Calibration and measurement capabilities for nitrogen dioxide in nitrogen and air†

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Abstract

This report describes the Calibration and Measurement Capabilities (CMCs) for mixtures of nitrogen dioxide in nitrogen/air at amount fractions from $0.1\,\mu\mathrm{mol\,mol^{-1}}$ to $1000\,\mu\mathrm{mol\,mol^{-1}}$. These CMCs are supported by participation in key comparisons and the standards maintenance and development work. This report details the performance of the static and dynamic gas mixture preparation, purity analysis, analytical verification and the long-term stability of mixtures of nitrogen dioxide in nitrogen. These mixtures are provided to customers with both a total amount fraction of nitric oxides, as well as the amount fraction nitrogen dioxide. In the latter, corrections are contained for the dimerisation of nitrogen dioxide as well as the formation of nitric acid.

Based this participation and the work done to maintain gas standards of nitrogen dioxide in nitrogen/air, the following capabilities have been demonstrated. From $0.1\,\mu\mathrm{mol\,mol^{-1}}$ to $1\,\mu\mathrm{mol\,mol^{-1}}$ a Calibration and Measurement Capability (CMC) is demonstrated of $3\,\%$ to $2\,\%$ ($k=2$), for $1\,\mu\mathrm{mol\,mol^{-1}}$ to $10\,\mu\mathrm{mol\,mol^{-1}}$ a CMC of $2\,\%$ to $1.5\,\%$, for $10\,\mu\mathrm{mol\,mol^{-1}}$ to $100\,\mu\mathrm{mol\,mol^{-1}}$ a CMC of $1.5\,\%$ to $1.0\,\%$ and finally from $100\,\mu\mathrm{mol\,mol^{-1}}$ to $1000\,\mu\mathrm{mol\,mol^{-1}}$ a CMC of $1.0\,\%$ to $0.5\,\%$.

1 Introduction

In 2016, the CCQM Gas Analysis Working Group (CCQM-GAWG) of the Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology (CCQM) introduced an extrapolation scheme to be used for translating the measurement uncertainty reported in a key comparison to a CMC [1]. This extrapolation scheme has a tipping point at $10\,\mu\mathrm{mol\,mol^{-1}}$. Below this amount fraction level, the expanded uncertainty is extrapolated absolute, and above relative. The GAWG extrapolation scheme has been developed based on the results from many key comparisons and studies in the gas analysis area. Most of the nominal amount fractions in these comparisons were at $10\,\mu\mathrm{mol\,mol^{-1}}$ or above.

It was demonstrated that for binary mixtures of propane, methane, carbon monoxide and carbon dioxide it is possible to relate the standard uncertainty to the amount fraction using a simple functional relationship. This function relates the standard uncertainty to the amount fraction

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using their logarithms, so $\lg u$ to $\lg x$. As the amount fraction intervals are very wide and using the double logarithm ensures that the data points (typically one per decade) are more or less evenly distributed. The VSL extrapolation scheme performs well over the entire amount fraction intervals, especially at the extremes [2] for gas mixtures that exhibit little stability effects [3–6].

In this paper, we apply the same approach to measurement standards and related calibration and reference material services of nitrogen dioxide in nitrogen and air, to support CMCs based on the result submitted in CCQM-K74.2018 [7] and the related degree of equivalence computed from it.

2   Key comparisons

The targeted measurand in CCQM-K74.2018 was the amount fraction nitrogen dioxide. In CCQM-K74 [8], all participating National Metrology Institutes (NMIs) interpreted this measurand as the total of the nitrogen oxides present in the mixture. In CCQM-K74.2018 [7], this measurand was interpreted partly in the same fashion is done in CCQM-K74, partly as the amount fraction of nitrogen dioxide alone, which requires an correction for the amount fraction nitric acid, as this compound is formed during gas mixture preparation. VSL used the latter interpretation and issues certificates that specify both results [9].

VSL participated in CCQM-K74.2018 [7]. The result submitted was consistent with the key comparison reference value (KCRV). The stated relative standard uncertainty is 0.7 %. VSL maintains measurement standards of nitrogen dioxide in nitrogen from $1\,\mu\text{mol}\,\text{mol}^{-1}$ to $1000\,\mu\text{mol}\,\text{mol}^{-1}$. The nominal amount fraction in CCQM-K74.2018 was $10\,\mu\text{mol}\,\text{mol}^{-1}$.

According to the GAWG Strategy [1], the CMC support would be at $1\,\mu\text{mol}\,\text{mol}^{-1}$ 7 % relative expanded uncertainty and at $1000\,\mu\text{mol}\,\text{mol}^{-1}$ 0.7 %. Neither of these relative expanded uncertainties reflect the performance of the calibration and reference material production and certification methods.

3   Method

The general approach of the uncertainty evaluation of calibrations and property values of primary reference materials has been described elsewhere [2]. The uncertainty evaluation is based on the standards ISO 6142-1, ISO 19229, ISO 6143 [10–12], and ISO Guide 35 [13]. The latter document is used with regard to the evaluation of stability study data [14], and the combination of that contribution with other uncertainty contributions [15, 16]. Unless stated otherwise, the uncertainty evaluations are performed using the law of propagation of uncertainty (LPU) of the Guide to the expression of Uncertainty in Measurement (GUM) [17].

Given that VSL prepares primary standard gas mixtures (PSMs) and primary reference materials (PRMs) starting from corresponding mixtures of nitrogen monoxide in nitrogen, several changes with respect to ISO 6142-1 have been implemented for the value assignment, as explained below.

4 Results

4.1 Purity analysis

PSMs and PRMs of nitrogen dioxide in nitrogen or air are prepared from gravimetric gas standards of nitrogen monoxide. These in turn are prepared, in the first step, from nominally pure nitrogen monoxide. A typical purity table of the nitrogen monoxide used for this purpose is given in the final report of CCQM-K137 [18].

4.2 Gravimetric gas mixture preparation

PSMs of nitrogen dioxide in nitrogen or air are prepared from gravimetrically prepared mixtures of nitrogen monoxide in nitrogen [19]. The gravimetric gas mixture preparation is done in accordance with ISO 6142-1 [10]. The value assignment differs, due to (1) the (deliberate) conversion of nitrogen monoxide to nitrogen dioxide, and the formation of nitric acid.

The following reaction describes the conversion of nitrogen monoxide into nitrogen dioxide

$$2\,NO + O_2 \rightleftharpoons 2\,NO_2 \tag{1}$$

This reaction is an equilibrium reaction. The Gibbs free energy of formation for NO is $86.55\,kJ\,mol^{-1}$ and that of NO_2 is $51.31\,kJ\,mol^{-1}$. So, the Gibbs free energy change $\Delta G^{\ominus} = -70.7\,kJ\,mol^{-1}$. The (rounded) value of R is $8.314\,46\,J\,mol^{-1}\,K^{-1}$. Hence, $K = 2.433 \times 10^{12}$. The fraction nitrogen monoxide unconverted is in the order of 10^{-5} at $101\,325\,Pa$. At this pressure the fraction unconverted is negligible and becomes even smaller at higher pressures (Le Chatelier's principle [20]) [19].

The targeted measurand in CCQM-K74.2018 was the amount fraction nitrogen dioxide. In the preparation process, an excess of $1000\,\mu mol\,mol^{-1}$ is maintained at minimum to ensure that the equilibrium reaction (1) shifts essentially to the side of nitrogen dioxide [19]. Nitric acid (HNO_3) is formed by the reaction of nitrogen dioxide with oxygen and water. The amount fraction water in the gas mixture has turned out to be a poor indicator of the nitric acid formation. In fact, there is much more water available, physically or chemically bound to the aluminium oxide of the cylinder and/or its passivation. A correction was developed for the amount fraction nitric acid [9]. Nitric acid is analysed using cavity ringdown spectroscopy (CRDS). The line strength is taken from the PNLL-database [21, 22] Tables 1 and 2 show two trends in the amount fraction nitric acid: (1) the amount fraction HNO_3 increases over time, and (2) it is approximately proportional to the amount fraction NO_2 calculated from gravimetry.

Table 1: Results of the nitric acid analysis in the first months after preparation [9]

Cylinder	Preparation date	amount fraction HNO_3 ($nmol\,mol^{-1}$)		
		17/01/2018	28/02/2018	29/03/2018
VSL105804	12/12/2017	70	78	113
VSL105805	11/12/2017	75	81	102
VSL105806	12/12/2017	80	81	113
VSL105808	08/12/2017	87	93	123

Thus, corrections are made for

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Table 2: Results of the measurement of the amount fraction nitric acid ($x(\mathrm{HNO_3})$) in selected PRMs of nitrogen dioxide in nitrogen [9]

Mixture	Preparation date	$x(\mathrm{NO_2})$ (nmol mol^{-1})	$x(\mathrm{HNO_3})$ (nmol mol^{-1})	Fraction converted (%)
VSL348086	14/07/2017	9990	166	1.66
VSL448105	23/07/2018	20 012	171	0.86
VSL244152	14/07/2017	20 034	241	1.20
VSL243949	10/07/2017	40 020	413	1.03
VSL243950	10/07/2017	60 072	581	0.97
VSL244071	06/07/2017	79 979	641	0.80
VSL243852	19/07/2018	80 083	396	0.50
VSL243985	31/05/2017	99 835	826	0.83
VSL243952	31/05/2017	99 645	976	0.98
PRM165026	03/09/2018	200 170	1686	0.84

1. the formation of nitric acid, and

2. the equilibrium with the dimer ($\mathrm{N_2O_4}$, dinitrogen tetraoxide).

to the amount fraction nitrogen dioxide as calculated from the gravimetric gas mixture preparation, including the conversion of nitrogen monoxide into nitrogen dioxide. The model equation takes the form [7]

$$x(\mathrm{NO_2}) = x(\mathrm{NO}_x) - x(\mathrm{HNO_3}) - 2x(\mathrm{N_2O_4}) \tag{2}$$

where the formula NO_x is used to denote the total nitrogen oxide amount fraction after preparation. The equilibrium constant for the dimerisation of $\mathrm{NO_2}$ to $\mathrm{N_2O_4}$ is based on spectroscopic work [23, 24]. The relative expanded uncertainty of the equilibrium constant is evaluated to be 5 % ($k = 2$) [9]. The fraction $\mathrm{N_2O_4}$ increases linearly with the amount fraction NO_x (figure 1). At 1000 µmol mol^{-1} NO_x, the amount of $\mathrm{N_2O_4}$ is 1 % of the total amount NO_x. At 10 µmol mol^{-1} NO_x however, there is only a negligible 0.01 % $\mathrm{N_2O_4}$ present.
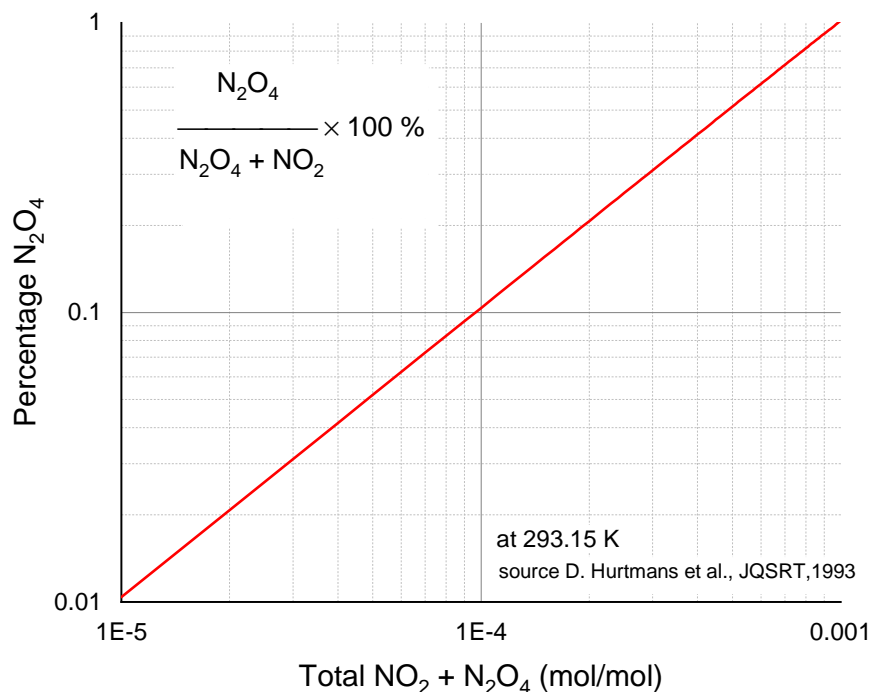
Figure 1: Equilibrium between NO_2 and N_2O_4 at 293.15 K [9]

Whether the speciation matters, depends very much on the analyser used. If that is specific for NO_2, such as a non-dispersive ultraviolet (NDUV) analyser, these corrections are relevant. For an analyser that detects all species, such as a chemiluminescence monitor, these corrections can be omitted, as the analyser will detect the total NO_x, including any nitric acid formed.

The effect of these corrections on the uncertainty computed from preparation is shown in table 3. The relative standard uncertainty of the nitric acid correction is evaluated to be 8.7 %, which includes a relative standard uncertainty of 6.4 % for the data from the PNNL-database and 5 % for measurement reproducibility.

Table 3: Uncertainty evaluation of the corrections for nitric acid and dinitrogen tetraoxide, assuming a relative standard uncertainty of 0.03 % for the gravimetric gas mixture preparation.

$x(NO_x)$ (mol mol^{-1})	$u(x(NO_x))$ (mol mol^{-1})	$u(x(HNO_3))$ (mol mol^{-1})	$u(x(N_2O_4))$ (mol mol^{-1})	$u(x(NO_2))$ (mol mol^{-1})	$u_{rel}(x(NO_2))$ (%)
1.00×10^{-6}	3.00×10^{-10}	8.70×10^{-10}	2.6×10^{-13}	9.20×10^{-10}	0.09
1.00×10^{-5}	3.00×10^{-9}	8.70×10^{-9}	2.6×10^{-11}	9.20×10^{-9}	0.09
1.00×10^{-4}	3.00×10^{-8}	8.70×10^{-8}	2.6×10^{-9}	9.21×10^{-8}	0.09
1.00×10^{-3}	3.00×10^{-7}	8.70×10^{-7}	2.6×10^{-7}	9.88×10^{-7}	0.10

4.3 Verification

Three analysers are available for the analysis of calibration gas mixtures of nitrogen dioxide in nitrogen, a Thermo 42i (chemiluminescence), an ABB Limas 01 (NDUV) and an ABB Limas 02 (NDUV). These analysers are calibrated using a multipoint calibration in accordance with ISO 6143 [12]. More details on their use has been provided elsewhere [7]. The calibration data used are shown in tables 7–10 in appendix A.
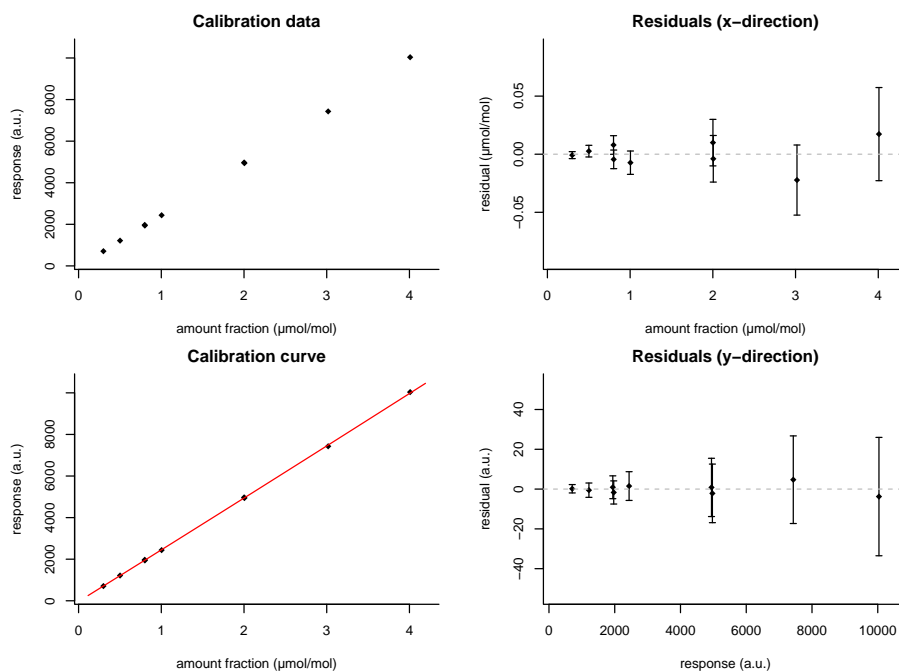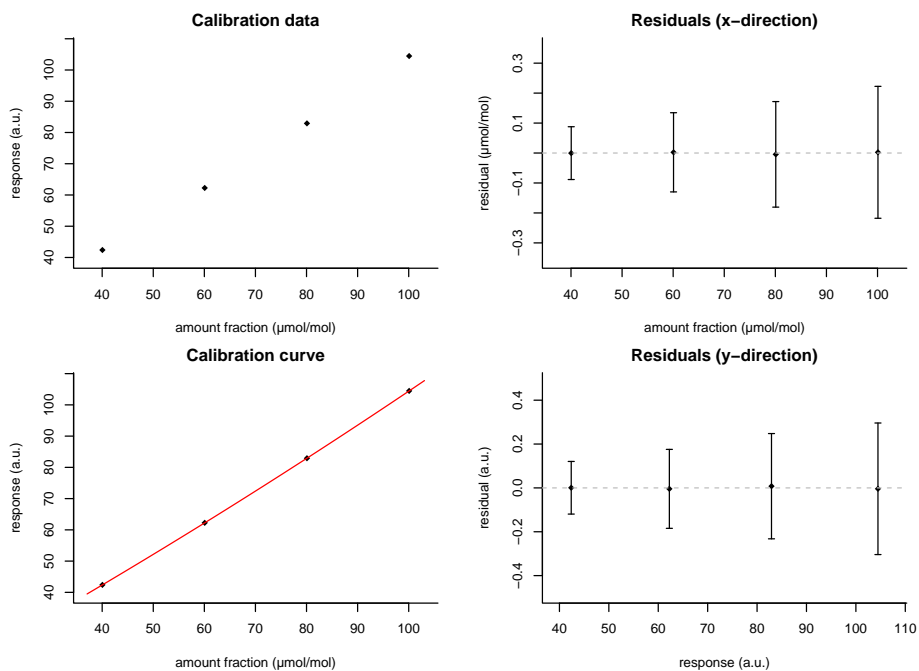

Figure 2: Calibration data, function and residuals for nitrogen dioxide in nitrogen according to the procedure of ISO 6143

The calibration results in the interval $0.3\,\mu\text{mol}\,\text{mol}^{-1}$ to $4\,\mu\text{mol}\,\text{mol}^{-1}$ using the Thermo 42i analyser are shown in figure 2. The calibration function is a parabola. All residuals meet the criteria of ISO 6143. The analytical relative standard uncertainty when using the calibration function ranges from $0.50\,\%$ to $0.30\,\%$. Gravimetric gas standards that have been analysed in this sequence show deviations from $-1\,\%$ to $1\,\%$, see table 4. Given the envisaged CMC of $3\,\%$ to $2\,\%$ ($k = 2$) for this interval, this calibration function is suitable for verification as required by ISO 6142-1 as well as for the calibration of gas mixtures. PRMs are currently not provided for this interval. The three mixtures with identifiers starting with "CGM" in table 4 are three calibrated gas mixtures (CGMs). As can be seen, the relative analytical standard uncertainty increases slightly with decreasing amount fraction, but it should also kept in mind that the largest standard uncertainties are at the ends of the interval (VSL165059 and CGM3710). Hence, the CMC of $3\,\%$ at $100\,\text{nmol}\,\text{mol}^{-1}$ (see table 6) is deemed sufficiently wide.

The calibration results in the interval $40\,\mu\text{mol}\,\text{mol}^{-1}$ to $100\,\mu\text{mol}\,\text{mol}^{-1}$ using the Limas) 02 analyser are shown in figure 3. The calibration function is a parabola. All residuals meet the criteria of ISO 6143. The analytical relative standard uncertainty when using the calibration function ranges from $0.30\,\%$ to $0.20\,\%$. Gravimetric gas standards that have been analysed in

Table 4: Responses (y) and amount fractions x computed by using the calibration function from figure 2. Amount fractions are given in $\mu\text{mol}\,\text{mol}^{-1}$.

Mixture	y a.u.	$u(y)$ a.u.	x_prep $\mu\text{mol}\,\text{mol}^{-1}$	x_anal $\mu\text{mol}\,\text{mol}^{-1}$	$u_\text{rel}(x)$ %	Δx $\mu\text{mol}\,\text{mol}^{-1}$	$\Delta x/x$ %
VSL165059	10 137.5	15.0	4.0334	4.0671	0.46	0.0337	0.84
VSL145022	4961.2	7.4	1.9855	2.0083	0.26	0.0228	1.15
VSL165017	2426.7	3.6	1.0018	0.9919	0.29	−0.0098	−0.98
VSL199166	2431.7	3.6	1.0007	0.9939	0.29	−0.0068	−0.68
VSL191138	2460.0	3.6	1.0005	1.0053	0.29	0.0048	0.48
CGM0078	1313.5	1.9		0.5438	0.27		
CGM2064	1220.1	1.8		0.5061	0.28		
CGM3710	762.6	1.1		0.3216	0.45		

Figure 3: Calibration data, function and residuals for nitrogen dioxide in nitrogen according to the procedure of ISO 6143

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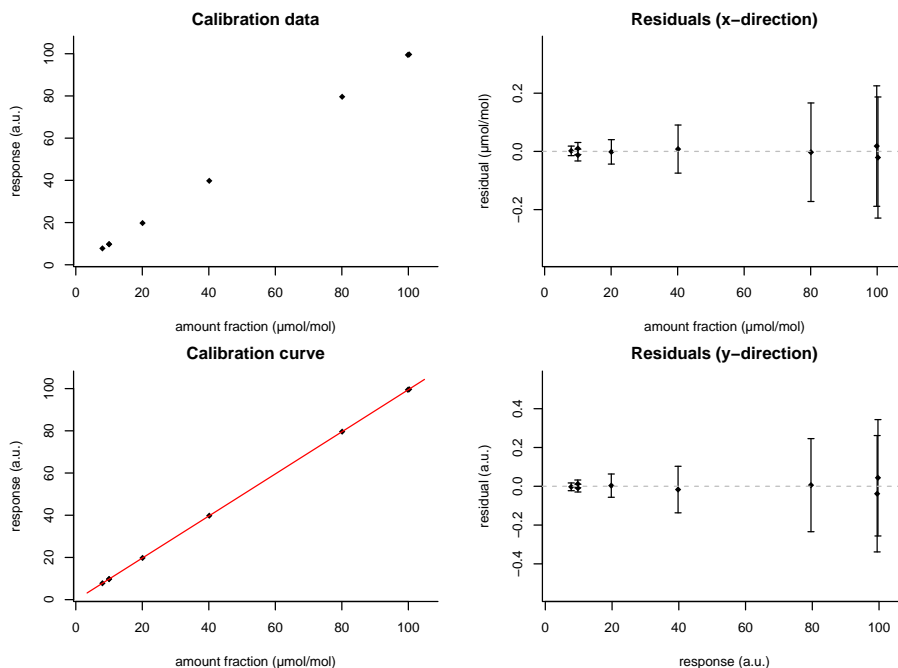this sequence show deviations from $-1\,\%$ to $1\,\%$.

Figure 4: Calibration data, function and residuals for nitrogen dioxide in nitrogen according to the procedure of ISO 6143

The calibration results in the interval $8\,\mu\mathrm{mol\,mol^{-1}}$ to $100\,\mu\mathrm{mol\,mol^{-1}}$ using the Limas) 02 analyser are shown in figure 4. The calibration function is a parabola. The relative standard uncertainty of the amount fractions is set to $0.10\,\%$ (see table 3). All residuals meet the criteria of ISO 6143. The analytical relative standard uncertainty when using the calibration function is $0.20\,\%$.

The calibration results in the interval $100\,\mu\mathrm{mol\,mol^{-1}}$ to $1000\,\mu\mathrm{mol\,mol^{-1}}$ using the Limas) 01 analyser are shown in figure 5. The calibration function is a parabola. The relative standard uncertainty of the amount fractions is set to $0.10\,\%$ (see table 3). All residuals meet the criteria of ISO 6143. The analytical relative standard uncertainty when using the calibration function is $0.22\,\%$.

4.4 Stability of measurement standards and primary reference materials

As part of the participation in CCQM-K74.2018, four mixtures of nominally $10\,\mu\mathrm{mol\,mol^{-1}}$ NO_2 were prepared. The stability study data are shown in figure 6. The behaviour of the four nominally the same cylinders is quite different: the mixture VSL105805 (figure 6b) is stable for well over two years, whereas mixture VSL105804 is only marginally so (figure 6a). The other two mixtures (figures 6c and 6d) show a rather steady decrease in the amount fraction NO_2, yet they are sufficiently stable for an expiry date on the certificate [25] of two years.

The uncertainty contributions and combined standard uncertainties for PRMs are summarised in table 5. The computed relative combined standard uncertainty for the $80\,\mu\mathrm{mol\,mol^{-1}}$ mixture exceeds the "best" measurement capability, which is probably due to the cylinder used. In the
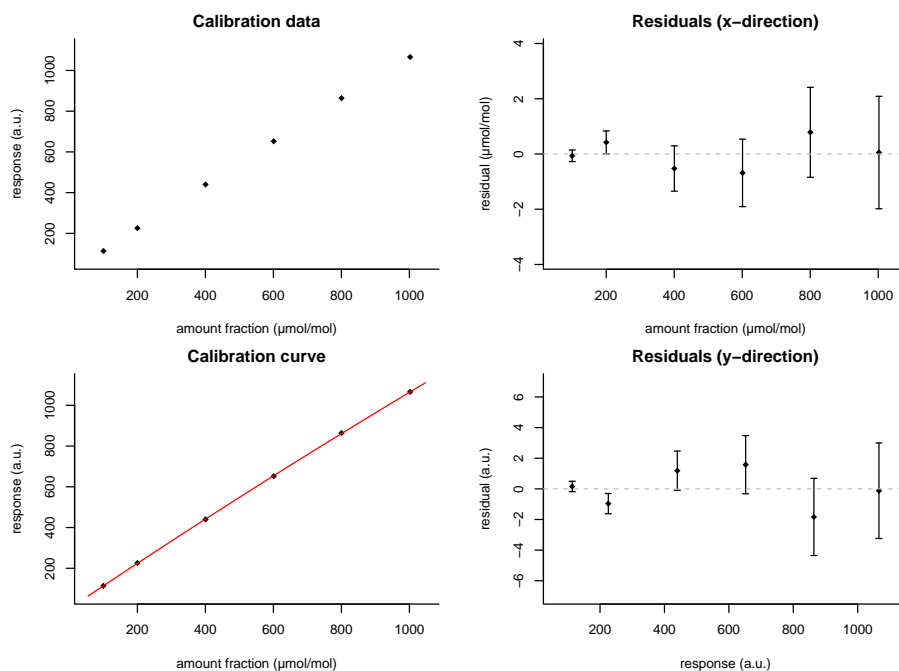
Figure 5: Calibration data, function and residuals for nitrogen dioxide in nitrogen according to the procedure of ISO 6143

recent years (2019-2021), the procedures for the preparation have been improved and optimised. The current state-of-the-art is shown in the $10\,\mu\mathrm{mol}\,\mathrm{mol}^{-1}$ mixtures prepared for CCQM-K74.2018 (figure 6).

4.5 CMCs

Based on the uncertainty budgets shown in table 5 and the analytical capabilities demonstrated for the ranges 3 and 4, the following CMCs are supported (table 6).

5 Conclusions

Based on the participation in CCQM-K74.2018 and the work done to maintain gas standards of nitrogen dioxide in nitrogen/air, the following capabilities have been demonstrated. From $0.1\,\mu\mathrm{mol}\,\mathrm{mol}^{-1}$ to $1\,\mu\mathrm{mol}\,\mathrm{mol}^{-1}$ a CMC is demonstrated of $3\,\%$ to $2\,\%$ ($k=2$), for $1\,\mu\mathrm{mol}\,\mathrm{mol}^{-1}$ to $10\,\mu\mathrm{mol}\,\mathrm{mol}^{-1}$ a CMC of $2\,\%$ to $1.5\,\%$, for $10\,\mu\mathrm{mol}\,\mathrm{mol}^{-1}$ to $100\,\mu\mathrm{mol}\,\mathrm{mol}^{-1}$ a CMC of $1.5\,\%$ to $1.0\,\%$ and finally from $100\,\mu\mathrm{mol}\,\mathrm{mol}^{-1}$ to $1000\,\mu\mathrm{mol}\,\mathrm{mol}^{-1}$ a CMC of $1.0\,\%$ to $0.5\,\%$.
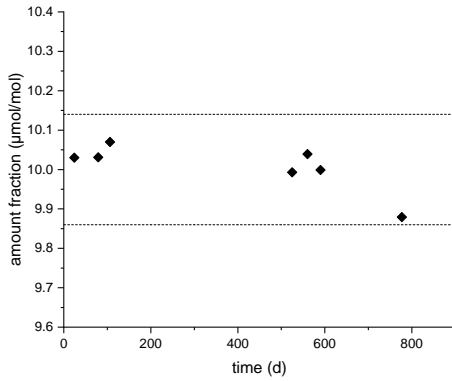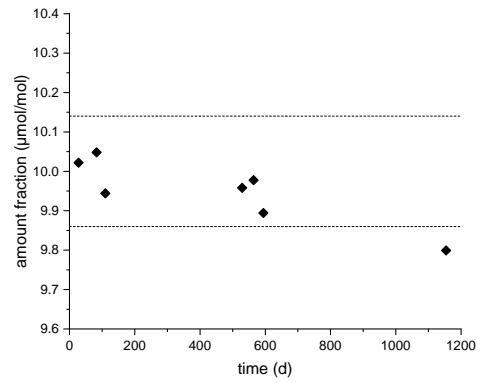
(a) VSL105804
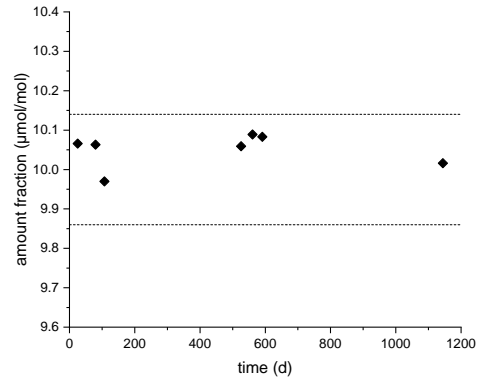
(b) VSL105805
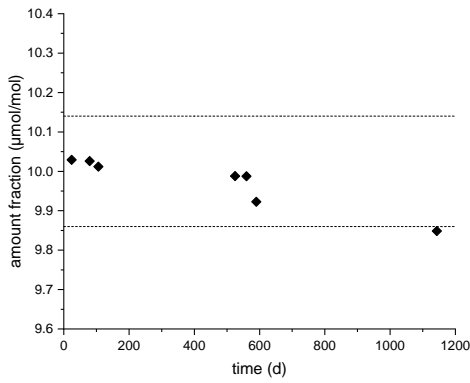
(c) VSL105806

(d) VSL105808

Figure 6: Stability study data of four mixtures containing $10\,\mu\mathrm{mol\,mol^{-1}}$ NO_2. The dotted lines indicate the coverage based on a relative expanded uncertainty of 1.4 %.

Table 5: Uncertainty contributions for PRMs of nitrogen dioxide in nitrogen/air for different amount fractions (x)

Mixture	x $\mu\mathrm{mol\,mol^{-1}}$	$u(\delta x_{\mathrm{stab}})$ %	$u(\delta x_{\mathrm{anal}})$ %	$u(\delta x_{\mathrm{prep}})$ %	$u(x_{\mathrm{total}})$ %
PRM144133	1000.7	0.04	0.22	0.11	0.25
PRM145036	900.91	0.26	0.22	0.11	0.35
PRM144012	496.67	0.08	0.22	0.11	0.26
PRM162926	450.53	0.13	0.22	0.11	0.28
VSL448122	200.16	0.26	0.22	0.11	0.36
VSL145035	100.03	0.44	0.22	0.11	0.50
PRM144130	80.082	0.82	0.22	0.11	0.86
VSL105804	10.005	0.61	0.22	0.11	0.66
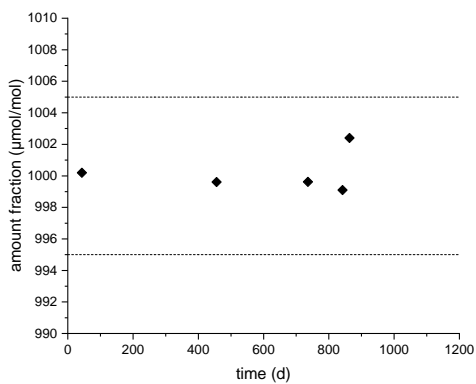
(a) PRM144133, 1000 μmol mol^{-1} NO$_2$
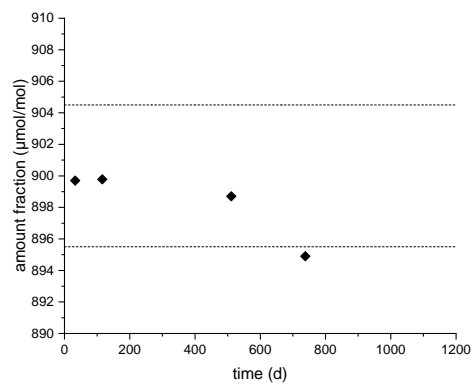
(b) PRM145036, 900 μmol mol^{-1} NO$_2$
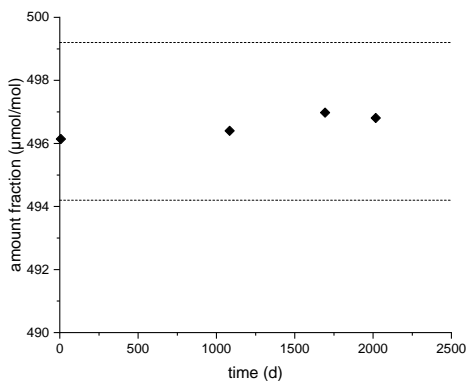
(c) PRM144012, 500 μmol mol^{-1} NO$_2$
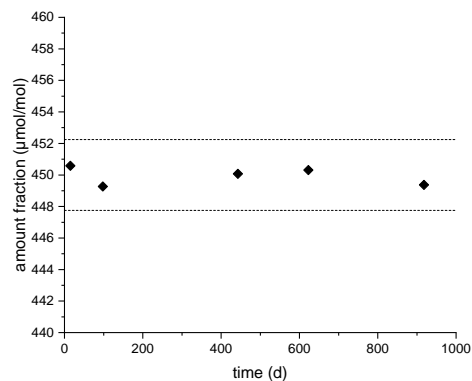
(d) PRM162926, 450 μmol mol^{-1} NO$_2$
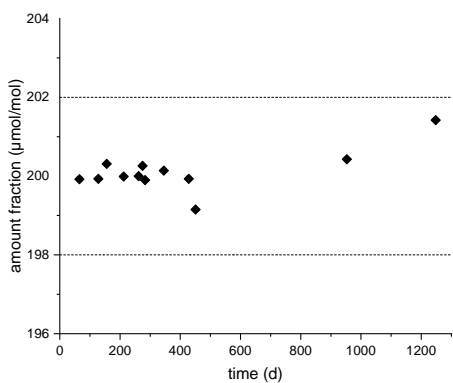
(e) VSL448122, 200 μmol mol^{-1} NO$_2$
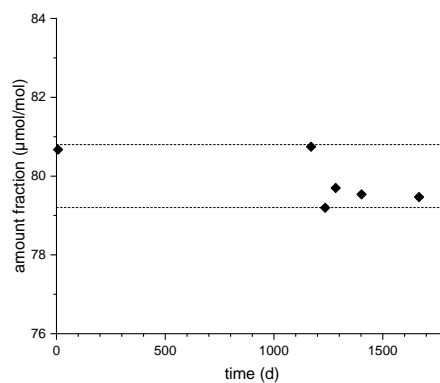
(f) PRM144130, 80 μmol mol^{-1} NO$_2$

Figure 7: Stability study data of NO$_2$ in nitrogen mixtures at various amount fraction levels.

Table 6: CMCs for nitrogen dioxide in nitrogen and air

Range	Amount fraction		Relative expanded uncertainty (%)		Standards
	Low	High	Low	High	
Range 4	1.00×10^{-7}	1.00×10^{-6}	3.0	2.0	Dynamic
Range 3	1.00×10^{-6}	1.00×10^{-5}	2.0	1.5	Dynamic
Range 2	1.00×10^{-5}	1.00×10^{-4}	1.5	1.0	Static
Range 1	1.00×10^{-4}	1.00×10^{-3}	1.0	0.5	Static

A   Calibration data

Table 7: Calibration data for nitrogen dioxide in nitrogen. Amount fractions (x) are given in $\mu mol\,mol^{-1}$, responses y in a.u.

Mixture	x	$u(x)$	y	$u(y)$
AN4004	4.0083	0.0200	10 036.4	14.9
AN4003	3.0173	0.0151	7430.4	11.0
AN4002	2.0053	0.0100	4943.1	7.3
AN2002	2.0013	0.0100	4970.9	7.4
AN2001	1.0038	0.0050	2436.6	3.6
AN2008	0.8014	0.0040	1941.2	2.9
AN1008	0.7994	0.0040	1969.5	2.9
AN1005	0.5012	0.0025	1215.0	1.8
AN1003	0.3002	0.0015	707.4	1.1

Table 8: Calibration data for nitrogen dioxide in nitrogen. Amount fractions (x) are given in $\mu mol\,mol^{-1}$, responses y in a.u.

Mixture	x	$u(x)$	y	$u(y)$
VSL243947	100.083	0.110	104.47	0.15
VSL243852	80.083	0.088	82.92	0.12
VSL345042	60.072	0.066	62.25	0.09
VSL243961	40.048	0.044	42.39	0.06

Table 9: Calibration data for nitrogen dioxide in nitrogen. Amount fractions (x) are given in $\mu mol\,mol^{-1}$, responses y in a.u.

Mixture	x	$u(x)$	y	$u(y)$
VSL245045	100.2319	0.104006	99.673	0.150
VSL245025	99.86657	0.103466	99.430	0.150
VSL165053	80.08822	0.084626	79.608	0.120
VSL344100	40.1276	0.041293	39.778	0.060
VSL345010	20.07022	0.02098	19.767	0.030
VSL243967	10.00759	0.010131	9.730	0.010
VSL548105	10.00238	0.010299	9.769	0.010
VSL448087	8.002645	0.008193	7.764	0.010

Table 10: Calibration data for nitrogen dioxide in nitrogen. Amount fractions (x) are given in $\mu mol\,mol^{-1}$, responses y in a.u.

Mixture	x	$u(x)$	y	$u(y)$
VSL343985	1002.15	1.02	1065.98	1.56
VSL245021	800.38	0.81	863.95	1.26
VSL348090	600.94	0.61	652.14	0.95
VSL399250	400.45	0.41	439.93	0.64
PRM165018	200.14	0.21	225.73	0.33
VSL243947	100.08	0.10	113.71	0.17

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[1] P. Brewer and A. M. H. van der Veen. GAWG strategy for comparisons and CMC claims. GAWG, Gas Analysis Working Group, Sèvres, France, October 2016.

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