CCQM-GAWG Guidance document for submitting and reviewing CMCs for purity analysis

Jennifer Carney, Bernhard Niederhauser, Takuya Shimosaka, Adriaan van der Veen, Janneke van Wijk

Rationale

How to provide support for CMCs is well documented, however purity CMCs are lacking support by key comparisons and therefore rely heavily on supporting evidence. For the past two EURAMET comparisons on purity analysis, no official conclusion was reached due to disagreement on data treatment. In the meantime, ISO 19229 provides better guidance on how to establish coverage intervals which enables a better treatment of data close to 'zero' and '100%'.
As data from supporting evidence is more ambiguous than results from key comparisons, some guidelines on supporting evidence are useful so that reviewers use the same method and all submitted CMCs are reviewed in the same manner.

Minimum requirements for supporting evidence

Information from key comparisons can be used especially for the analyte tested in the key comparison both for purity of the analyte and for the detection limit of the analyte in the matrix gas used. The underpinning of the CMC should always include:

- A description of the measurement method used and a description of the evaluation of the measurement results, including the measurement uncertainty.
- Some proof of measurements is required like chromatograms or spectra to demonstrate the sensitivity and performance of the methods used. LoD/noise level measurements for dedicated analyzers can also be used.
- Examples of measurement data and the use of extrapolation and interpretation employed to arrive at the proposed CMC.

Scientific knowledge can also be used to support CMCs:

- For similar components proof for only one component is required. When an NMI has CMCs for purity analysis on nitrogen for propane and methane there is no reason to assume the NMI cannot determine ethane in nitrogen at trace levels using response factors. The determination of eg. hydrogen is not supported by those two components The rationale on which the equivalence of components is assumed should be stated when the CMC is submitted.
- Databases like the NIST webbook or HITRAN can also be used to extend the analysis of a component to a component that is similar under the measurement technique.
- The extrapolation of measurements from one technique to another should always include an uncertainty budget for using databases, response factors etc.

Example: Use of information from key comparisons

The participation of VSL in the CCQM-K111 1000 µmol mol^{-1} of propane in nitrogen is used and two purity tables were submitted as part of the measurement report of VSL.

Table 1: Purity table of propane.

Chemical symbol	Amount fraction x (mol/mol)	Standard uncertainty u_x (mol/mol)
C_2H_6	0.0000001	0.00000001
C_3H_6	0.000114	0.000011
C_3H_8	**0.9998556**	**0.000015**
C_4H_8	0.00000006	0.00000003
n-C_4H_{10}	0.0000016	0.00000016
i-C_4H_{10}	0.00000023	0.00000003
1-C_5H_{10}	0.0000004	0.0000002
n-C_5H_{10}	0.00000004	0.00000002

Table 2: Purity table of nitrogen.

Chemical symbol	Amount fraction x (mol/mol)	Standard uncertainty u_x (mol/mol)
H_2	0.000005	0.000003
H_2O	0.00000001	0.000000006
CH_4	0.000000008	0.000000005
N_2	**0.999994927**	**0.000006**
CO	0.000000015	0.000000009
O_2	0.000000005	0.000000003
Ar	0.000005	0.000003
CO_2	0.00000001	0.000000006

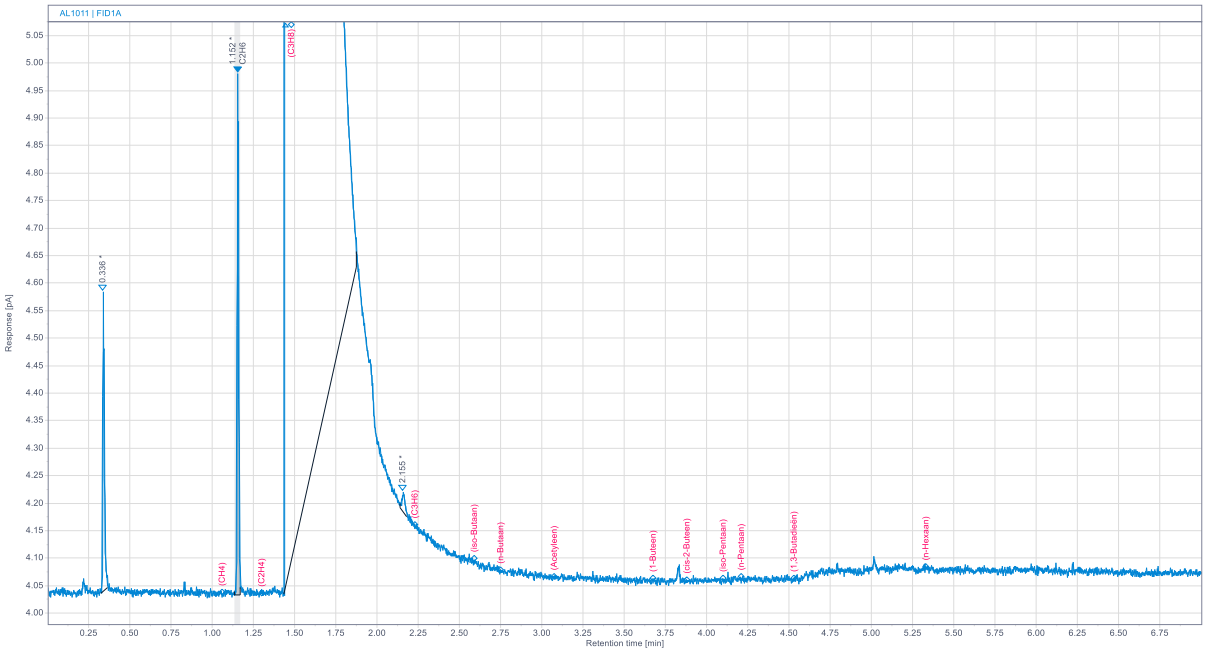
The uncertainty given by an NMI in a key comparison is calculated from the preparation and analysis of standards including purity analysis. When the NMI is in agreement with the KCRV this means that the presented purity table for the main component can be used for underpinning of CMCs but only for the main component; all other components are not tested in the key comparison and more supporting evidence is necessary.

As VSL demonstrates equivalence with the key comparison reference value, it can claim to be able to perform the purity analysis of propane with the uncertainty given in table 1. However, as the other components in the purity table were not tested in the key comparison, no CMC for the stated impurities in propane can be claimed without supporting evidence.

The extrapolation scheme for propane in nitrogen gives a cut-off value of 10 nmol mol^{-1} and therefore a claim for purity analysis of propane in nitrogen of 10 nmol mol^{-1} is also supported by this key comparison. None of the other components given in the purity able for nitrogen are supported by this key comparison.

Example: Supporting evidence for purity analysis claims for Propane by VSL

VSL uses two different GCs and three measurements performed against VSL standards. One of the chromatograms is presented here and expert information is used to look for impurities in the pure propane. The results of the measurement are given in the different tables. Note that this is not the same propane used in the CCQM-K111.



AL1011							
Rt	component		avg area	stdev	rsd%	calc. amount fraction mol/mol	uncertainty mol/mol
0.34	?						
1.15	ethaan		0.57	0.0017	0.29	2.69E-05	5.65E-07
2.15	propeen		0.04	0.0025	5.94	1.29E-06	8.08E-08
VSL223923							
Rt	component			cor. Mol fractie	cor. Uncertainty	stdv(Area)	rsd(area)
1.15	ethaan		0.11	5.00E-06	1.89E-09	2.21E-03	2.08
1.25	etheen						
1.48	propaan						
2.16	propeen		0.17	5.00E-06	2.16E-09	3.34E-03	2.01
2.57	iso-butaan						
2.72	n-butaan						
3.00	acetyleen						
3.54	cis-2-buteen/trans-2-buteen						
3.64	1-buteen						
3.76	cis-2-buteen/trans-2-buteen						
3.86	neopentaan/iso-butaan						
4.07	iso-pentaan						
4.19	n-pentaan						
4.39	1,3-butadieen						

		split 1:1						
AL1011								
Rt	component		avg area	stdev	rsd%	calc amount fraction mol/mol	uncertainty mol/mol	
3.88	neopentaan/isobutaan		0.13	0.00680	5.37	4.82E-07	2.64E-08	
5.03	Methylcyclopentaan		0.07	0.00281	3.83	1.11E-06	4.28E-08	
VSL223923								
Rt	component			cor. Mol fractie	cor. Uncertainty	stdv(area)	rsd(area)	
3.71	1-buteen							
3.82	neopentaan/ iso-butaan		1.31	4.97E-06	1.84E-09	0.0142	1.09	
3.91	cis-2-buteen							
4.12	iso-pentaan							
4.23	n-pentaan							
4.43	1,3-butadieen							
VSL144617	gemeten op 2022/06/01 (GC-02)							
	2-methyl-pentaan	5.178	1.91	3.01E-05	6.52E-09	0.02167	0.66	
	methyl-cyclopentaan	5.056	6.57	9.99E-05	2.18E-08	0.02183	0.21	

		split 1:1						
AL1011								
Rt	component		avg area	stdev	rsd%	calc amount fraction mol/mol	uncertainty mol/mol	
3.88	neopentaan/isobutaan		0.13	0.00680	5.37	4.82E-07	2.64E-08	
5.03	Methylcyclopentaan		0.07	0.00281	3.83	1.11E-06	4.28E-08	
VSL223923								
Rt	component			cor. Mol fractie	cor. Uncertainty	stdv(area)	rsd(area)	
3.71	1-buteen							
3.82	neopentaan/ iso-butaan		1.31	4.97E-06	1.84E-09	0.0142	1.09	
3.91	cis-2-buteen							
4.12	iso-pentaan							
4.23	n-pentaan							
4.43	1,3-butadieen							
VSL144617	gemeten op 2022/06/01 (GC-02)							
	2-methyl-pentaan	5.178	1.91	3.01E-05	6.52E-09	0.02167	0.66	
	methyl-cyclopentaan	5.056	6.57	9.99E-05	2.18E-08	0.02183	0.21	

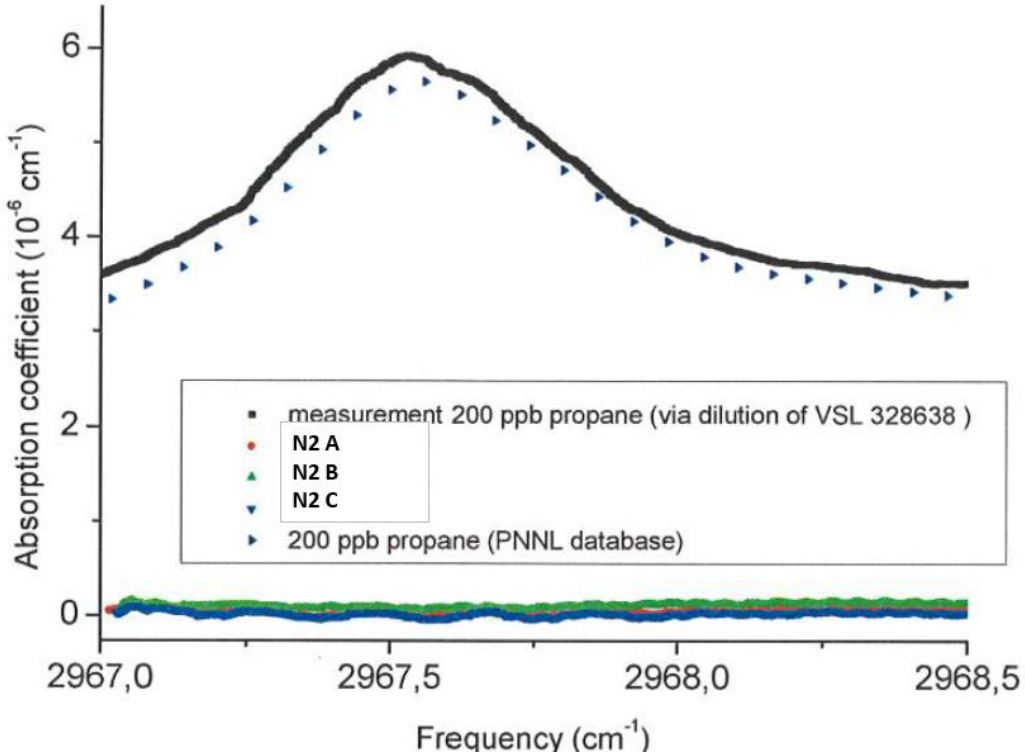
		split 1:1						
AL1011								
Rt	component		avg area	stdev	rsd%	calc amount fraction mol/mol	uncertainty mol/mol	
3.88	neopentaan/isobutaan		0.13	0.00680	5.37	4.82E-07	2.64E-08	
5.03	Methylcyclopentaan		0.07	0.00281	3.83	1.11E-06	4.28E-08	
VSL223923								
Rt	component			cor. Mol fractie	cor. Uncertainty	stdv(area)	rsd(area)	
3.71	1-buteen							
3.82	neopentaan/ iso-butaan		1.31	4.97E-06	1.84E-09	0.0142	1.09	
3.91	cis-2-buteen							
4.12	iso-pentaan							
4.23	n-pentaan							
4.43	1,3-butadieen							
VSL144617	gemeten op 2022/06/01 (GC-02)							
	2-methyl-pentaan	5.178	1.91	3.01E-05	6.52E-09	0.02167	0.66	
	methyl-cyclopentaan	5.056	6.57	9.99E-05	2.18E-08	0.02183	0.21	

These measurement results in the following purity table. As some of the reference standards are in helium and nitrogen this is added as a contribution to the uncertainty of the final composition. An extra uncertainty contribution is also added for the more than a factor 20 extrapolation for oxygen and argon.

Component	Formule	Mol fractie	ppm	u (mol/mol)	rsd%	absolute onzekerheid	rsd%
propaan	C3H8	9.99963E-01	9.99963E+05	7.36124E-07	0.00007	1.713E-06	0.000171
ethaan	C2H6	2.69E-05	26.88	5.65E-07	2	1.344E-06	5.00
propeen	C3H6	1.29E-06	1.29	8.08E-08	6	1.289E-07	10.00
neopentaan/isobutaan	iso-C4H10	4.82E-07	0.48	2.64E-08	5	4.823E-08	10.00
Methylcyclopentaan	C6H12	1.11E-06	1.11	4.28E-08	4	1.115E-07	10.00
Argon	Ar	1.30E-07	0.13	3.90E-09	3	1.305E-08	10.00
Zuurstof	O2	5.61E-07	0.56	2.52E-08	4	5.612E-08	10.00
Stikstof	N2	6.97E-06	6.97	4.62E-07	7	1.045E-06	15.00
Methaan	CH4	6.32E-08	0.06	9.48E-09	15	1.265E-08	20.00

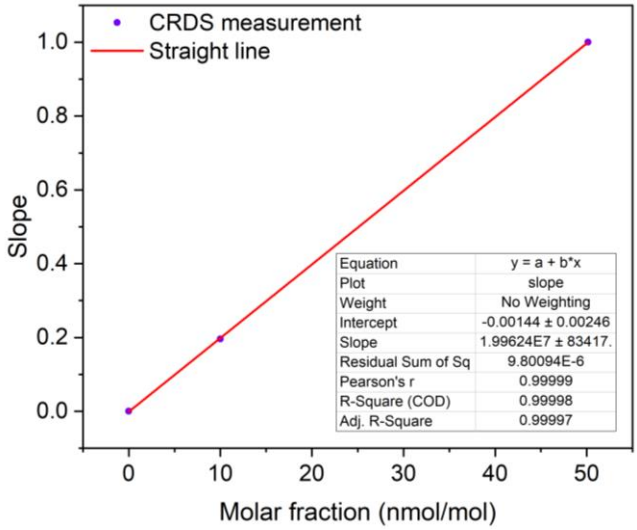
Example: Purity analysis of propane in nitrogen with CRDS

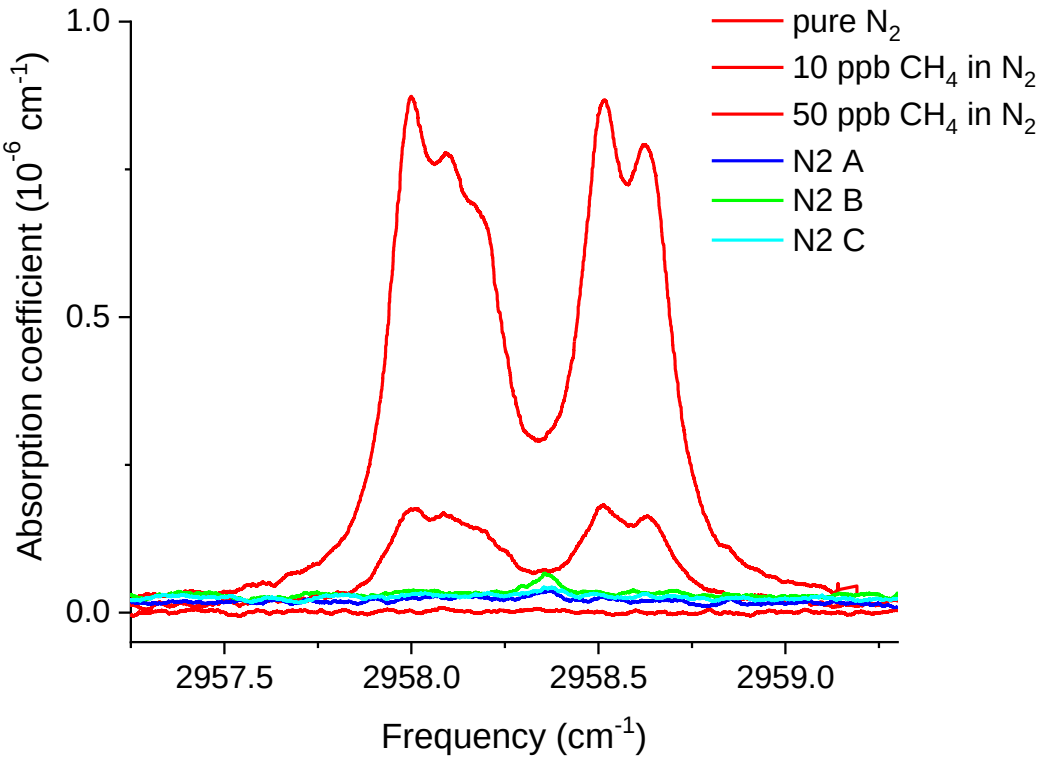
The reference standard used is a 1 µmol mol^{-1} propane in nitrogen standard. As the absorption of this amount fraction is too strong for the chosen adsorption line, the standard is dynamically diluted using thermal mass flow controllers to an amount fraction of 200 nmol mol^{-1} of propane. As an extra control on the dilution comparison with a calculated spectrum using the PNNL database is used.
The measurement spectra of the diluted standard, a number of pure nitrogen cylinders and the calculated spectrum for 200 nmol mol^{-1} is given. Resulting in a value of 5 ± 3 nmol mol^{-1} of propane in the measured nitrogen. This value looks high for the figure but it is a representation of a comparison with only 1 reference standard and extrapolation of the 200 nmol mol^{-1} value of the standard to a detection limit.



Example: Purity analysis of methane in nitrogen with CRDS

The methane amount fraction of the sample was calculated by plotting the CRDS signals collected at varying amount fractions against the CRDS spectrum corresponding to the highest amount fraction methane standard. The slopes of the resulting curves were determined by linear fitting and consecutively plotted as a function of amount fraction. The methane amount fraction of the analyzed mixtures (cylinders 396128, 439382 and G28267) is below the limit of detection of the instrument < 1 nmol mol^{-1}. As much more emphasis is made on measuring at different amount fractions no extra uncertainty budget has to be incorporated for extrapolation.





Suggestions regarding uncertainty budgets close to or at detection limits

In general: do not be too optimistic about uncertainties close to or at a detection limit. Extrapolation over more than 1 decade is often used and information about linearity of instrumentation close to 'zero' is often limited. Multiple reference standards are often not available and contribute to a larger uncertainty than just repeatability.

Detection limits are often calculated by applying a rectangular distribution. When using k=2, the uncertainty at the half width of the rectangle is more than 100 %. It is advisable to use k=1 to avoid this and avoid issues with non-symmetric coverage intervals.

To extrapolate uncertainties for purity analysis to higher amount fractions should be underpinned by proof of measurement.