METROLOGY for
HYDROGEN VEHICLES

REPORT:

Deliverable 4: Report on the results of the interlaboratory comparison for offline hydrogen purity analysis with conclusions on the participant agreement and recommendations for future improvements

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This report was written as part of activity A2.6.6 from the EMPIR Metrology for Hydrogen Vehicles (MetroHyVe) project. This report is the Deliverable 4 of the EMPIR MetroHyVe project. The three-year European project commenced on 1st June 2017 and focused on providing solutions to four measurement challenges faced by the hydrogen industry (flow metering, quality assurance, quality control and sampling). For more details about this project please visit www.metrohyve.eu.

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Contents

Glossary / Abbreviations

ATD	Automated thermal desorption
BID	Dielectric barrier discharge
BIP	Built-in purifier
CRDS	Cavity ring-down spectroscopy
DIN	Deutsches institut für normung
EMPIR	European metrology programme for innoavation and research
EURAMET	European association of national metrology institutes
FID	Flame ionisation detector
FPD	Flame photometric detector
FTIR	Fourier transform infrared spectrometer
GC	Gas chromatography
ISO	International organization for standardization
MFC	Mass flow controller
MS	Mass spectrometer
NMI	National metrology institute
PDHID	Pulsed discharge helium ionization detector
PED	Plasma emission detector
ppb	part per billion
ppm	part per million
OFCEAS	Optical feedback cavity-enhanced absorption spectroscopy
QCM	Quartz crystal microbalance
SCD	Sulphur chemiluminescence detector
TCD	Thermal conductivity detector
TD	Thermal desorption
UHP	Ultra-high purity

Participant name / Abbreviated name

AAL	Atlantic Analytical Laboratory
ALI	Airborne Labs International
CEMIAG	Centre d’Expertise et de Micro-Analyse des Gaz
GAS	Gas Analysis Services
IW	Iwatani Corporation
LD	Linde
NICE	National Institute of Clean and Low-Carbon Energy
NPL	National Physical Laboratory
SC	Smart Chemistry
VSL	Van Swinden Laboratory
VTT	VTT Technical Research Centre of Finland
ZBT	Zentrum für BrennstoffzellenTechnik
ZSW	Zentrum für Sonnenenergie- und Wasserstoff-Forschung Baden-Württemberg

1. Introduction

Currently there is a global push to reduce emissions of greenhouse gases with many nations having set stringent targets to reduce their carbon dioxide emissions [1]. One way to achieve this is to switch from petrol- or diesel-powered transportation to hydrogen fuel cell vehicles. Many countries (including the United Kingdom, France, Norway, India and China [2]) have already announced that they will ban new sales of petrol and diesel cars within the next 20 years. Although fuel cell vehicles are a suitable alternative to conventional vehicles in terms of emissions, fuel cells contain a catalyst that is very susceptible to chemical degradation [3]. The presence of certain contaminants in the hydrogen utilised, even at trace amount fractions (for example nmol/mol of hydrogen sulphide) can detrimentally damage the fuel cell due to poisoning of the catalyst, resulting in loss of power to the vehicle [4].

The globally recognised quality standard for hydrogen provided to fuel cell vehicles is ISO 14687:2019 Grade D [5]; which lists 13 different chemical contaminants with set threshold limits stated in Table 1. Refueling station operators must demonstrate compliance with ISO 14687:2019 (EN 17124:2018 [6] in Europe) before supplying hydrogen fuel to customers which in turn requires analytical laboratories to undertake quality assurance measurements of the hydrogen dispensed. Several laboratories across Europe are developing capability to provide these measurements with new challenges arising as a result, such as reliability, reproducibility and comparability. It is critical to ensure that the results provided are accurate and comparable between laboratories.

Table 1: Hydrogen purity requirements as specified in ISO 14687:2019

Component	Maximum concentration [µmol/mol]
Water	5
Total hydrocarbons except methane	2
Methane	100
Oxygen	5
Helium	300
Nitrogen	300
Argon	300
Carbon dioxide	2
Carbon monoxide	0.2
Total sulphur compounds	0.004
Formaldehyde	0.2
Formic acid	0.2
Ammonia	0.1
Halogenated compounds	0.05

EURAMET 1220 was the world's first interlaboratory comparison focusing on analysis of impurities in hydrogen [7]. The comparison exercise was performed in 2016 and involved analysis of hydrogen containing carbon monoxide at 1 µmol/mol and 0.1 µmol/mol and hydrogen sulphide at 1 µmol/mol. This work indicated that analytical results can vary significantly between laboratories, highlighting the need for further work and development of more complex and representative comparison exercises. As a result, a more complex interlaboratory comparison was organised and managed as part of the EMPIR MetroHyVe project.

This report presents the results of the MetroHyVe Interlaboratory comparison undertaken to evaluate the performance of analytical laboratories for measuring the concentration of several critical hydrogen impurities, including water (H_2O), nitrogen (N_2), carbon monoxide (CO) and hydrogen sulphide (H_2S), at ISO 14687:2019 threshold levels. These contaminants were selected based on a review of the literature [8] and feedback from the stakeholder advisory board for the MetroHyVe project due to their impact upon the fuel cell system (H_2S and CO) or their current prevalence as a hydrogen fuel contaminant (N_2 and H_2O)

Thirteen laboratories participated in the comparison exercise: NPL (UK) and VSL (NL) as coordinating laboratories, Atlantic Analytical Laboratory (US), Airborne Labs International (US), CEMIAG (FR), GAS Analysis Services (IE), Iwatani (JP), Linde (DE), NICE (CN), Smart Chemistry (US), VTT (FI), ZBT (DE) and ZSW (DE) as participating laboratories.

2. Scope of work

The objectives of the interlaboratory comparison described in this report are to provide a benchmark of analytical performance for laboratories undertaking measurements of critical hydrogen impurities, including H_2O, N_2, CO and H_2S at ISO 14687 threshold levels, and to identify significant differences in performance between laboratories and provide recommendations for future improvement.

2.1. Gas mixture provision

The compositions of the hydrogen gas mixtures were selected with consideration of the following points:

- The analyte amount fractions should be close to the maximum concentration specified in ISO 14687:2019 (see Table 1).
- The analyte amount fractions should be sufficiently low as to challenge the measurement capabilities of participants.
- The analyte amount fractions should not be too low as to cause the gas mixtures to lose stability over the timeframe of the comparison exercise.
- The laboratories preparing the hydrogen gas mixtures must have the capability to provide an accurate reference value for the analyte amount fractions.

For these reasons, two gas mixture compositions were selected:

- 250 nmol/mol carbon monoxide, 200 µmol/mol nitrogen and 9 µmol/mol water in hydrogen.
- 40 nmol/mol hydrogen sulphide in hydrogen.

A relatively high amount fraction for hydrogen sulphide was selected (with regards to the ISO 14687:2019 threshold limit) as hydrogen sulphide at low amount fractions is known to be unstable within static gas mixtures, however the amount fraction selected is still very challenging to perform. To confirm the stability of hydrogen sulphide at the selected amount fraction over the duration of the interlaboratory comparison exercise, a preliminary stability study was performed. See section 2.2. below for details.

Participants were provided with the amount fraction ranges and uncertainty targets stated in Table 2. The uncertainty targets are considered realistic and representative of a real hydrogen sample.

Table 2: Analyte amount fraction range of each component in hydrogen

Analyte	Amount fraction [µmol/mol]	Uncertainty (*k*=2) [%]
Carbon monoxide	0.02 – 0.4	10
Nitrogen	50 – 500	5
Water	1 – 10	5
Hydrogen sulphide	0.01 – 0.4	10

A total of 20 gas mixtures (10 of each composition) were prepared and validated or certified for use in this comparison exercise. This allowed for most participants to receive a set of gas mixtures to perform measurements on. It was necessary however for some participants in Europe and the United States of America to share a set of gas mixtures with one other European or American participant as shown by the schematic in Figure 1.

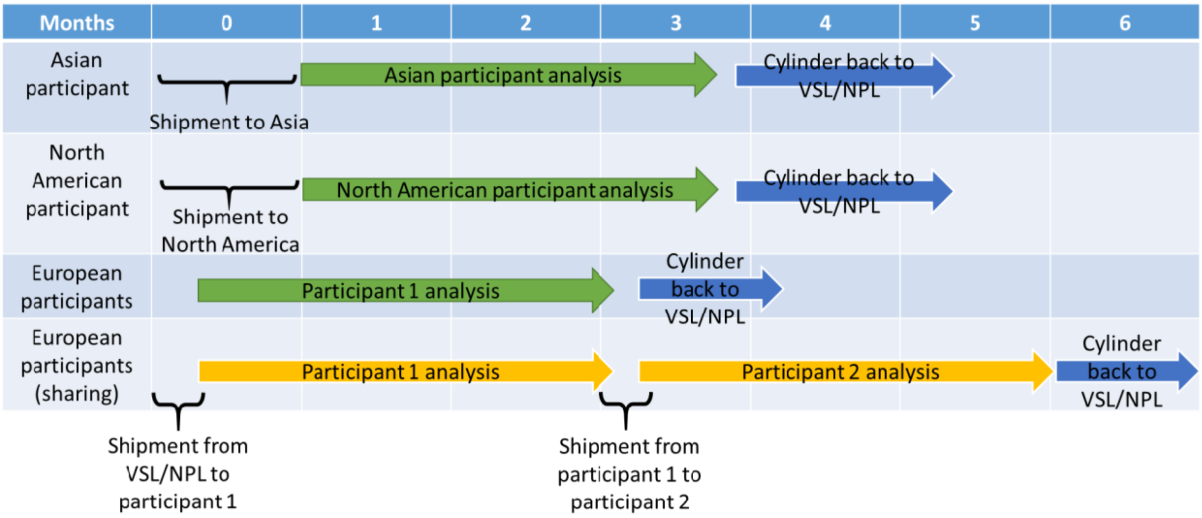

Figure 1: Schematic of logistic plan across timeframe of interlaboratory comparison

2.1.1. Hydrogen sulphide in hydrogen mixture preparation

A set of NPL Certified Reference Materials (NPL CRMs) were prepared gravimetrically and certified reference values assigned using traceable gas reference standards (dynamically generated) following the guidance of ISO 17034:2016 [9]. Gas mixtures were prepared in 10 L aluminium cylinders that had undergone BOC's SPECTRA-SEAL® treatment to render the internal surface chemically inert (BOC, UK) and fitted with DIN 477 No. 1 valve outlets. These NPL CRMs were prepared to contain nominally 40 nmol/mol hydrogen sulphide in a hydrogen balance. Mixtures were prepared in one stage by dilution of a nominally 1 µmol/mol NPL Primary Reference Material (NPL PRM) by direct filling followed by addition of hydrogen balance gas (direct filling). The nominally 1 µmol/mol NPL PRM was prepared in the same way by dilution of a nominally 10 µmol/mol NPL PRM, which was also prepared in the same way by dilution of a nominally 100 µmol/mol NPL PRM. The nominally 100 µmol/mol NPL PRM was prepared by indirect addition via a transfer vessel of pure hydrogen sulphide followed by direct filling of hydrogen. The purity of the source chemicals was analysed and determined to be > 99.69 %.

2.1.2. Carbon monoxide, nitrogen and water in hydrogen mixture preparation

VSL prepared gravimetrically a set of CRMs. Certified reference values were assigned using traceable gas reference standards (see section 2.4.2). Gas mixtures were prepared in Aculife IV 10 L aluminium cylinders fitted with DIN 477 No. 1 valve outlets (Air Liquide, BE). The mixtures sent to the participants were prepared to contain nominally 250 nmol/mol carbon monoxide, 9 µmol/mol water and 199 µmol/mol nitrogen in a hydrogen balance. These mixtures were prepared in one stage by dilution of a nominally 1.25 µmol/mol carbon monoxide, 44 µmol/mol water and 996 µmol/mol nitrogen in hydrogen mixture. The latter mixture in turn was prepared in one stage by dilution of a nominally 6.25 µmol/mol carbon monoxide, 219 µmol/mol water and 0.499 % mol/mol nitrogen in hydrogen mixture. The latter mixture was prepared from a 31 µmol/mol carbon monoxide in hydrogen mixture, hydrogen and nitrogen were added using gas injection and water was added using liquid injection.

2.2. Preliminary stability study

To evaluate the stability of the selected analyte amount fractions and gas mixture compositions over the duration of the comparison exercise, preliminary stability studies were performed by NPL and VSL before the start of the comparison.

For 40 nmol/mol hydrogen sulphide in hydrogen, six gas mixtures were prepared as outlined in sections 2.1.1 on different dates over a period of approximately 18 months between June 2017 to October 2018. Five gas mixtures were prepared in 10 L aluminium cylinders that had undergone BOC's SPECTRA-SEAL® treatment to render the internal surface chemically inert (BOC, UK) and fitted with DIN 477 No. 1 or BS341 No. 15 valve outlets. One gas mixture was prepared in an Aculife IV 10 L aluminium cylinder fitted with a DIN 477 No. 1 valve (Air Liquide, BE). Analyte amount fractions were certified on 18th December 2018 using traceable gas reference standards (dynamically generated) using the method outlined in section 2.4.1. Analyte amount fractions were considered to be significantly stable if the uncertainties associated with the certified amount fractions overlapped. The results of the stability study indicated that hydrogen sulphide in hydrogen at 40 nmol/mol was significantly stable in both cylinder types tested at the 95 % confidence level (considering measurement uncertainties) over a period of more than one year. Based on this preliminary stability study, the interlaboratory comparison gas mixtures were considered to be suitable for preparation within 10 L aluminium cylinders that had undergone BOC's SPECTRA-SEAL® treatment.

Before the interlaboratory comparison, a stability study was carried out at VSL over a period of four months on a set of gas mixtures containing 9 µmol/mol water and 250 nmol/mol carbon monoxide in hydrogen. Gas mixtures were prepared in Aculife IV 10 L aluminium cylinders fitted with DIN 477 No. 1 valve outlets (Air Liquide, BE) and in 10 L aluminium cylinders SPECTRA-SEAL® treatment (BOC, UK) fitted with DIN 477 No. 1. For nitrogen, a stability study was not carried out as no instabilities were anticipated based on previous experience. This short stability study indicated that 9 µmol/mol water and 250 nmol/mol carbon monoxide in hydrogen was significantly stable at the 95 % confidence level.

2.3. Concluding validation study

To ensure an appropriate reference value was assigned and to confirm that the gas mixtures had remained stable over the duration of the comparison exercise (with respect to the reference value assignment), the gas mixtures were measured before dispatch to the participants and once again upon return to NPL and VSL following measurement by the participants.

- For hydrogen sulphide, measurements were performed by NPL in May 2019 and March 2020. Remark: all participant analysis was undertaken between July 2019 and March 2020.
- For water, measurements were performed by VSL in March 2019 and March 2020. Remark: all participant analysis was undertaken between June 2019 and March 2020.

The analytical methods used for the reference value assignments are detailed in section 2.4.

2.4. Analytical Methods

2.4.1. Hydrogen sulphide

Hydrogen sulphide was measured using NPL validated methods and an Agilent 7890A GC coupled with an Agilent 355 SCD detector (Agilent Technologies, UK) that had all internal tubing Sulfinert®-treated. Dynamic reference gas standards were used to assign reference values to the interlaboratory comparison gas mixtures rather than static reference gas standards as hydrogen sulphide at low amount fractions is known to be unstable over time within static mixtures due to reactions or adsorption to the cylinder walls. The dynamic reference gas standards were prepared by blending gravimetrically prepared 1 µmol/mol hydrogen sulphide in hydrogen PRMs with ultra-pure hydrogen (purity grade BIP®+. 99.9999 % from Air Products, UK) using hydrogen calibrated mass-flow controllers (Bronkhorst, NL), thus producing the desired gas mixture at an amount fraction between 10 – 44 µmol/mol at the point-of-use. The amount fractions of the dynamic reference gas standards were calculated following the guidance of ISO 6145-7:2018 [10].

The high amount fraction PRMs were prepared at NPL for calibration of the analytical measurements. The purity of the parent gases (H_2S and H_2) were tested to ensure that impurity levels were complaint with the measurement test objective. The purity analyses determined that the hydrogen sulphide was > 99.7 % pure. Ultra-pure Hydrogen (purity grade BIP®+. 99.9999 % from Air Products, United Kingdom) was tested using the methods mentioned above and no significant impurity was detected. The assigned values for this impurity within the ultra-pure hydrogen cylinders were calculated using the limit of detection of the GC-SCD instrument.

To assign the amount fraction of hydrogen sulphide in the interlaboratory comparison gas mixtures, the gas mixtures were compared to dynamic reference gas standards of hydrogen sulphide in hydrogen at 36, 38, 40, 42 and 44 nmol/mol. Upon return of the interlaboratory comparison gas mixtures to NPL, a concluding validation study was performed. The cylinders that contained sufficient pressure were compared to dynamic reference gas standards of hydrogen sulphide in hydrogen at 10, 20, 30 and 40 nmol/mol.

The validated software XLGenline version 2 [11] was then used to quantify the measured amount fraction in the interlaboratory comparison mixtures. The uncertainties associated with the dynamic reference gas standard amount fractions (u_{ref}) were calculated using equation 1:

$$u_{ref} = \sqrt{u_{PRM}^2 + u_{MFC}^2} \qquad \text{Equation 1}$$

where u_{PRM} is uncertainty associated with the amount fraction of the static primary reference material used,

u_{MFC} is the uncertainty of the mass-flow controller based dynamic dilution system.

The uncertainties associated with the instrument response to the dynamic reference gas standards and the mixtures being quantified were the standard deviation of the corresponding measurements. XLGenline generates a weighted linear calibration curve which was used to quantify the amount fractions in the mixtures of interest. XLGenline also generates an uncertainty following a generalised least square fitting directional regression model [11].

2.4.2. Carbon monoxide, nitrogen and water

Nitrogen was measured using a GC (Agilent 7890A) equipped with a TCD detector and Porapack column. Nitrogen in hydrogen standards in the range of 40 and 1000 µmol/mol were used. Three analyses were performed during the period of 30th April – 8th May 2019 and the nitrogen amount fraction was determined using linear regression following ISO 6143:2006 [12].

Water in the gas mixtures was measured using a CRDS spectrometer (Spark$^+$) from Tiger optics (US). The laser was tuned using temperature scanning of the laser over a water absorption line. Further high purity nitrogen and high purity hydrogen were analysed to determine the background signal (so-called tau zero). The area of the absorption curve was compared to the area of water in nitrogen standards certified by the VSL humidity department. Data was analysed using linear regression with CurveFit software [13] which is based on ISO 6143:2006.

Carbon monoxide was measured using a custom-built direction absorption spectroscopy using a tunable diode laser equipped with a multipass cell with an effective optical path length of 76 m. The carbon monoxide line at 2190 nm was probed. Three gravimetric carbon monoxide in nitrogen reference gas mixtures were used as standards. In total three series of measurements were made on 28th and 29th March 2019. Data was analysed using linear regression with CurveFit software which is based on ISO 6143:2006.

2.5. Stability evaluation

The significance of instability was evaluated by comparison of the certified amount fractions assigned before dispatch to the participants and the certified amount fractions assigned upon return of the gas mixtures to NPL and VSL, taking into consideration the uncertainty associated with the certified amount fractions. Analyte amount fractions were considered to be significantly unstable if the uncertainties associated to the certified amount fractions from the two measurements did not overlap. Results of the stability assessment can be found in Annex A.

The amount fractions of carbon monoxide and nitrogen were significantly stable over the duration of the comparison exercise, whereas hydrogen sulphide and water were significantly unstable over the same time period. Based on these observations, the reference values and uncertainties were determined differently if the analytes were significantly stable or unstable. The degree of instability of hydrogen sulphide and water were also significantly different, resulting in the reference values and uncertainties being determined differently for these analytes. Possible sources of instability are related to the gas cylinder production and proprietary treatments performed as well as cylinder transportation to and from participating laboratories (e.g. temperature, handling).

2.5.1. Reference value and uncertainty assignment for carbon monoxide and nitrogen

As the amount fractions of carbon monoxide and nitrogen in hydrogen were stable, the reference values were assigned by comparison of the interlaboratory comparison mixtures with traceable reference gas standards before dispatch to the participants.

Data was analysed using linear regression with CurveFit software which is based on ISO 6143:2006.

2.5.2. Reference value and uncertainty assignment for hydrogen sulphide

Due to the significant instability of hydrogen sulphide in the interlaboratory comparison gas mixtures, analyses of each individual gas mixture were required in order to accurately assign the reference values and uncertainties.

Following return of the interlaboratory comparison gas mixtures in March 2020, it was found that some cylinders did not contain enough gas to allow for further analyses, even though it was required that gas mixtures were returned containing at least 10 bar pressure of gas. Gas mixtures that contained enough gas were subsequently re-analysed by comparison with dynamic reference gas standards to assess the rate of instability of hydrogen sulphide over the duration of the interlaboratory comparison exercise. Results of the stability assessment can be found in Annex A, Table A.2.

As it was not possible to re-analyse all interlaboratory comparison gas mixtures, the average rate of instability was determined based on the measurements before dispatch to the participants and upon return to NPL after measurements by the participants.

The dates of analyses and certified reference values for all gas mixtures analysed were normalised so that a linear regression analysis could be performed to determine an average rate of instability. Dates of analyses were normalised to consider the measurement performed before dispatch to the participants as Day 0. The uncertainty associated with the date of analyses were conservatively set to 1 day. Certified reference values were normalised to a value of 100 and the associated uncertainties normalised accordingly.

Using the validated software XLGENLINE version 2, a linear regression analysis was performed using the normalised data to determine the average rate of instability. The reference values for hydrogen sulphide in hydrogen were considered time-dependent and this rate of instability was then used to determine the reference value and uncertainty for the interlaboratory comparison gas mixture measured by each participant at the time of analysis.

The hydrogen sulphide reference values $[H_2S]_{x,t}$ were calculated using equation 2 and equation 3 in order to accurately assign hydrogen sulphide amount fractions based on the date of measurement by the participant considering the average rate of instability of hydrogen sulphide in the interlaboratory comparison gas mixtures.

$$[H_2S]_{x,t} = \frac{D_{norm,x,t} \times [H_2S]_{x,0}}{100} \qquad \text{Equation 2}$$

where $[H_2S]_{x,0}$ is the amount fraction of hydrogen sulphide determined for the interlaboratory comparison gas mixtures before dispatch to the participants,

$D_{norm,x,t}$ is the average rate of instability for hydrogen sulphide at date t as calculated in equation 3.

$$D_{norm,x,t} = \frac{t_{norm} - c}{m} \qquad \text{Equation 3}$$

where t_{norm} is the normalised date of analysis,

m is the gradient (m is equal to -7.8071 days/arbitrary unit),

c is the intercept with the y-axis (c is equal to 780.66 days).

The uncertainties associated with the hydrogen sulphide amount fractions were determined using the uncertainties from the measurement of hydrogen sulphide performed before dispatch of the interlaboratory comparison gas mixtures to the participants and the uncertainty associated with the average rate of instability of hydrogen sulphide (obtained using XLGenline software version 2).

2.5.3. Reference value and uncertainty assignment for water

Data was analysed using linear regression with CurveFit software which is based on ISO 6143:2006. Three standards were measured after return from the participants. An unexpected high drift was observed with regards to the amount fraction of water in hydrogen (two mixtures indicated an increase in water amount fraction and one mixture indicated a decrease in a water amount fraction, however it should be noted that the pressure in two of the cylinders measured was less than the minimum 10 bar pressure of gas required). To compensate for this the uncertainty of all interlaboratory comparison gas mixtures was increased.

2.6. Data treatment

Interlaboratory comparison results were calculated following the guidelines of ISO 17034:2016 to provide a statistical means of measuring the deviation of participants results from the assigned references values in a manner that allows comparison with performance criteria.

Zeta-scores (ζ) were calculated from the data obtained using equation 4:

$$\zeta = \frac{x - X}{\sqrt{u_x^2 + u_X^2}} \qquad \text{Equation 4}$$

where x is the result reported by the participant,

X is the assigned value,

u_x is the participant's own estimate of the standard uncertainty of its result x,

u_X is the standard uncertainty of the assigned value X.

Note: Where participants reported two sets of results for the same analyte, the result reported by the participant was assigned as the mean of the two reported results. The participant's own estimate of the standard uncertainty was assigned by combining the two corresponding uncertainties associated with the reported results using equation 5:

$$u_x = \sqrt{u_{x,i}^2 + u_{x,ii}^2} \qquad \text{Equation 5}$$

where $u_{x,i}$ is the uncertainty associated with the first reported result,

$u_{x,ii}$ is the uncertainty associated with the second reported result.

Calculated zeta-scores were assigned as defined in Table 4:

Table 3: Zeta-score assignment key

Zeta-score	Assignment
$\lvert\zeta\rvert \leq 2$	Satisfactory
$2 < \lvert\zeta\rvert < 3$	Questionable
$\lvert\zeta\rvert \geq 3$	Unsatisfactory

3. Participant methods

A range of analytical methods were used by participants to perform analysis of carbon monoxide, hydrogen sulphide, nitrogen and water for this comparison. This section summarises the methods with detailed descriptions of the measurements performed given in Annex B.

Table 4: Summary of the methods used by participants for the determination of CO amount fraction in hydrogen

Participant code	Technique	Calibration
L01	OFCEAS	Certified standard produced by Air Liquide
L02	GC-PDHID	Internal static calibration standards used
L03	GC-FID (methaniser)	Static calibration standards produced by Sumitomo Seika Chemicals
L04	Direct absorption spectroscopy	Internal primary standard gas mixtures used to perform calibration according to ISO 6143
L05	GC-FID (methaniser)	Dynamic dilution of internal Primary Reference Material
L06	FTIR	Primary standard gas mixture produced by Airgas
L07	GC-PDHID	Calibration gas standard produced by Air Liquide
L08	GC-PDID	Internal calibration gas mixture used
L09	GC-FID (methaniser)	Premixed calibration gases produced by Aga
L10	FTIR	Dynamic dilution of NIST traceable certified standard produced by Airgas
L11	GC-PED	Calibration gas standard produced by Air Liquide
L12	PHID	n.a.*
L13	GC-PDD	Calibrants produced by Dalian Special Gases

*n.a. means not available

Table 5: Summary of the methods used by participants for the determination of H_2S amount fraction in hydrogen

Participant code	Technique	Calibration
L01	TD-GC-FPD	Dynamic dilution of certified standard produced by MTI
L02	GC-SCD	Static calibration standard produced by Matheson
L03	GC-FPD	Static calibration standard produced by Sumitomo Seika Chemicals. Diluter used to perform calibration
L04	GC-SCD	Internal primary standard gas mixtures used to perform calibration according to ISO 6143
L05	GC-SCD	Dynamic dilution of internal Primary Reference Material
L06	GC-SCD	Primary standard gas mixture produced by Airgas
L07	ATD-GC-FPD	Dynamic dilution of calibration gas standard produced by Air Liquide
L08	GC-SCD	Internal calibration gas mixture used
L09	n.m.*	n.m.*
L10	GC-SCD	Dynamic dilution of NIST traceable primary standard produced by Airgas. Secondary standard used as a check
L11	GC-SCD	Standard gas mixture produced by Air Liquide
L12	GC-SCD	n.a.*
L13	GC-FPD	Calibrants produced by Sichaun Standard Material Technology

*n.a. means not available

*n.m. means not measured

Table 6: Summary of the methods used by participants for the determination of N_2 amount fraction in hydrogen

Participant code	Technique	Calibration
L01	GC-TCD	Certified standard produced by Air Liquide
L02	GC-MS	Internal static calibration standard used
L03	GC-TCD	Static calibration standards produced by Sumitomo Seika Chemicals
L04	GC-PDHID	Internal primary standard gas mixtures used to perform calibration according to ISO 6143
L05	GC-PDHID	Internal Primary Reference Material used
L06	MS	Primary standard gas mixture produced by Airgas
L07	GC-PDHID	Calibration gas standard produced by Air Liquide
L08	GC-TCD	Internal calibration gas mixture used
L09	GC-BID-TCD	Premixed calibration gases produced by Aga
L10	GC-PDID	Dynamic dilution of NIST traceable certified standard produced by Airgas
L11	GC-PED	Primary reference gas mixtures produced by Air Liquide
L12	PHID	n.a.*
L13	GC-PDD	Calibrants produced by Dalian Special Gases

*n.a. means not available

Table 7: Summary of the methods used by participants for the determination of H_2O amount fraction in hydrogen

Participant code	Technique	Calibration
L01	Chilled mirror	Certified standard device produced by MTI. Device calibrated by manufacturer only
L02	GC-MS	Static calibration standards produced by Airgas
L03	CRDS	Calibrated device used
L04	CRDS	Gas mixtures produced by Air Liquide and certified by internal humidity group. Calibrated gas mixtures used to perform calibration according to ISO 6143
L05	QCM	Internal Primary Reference Materials used
L06	Electrolytic hygrometry	Calibrated device used
L07	OFCEAS	Calibration gas standards produced by Air Liquide
L08	CRDS	No calibration performed
L09	CRDS	NIST traceable calibrated device used
L10	FTIR	GE Panametrics conductimetric hygrometer calibration device used
L11	QCM	Internal standard (internal moisture generator)
L12	Silicon sensor	n.a.*
L13	Aluminium oxide sensor	n.a.*

*n.a. means not available

4. Results

Measurement reports were provided by each participating laboratory and these can be found in Annex C. Each participating laboratory provided an overall result including an assigned uncertainty for each impurity measured. The results of the interlaboratory comparison are presented as zeta-scores in Table 8 and Figures 2 – 5.

Note: Results for participant L02 are presented as L02A and L02B as results were reported following two different analytical procedures (details given in Annex B).

Table 8: Zeta-scores for measurement of CO, H_2S, N_2 and H_2O analyte amount fractions in hydrogen.

Participant code	Carbon monoxide	Hydrogen sulphide	Nitrogen	Water
L01	-1.06	0.97	0.12	1.62
L02A	-23.31	-8.15	7.44	-2.98
L02B	n.m.*	n.m.*	n.m.*	-11.24
L03	-0.60	0.72	0.17	1.95
L04	-1.68	5.82	0.42	3.60
L05	-1.03	-0.72	0.73	1.70
L06	2.08	4.56	9.70	2.71
L07	0.52	-6.77	0.35	2.94
L08	-0.89	-2.92	4.23	2.03
L09	-2.17	n.m.*	12.96	1.96
L10	0.88	0.29	-9.59	-14.59
L11	-2.07	4.81	-0.52	2.86
L12	-13.64	15.18	-75.68	3.82
L13	-0.88	-17.32	-1.19	-0.73

*n.m. means not measured

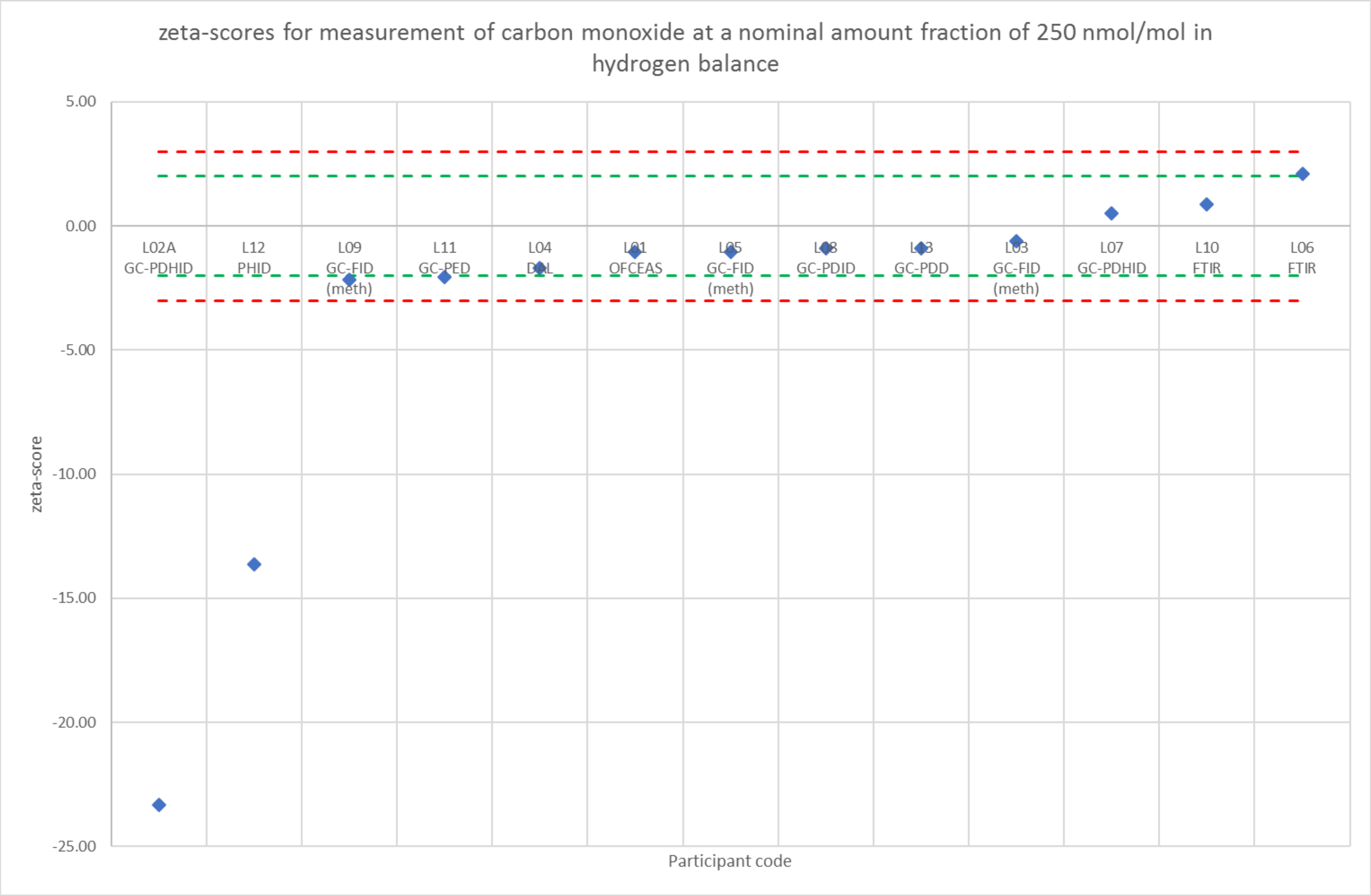

Figure 2: Zeta-scores for CO at nominally 250 nmol/mol in hydrogen for each laboratory ordered from lowest to highest

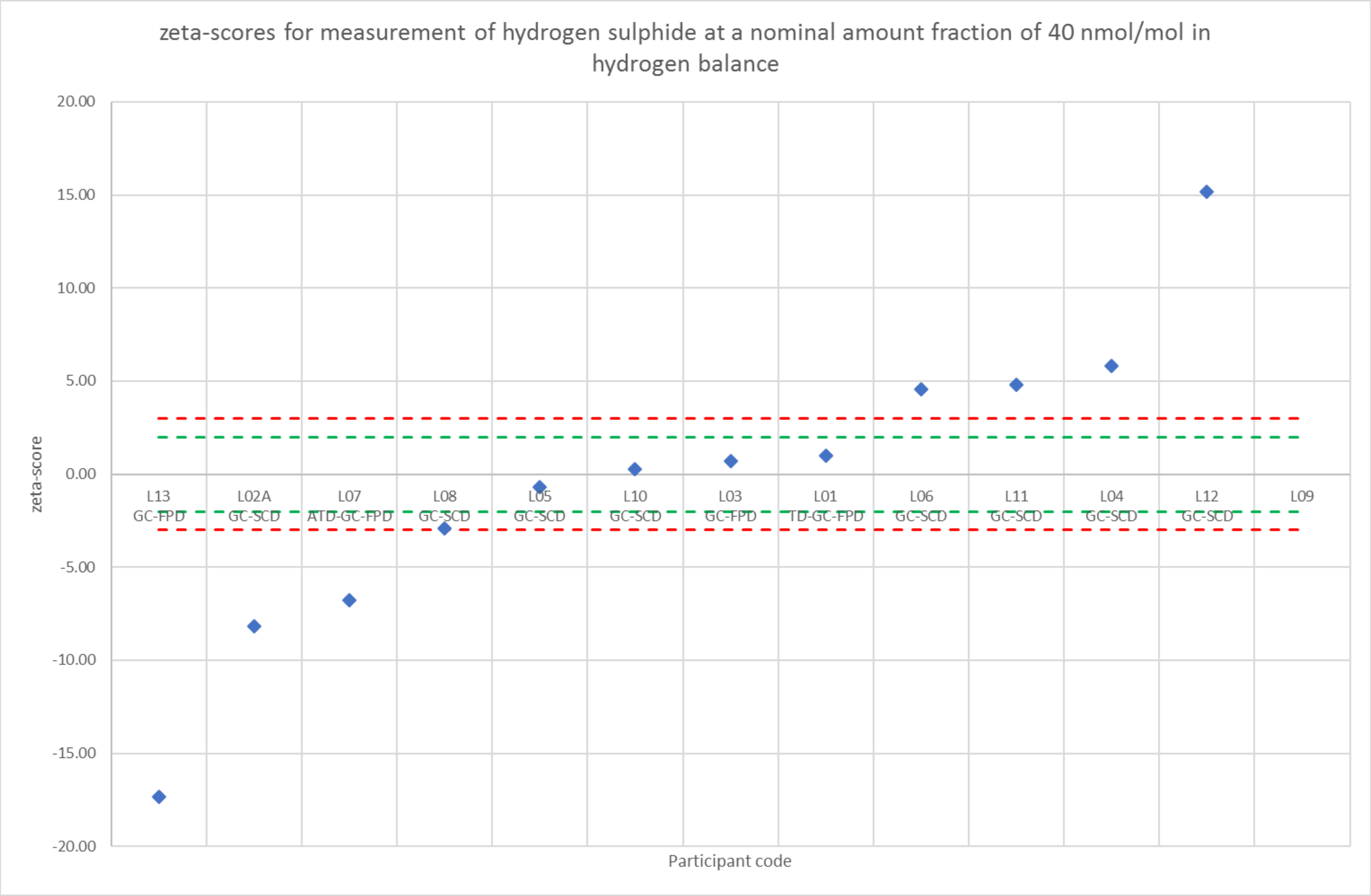

Figure 3: Zeta-scores for H_2S at nominally 40 nmol/mol in hydrogen for each laboratory ordered from lowest to highest

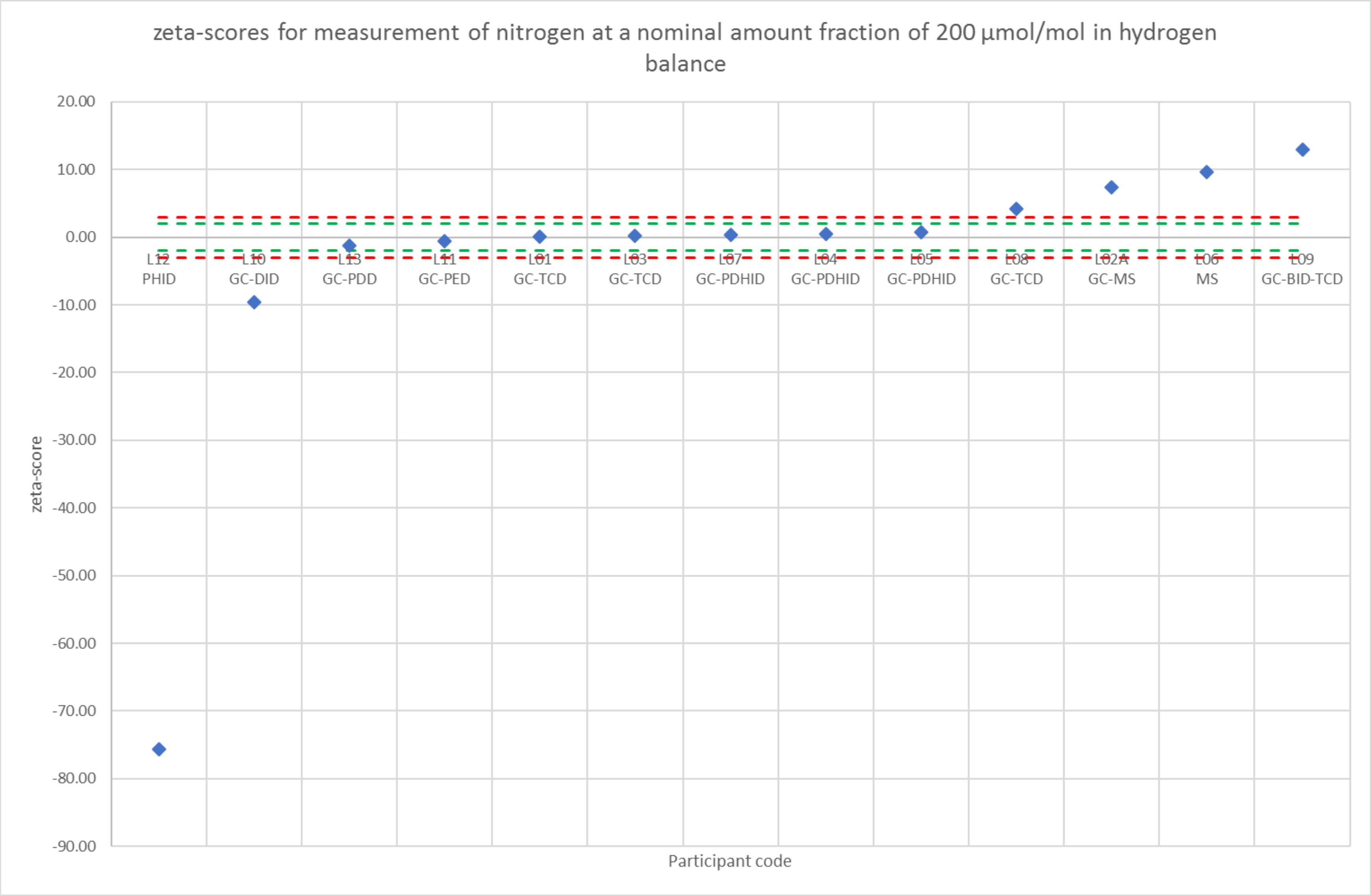

Figure 4: Zeta scores for N_2 at nominally 200 µmol/mol in hydrogen for each laboratory ordered from lowest to highest

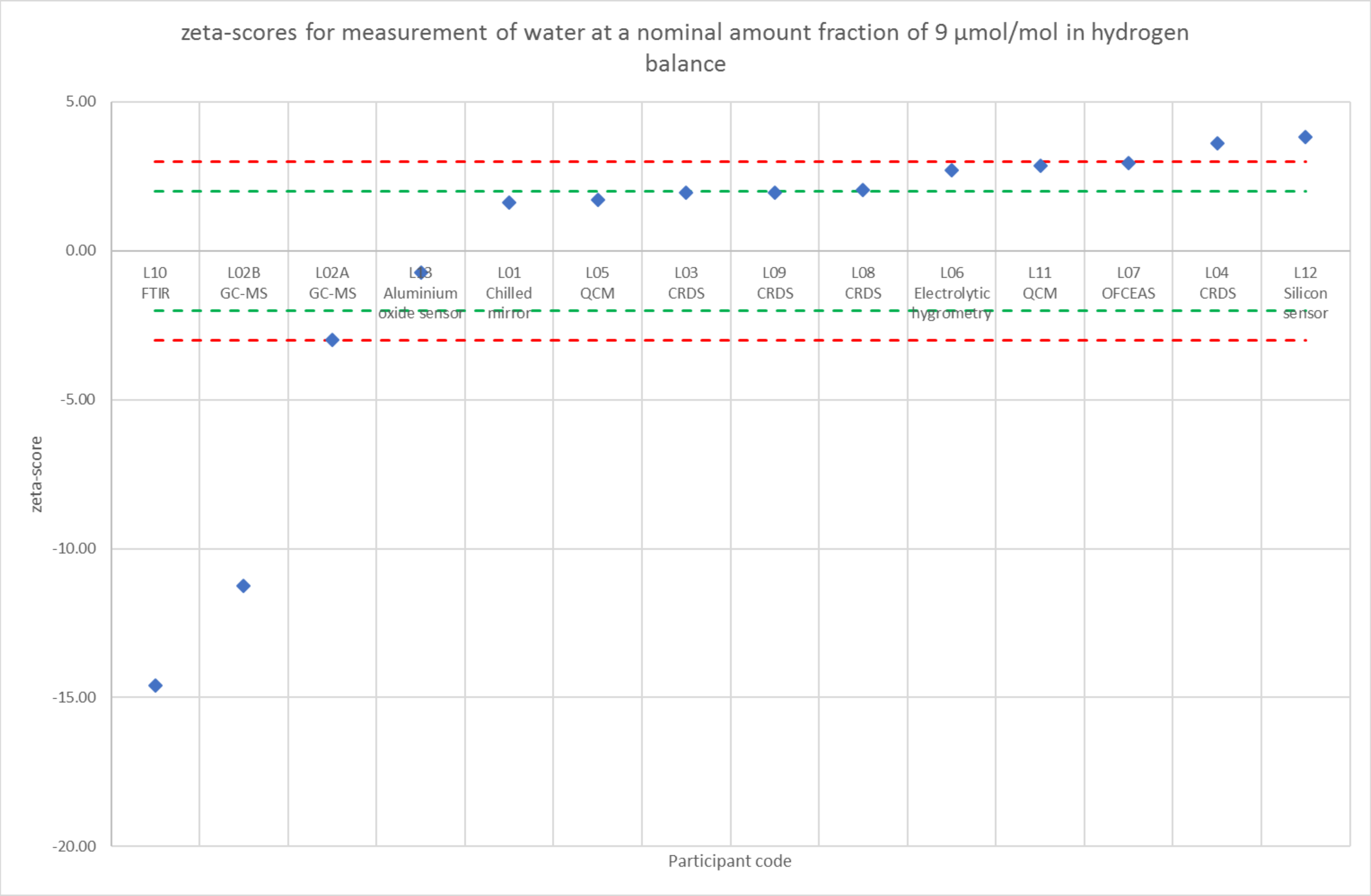

Figure 5: Zeta-scores for H_2O at nominally 9 µmol/mol in hydrogen for each laboratory ordered from lowest to highest

5. Conclusions and recommendations

The interlaboratory comparison for offline hydrogen purity analysis performed as part of the MetroHyVe project has given an important insight into the performance of the participating laboratories for measuring key analytes in hydrogen gas for quality assurance purposes against ISO 14687:2019. The comparison exercise has highlighted several points (i.e. calibration gas, measurement uncertainty) across the range of analytes that some of the participants should look to address in order to improve and maintain their gas analytical capabilities. A summary of zeta-scores is presented in Table 9.

Table 9: Summary of zeta-scores per compound

Analyte	Zeta-scores			
	Satisfactory	Questionable	Unsatisfactory	Total
Carbon monoxide	8	3	2	13
Hydrogen sulphide	4	1	7	12
Nitrogen	7	0	6	13
Water	5	5	4	14

For measurement of carbon monoxide in hydrogen at the ISO 14687:2019 threshold limit, 62 % of the reported results were assigned as satisfactory and approximately 85 % of the zeta-scores were less than 3. For the two participating laboratories that reported results assigned as unsatisfactory (L02A and L12), corrective actions would be required to improve analytical performance. Following a review of the method information and results provided by participant L02A, it is recommended that an investigation into the gas transfer procedure and the calibrants used is undertaken. Participant L12 did not provide any method information and therefore no recommendations were provided.

The results for hydrogen sulphide in hydrogen at ten-times the ISO 14687:2019 threshold limit cannot be considered successful with only 33 % of reported results assigned as satisfactory and approximately 58 % of reported results assigned as unsatisfactory, highlighting the need for improvement. For the seven participating laboratories that reported results assigned as unsatisfactory (L02A, L04, L06, L07, L11, L12 and L13), corrective actions plan will be required in order to improve analytical performance. Following a review of the method information and results provided, it was noted that some of the calibrations performed were undertaken using fewer calibration points and at higher amount fractions than were being tested. Therefore, it is recommended to review the calibration strategy to ensure a fit-for-purpose calibration is performed prior to measurement. Additionally, some participants reported the standard deviation of the measurements as the expanded uncertainty, therefore providing an underestimation of the overall measurement uncertainty. It is therefore recommended to review the uncertainty calculations to ensure a more representative measurement uncertainty is reported. The results indicate that there is a clear requirement for most participating laboratories to improve their analytical performance, however the instability of the gas mixtures used to evaluate laboratory performance made this task more challenging. For future interlaboratory comparisons, it will be important to improve the protocol to ensure that stable gas mixtures are provided to participants.

The results for nitrogen in hydrogen at close to the ISO 14687:2019 threshold limit were quite divided with 54 % of the reported results assigned as satisfactory. Even though the measurement results were not aberrant (except for the results reported by participant L12), approximately 46 % of the reported results were assigned as unsatisfactory. For the six participating laboratories that reported results assigned as unsatisfactory (L02A, L06, L08, L09, L10 and L12), corrective actions plan will be required in order to improve analytical performance. Following a review of the method information and results provided, it was noted that some of the reported uncertainties associated with the nitrogen amount fractions were very low in comparison with other reported results. It is therefore recommended to review the uncertainty calculations to ensure a more representative measurement uncertainty is reported.

The results for water in hydrogen at close to the ISO 14687:2019 threshold limit were quite good with approximately 71 % of the zeta-scores greater than or equal to 3. For the four participating laboratories that reported results assigned as unsatisfactory (L02A, L02B, L04, L10 and L12), corrective actions plan will be required in order to improve analytical performance. Following a review of the method information and results provided by participant L02, it is recommended that to review the two methodologies reported (L02A and L02B) and undertake improvements or consider the method unsuitable for this kind of activity. For participants L04, L10 and L12, it was noted that all the reported amount fraction results were higher than the reference values. Following review, it is recommended to investigate the calibrants used and review the applied methodologies to ensure sufficient system purging is performed (to remove ambient moisture) and that sufficient stabilisation time is allowed before performing measurements. As with hydrogen sulphide, the instability of the gas mixtures used to evaluate laboratory performance made this task more challenging. For future interlaboratory comparisons, it will be important to improve the protocol to ensure that stable gas mixtures are provided to participants.

These results indicate that further work is required to improve the capability of laboratories for the measurement of low amount fractions of hydrogen sulphide in hydrogen as this measurement reported the highest number of zeta-score results assigned as unsatisfactory. Further work is also required for the measurement of nitrogen in hydrogen as this measurement reported the second highest number of zeta-score results assigned as unsatisfactory. The results also indicate that some additional work is required for the measurement of water in hydrogen as this measurement reported the highest number of zeta-score results assigned as questionable.

In general, the interlaboratory comparison results highlight the need to undertake further interlaboratory comparisons in future in order to benchmark and improve analytical performance of laboratories. This comparison provided proficiency testing for only four of the impurities specified in ISO 14687:2019; a future comparison should include more or all impurities. Regular interlaboratory comparison exercises (for example annually) would allow participating laboratories to create vital evidence required to obtain a scope of accreditation for hydrogen purity analysis under ISO 17025, or in the case of bad performance, assess the improvements from implementation of actions from a corrective action plan (CAP) and identify areas of further improvement. In accordance with the enforcement of the new ISO 21087:2019 standard [14], there is a clear requirement for analytical laboratories to investigate their uncertainty evaluation as underestimation of measurement uncertainty may have been the cause of reported results being assigned as unsatisfactory in some instances.

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Annex A: Reference value determination

Note: Stability measurements were not performed for nitrogen amount fraction in hydrogen.

Table A.1: Results of stability measurements for CO amount fraction in hydrogen

Cylinder	Analysis date	Amount fraction [nmol/mol]	Expanded uncertainty [nmol/mol]	Significant instability
5707088	28-29/03/2019	248	11	No
	27/02/2020	251	5	
5707097	28-29/03/2019	246	5	No
	27/02/2020	252	5	
5705785	28-29/03/2019	252	8	No
	27/02/2020	250	6	

Table A.2: Results of stability measurements for H_2S amount fraction in hydrogen

Cylinder	Analysis date	Amount fraction [nmol/mol]	Expanded uncertainty [nmol/mol]	Significant instability
NG817R	23/05/2019	35.6	3.5	Yes
	11/03/2020	24.0	2.1	
NG815R	23/05/2019	34.3	3.7	Yes
	11/03/2020	21.4	1.9	
NG897	23/05/2019	38.4	2.6	Yes
	11/03/2020	24.8	2.7	
NG812R	23/05/2019	38.0	2.8	Yes
	11/03/2020	21.4	1.8	
NG846R	23/05/2019	36.0	3.3	Yes
	13/03/2020	23.8	2.6	

Table A.3: Results of stability measurements for H_2O amount fraction in hydrogen

Cylinder	Analysis date	Amount fraction [µmol/mol]	Expanded uncertainty [µmol/mol]	Significant instability
5707088	26-27/03/2019	6.00	0.16	Yes
	06/03/2020	7.16	0.26	
5707097	26-27/03/2019	6.98	0.26	Yes*
	06/03/2020	7.76	0.21	
5705785	26-27/03/2019	6.69	0.15	Yes*
	06/03/2020	5.98	0.25	

*Cylinder pressure below recommended pressure for measurement performed on 06/03/2020

Annex B: Summary of participant analytical methods

Table B.1: Analytical method information used for the measurement of CO in hydrogen by the participants of the MetroHyVe interlaboratory comparison for offline hydrogen purity analysis

Participant code	Sample preparation	Calibration	Method	Uncertainty calculation	Additional remark
L01	Injection through a sulfinert coated transfer line at an inlet pressure of 0.6 bar(g). 10 purges and 10+ mins stabilisation before performing measurements	1-point calibration at 0.48 µmol/mol using a certified standard produced by Air Liquide	Technique: OFCEAS Instrument: Proceas (Ap2E) Condition: 75 mbar(a) - cavity temp: 45°C; Stabilisation time: ~ 5 mins	Measurement uncertainty is given with a coverage factor of k = 2 including: uncertainty budgets from cal gas standard analysis, deviation of calibration samples and deviation of measured samples under reproducibility conditions	n.a.*
L02A	Gas transferred into non-treated sampling cylinder (1LS1) prior to dispatch. Injection through a 1/16" SS tubing without coating at an inlet pressure of 110 psi	2-point calibration using internal standards at 0.217 and 0.101 µmol/mol. Calibration before each sample analysis with 4 sample replicate analysis	Technique: GC-PDHID Instrument: Agilent – VICI Condition: Helium carrier; 30 m x 0.53 mm ID molecular sieve column; Detector parameters: 110° C	Standard deviation	According to ASTM D5466. Volume of gas used: 154 – 230 mL
L03	Injection through a non-treated transfer line at an inlet pressure of 0.2 MPa	1-point calibration at 1 µmol/mol using a non-certified standard produced by Sumitomo Seika Chemicals Co. Ltd	Technique: GC-meth-FID Instrument: J-SCIENCE LAB Co. Condition: Hydrogen carrier; packed column	Uncertainty of the standard substance was evaluated with Type A, and the uncertainty was calculated assuming a rectangular distribution with a guaranteed value of ±. The uncertainty of repetition was evaluated with Type B, and the uncertainty was calculated from the standard deviation	Volume of gas used: 80 L
L04	Injection through a stainless-steel transfer line at an inlet pressure of ~1.5 bar(a)	2-point calibration at 0.1 and 0.5 µmol/mol using internal standards	Technique: DA spectroscopy Instrument: no information provided Condition: Wavelength 2190 nm; Stabilisation time: ~ 1 min	95 % uncertainty based on k=2	Volume of gas used: ~5 L
L05	Injection through a sulfinert-coated stainless-steel transfer line at an inlet pressure of ~ 1 bar. Purges performed and conditioning time allowed prior to injection	5-point calibration at 0.22, 0.24, 0.24, 0.28 and 0.3 µmol/mol using dynamic dilution of an internal primary standard	Technique: GC-meth-FID Instrument: Agilent Condition: Nitrogen carrier; Haysep D packed column; 5 cc loop, 30°C oven, 30 mL/min flowrate; Stabilisation time: ~ 10 mins (1 discarded measurement)	Measurement uncertainties are stated with a coverage factor k = 2, providing a coverage probability of approx. 95 %. Uncertainty budgets include contributions from calibration gas standard validation, repeatability of calibration standard measurements, repeatability of sample measurements and, for dynamic calibration curve production, uncertainties associated with the gas flow control devices	Volume of gas used: ~ 100 L
L06	Injection performed directly from sample cylinder provided	1-point calibration at 1 µmol/mol using a primary standard produced by Airgas	Technique: FTIR Instrument: Nicolet - DGTS Condition: Background correction: vacuum; Blank correction: UHP Nitrogen	Method uncertainty values based on validations performed for initial ISO 17025 accreditation and ongoing QA monitoring including SPC data collection	n.a.*

L07	Injection performed directly into analyser at an inlet pressure of 1 bar	1-point calibration at 0.2 µmol/mol using a standard in a hydrogen balance produced by Air Liquide	Technique: GC-PDHID Instrument: no information provided Condition: Helium carrier; filled column; Detector parameters: 150°C; Stabilisation time: 60 mins	Used the criteria for the measurement uncertainty defined in the standard ISO 21087, published in September 2019. Calculated the uncertainties with the standard NF ISO 11352 published in February 2013. This method is described in the sections 8, 9, 10. The uncertainty estimation was realised on ten replicates for each concentration level on working range. To determine measurement uncertainty, two parameters were calculated: uncertainty of replicate reproducibility intralaboratory (section 8.2.2) and bias of the method and laboratory (section 8.3.2)	n.a.*
L08	n.a.*	1-point calibration at 0.7 µmol/mol using an internal calibration standard with a strict preparation tolerance (PEH)	Technique: GC-PDID Instrument: Unicam ThermoOnix Protrace GC Conditions: Helium carrier	According to GUM	n.a.*
L09	Injection through a non-treated transfer line at atmospheric pressure	2-point calibration at 1.73 and 10 µmol/mol using premixed standards produced by Aga	Technique: GC-meth-FID Instrument: Agilent 6890 Condition: Helium carrier; packed column	n.a.*	Volume of gas used: 2 L
L10	Injection through a sulfinert treated 1/4” transfer line at an inlet pressure of 1000 torr through a leak-tight evacuated manifold	1-point calibration using dynamic dilution of a 10.1 µmol/mol NIST traceable certified standard produced by Airgas	Technique: FTIR Instrument: Thermofisher Nicolet 6700 Condition: Background correction: yes; Detector parameters: 50°C; 10 m gas cell – 4.0 mm thick zinc selenide windows	Standard deviation of the mean	Volume of gas used: 4600 mL
L11	Injection through a sulfinert treated transfer line at an inlet pressure of 0.7 bar	1-point calibration at 2.042 µmol/mol using a standard in a hydrogen balance produced by Air Liquide	Technique: GC-PED Instrument: no information provided Condition: Helium carrier; packed column	X1: repeatability X2: massflow -controller X3: uncertainty calibration gas mixture k=2 k*SQRT(X1^2+X2^2+X3^2)	Volume of gas used: 10 L per analysis
L12	n.a.*	n.a.*	n.a.*	n.a.*	n.a.*
L13	n.a.*	2-point calibration using standards produced by Dalian Special Gases Co.LTD	Technique: GC-PDD Instrument: GC-2014/PDD (Shimadzu) Condition: 0.1 MPa inlet pressure; helium carrier	The main sources of uncertainty come from calibration models, calibration gas and pre-processing step of samples. u^2=ur(calibration gas)^2+ur(calibration curve)^2+ ur(RSD)^2	n.a.*

*n.a. means not available

Table B.2: Analytical method information used for the measurement of H_2S in hydrogen by the participants of the MetroHyVe interlaboratory comparison for offline hydrogen purity analysis

Participant code	Sample preparation	Calibration	Method	Uncertainty calculation	Additional remark
L01	Injection through a sulfinert-coated transfer line and sulfiner-coated pressure transducer at an inlet pressure of 0.6 bar(g). 10 purges and 10+ min stabilisation before performing measurements	2-point calibration at 0 - 0.013 and 0.013 - 0.025 µmol/mol using dynamic dilution of a certified standard produced by MTI	Technique: TD-GC-FPD Instrument: PerkinElmer Clarus 680 Condition: Helium 6.0 carrier; blind column; 300°C sensor heater - H2 (6.0) /syn. air flame; Stabilisation time: ~ 20 mins (1 discarded sample)	Measurement uncertainty is given with a coverage factor of k = 2 including: uncertainty budgets from cal gas standard analysis, deviation of calibration samples and deviation of measured samples under reproducibility conditions. In the case of dynamic calibration of sulphur, the uncertainty budget is expanded by uncertainties of the dilution process	n.a.*
L02A	Gas transferred into sampling cylinder (1LL14) prior to dispatch. Injection through a PTFE tubing at sample pressure	1-point calibration at 10 µmol/mol using a standard produced by Matheson. Calibration before each sample analysis with 5 sample replicate analysis	Technique: GC-SCD Instrument: Agilent – Sievers Condition: Hydrogen carrier; Restek 60 m x 0.53 mm ID 7µm MXT-1; Detector parameters: 800° C	Standard deviation	According to ASTM D7652. Volume of gas used: 10 mL
L03	Injection through a sulfinert-treated transfer line at an inlet pressure of 0.2 MPa. Sample collected in sulphur-treated cylinder before analysis	3-point calibration at 10, 20 and 30 nmol/mol using dynamic dilution of a non-certified standard produced by Sumitomo Seika Chemicals Co. Ltd. Calibration performed on a different date to measurements	Technique: GC-FPD Instrument: J-SCIENCE LAB Co. Condition: Inlet pressure of 0.25 MPa; nitrogen carrier; packed column	Uncertainty of the standard substance was evaluated with Type A, and the uncertainty was calculated assuming a rectangular distribution with a guaranteed value of ±. The uncertainty of repetition was evaluated with Type B, and the uncertainty was calculated from the standard deviation	Volume of gas used: 880 L
L04	Injection through a coated transfer line at an inlet pressure of 20 psi. Direct injection, pulsed splitless, coated inlet	2-point calibration at 0.02 and 0.2 µmol/mol using internal standards	Technique: GC-SCD Instrument: no information provided Condition: Helium carrier; DB-1 60 m, 0.32 mm, 5 µm column; 800 °C burner	95 % uncertainty based on k=2	Volume of gas used: 1 mL sample loop
L05	Injection through a sulfinert-coated stainless-steel transfer line at an inlet pressure of ~ 1 bar. Purges performed and conditioning time allowed prior to injection	5-point calibration at 0.024, 0.028, 0.032, 0.036 and 0.04 µmol/mol using dynamic dilution of an internal primary standard	Technique: GC-SCD Instrument: Agilent Condition: Helium carrier; HP-1 column; 0.5 cc loop, 30°C oven, 30 mL/min flowrate; Stabilisation time: ~ 20 mins (10 discarded measurement)	Measurement uncertainties are stated with a coverage factor k = 2, providing a coverage probability of approx. 95 %. Uncertainty budgets include contributions from calibration gas standard validation, repeatability of calibration standard measurements, repeatability of sample measurements and, for dynamic calibration curve production, uncertainties associated with the gas flow control devices	Volume of gas used: ~ 3 L
L06	Injection performed directly from sample cylinder provided	1-point calibration at 1 µmol/mol using a primary standard produced by Airgas	Technique: GC-SCD Instrument: Agilent - Sievers Condition: UHP helium carrier; CP-Sil 5CB column	Method uncertainty values based on validations performed for initial ISO 17025 accreditation and ongoing QA monitoring including SPC data collection	n.a.*

L07	Injection performed directly into analyser at an inlet pressure of 1 bar. Analyser coupled with an automated preconcentrator	5-point calibration at 4, 6, 8, 10, 20 nmol/mol using dynamic dilution of a standard in a hydrogen balance produced by Air Liquide	Technique: ATD-GC-FPD Instrument: no information provided Condition: Helium carrier; capillary column; Detector parameters: 300°C; Stabilisation time: 120 mins	Used the criteria for the measurement uncertainty defined in the standard ISO 21087, published in September 2019. Calculated the uncertainties with the standard NF ISO 11352 published in February 2013. This method is described in the sections 8, 9, 10. The uncertainty estimation was realised on ten replicates for each concentration level on working range. To determine measurement uncertainty, two parameters were calculated: uncertainty of replicate reproducibility intralaboratory (section 8.2.2) and bias of the method and laboratory (section 8.3.2)	n.a.*
L08	n.a.*	1-point calibration at 0.208 µmol/mol using an internal calibration standard with a strict preparation tolerance (PEH)	Technique: GC-SCD Instrument: Agilent 7890B Conditions: Helium carrier	According to GUM	n.a.*
L09	n.m.*	n.m.*	n.m.*	n.m.*	n.m.*
L10	Injection through a dual-stage pressure regulator and sulfinert treated 1/16” transfer line at an inlet pressure of 20 psig. Sample allowed to flow through at 100 mL/min for 30secs before injection	1-point calibration at 0.14 µmol/mol using dynamic dilution of a 300 µmol/mol NIST traceable primary standard produced by Airgas. Checked against a secondary standard certified at 0.22 µmol/mol	Technique: GC-SCD Instrument: Perkin Elmer Clarus 580 Condition: Helium carrier; Supelco PDMS column; Detector parameters: 800°C; Stabilisation time: 0.5 mins	Standard deviation of the mean	Volume of gas used: 1 mL
L11	Injection through a sulfinert-treated transfer line at atmospheric pressure	1-point calibration at 0.970 µmol/mol using a standard in a hydrogen balance produced by Air Liquide	Technique: GC-SCD Instrument: no information provided Condition: Helium carrier	X1: repeatability X2: massflow -controller X3: uncertainty calibration gas mixture k=2 k*SQRT(X1^2+X2^2+X3^2)	Volume of gas used: 16.5 L per analysis
L12	n.a.*	n.a.*	n.a.*	n.a.*	n.a.*
L13	n.a.*	5-point calibration using standards produced by Sichuan Standard Material Technology Co., Ltd.	Technique: GC-FPD Instrument: no information provided Condition: 0.1 MPa inlet pressure; helium carrier	u^2=ur(calibration gas)^2+ur(calibration curve)^2+ ur(RSD)^2	n.a.*

*n.a. means not available

*n.m. means not measured

Table B.3: Analytical method information used for the measurement of N_2 in hydrogen by the participants of the MetroHyVe interlaboratory comparison for offline hydrogen purity analysis

Participant code	Sample preparation	Calibration	Method	Uncertainty calculation	Additional remark
L01	Injection through a sulfinert-coated transfer line at an inlet pressure of 0.6 bar(g). 10 purges and 10+ min stabilisation before performing measurements	1-point calibration at 99.5 µmol/mol using a certified standard produced by Air Liquide	Technique: GC-TCD Instrument: Agilent Technologies 490 micro GC Condition: Helium 6.0 carrier; MS 5A – 25 m column; 32°C column and injector temp; Stabilisation time: ~ 30 mins (10 discarded samples)	Measurement uncertainty is given with a coverage factor of k = 2 including: uncertainty budgets from cal gas standard analysis, deviation of calibration samples and deviation of measured samples under reproducibility conditions	n.a.*
L02A	Gas transferred into non-treated sampling cylinder (1LS1) prior to dispatch. Injection through a 1/4" heated line without coating at sample pressure	1-point calibration using an internal standard at 197 µmol/mol. Initial calibration with 6 sample replicate analysis	Technique: GC-MS Instrument: Agilent 5973 Condition: Hydrogen carrier; 30 m x 0.25 µm capillary column	Standard deviation	According to ASTM D7649. Volume of gas used: ~60 mL
L03	Injection through a non-treated transfer line at an inlet pressure of 0.2 MPa	2-point calibration at 100 and 600 µmol/mol using non-certified standards produced by Sumitomo Seika Chemicals Co. Ltd	Technique: GC-TCD Instrument: J-SCIENCE LAB Co. Condition: Hydrogen carrier; packed column	Uncertainty of the standard substance was evaluated with Type A, and the uncertainty was calculated assuming a rectangular distribution with a guaranteed value of ±. The uncertainty of repetition was evaluated with Type B, and the uncertainty was calculated from the standard deviation	Volume of gas used: 80 L
L04	Injection through a stainless-steel transfer line at an inlet pressure of 15 psi. Direct injection, split ratio 1:5	2-point calibration at 190 and 210 µmol/mol using internal standards	Technique: GC-PDHID Instrument: no information provided Condition: Helium carrier; CP Molsieve 5A 50 m, 0.53 mm, 50 µm column; 120 °C PDHID	95 % uncertainty based on k=2	Volume of gas used: 1 mL sample loop
L05	Injection through a sulfinert-coated stainless-steel transfer line at an inlet pressure of ~ 1 bar. Purges performed and conditioning time allowed prior to injection	1-point calibration at 200 µmol/mol using an internal primary standard	Technique: GC-PDHID Instrument: Agilent Condition: Helium carrier; Molsieve 5A and HS-A packed column; 1 cc loop, 30°C oven, 30 mL/min flowrate; Stabilisation time: ~ 10 mins (1 discarded measurement)	Measurement uncertainties are stated with a coverage factor k = 2, providing a coverage probability of approx. 95 %. Uncertainty budgets include contributions from calibration gas standard validation, repeatability of calibration standard measurements, repeatability of sample measurements and, for dynamic calibration curve production, uncertainties associated with the gas flow control devices	Volume of gas used: ~ 100 L
L06	Injection performed directly from sample cylinder provided	1-point calibration at 1 µmol/mol using a primary standard produced by Airgas	Technique: MS Instrument: MKS - Hiden Condition: Background correction: UHP hydrogen; Blank correction: vacuum; Detector parameters: electron multiplier	Method uncertainty values based on validations performed for initial ISO 17025 accreditation and ongoing QA monitoring including SPC data collection	n.a.*
L07	Injection performed directly into analyser at an inlet pressure of 1 bar	1-point calibration at 308 µmol/mol using a standard in a hydrogen balance produced by Air Liquide	Technique: GC-PDHID Instrument: no information provided	Used the criteria for the measurement uncertainty defined in the standard ISO 21087, published in September 2019. Calculated the uncertainties with the standard NF ISO 11352 published in February 2013. This method is described in the sections 8, 9, 10.	n.a.*

			Condition: Helium carrier; filled column; Detector parameters: 150°C; Stabilisation time: 60 mins	The uncertainty estimation was realised on ten replicates for each concentration level on working range. To determine measurement uncertainty, two parameters were calculated: uncertainty of replicate reproducibility intralaboratory (section 8.2.2) and bias of the method and laboratory (section 8.3.2)	
L08	No information provided	1-point calibration at 249 µmol/mol using an internal calibration standard with a strict preparation tolerance (PEH)	Technique: GC-PDID Instrument: Unicam Pro GC Condition: Helium carrier	According to GUM	n.a.*
L09	Injection through a non-treated transfer line at atmospheric pressure	2-point calibration at 413 and 1001 µmol/mol using premixed standards produced by Aga	Technique: GC-BID-TCD Instrument: Shimadzu 2010 Condition: Helium carrier; µ-packed column; Detector parameters: BID	n.a.*	Volume of gas used: 2 L
L10	Injection through a sulfinert treated 1/16" transfer line at an inlet pressure of 760 torr through a leak-tight evacuated manifold. Manifold filled with sample to 760 torr before injection	1-point calibration using dynamic dilution of a 5.3 µmol/mol NIST traceable certified standard produced by Airgas	Technique: GC-PDID Instrument: Perkin Elmer Clarus 500 Condition: Helium carrier; Agilent molesieve column; Detector parameters: 240°C; Stabilisation time: 0.5 mins	Standard deviation of the mean	Volume of gas used: 1 mL
L11	Injection through a sulfinert treated transfer line at atmospheric pressure	1-point calibration at 106.2 µmol/mol using a standard in a hydrogen balance produced by Air Liquide	Technique: GC-PED Instrument: no information provided Condition: Helium carrier	X1: repeatability X2: massflow -controller X3: uncertainty calibration gas mixture k=2 k*SQRT(X1^2+X2^2+X3^2)	Volume of gas used: 10 L per analysis
L12	n.a.*	n.a.*	n.a.*	n.a.*	n.a.*
L13	n.a.*	2-point calibration using standards produced by Dalian Special Gases Co.LTD	Technique: GC-PDD Instrument: GC-2014/PDD (Shimadzu) Condition: 0.1 MPa inlet pressure; helium carrier	The main sources of uncertainty come from calibration models, calibration gas and pre-processing step of samples. u^2=ur(calibration gas)^2+ur(calibration curve)^2+ ur(RSD)^2	n.a.*

*n.a. means not available

Table B.4: Analytical method information used for the measurement of H_2O in hydrogen by the participants of the MetroHyVe interlaboratory comparison for offline hydrogen purity analysis

Participant code	Sample preparation	Calibration	Method	Uncertainty calculation	Additional remark
L01	Injection through a sulfinert-coated transfer line at an inlet pressure of 0.6 bar(g). 10 purges and 10+ min stabilisation before performing measurements	1-point calibration at 10 µmol/mol using a certified standard produced by MTI. Device can only be calibrated by the manufacturer; calibration sample used for QC purposes. Device calibrated by Michell in 07/2019	Technique: Chilled mirror Instrument: Michell Instruments S8000RS Condition: 750 ml/min continuous flow; dew point: -90 to +20°C; stabilisation time: ~ 30 mins	Measurement uncertainty is given with a coverage factor of k = 2 including: uncertainty budgets from cal gas standard analysis, deviation of calibration samples and deviation of measured samples under reproducibility conditions	n.a.*
L02A	Gas transferred into non-treated sampling cylinder (1LS1) prior to dispatch. Injection through a 1/4" heated line without coating at sample pressure	2-point calibration at 8.28 and 5.93 µmol/mol using standards produced by Airgas. Initial calibration with 6 sample replicate analysis	Technique: GC-MS Instrument: Agilent 5973 Condition: Hydrogen carrier; 30 m x 0.25 µm capillary column	Standard deviation	According to ASTM D7649. Volume of gas used: ~60 mL
L02B	Gas transferred into silicon-coated sampling cylinder (1LL15) prior to dispatch. Injection through a 1/4" heated line without coating at sample pressure	2-point calibration at 8.28 and 5.93 µmol/mol using standards produced by Airgas. Initial calibration with 6 sample replicate analysis	Technique: GC-MS Instrument: Agilent 5973 Condition: Hydrogen carrier; 30 m x 0.25 µm capillary column	Standard deviation	According to ASTM D7649. Volume of gas used: ~60 mL
L03	Injection through a non-treated transfer line at an inlet pressure of 0.2 MPa	1-point calibration of device at 1000 µmol/mol. Device calibrated once a year	Technique: CRDS Instrument: Tiger Optics Condition: wavelength: 1392.18 nm; stabilisation time: 30 min	Uncertainty of the standard substance was evaluated with Type A, and the uncertainty was calculated assuming a rectangular distribution with a guaranteed value of ±. The uncertainty of repetition was evaluated with Type B, and the uncertainty was calculated from the standard deviation	Volume of gas used: 180 L
L04	Injection through a coated transfer line at an inlet pressure of ~2 bar(a)	2-point calibration at 1.5 and 25 µmol/mol using standards produced by Air Liquide. Standards certified by internal humidity group. The 1.5 µmol/mol certified standard was low in pressure. Linearity of instrument good. Zero determined with N2 BIP and H2 BIP	Technique: CRDS Instrument: Tiger Optics Spark+ Condition: Wavelength: 1.39 µm; stabilisation time: ≥ 30 mins 4 temperature scans were made and the area under the absorption spectrum was fitted and compared to the area of the absorption spectra of the certified standards	95 % uncertainty based on k=2	Volume of gas used: ~60 L
L05	Injection through a sulfinert-coated stainless-steel transfer line and non-treated HF-series	3-point calibration at 2, 5 and 10 µmol/mol using internal primary standards	Technique: QCM Instrument: Michell	Measurement uncertainties are stated with a coverage factor k = 2, providing a coverage probability of approx. 95 %. Uncertainty budgets include contributions from calibration gas standard	Volume of gas used: ~ 300 L

	regulator at an inlet pressure of ~ 1 bar. Purges performed and conditioning time allowed prior to injection		Conditions: 330 - 360 mL/min flowrate; Stabilisation time: ~ 30 mins	validation, repeatability of calibration standard measurements, repeatability of sample measurements and, for dynamic calibration curve production, uncertainties associated with the gas flow control devices	
L06	Injection performed directly from sample cylinder provided	1-point calibration of device at 10 µmol/mol. Device calibrated once a year	Technique: Electrolytic hygrometry Instrument: GE/Panametrics Condition: Detector parameters: aluminium oxide; Stabilisation time: 10 mins	Method uncertainty values based on validations performed for initial ISO 17025 accreditation and ongoing QA monitoring including SPC data collection	n.a.*
L07	Injection performed directly into analyser at an inlet pressure of 1 bar	2-point calibration at 0 and 4.75 µmol/mol using standards in a nitrogen balance produced by Air Liquide.	Technique: OFCEAS Instrument: no information provided Condition: Wavelength: 1.6 to 2.0 µm; Detector parameters: 50°C; Stabilisation time: 60 mins	Used the criteria for the measurement uncertainty defined in the standard ISO 21087, published in September 2019. Calculated the uncertainties with the standard NF ISO 11352 published in February 2013. This method is described in the sections 8, 9, 10. The uncertainty estimation was realised on ten replicates for each concentration level on working range. To determine measurement uncertainty, two parameters were calculated: uncertainty of replicate reproducibility intralaboratory (section 8.2.2) and bias of the method and laboratory (section 8.3.2)	n.a.*
L08	n.a.*	No calibration performed	Technique: CRDS Instrument: Tiger Optics Halo+ H2O Analysator Condition: no information provided	According to GUM	n.a.*
L09	Injection through a SilcoNert-treated transfer line at an inlet pressure of 3 bar(a)	NIST traceable internal calibration of analyser. Accuracy is 4% of reading	Technique: CRDS Instrument: Tiger Optics HALO M7003 L4700-Type3 Condition: Background correction: internal tuning with sample gas; Stabilisation time: 1 hour; Blank correction: internal tuning with sample gas	n.a.*	Volume of gas used: 600 L
L10	Injection through a sulfinert treated 1/4" transfer line at an inlet pressure of 125 torr through a leak-tight evacuated manifold	Multiple-point calibration in correlation to a GE Panametrics conductimetric hygrometer using internal standards	Technique: FTIR Instrument: Thermofisher Nicolet 6700 Condition: Background correction: yes; Detector parameters: 50°C; 10 m gas cell – 4.0 mm thick zinc selenide windows	Standard deviation of the mean	Volume of gas used: 2300 mL
L11	Injection through a sulfinert treated transfer line at an inlet pressure of 0.2 bar	1-point calibration at 4.9648 µmol/mol using an internal standard	Technique: QCM Instrument: no information provided Condition: Stabilisation time: 30 mins	X1: repeatability X2: massflow -controller X3: uncertainty calibration gas mixture k=2 k*SQRT(X1^2+X2^2+X3^2)	Volume of gas used: 18 L per analysis
L12	n.a.*	n.a.*	n.a.*	n.a.*	n.a.*
L13	n.a.*	n.a.*	Technique: Aluminium oxide sensor Instrument: Xentaur portable dewpoint meter Condition: 0.1 MPa inlet pressure; Stabilisation time: 30 mins	u^2=ur(calibration gas)^2+ur(calibration curve)^2+ ur(RSD)^2	n.a.*

*n.a. means not available

Annex C: Participant results

The results below are as reported by the participants. No rounding has been performed.

Table C.1: Participant results for the measurement of CO in hydrogen in the MetroHyVe interlaboratory comparison for offline hydrogen purity analysis

Participant code	Cylinder reference	Date B [dd/mm/yyyy]	Result 1 [µmol/mol]	Result 2 [µmol/mol]	Result 3 [µmol/mol]	Average [µmol/mol]	Expanded uncertainty [µmol/mol]	Date B [dd/mm/yyyy]	Result 1 [µmol/mol]	Result 2 [µmol/mol]	Result 3 [µmol/mol]	Average [µmol/mol]	Expanded uncertainty [µmol/mol]
L01	5707098	30/07/2019	0.243	0.243	0.243	0.243	0.0037	01/08/2019	0.243	0.246	0.243	0.244	0.0037
L02A	5707102	09/07/2019	0.1074	0.101	n.r.*	0.104	0.005	10/07/2019	0.1078	0.1119	n.r.*	0.110	0.003
L03	5707088	03/09/2019	0.241	0.242	0.240	0.241	0.014	04/09/2019	0.246	0.239	0.241	0.242	0.015
L04	5707111	29/07/2019	0.242	0.239	0.239	n.r.*	n.r.*	29/07/2019	0.243	n.r.*	n.r.*	0.241	0.004
L05	5707097	23/10/2019	0.234	0.235	0.236	0.235	0.009	28/10/2019	0.242	0.243	0.245	0.243	0.008
L06	5707090	06/08/2019	0.31	0.29	0.30	0.30	0.05	07/08/2019	0.37	0.34	0.32	0.34	0.05
L07	5707101	16/10/2019	0.25	0.24	0.28	0.26	0.03	n.r.*	n.r.*	n.r.*	n.r.*	n.r.*	n.r.*
L08	5707089	12/12/2019	0.24	n.r.*	n.r.*	0.24	0.024	13/12/2019	0.23	n.r.*	n.r.*	0.23	0.023
L09	5705785	19/11/2019	0.19	0.2	0.19	0.19	0.04	20/11/2019	0.2	0.19	0.19	0.19	0.04
L10	5707090	20/01/2020	0.25	0.25	0.25	0.25	0.00083	24/01/2020	0.25	0.25	0.25	0.25	0.00048
L11	5707098	12/02/2020	0.235	0.233	0.231	0.233	0.010	13/02/2020	0.232	0.230	0.229	0.230	0.010
L12	5707102	27/02/2020	0.121	0.122	0.123	0.122	0.01	04/03/2020	0.129	0.134	0.136	0.133	0.01
L13	5707087	03-04/03/2020	0.246	0.25	0.246	0.247	0.015	05-06/03/2020	0.247	0.243	0.243	0.244	0.15

*n.r. means not reported

Table C.2: Participant results for the measurement of H_2S in hydrogen in the MetroHyVe interlaboratory comparison for offline hydrogen purity analysis

Participant code	Cylinder reference	Date B [dd/mm/yyyy]	Result 1 [µmol/mol]	Result 2 [µmol/mol]	Result 3 [µmol/mol]	Average [µmol/mol]	Expanded uncertainty [µmol/mol]	Date B [dd/mm/yyyy]	Result 1 [µmol/mol]	Result 2 [µmol/mol]	Result 3 [µmol/mol]	Average [µmol/mol]	Expanded uncertainty [µmol/mol]
L01	NG890	30/07/2019	0.02948	0.03183	0.03242	0.03124	0.0046	01/08/2019	0.045	0.04535	0.04545	0.045	0.0048
L02A	NG812R	09/07/2019	0.0191	n.r.*	n.r.*	n.r.*	n.r.*	09/07/2019	0.0236	0.0193	0.0177	0.020	0.003
L03	NG897	19/09/2019	0.035	0.036	0.036	0.036	0.0065	20/09/2019	0.035	0.036	0.036	0.036	0.0065
L04	NG817R	22/08/2019	0.04073	n.r.*	n.r.*	n.r.*	n.r.*	26-27/08/2019	0.0393	0.03923	n.r.*	0.0398	0.0012
L05	NG812R	26/09/2019	0.0309	0.0308	0.0313	0.0310	0.0018	03/10/2019	0.0292	0.029	0.0301	0.0294	0.0027
L06	NG815R	12/02/2020	0.030	0.030	0.031	0.030	0.002	14/02/2020	0.031	0.032	0.032	0.032	0.002
L07	NG846R	21/10/2019	0.01963	0.01775	0.02328	0.02022	0.00202	n.r.*	n.r.*	n.r.*	n.r.*	n.r.*	n.r.*
L08	NG812R	18/12/2019	0.020	n.r.*	n.r.*	0.020	0.0020	15/01/2019	0.023	n.r.*	n.r.*	0.023	0.0023
L09	NG817R	n.m.*	n.m.*	n.m.*	n.m.*	n.m.*	n.m.*	n.m.*	n.m.*	n.m.*	n.m.*	n.m.*	n.m.*
L10	NG815R	08/01/2020	0.024	0.025	0.024	0.024	0.00027	09/01/2020	0.026	0.025	0.024	0.025	0.00047
L11	NG890	11/02/2020	0.038	0.039	0.041	0.040	0.003	12/02/2020	0.036	0.037	0.039	0.037	0.004
L12	NG888	27/02/2020	0.24	0.249	0.24	0.243	0.02	04/03/2020	0.231	0.233	0.235	0.233	0.02
L13	NG845R	12/03/2020	0.005378	0.005023	0.005055	0.005152	0.000641	n.r.*	n.r.*	n.r.*	n.r.*	n.r.*	n.r.*

*n.r. means not reported

*n.m. means not measured

Table C.3: Participant results for the measurement of N_2 in hydrogen in the MetroHyVe interlaboratory comparison for offline hydrogen purity analysis

Participant code	Cylinder reference	Date B [dd/mm/yyyy]	Result 1 [µmol/mol]	Result 2 [µmol/mol]	Result 3 [µmol/mol]	Average [µmol/mol]	Expanded uncertainty [µmol/mol]	Date B [dd/mm/yyyy]	Result 1 [µmol/mol]	Result 2 [µmol/mol]	Result 3 [µmol/mol]	Average [µmol/mol]	Expanded uncertainty [µmol/mol]
L01	5707098	30/07/2019	204.9	194.8	204	201.24	25	01/08/2019	198.6	201.4	202.7	200.9	24
L02A	5707102	18/06/2019	210	209	214	211.0	2.6	12/07/2019	202	n.r.*	n.r.*	n.r.*	n.r.*
L03	5707088	03/09/2019	200	200	200	200	14	04/09/2019	201	202	200	201	14
L04	5707111	14-19/08/2019	199.2	200.7	n.r.*	n.r.*	n.r.*	21-26/08/2019	199.4	199.4	n.r.*	199.7	2.0
L05	5707097	06/09/2019	201.15	200.95	201.24	201.1	4.0	09/09/2019	200.94	200.54	200.51	200.7	4.0
L06	5707090	20/08/2019	202	218	221	214	2	23/08/2019	222	216	207	215	2
L07	5707101	16/10/2019	201	203	204	203	20	n.r.*	n.r.*	n.r.*	n.r.*	n.r.*	n.r.*
L08	5707089	27/11/2019	213	n.r.*	n.r.*	213	4.3	28/11/2019	211	n.r.*	n.r.*	211	4.2
L09	5705785	20/11/2019	221.1	221.2	221.2	221.2	2	21/11/2019	221.4	221.6	221.5	221.5	2
L10	5707090	20/01/2020	170	180	170	170	2.7	24/01/2020	160	180	170	170	4.7
L11	5707098	12/02/2020	206.909	191.306	166.451	188.2	39.0	13/02/2020	205.446	176.297	157.045	179.6	42.8
L12	5707102	27/02/2020	51.18	51.42	50.98	51.19	2.5	04/03/2020	39	39	38	39	2.5
L13	5707087	03-04/03/2020	174.183	173.311	174.662	174.052	28.705	05-06/03/2020	175.701	174.638	176.841	175.727	29.037

*n.r. means not reported

Table C.4: Participant results for the measurement of H_2O in hydrogen in the MetroHyVe interlaboratory comparison for offline hydrogen purity analysis

Participant code	Cylinder reference	Date B [dd/mm/yyyy]	Result 1 [µmol/mol]	Result 2 [µmol/mol]	Result 3 [µmol/mol]	Average [µmol/mol]	Expanded uncertainty [µmol/mol]	Date B [dd/mm/yyyy]	Result 1 [µmol/mol]	Result 2 [µmol/mol]	Result 3 [µmol/mol]	Average [µmol/mol]	Expanded uncertainty [µmol/mol]
L01	5707098	30/07/2019	8.36	8.6	8.74	8.56	0.6	01/08/2019	8.4	8.7	8.84	8.64	0.7
L02A	5707102	18/06/2019	4.5	5.5	5.5	5.2	0.58	n.r.*	n.r.*	n.r.*	n.r.*	n.r.*	n.r.*
L02B	5707102	12/07/2019	1.9	1.5	1.7	1.7	0.20	n.r.*	n.r.*	n.r.*	n.r.*	n.r.*	n.r.*
L03	5707088	28/08/2019	6.90	6.89	6.90	6.90	0.21	29/08/2019	6.90	6.92	6.91	6.91	0.21
L04	5707111	30/07/2019	8.41	8.17	8.31	n.r.*	n.r.*	30/07/2019	8.42	n.r.*	n.r.*	8.33	0.34
L05	5707097	15/08/2019	8.28	8.25	8.22	8.25	0.48	12/09/2019	7.55	7.57	7.58	7.57	0.44
L06	5707090	06/08/2019	7.4	6.8	6.4	6.9	0.5	07/08/2019	10.8	9.9	8.3	9.7	0.5
L07	5707101	16/10/2019	9.41	9.39	9.39	9.40	0.94	n.r.*	n.r.*	n.r.*	n.r.*	n.r.*	n.r.*
L08	5707089	05/12/2019	7.58	n.r.*	n.r.*	7.58	0.76	06/12/2019	7.60	n.r.*	n.r.*	7.60	0.76
L09	5705785	22/01/2020	7.68	7.58	7.66	7.68	0.35	23/01/2020	7.71	7.66	7.67	7.68	0.35
L10	5707090	20/01/2020	0.4	0.4	0.4	0.4	0.0047	27/01/2020	0.3	0.3	0.3	0.3	0.014
L11	5707098	14/02/2020	10.61	10.57	10.53	10.34	1.1	14/02/2020	9.95	9.96	9.94	9.72	1.0
L12	5707102	27/02/2020	10	10	10	10	1	04/03/2020	9.8	9.9	9.9	9.9	1
L13	5707087	01/03/2020	5.13	5.13	5.13	5.13	1.2	05/03/2020	4.53	4.53	4.53	4.558	1.1

*n.r. means not reported

Annex D: Zeta scores

Table D.1: Participants results for the measurement of CO at nominally 250 nmol/mol in hydrogen, the corresponding reference value and zeta-score. If the first significant figure of the uncertainty was 5 or greater, the uncertainty was stated to one significant figure. If the first significant figure of the uncertainty was 4 or less, the uncertainty was stated to two significant figures. The reported results and reference values were rounded accordingly. zeta-scores were rounded to two decimal places.

Participant code	Technique used	Reported result [nmol/mol]	Uncertainty (*k*=2) [nmol/mol]	Reference value [nmol/mol]	Uncertainty of the reference value (*k*=2) [nmol/mol]	Zeta-score
L01	OFCEAS	244	5	250	10	-1.06
L02A	GC-PDHID	107	6	248	11	-23.31
L03	GC-FID (meth)	242	21	248	11	-0.60
L04	DAL	241.0	4.0	249	9	-1.68
L05	GC-FID (meth)	239	12	246	5	-1.03
L06	FTIR	320	71	246	10	2.08
L07	GC-PDHID	260	30	252	10	0.52
L08	GC-PDID	235	33	250	8	-0.89
L09	GC-FID (meth)	190	57	252	8	-2.17
L10	FTIR	250.0	1.0	246	10	0.88
L11	GC-PED	232	14	250	10	-2.07
L12	PHID	128	14	248	11	-13.64
L13	GC-PDD	246	21	255	7	-0.88

Table D.2: Participants results for the measurement of H_2S at nominally 40 nmol/mol in hydrogen, the corresponding reference value and zeta-score. If the first significant figure of the uncertainty was 5 or greater, the uncertainty was stated to one significant figure. If the first significant figure of the uncertainty was 4 or less, the uncertainty was stated to two significant figures. The reported results and reference values were rounded accordingly. zeta-scores were rounded to two decimal places.

Participant code	Technique used	Reported result [nmol/mol]	Uncertainty (*k*=2) [nmol/mol]	Reference value [nmol/mol]	Uncertainty of the reference value (*k*=2) [nmol/mol]	Zeta-score
L01	TD-GC-FPD	38	7	34.4	3.1	0.97
L02A	GC-SCD	20.0	3.0	35.7	2.4	-8.15
L03	GC-FPD	36	9	32.5	2.7	0.72
L04	GC-SCD	39.8	1.2	31.2	2.7	5.82
L05	GC-SCD	30.2	3.2	31.7	2.6	-0.72
L06	GC-SCD	31.0	2.8	22.6	2.4	4.56
L07	ATD-GC-FPD	20.2	2.0	29.0	1.6	-6.77
L08	GC-SCD	21.5	3.0	27.1	2.4	-2.92
L10	GC-SCD	24.5	0.5	24.2	2.2	0.29
L11	GC-SCD	38.5	5	25.0	2.6	4.81
L12	GC-SCD	238	28	22.5	2.5	15.18
L13	GC-FPD	5.2	0.6	22.9	1.9	-17.32

Table D.3: Participants results for the measurement of N_2 at nominally 200 µmol/mol in hydrogen, the corresponding reference value and zeta-score. If the first significant figure of the uncertainty was 5 or greater, the uncertainty was stated to one significant figure. If the first significant figure of the uncertainty was 4 or less, the uncertainty was stated to two significant figures. The reported results and reference values were rounded accordingly. zeta-scores were rounded to two decimal places.

Participant code	Technique used	Reported result [nmol/mol]	Uncertainty (*k*=2) [nmol/mol]	Reference value [nmol/mol]	Uncertainty of the reference value (*k*=2) [nmol/mol]	Zeta-score
L01	GC-TCD	201	35	198.9	2.0	0.12
L02A	GC-MS	211.0	2.6	198.8	2.0	7.44
L03	GC-TCD	201	20	198.8	2.0	0.17
L04	GC-PDHID	199.7	2.0	199.1	2.0	0.42
L05	GC-PDHID	201	6	198.7	2.0	0.73
L06	MS	214.5	2.8	197.7	2.0	9.70
L07	GC-PDHID	203	20	199.5	2.0	0.35
L08	GC-TCD	212.0	6.0	198.6	2.0	4.23
L09	GC-BID-TCD	221.4	2.8	198.9	2.0	12.96
L10	GC-DID	170	5	197.7	2.0	-9.59
L11	GC-PED	184	58	198.9	2.0	-0.52
L12	PHID	45.1	3.5	198.8	2.0	-75.68
L13	GC-PDD	175	41	199.2	2.0	-1.19

Table D.4: Participants results for the measurement of H_2O at nominally 9 µmol/mol in hydrogen, the corresponding reference value and zeta-score. If the first significant figure of the uncertainty was 5 or greater, the uncertainty was stated to one significant figure. If the first significant figure of the uncertainty was 4 or less, the uncertainty was stated to two significant figures. The reported results and reference values were rounded accordingly. zeta-scores were rounded to two decimal places.

Participant code	Technique used	Reported result [nmol/mol]	Uncertainty (*k*=2) [nmol/mol]	Reference value [nmol/mol]	Uncertainty of the reference value (*k*=2) [nmol/mol]	Zeta-score
L01	Chilled mirror	8.6	0.9	7.6	0.9	1.62
L02A	GC-MS	5.2	0.6	6.8	0.9	-2.98
L02B	GC-MS	1.70	0.20	6.8	0.9	-11.24
L03	CRDS	6.91	0.30	6.0	0.9	1.95
L04	CRDS	8.33	0.34	6.6	0.9	3.60
L05	QCM	7.9	0.7	7.0	0.9	1.70
L06	Electrolytic hygrometry	8.3	0.7	6.8	0.9	2.71
L07	OFCEAS	9.4	0.9	7.5	0.9	2.94
L08	CRDS	7.6	1.1	6.2	0.9	2.03
L09	CRDS	7.68	0.49	6.7	0.9	1.96
L10	FTIR	0.350	0.015	6.8	0.9	-14.59
L11	QCM	10.0	1.5	7.6	0.9	2.86
L12	Si sensor	10.0	1.4	6.8	0.9	3.82
L13	Al_2O_3 sensor	4.8	1.6	5.5	0.9	-0.73

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