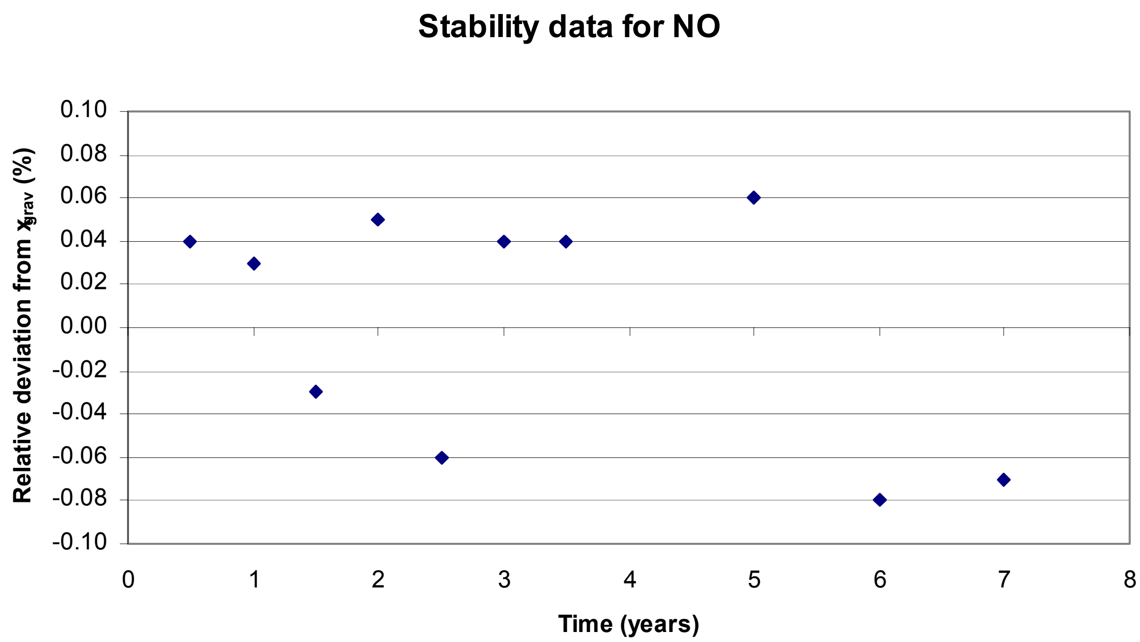

Figure 1: Stability data of 500 μmol/mol NO in nitrogen

From the stability data, a mean relative deviation of 0.002% has been obtained, with a standard deviation of 0.055%. This standard deviation accounts for both the instability, as well as for the uncertainty from verification. From the stability data, it is clear that there is no drift.

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

Table 1: Uncertainty components

	u_{grav} (%,rel.)	u_{ver} (%,rel.)
NO	0,028	0,055

The results from table 3 have been used to compute the uncertainty in the assigned (reference) value

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

where

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

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

Measurement methods

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

Table 2: Measurement and calibration methods

Laboratory	Measurement method	Calibration method	Traceability
NMi	ND-UV	Polynomial regression (8 points), weighted	NMi Gravimetric PSMs
METAS	Chemiluminescence	Linear regression (6 points)	METAS Certified Gas Mixtures
VNIIM	UV absorption	Linear regression (6 points)	VNIIM Gravimetric PSM's
CMI-CHMI	Chemiluminescence	manometric static injection	Diluted NMi PRM
LNE	Chemiluminescence	dynamic dilution + single point calibration	LNE Gravimetric PSM; dilution calibrated by LNE using gravimetry
NPL	Chemiluminescence	bracketing with 4 pairs of cylinders	NPL Primary gravimetric Standards
IPQ	ND-IR	Linear regression (4 points)	NMi PRMs
FMI	Chemiluminescence	dynamic dilution + linear regression (6 points)	NPL Secondary Standard; dilutor calibrated by LNE
GUM	Chemiluminescence	bracketing (2 points)	GUM Gravimetric PSMs
CEM	Chemiluminescence	Linear regression (3 points)	NMi PRMs

Results

Usually all participants perform analyses on the same artefact and the key comparison reference value is calculated from the mean of the individual results. In the current comparison on gas mixtures, measurements were performed on individually prepared gas mixtures with (slightly) different concentrations. Since the pilot laboratory prepared these mixtures using the same methods and materials, the individual gravimetric values can be adopted as reference values, despite of the small differences that exist. The problem is that these small differences are of the same order of the differences found between the national metrological institutes, and thus influencing the outcome of the key comparison if it would be 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 degree of equivalence, defined as

$$D_i = x_{lab} - x_{grav} \quad (4)$$

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

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

and the expanded uncertainty, at a 95% confidence level

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

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

In the table 3 the results of this key comparison are presented. The table contains the following information

Cylinder	Identification code of cylinder
x_{grav}	Assigned amount of substance fraction of a component
u_{gravR}	Standard 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 value 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}. This implies that if a laboratory used a *k* value deviating from *k* = 2, this information has been appreciated to obtain an estimate for the combined standard uncertainty of the result.

Table 3: Results and degrees of equivalence for NO (μmol/mol)

Code	Cylinder	x_{grav}	u_{gravR}	x_{lab}	k_{lab}	U_{lab}	D_i	$U(D_i)$
LNE	153262	95.070	0.062	95.08	2	0.65	0.01	0.66
NPL	153673	95.094	0.062	95.2	2	0.3	0.11	0.32
VNIIM	153823	95.055	0.062	96.6	2	0.9	1.55	0.91
NMi VSL	152994	94.732	0.062	94.8	2	0.3	0.07	0.32
GUM	153596	95.172	0.062	95.8	2	1.5	0.63	1.51
CEM	153255	95.228	0.062	95.8	2	0.9	0.57	0.91
METAS	153181	94.843	0.062	95.12	2	0.42	0.28	0.44
CMI/CHMI	153418	95.064	0.062	94.87	2	1.6	-0.19	1.61
FMI	153038	95.158	0.062	94.8	2	1.5	-0.36	1.51
LNM-IPQ	153690	95.120	0.062	95.22	2	0.39	0.10	0.41

The unilateral degrees of equivalence are visualised in figure 2.

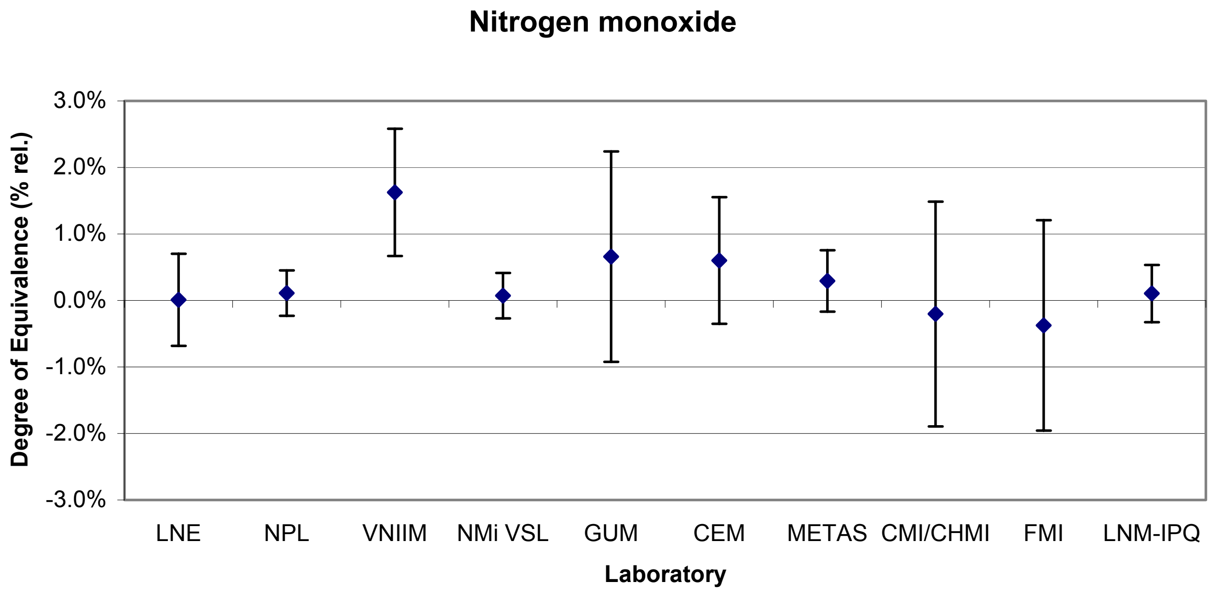

Figure 2: Degree of equivalence for nitrogen monoxide

Degrees of equivalence between this comparison and CCQM-K1c

The bilateral degrees of equivalence in the CCQM-K1c have been defined as

$$D_{ij} = D_i - D_j, \tag{7}$$

and the uncertainty has been approximated by

$$\begin{aligned} u^2(D_{ij}) &= u^2(D_i) + u^2(D_j) = \\ &= u^2(x_{lab,i}) + u^2(x_{grav,i}) + u^2(x_{lab,j}) + u^2(x_{grav,j}), \end{aligned} \tag{8}$$

thus ignoring effects of the uncertainty from verification. The same approximation has been used for the degrees of equivalence between this key comparison and CCQM-K1c. The rationale for deviating from the ideas in [8] is that following those recommendations would lead to inconsistencies in the degrees of equivalence tables.

One remark should be made about the linking. Conditions for a useful linking include [8]

- the artefact(s) used should be the same
- the nominal values should be the same
- the key comparisons should take place in a reasonably short period of time
- a link must be demonstrable between the pilot laboratories, if there is more than one.[1]

The third condition is not met in this case; there are more than 6 years between the two comparisons.

[1] Such a link can be established through, for example, participation of one pilot laboratory in the key comparison of the other, or through a bilateral comparison.

Discussion and conclusions

All laboratories except VNIIM, have shown very good performance and in some cases even extremely good. The results of this NMI show larger deviations from the gravimetric value, which are also not covered by the reported uncertainty.

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