Calibration and Measurement Capabilities for hydrogen sulfide in nitrogen and methane†

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Abstract

In 2016, the Gas Analysis Working Group of the Consultative Committee on Amount-of-Substance (GAWG) introduced an extrapolation scheme to be used for translating the measurement uncertainty reported in a key comparison to a measurement capability. This extrapolation scheme has a tipping point at 10 µmol mol^{-1}. Below this amount fraction level, the expanded uncertainty is assumed to be independent of the amount fraction, and above the relative expanded uncertainty is assumed to constant. It provides conservative values for the relative expanded uncertainty at the end points of the interval of services related to hydrogen sulfide. In this paper, we revisit the results of the latest key comparison, the maintenance of the measurement standards, and the re-verification of returned primary reference materials and provide evidence for the calibration and measurement capability. We demonstrate that the relative expanded uncertainty in the interval from 1 µmol mol^{-1} to 1000 µmol mol^{-1} range from 2.5 % to 0.4 % ($k = 2$). We note that due to the steep increase in the uncertainty at the low amount fraction end, it is difficult to describe the relationship between the expanded uncertainty and the amount fraction by a simple formula.

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 Calibration and Measurement Capability (CMC) [1]. This extrapolation scheme has a tipping point at 10 µmol 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 µmol 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 using their logarithms, so $\lg u$ to $\lg x$. As the amount fraction intervals are very wide and using

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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 approach applied previously for the said binary mixtures to mixtures of hydrogen sulfide nitrogen. The result submitted the result submitted in CCQM-K41.2017 [7] and the related degree of equivalence computed from it is the focal point. To characterise the relative expanded uncertainty over the interval 1 μmol mol^{-1} to 1000 μmol mol^{-1}, the evidence is supplemented by data showing the long-term behaviour of these calibration gas mixtures, performance of the analysers used, performance of the static gravimetric gas mixture preparation, to support CMCs based on the result submitted in CCQM-K41.2017.

2 Key comparisons

VSL participated in CCQM-K41.2017 [7]. The result submitted was consistent with the key comparison reference value (KCRV). The stated relative expanded uncertainty is 0.6 %. VSL maintains measurement standards of hydrogen sulfide in nitrogen from 1 μmol mol^{-1} to 1000 μmol mol^{-1}. The nominal amount fraction in CCQM-K41.2017 was 10 μmol mol^{-1}.

According to the GAWG Strategy [1], the CMC support would be at 1 μmol mol^{-1} 6 % relative expanded uncertainty and at 1000 μmol mol^{-1} 0.6 %. 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 [8–10], and ISO Guide 35 [11]. The latter document is used with regard to the evaluation of stability study data [12], and the combination of that contribution with other uncertainty contributions [13, 14]. 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) [15].

4 Results

4.1 Purity analysis

Nominally pure hydrogen sulfide is assessed for purity in accordance with ISO 19229 [9]. The main impurities are nitrogen, carbon dioxide, carbonyl sulfide. The purity table is given in table 1. Nitrogen used for both primary standard gas mixtures (PSMs) and primary reference materials (PRMs) is grade 6.0, BIP+. A purity table is shown elsewhere [16].

4.2 Gravimetric gas mixture preparation

All PSMs and PRMs are prepared using the procedure of ISO 6142-1 [8, 17]. The uncertainty evaluation is described elsewhere [2, 18]. PSMs are prepared using a hierarchy as described

Table 1: Purity table of the nominally pure hydrogen sulfide (AP7947)

Component	x $\mu mol\,mol^{-1}$	$u(x)$ $\mu mol\,mol^{-1}$
Carbon dioxide	78.0	4
Nitrogen	4.4	2.5
Hydrogen sulfide	999 914.2	5
Carbonyl sulfide	3.4	0.2

in ISO 14167 [19] by means of gravimetric dilution. In the first step, a gas mixture is prepared with nominally 4 % hydrogen sulfide. Typical compositions of gravimetrically prepared mixtures are given in tables 2 (1000 $\mu mol\,mol^{-1}$), 3 (100 $\mu mol\,mol^{-1}$), 4 (20 $\mu mol\,mol^{-1}$), and 5 (1 $\mu mol\,mol^{-1}$).

Table 2: Composition of a nominally 1000 $\mu mol\,mol^{-1}$ H_2S mixture

Component	x $mol\,mol^{-1}$	$u_{rel}(x)$ %
Argon	4.9950×10^{-6}	58
Methane	7.9920×10^{-9}	60
Carbon monoxide	1.4985×10^{-8}	58
Carbon dioxide	9.2081×10^{-8}	7.7
hydrogen	2.4974×10^{-8}	58
water	9.9900×10^{-9}	58
Nitrogen	9.9899×10^{-1}	0.0006
Oxygen	9.6829×10^{-8}	30
hydrogen sulfide	1.0010×10^{-3}	0.0335
carbonyl sulfide	7.0076×10^{-9}	29

4.3 Verification

The verification of gravimetrically prepared gas mixtures is done using an Interscan RM17 gas analyser based on electrochemical analysis with a continuous flow gas cell (1 $\mu mol\,mol^{-1}$ to 10 $\mu mol\,mol^{-1}$) [7] and a multipoint calibration in accordance with ISO 6143 [10]. For the intervals 10 $\mu mol\,mol^{-1}$ to 100 $\mu mol\,mol^{-1}$ and 100 $\mu mol\,mol^{-1}$ to 1000 $\mu mol\,mol^{-1}$, an ABB AO2020 analyser equipped with a Limas 11 UV module is used. This analyser is also calibrated using a multipoint calibration.

A typical calibration function for the range 1 $\mu mol\,mol^{-1}$ to 10 $\mu mol\,mol^{-1}$ is shown in figure 1. The standard uncertainty calculated from ISO 6142-1 is used for the amount fractions. The standard uncertainty of the responses is evaluated by averaging the three runs of the analyser and using the standard deviation of the responses as standard uncertainty for the average. This approach is consistent with the uncertainty budget submitted in CCQM-K41.2017 [7]. The calibration function is a parabola.

Table 3: Composition of a nominally 100 µmol mol^{-1} H_2S mixture

Component	x mol mol^{-1}	$u_{rel}(x)$ %
Argon	4.9995×10^{-6}	59
Methane	1.0062×10^{-9}	58
Carbon monoxide	1.0125×10^{-9}	58
Carbon dioxide	1.7809×10^{-8}	33
Hydrogen	2.4998×10^{-8}	59
Water	9.9990×10^{-9}	59
Nitrogen	9.9989×10^{-1}	0.0006
Oxygen	9.9904×10^{-8}	29
Hydrogen sulfide	1.0011×10^{-4}	0.0168
Carbonyl sulfide	3.4042×10^{-10}	5.9

Table 4: Composition of a nominally 20 µmol mol^{-1} H_2S mixture

Component	x mol mol^{-1}	$u_{rel}(x)$ %
Argon	5.0000×10^{-6}	57
Methane	8.0000×10^{-9}	59
Carbon monoxide	1.5000×10^{-8}	57
Carbon dioxide	1.0078×10^{-8}	56
Hydrogen	2.5000×10^{-8}	57
Water	1.0000×10^{-8}	57
Nitrogen	9.9999×10^{-1}	0.0006
Oxygen	5.0000×10^{-9}	57
Hydrogen sulfide	1.0014×10^{-6}	0.0304
Carbonyl sulfide	3.4051×10^{-12}	5.9

Table 5: Composition of a nominally 1 µmol mol^{-1} H_2S mixture

Component	x mol mol^{-1}	$u_{rel}(x)$ %
Argon	5.0000×10^{-6}	57
Methane	8.0000×10^{-9}	59
Carbon monoxide	1.5000×10^{-8}	57
Carbon dioxide	1.0078×10^{-8}	56
Hydrogen	2.5000×10^{-8}	57
Water	1.0000×10^{-8}	57
Nitrogen	9.9999×10^{-1}	0.0006
Oxygen	5.0000×10^{-9}	57
Hydrogen sulfide	1.0014×10^{-6}	0.0304
Carbonyl sulfide	3.4051×10^{-12}	5.9

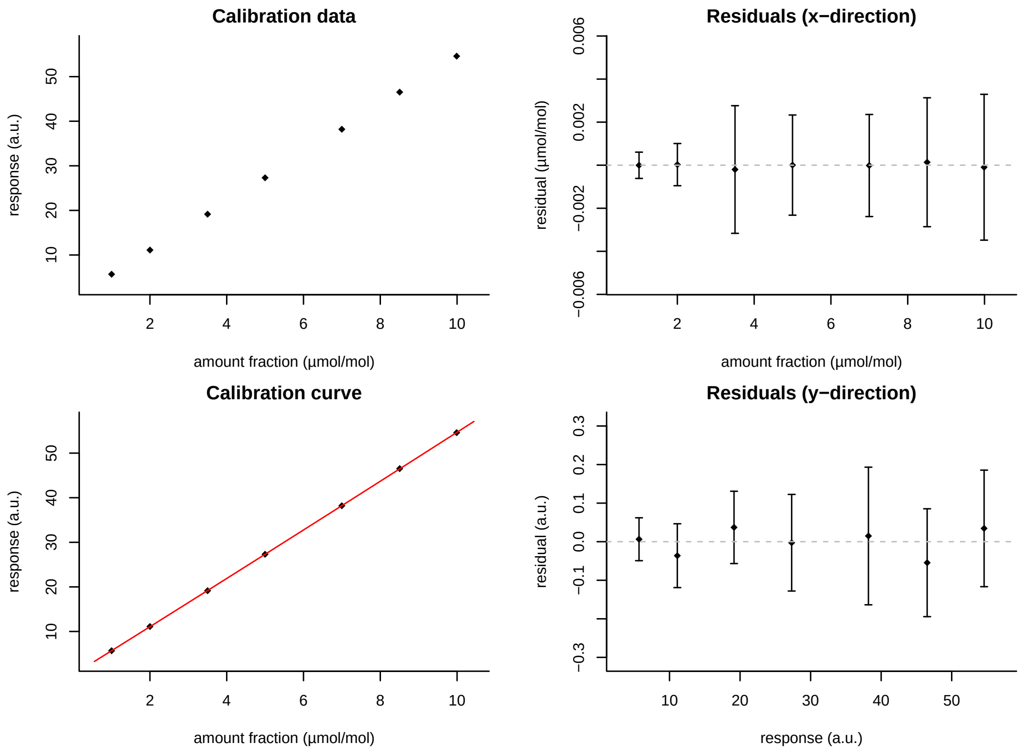

Figure 1: Calibration function for hydrogen sulfide in the range 1 µmol mol^{-1} to 10 µmol mol^{-1} and residuals after weighted total least squares (WTLS) regression in accordance with ISO 6143

The results of the use of the calibration function are shown in table 6. The relative standard uncertainty of the amount fractions ranges from around 1 % at 1 µmol mol^{-1} down to 0.20 % at 10 µmol mol^{-1}. For the vast majority of the gas mixtures, the results pass the verification criterion of ISO 6142-1 [8, eqn (8)]. Such mixtures are provided with relative expanded uncertainties from 2.5 % to 1.5 %.

Calibration data and a calibration function for the range 10 µmol mol^{-1} to 100 µmol mol^{-1} is shown in figure 2. The calibration function is a parabola. The uncertainty evaluation of the responses is the same as done for the range 1 µmol mol^{-1} to 10 µmol mol^{-1}. The use of the calibration function for interpolation is shown in table 7. The relative standard uncertainty of the interpolated amount fraction ranges from 0.20 % to 0.05 %. Mixtures in this range are certified with an expanded uncertainty from 1.5 % to 1.0 %.

Table 6: Verification data for hydrogen sulfide in nitrogen in the range 1 µmol mol^{-1} to 10 µmol mol^{-1}

Mixture	y a.u.	$u(y)$ a.u.	x µmol mol^{-1}	$u(x)$ µmol mol^{-1}	$u(x)/x$	Δx µmol mol^{-1}	$\Delta x/u(x)$	$\Delta x/x$
VSL199579	5.674	0.043	0.999	0.009	0.93%	-0.001	-0.13	-0.12%
VSL299619	5.724	0.055	1.008	0.011	1.12%	0.009	0.84	0.95%
VSL144973	5.529	0.023	0.972	0.006	0.66%	-0.030	-4.71	-3.03%
VSL199626	10.914	0.043	1.972	0.009	0.45%	-0.028	-3.20	-1.41%
VSL399581	11.015	0.046	1.990	0.009	0.47%	-0.011	-1.15	-0.54%
VSL144592	10.893	0.042	1.968	0.009	0.44%	-0.035	-4.03	-1.73%
VSL144969	16.361	0.053	2.980	0.011	0.37%	-0.020	-1.83	-0.67%
VSL149093	16.351	0.051	2.978	0.011	0.35%	-0.023	-2.16	-0.76%
VSL458440	16.858	0.022	3.072	0.006	0.21%	0.069	10.68	2.30%
VSL144573	16.545	0.035	3.014	0.008	0.27%	0.007	0.84	0.22%
VSL144993	27.331	0.058	5.002	0.013	0.25%	0.003	0.23	0.06%
PRM144963	27.264	0.060	4.990	0.013	0.26%	-0.013	-1.02	-0.26%
VSL299572	27.340	0.056	5.004	0.012	0.25%	-0.015	-1.19	-0.29%
VSL258426	38.112	0.076	6.980	0.015	0.22%	-0.008	-0.51	-0.11%
VSL299568	46.348	0.087	8.484	0.017	0.21%	-0.018	-1.04	-0.21%
VSL149078	46.255	0.078	8.467	0.016	0.19%	-0.038	-2.41	-0.45%
VSL299623	54.668	0.067	9.997	0.017	0.17%	-0.003	-0.20	-0.03%

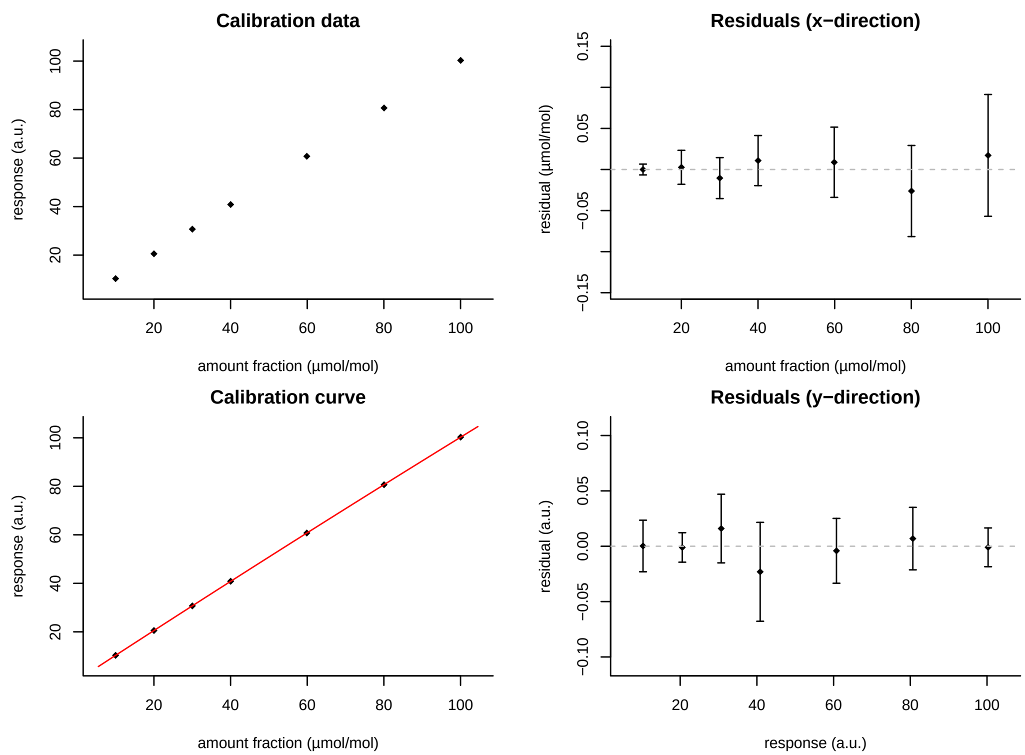

Figure 2: Calibration function for hydrogen sulfide in the range 10 µmol mol^{-1} to 100 µmol mol^{-1} and residuals after WTLS regression in accordance with ISO 6143

Table 7: Verification data for hydrogen sulfide in nitrogen in the range 10 µmol mol^{-1} to 100 µmol mol^{-1}

Mixture	y a.u.	$u(y)$ a.u.	x µmol mol^{-1}	$u(x)$ µmol mol^{-1}	$u(x)/x$	Δx µmol mol^{-1}	$\Delta x/u(x)$	$\Delta x/x$
VSL105799	10.296	0.014	9.984	0.017	0.18%	-0.005	-0.28	-0.05%
VSL658444	10.311	0.011	10.000	0.015	0.15%	0.000	0.01	0.00%
VSL299558	10.276	0.015	9.965	0.018	0.18%	-0.038	-2.08	-0.38%
PRM291149	20.561	0.015	20.028	0.017	0.08%	0.019	1.13	0.09%
VSL244576	20.573	0.027	20.039	0.027	0.14%	0.015	0.56	0.08%
PRM244593	20.553	0.022	20.020	0.022	0.11%	-0.005	-0.23	-0.03%
VSL199640	30.633	0.022	29.938	0.024	0.08%	-0.045	-1.86	-0.15%
VSL244428	30.689	0.009	29.994	0.013	0.05%	-0.009	-0.67	-0.03%
VSL358460	40.776	0.006	39.974	0.014	0.04%	-0.012	-0.85	-0.03%
PRM191147	48.939	0.008	48.094	0.016	0.03%	-0.033	-2.06	-0.07%
VSL399573	60.888	0.019	60.047	0.024	0.04%	0.033	1.37	0.06%
VSL299559	80.726	0.002	80.076	0.018	0.02%	0.038	2.15	0.05%
VSL299562	100.279	0.011	100.049	0.035	0.04%	0.015	0.42	0.02%
VSL299632	100.367	0.012	100.139	0.035	0.04%	0.025	0.72	0.03%

Calibration data and a calibration function for the range 100 µmol mol^{-1} to 1000 µmol mol^{-1} is shown in figure 3. The calibration function is a parabola. The relative standard uncertainty of the responses is set at 0.04 %. The use of the calibration function for interpolation is shown in table 8. The relative standard uncertainty of the interpolated amount fraction is 0.06 %. Mixtures in this range are certified with an expanded uncertainty from 1.0 % to 0.5 %.

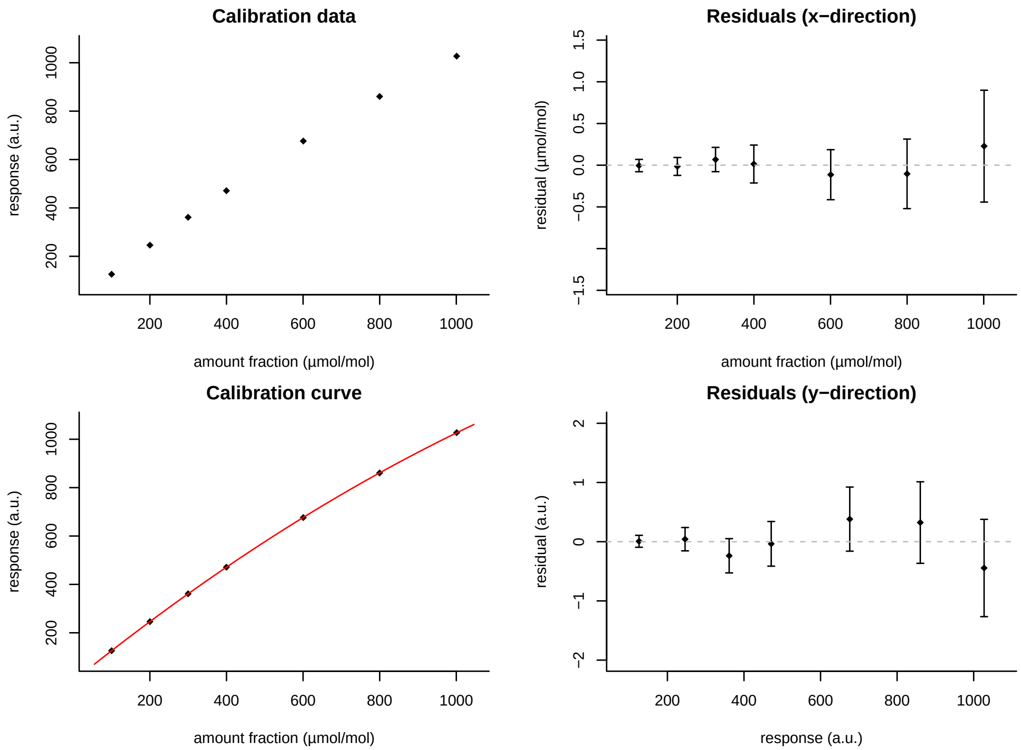

Figure 3: Calibration function for hydrogen sulfide in the range 100 µmol mol^{-1} to 1000 µmol mol^{-1} and residuals after WTLS regression in accordance with ISO 6143

Table 8: Verification data for hydrogen sulfide in nitrogen in the range 10 µmol mol^{-1} to 100 µmol mol^{-1}

Mixture	y a.u.	$u(y)$ a.u.	x µmol mol^{-1}	$u(x)$ µmol mol^{-1}	$u(x)/x$	Δx µmol mol^{-1}	$\Delta x/u(x)$	$\Delta x/x$
VSL399563	125.98	0.05	100.10	0.07	0.07%	0.02	0.37	0.03%
VSL299632	126.03	0.05	100.14	0.07	0.07%	0.03	0.40	0.03%
VSL247963	246.43	0.10	200.33	0.10	0.05%	0.21	2.13	0.11%
VSL299754	361.03	0.14	299.86	0.15	0.05%	0.11	0.69	0.04%
VSL300241	361.58	0.14	300.35	0.15	0.05%	0.19	1.26	0.06%
VSL449656	470.98	0.19	399.72	0.21	0.05%	-0.16	-0.78	-0.04%
VSL163012	675.70	0.27	599.36	0.32	0.05%	-0.25	-0.79	-0.04%
VSL238588	852.04	0.34	789.57	0.45	0.06%	-0.73	-1.62	-0.09%
VSL163013	851.34	0.34	788.78	0.45	0.06%	-11.01	-24.30	-1.38%
VSL238370	1026.48	0.41	1000.81	0.74	0.07%	0.28	0.38	0.03%

4.4 Stability of measurement standards and primary reference materials

The largest uncertainty contribution is due to long-term stability of the amount fraction hydrogen sulfide. The data from three calibration gas mixtures is shown in figure 4. The relative deviation with respect to the amount fraction calculated from preparation is shown. The mixtures represent three different nominal amount fractions: 790 µmol mol^{-1}, 200 µmol mol^{-1} and 60 µmol mol^{-1}. The data demonstrate stability for well over three year. The standard deviations are respectively 0.15 %, 0.21 % and 0.06 %. A cautious relative standard uncertainty would be 0.20 %, for mixtures with an amount fraction hydrogen sulfide down to 10 µmol mol^{-1}. This limit is confirmed by an overview of the re-analysis of returned PRMs (table 9). For lower amount fractions, the standard uncertainty due to long-term stability increases. For example, mixtures with 3 µmol mol^{-1} hydrogen sulfide would have at least a relative standard uncertainty of 1 % to address stability effects, and an expiry date of two years. The result for PRM158448 is in that sense not extraordinary; actually, the results for PRM299564 and PRM258451 are exceptionally good. Table 9 also demonstrates that nominally identical cylinders can show quite different stability behaviour, especially at low-µmol mol^{-1} levels.

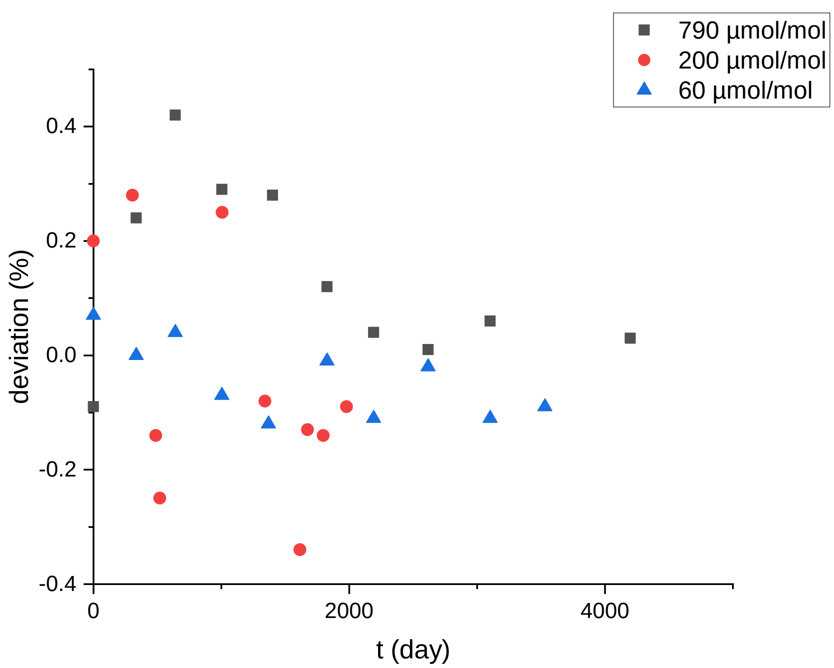

Figure 4: Long-term stability data of three mixtures of hydrogen sulfide in nitrogen

4.5 CMCs

The Calibration and Measurement Capabilities (CMCs) can now be computed by combining the relative standard uncertainties of preparation, analysis, and long-term stability [2,14]. The results are shown in table 10.

Based on the evidence provided, the CMCs that are underpinned by on one hand the result in CCQM-K41.2017 and on the other the long-term stability study data are shown in table 11.

Table 9: Relative differences (Δx) with respect to gravimetry for returned PRMs

Mixture	x $\mu mol\,mol^{-1}$	preparation	re-analysis	Δx %
PRM149214	1000.70	18/01/2012	18/02/2016	0.04
PRM148251	100.11	09/04/2010	29/08/2016	0.02
PRM158517	100.07	12/07/2007	29/08/2016	−0.19
PRM149262	100.06	06/04/2012	29/08/2016	0.07
PRM144970	50.031	30/01/2018	19/10/2020	−0.14
PRM299574	50.027	06/06/2016	15/01/2020	−0.20
PRM144976	20.007	30/01/2018	19/10/2020	−0.18
PRM144975	10.017	28/08/2017	15/01/2020	−0.08
PRM258451	4.014	26/03/2012	17/01/2016	0.03
PRM299561	4.002	19/05/2014	27/01/2016	−0.28
PRM299564	3.502	13/06/2016	18/06/2018	−0.06
PRM158448	3.014	08/05/2007	13/08/2014	−1.50

Table 10: CMCs calculated for different amount fractions

x	Uncertainty contribution				Mixture
$mol\,mol^{-1}$	prep %	anal %	stab %	total %	
1.00×10^{-6}	0.04	0.93	0.80	1.23	VSL199579
5.00×10^{-6}	0.04	0.30	0.50	0.58	VSL299572
1.00×10^{-5}				0.30	CCQM-K41.2017
1.00×10^{-5}	0.03	0.18	0.25	0.31	VSL658444
5.00×10^{-4}	0.03	0.10	0.20	0.23	PRM299574
1.00×10^{-4}	0.03	0.10	0.15	0.18	PRM158517
1.00×10^{-3}	0.03	0.10	0.10	0.14	PRM149214

Table 11: Measurement ranges and CMCs (expressed as relative expanded uncertainty)

Range	Amount fraction		Expanded uncertainty (%)	
	Low end	High end	Low end	High end
Range 3	1.00×10^{-6}	1.00×10^{-5}	2.5	0.6
Range 2	1.00×10^{-5}	1.00×10^{-4}	0.6	0.5
Range 1	1.00×10^{-4}	1.00×10^{-3}	0.5	0.4

The extrapolation model developed previously is not capable to describe the data in table 10, largely due to the steep increase of the analytical (verification) uncertainty and the uncertainty due to long-term stability below 10 µmol mol^{-1}.

5 Conclusions

In this paper, we revisited the results of the latest key comparison, the maintenance of the measurement standards, and the re-verification of returned primary reference materials for mixtures of hydrogen sulfide in nitrogen. Thereby, evidence is provided for the calibration and measurement capability over the interval from 1 µmol mol^{-1} to 1000 µmol mol^{-1}. We demonstrate that the relative expanded uncertainty ranges from 2.5 % to 0.4 % ($k = 2$). We note that due to the steep increase in the uncertainty at the low amount fraction end, it is difficult to describe the relationship between the expanded uncertainty and the amount fraction by a simple formula.

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