International Comparison CCQM-K118 Natural Gas. Support to measurement capabilities[†]

1 Premable

This guidance note is aimed at reviewers of Calibration and Measurement Capabilitys (CMCs), supported by the participation in a key comparison. In principle, support to measurement capabilities is limited to those measurement results that are consistent with the key comparison reference value (KCRV). In this key comparison [1], several measurement results were not consistent with the KCRV. For those results, this guidance note provides larger expanded uncertainties, based on the GAWG strategy document [2]. The idea behind these larger uncertainties is that

1. National Metrology Institutes (NMIs) can still use their participation in a key comparison to support their measurement service;
2. The stated uncertainty is large enough to ensure comparability with the KCRV and the results of other NMIs;
3. There is a harmonised way of dealing with discrepant results in relation to CMCs.

Discrepant measurement results can occur for a number of reasons. For a discussion of the measurement results in CCQM-K118, see the final report [1]. In case of incidental discrepant results, the default response would be to investigate the cause of the discrepancy and to resolve it [3]. Hence, the attached table should not be viewed as

- A substitute for appropriate corrective measures from the side of the NMI to resolve the discrepancy;
- A consent from the CCQM Gas Analysis Working Group (CCQM-GAWG) that the submitted measurement result is acceptable;
- A guarantee that a CMC submitted in accordance with this guidance note will be accepted by reviewers in the review process by the Regional Metrology Organisations;
- Support for the metrological traceability of the measurement result submitted;
- A direction or recommendation to assessors in peer reviews or accreditation visits.

[†]This document cancels and replaces guidance note CCQM-GAWG CMC-06 A.

2 Support to CMCs

The support of CMC claims is described in more detail in the ”GAWG strategy for comparisons and CMC claims” [2]. The results of this key comparison can be used to support CMC claims for the composition of natural gas in the following ranges (see table 1). CMCs outside the listed ranges are not supported by the results of this key comparison without further evidence.

If an NMI participated only for one of the mixtures, then the respective columns in table 1 apply.

Table 1: Support to CMCs ($\mathrm{cmol\,mol^{-1}}$) [1]

Component	Both mixtures		Low calorific mixture			High calorific mixture		
	x_{LB}	x_{UB}	x	x_{LB}	x_{UB}	x	x_{LB}	x_{UB}
Nitrogen	0.1	25	12	0.5	25	0.12	0.1	20
Carbon dioxide	0.02	20	4	0.5	20	0.02	0.02	10
Hydrogen	0.5	10	3	0.5	10			
Helium	0.05	2.5	0.5	0.05	2.5			
Ethane	0.2	25	0.75	0.2	20	10	0.5	25
Propane	0.05	12	0.3	0.05	10	2	0.1	12
iso-Butane	0.05	1.5	0.2	0.05	1.5	0.15	0.05	1.5
n-Butane	0.05	1.5	0.2	0.05	1.5	0.15	0.05	1.5
neo-Pentane	0.01	0.25	0.05	0.01	0.25			
iso-Pentane	0.01	0.25	0.05	0.01	0.25	0.02	0.01	0.25
n-Pentane	0.01	0.25	0.05	0.01	0.25	0.02	0.01	0.25
n-Hexane	0.01	0.25	0.05	0.01	0.25			
Methane	50	99.9	78.85	50	99.9	87.52	50	99.9

3 Supported capabilities

3.1 Nitrogen

Table 2: Supported CMCs for nitrogen (%). Lower and upper bounds given in cmol mol^{-1}.

Lab	x_{LB} cmol mol^{-1}	x_{UB} cmol mol^{-1}	a_0	a_1	U_{CMC} %
VSL	0.10	25.0	-5.8596	-0.2073	0.17
VNIIM	0.10	25.0	-2.7424	0.8541	0.78
SMU	0.50	25.0			0.31
NIM	0.10	25.0	-7.7438	-1.1016	0.25
NPL	0.10	25.0	-5.3432	-0.0183	0.20
NMIA	0.10	25.0	-6.0894	-0.2736	0.14
BAM	0.10	25.0	-6.1241	-0.2954	0.14
GUM	0.10	25.0	-3.7449	0.5361	0.42
CMI	0.10	25.0	-7.9930	-1.1484	0.18
NMISA	0.10	25.0	-6.3606	-0.6870	0.66
BFKH	0.10	20.0			0.82
NMIJ	0.10	25.0	-3.3890	0.6590	0.50
KRISS	0.50	25.0			1.24
UME	0.10	25.0	-4.6835	0.2344	0.24

For laboratories for which the cells in the columns a_0 and a_1 in table 2 are populated, the interpolation formula [4]

$$\lg u_{CMC} = a_0 + a_1 \lg x$$

applies, where x denotes the amount fraction nitrogen and u_{CMC} the supported absolute standard uncertainty, both expressed in mol mol^{-1}. The relative expanded uncertainty $U_{CMC} = ku_{CMC}/x$ is calculated as

$$U_{CMC} = \frac{k}{x} \cdot 10^{a_0 + a_1 \lg x}$$

where x denotes the amount fraction in mol mol^{-1} and k the coverage factor. For $x > 0.5$ cmol mol^{-1}, the relative expanded uncertainty in the column U_{CMC} applies.

If a_0 and a_1 in table 2 are not populated, the supported range is limited as given in table 2. The relative expanded uncertainty in the column U_{CMC} of table 2 applies.

As an example, consider the data of NIM. At $x = 0.5$ cmol mol^{-1}, their CMC is

$$U_{CMC} = \frac{2}{0.005} \cdot 10^{-7.7438 - 1.1016 \lg 0.005} = 0.25\,\%$$

For an amount fraction of 20 cmol mol^{-1}, $U_{CMC} = 0.25\,\%$ (see also table 2).

3.2 Carbon dioxide

Table 3: Supported CMCs for carbon dioxide (%). Lower and upper bounds given in cmol mol^{-1}.

Lab	x_{LB} cmol mol^{-1}	x_{UB} cmol mol^{-1}	a_0	a_1	U_{CMC} %
VSL	0.02	20.0	-4.2317	0.5116	0.16
VNIIM	0.02	20.0	-2.5466	0.9402	0.78
SMU	0.50	20.0			0.42
NIM	0.02	20.0	-3.6640	0.6639	0.26
NPL	0.02	20.0	-4.9583	0.1957	0.16
NMIA	0.02	20.0	-4.8946	0.2423	0.14
BAM	0.02	20.0	-3.8666	0.6282	0.20
GUM	0.02	20.0	-2.5051	1.0049	0.61
CMI	0.02	20.0	-4.1926	0.4726	0.21
NMISA	0.02	20.0	0.9901	1.6580	59.84
BFKH	0.02	10.0			1.16
NMIJ	0.02	20.0	-0.1352	1.6451	4.80
KRISS	0.50	20.0			0.96
UME	0.02	20.0	-3.8372	0.6078	0.23

For laboratories for which the cells in the columns a_0 and a_1 in table 3 are populated, the interpolation formula [4]

$$\lg u_{CMC} = a_0 + a_1 \lg x$$

applies, where x denotes the amount fraction carbon dioxide and u_{CMC} the supported absolute standard uncertainty, both expressed in mol mol^{-1}. The relative expanded uncertainty $U_{CMC} = k u_{CMC}/x$ is calculated as

$$U_{CMC} = \frac{k}{x} \cdot 10^{a_0 + a_1 \lg x}$$

where x denotes the amount fraction in mol mol^{-1} and k the coverage factor. The interpolation formula applies up to an amount fraction of 0.5 cmol mol^{-1}. For $x \geq 0.5$ cmol mol^{-1}, the relative expanded uncertainty in the column U_{CMC} applies in table 3.

If a_0 and a_1 in table 3 are not populated, the supported range is limited as given in table 3. The relative expanded uncertainty in the column U_{CMC} of table 3 applies.

3.3 Hydrogen

Table 4: Supported CMCs for hydrogen (%). Lower and upper bounds given in cmol mol^{-1}.

Lab	x_{LB} cmol mol^{-1}	x_{UB} cmol mol^{-1}	U_{CMC} %
VSL	0.50	10.00	0.34
VNIIM	0.50	10.00	0.53
SMU	0.50	10.00	1.11
NIM	0.50	10.00	0.39
NPL	0.50	10.00	0.59
NMIA	0.50	10.00	0.35
BAM	0.50	10.00	0.33
GUM	0.50	10.00	0.86
CMI	0.50	10.00	0.73
NMISA	0.50	10.00	4.22
NMIJ	0.50	10.00	5.88
KRISS	0.50	10.00	1.29
UME	0.50	10.00	0.33

3.4 Helium

Table 5: Supported CMCs for helium (%). Lower and upper bounds given in cmol mol^{-1}.

Lab	x_{LB} cmol mol^{-1}	x_{UB} cmol mol^{-1}	U_{CMC} %
VSL	0.05	2.50	0.28
VNIIM	0.05	2.50	0.53
SMU	0.05	2.50	1.09
NIM	0.05	2.50	0.34
NPL	0.05	2.50	0.53
NMIA	0.05	2.50	0.29
BAM	0.05	2.50	0.24
GUM	0.05	2.50	0.63
CMI	0.05	2.50	0.87
NMISA	0.05	2.50	5.55
NMIJ	0.05	2.50	2.54
KRISS	0.05	2.50	1.61
UME	0.05	2.50	2.47

3.5 Ethane

Table 6: Supported CMCs for ethane (%). Lower and upper bounds given in cmol mol^{-1}.

Lab	x_{LB} cmol mol^{-1}	x_{UB} cmol mol^{-1}	U_{CMC} %
VSL	0.2	25.0	0.19
VNIIM	0.2	25.0	0.53
SMU	0.2	20.0	0.32
NIM	0.2	25.0	0.27
NPL	0.2	25.0	0.23
NMIA	0.2	25.0	0.17
BAM	0.2	25.0	0.33
GUM	0.2	25.0	0.81
CMI	0.2	25.0	0.65
NMISA	0.2	25.0	2.42
BFKH	0.5	25.0	0.14
NMIJ	0.2	25.0	0.16
KRISS	0.2	20.0	1.16
UME	0.2	25.0	0.18

3.6 Propane

Table 7: Supported CMCs for propane (%). Lower and upper bounds given in cmol mol^{-1}.

Lab	x_{LB} cmol mol^{-1}	x_{UB} cmol mol^{-1}	U_{CMC} %
VSL	0.05	12.00	0.27
VNIIM	0.05	12.00	0.57
SMU	0.05	10.00	0.54
NIM	0.05	12.00	0.30
NPL	0.05	12.00	0.21
NMIA	0.05	12.00	0.24
BAM	0.05	12.00	0.30
GUM	0.05	12.00	1.13
CMI	0.05	12.00	0.64
NMISA	0.05	12.00	2.33
BFKH	0.10	12.00	0.13
NMIJ	0.05	12.00	1.14
KRISS	0.05	10.00	1.26
UME	0.05	12.00	0.22

3.7 iso-Butane

Table 8: Supported CMCs for iso-butane (%). Lower and upper bounds given in cmol mol^{-1}.

Lab	x_{LB} cmol mol^{-1}	x_{UB} cmol mol^{-1}	U_{CMC} %
VSL	0.05	1.50	0.14
VNIIM	0.05	1.50	0.72
SMU	0.05	1.50	0.56
NIM	0.05	1.50	0.27
NPL	0.05	1.50	0.36
NMIA	0.05	1.50	0.33
BAM	0.05	1.50	0.14
GUM	0.05	1.50	4.97
CMI	0.05	1.50	0.69
BFKH	0.05	1.50	0.35
NMIJ	0.05	1.50	0.20
KRISS	0.05	1.50	0.94
UME	0.05	1.50	0.19

3.8 n-Butane

Table 9: Supported CMCs for n-butane (%). Lower and upper bounds given in cmol mol^{-1}.

Lab	x_{LB} cmol mol^{-1}	x_{UB} cmol mol^{-1}	U_{CMC} %
VSL	0.05	1.50	0.19
VNIIM	0.05	1.50	0.93
SMU	0.05	1.50	0.58
NIM	0.05	1.50	0.30
NPL	0.05	1.50	0.38
NMIA	0.05	1.50	0.36
BAM	0.05	1.50	0.19
GUM	0.05	1.50	0.82
CMI	0.05	1.50	0.73
NMISA	0.05	1.50	4.27
BFKH	0.05	1.50	0.30
NMIJ	0.05	1.50	0.59
KRISS	0.05	1.50	1.49
UME	0.05	1.50	0.23

3.9 iso-Pentane

Table 10: Supported CMCs for iso-pentane (%). Lower and upper bounds given in cmol mol^{-1}.

Lab	x_{LB} cmol mol^{-1}	x_{UB} cmol mol^{-1}	U_{CMC} %
VSL	0.01	0.25	0.50
VNIIM	0.01	0.25	1.05
SMU	0.01	0.25	0.98
NIM	0.01	0.25	0.53
NPL	0.01	0.25	0.55
NMIA	0.01	0.25	1.44
BAM	0.01	0.25	0.44
GUM	0.01	0.25	2.79
CMI	0.01	0.25	2.12
NMISA	0.01	0.25	2.88
BFKH	0.01	0.25	2.08
NMIJ	0.01	0.25	2.91
KRISS	0.01	0.25	3.02
UME	0.01	0.25	3.52

3.10 n-Pentane

Table 11: Supported CMCs for n-pentane (%). Lower and upper bounds given in cmol mol^{-1}.

Lab	x_{LB} cmol mol^{-1}	x_{UB} cmol mol^{-1}	U_{CMC} %
VSL	0.01	0.25	0.46
VNIIM	0.01	0.25	0.82
SMU	0.01	0.25	0.82
NIM	0.01	0.25	0.46
NPL	0.01	0.25	0.52
NMIA	0.01	0.25	0.53
BAM	0.01	0.25	0.48
GUM	0.01	0.25	0.68
CMI	0.01	0.25	1.52
NMISA	0.01	0.25	2.19
BFKH	0.01	0.25	0.59
NMIJ	0.01	0.25	0.42
KRISS	0.01	0.25	2.54
UME	0.01	0.25	1.71

3.11 neo-Pentane

Table 12: Supported CMCs for neo-pentane (%). Lower and upper bounds given in cmol mol^{-1}.

Lab	x_{LB} cmol mol^{-1}	x_{UB} cmol mol^{-1}	U_{CMC} %
VSL	0.01	0.25	0.39
VNIIM	0.01	0.25	0.69
SMU	0.01	0.25	1.06
NIM	0.01	0.25	0.47
NPL	0.01	0.25	0.60
NMIA	0.01	0.25	0.47
BAM	0.01	0.25	0.41
GUM	0.01	0.25	2.03
CMI	0.01	0.25	1.06
NMIJ	0.01	0.25	0.43
KRISS	0.01	0.25	2.03
UME	0.01	0.25	1.24

3.12 n-Hexane

Table 13: Supported CMCs for n-hexane (%). Lower and upper bounds given in cmol mol^{-1}.

Lab	x_{LB} cmol mol^{-1}	x_{UB} cmol mol^{-1}	U_{CMC} %
VSL	0.01	0.25	0.48
VNIIM	0.01	0.25	1.28
SMU	0.01	0.25	0.88
NIM	0.01	0.25	0.51
NPL	0.01	0.25	0.59
NMIA	0.01	0.25	1.67
BAM	0.01	0.25	0.54
GUM	0.01	0.25	0.74
CMI	0.01	0.25	0.74
NMISA	0.01	0.25	2.38
NMIJ	0.01	0.25	1.32
KRISS	0.01	0.25	2.04
UME	0.01	0.25	0.62

3.13 Methane (natural gas)

Table 14: Supported CMCs for methane (%). Lower and upper bounds given in cmol mol^{-1}.

Lab	x_{LB} cmol mol^{-1}	x_{UB} cmol mol^{-1}	U_{CMC} %
VSL	50.00	99.90	0.10
VNIIM	50.00	99.90	0.06
NIM	50.00	99.90	0.04
NPL	50.00	99.90	0.05
NMIA	50.00	99.90	0.06
BAM	50.00	99.90	0.03
GUM	50.00	99.90	0.10
CMI	50.00	99.90	0.04
NMISA	50.00	99.90	1.87
BFKH	50.00	99.90	0.04
NMIJ	50.00	99.90	0.89
UME	50.00	99.90	0.08

3.14 Methane (hydrogen-enriched natural gas)

Table 15: Supported CMCs for methane (%). Lower and upper bounds given in cmol mol^{-1}.

Lab	x_{LB} cmol mol^{-1}	x_{UB} cmol mol^{-1}	U_{CMC} %
VSL	50.00	99.90	0.38
VNIIM	50.00	99.90	0.07
SMU	50.00	99.90	0.16
NIM	50.00	99.90	0.06
NPL	50.00	99.90	0.06
NMIA	50.00	99.90	0.08
BAM	50.00	99.90	0.05
GUM	50.00	99.90	0.11
CMI	50.00	99.90	0.06
NMISA	50.00	99.90	2.06
NMIJ	50.00	99.90	0.42
KRISS	50.00	99.90	0.30
UME	50.00	99.90	0.20

A List of symbols

A.1 Symbols

a_0 intercept
a_1 slope
U expanded uncertainty
u standard uncertainty
x amount fraction

A.2 Subscripts

CMC	calibration and measurement capability
LB	lower bound (of the amount fraction interval)
UB	upper bound (of the amount fraction interval)

References

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[2] P. Brewer and A. M. H. van der Veen. GAWG strategy for comparisons and CMC claims. GAWG 19/41, Gas Analysis Working Group, Sèvres, France, October 2019.

[3] ISO/IEC 17025 General requirements for the competence of testing and calibration laboratories. ISO, International Organization for Standardization, Geneva, Switzerland, 2017. Third edition.

[4] Adriaan M.H. van der Veen and Heleen Meuzelaar. Extrapolation schemes of key comparison results in gas analysis. *Metrologia*, 58:045004, may 2021.