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**EURAMET 1220: INTERNATIONAL COMPARISON ON HYDROGEN
PURITY ANALYSIS**

**T. BACQUART, A.M.H. VAN DER VEEN, S. BARTLETT, H. ENT, J.I.T.
VAN WIJK, M.D. MINARRO, R. E. HILL-PEARCE, P.J. BREWER,
R.J.C. BROWN, A.S. BROWN AND A. MURUGAN**

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T. Bacquart¹, A.M.H. van der Veen², S. Bartlett¹, H. Ent², J.I.T. van Wijk²,
M.D. Minarro¹, R. E. Hill-Pearce¹, P.J. Brewer¹, R.J.C. Brown¹, A.S.
Brown¹, A. Murugan¹

¹NPL, Environmental Division, Teddington, United Kingdom

²VSL, Chemistry Group, Delft, the Netherlands

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National Physical Laboratory
Hampton Road, Teddington, Middlesex, TW11 0LW

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J. Burston, Head of NPL Environment division.

CONTENTS

GLOSSARY/ABBREVIATIONS

1. INTRODUCTION 1

2. PREPARATION OF THE MIXTURES 1

 A. MIXTURE SELECTION AND DISTRIBUTION 1

 B. MIXTURE PREPARATION 2

 i. Air Liquide mixture preparation 2

 ii. Linde mixture preparation 2

 C. REFERENCE VALUES AND STABILITY EVALUATION 2

 i. Measurements setup 3

 ii. Analytical methods 3

 iii. Data treatment 4

 iv. Set (1) - data evaluation 6

 v. Set (2) - data evaluation 6

3. METHODS 7

4. RESULTS 11

5. ANNEX 14

 ANNEX A. KEY COMPARISON REFERENCE VALUE DETERMINATION AND STABILITY ASSESSMENT. 14

 ANNEX B. SUMMARY OF PARTICIPANTS ANALYTICAL METHODS 16

 ANNEX C. PARTICIPANT’S RESULTS. 27

 ANNEX D. DEGREE OF EQUIVALENCE RESULTS. 36

6. REFERENCES 38

GLOSSARY/ABBREVIATIONS

BIP	Built-in purifier
CEN	Comité européen de normalisation
CENELEC	Comité Européen de Normalisation Electrotechnique
CRDS	Cavity ring-down spectroscopy
df	Degrees of freedom
DIN	Deutsches institut für normung
ED	Enrichment device
EU	European Union
EURAMET	European Association of National Metrology Institutes
FID	Flame ionisation detector
FTIR	Fourier transform infrared spectrometer
GC	Gas chromatography
GUM	Guide to the expression of uncertainty in measurement
HEMS	Hydrogen Elimination Measurement System
IMR	Ion molecule reaction
ISO	International Organization for Standardization
MFC	Mass flow controller
MS	Mass spectrometer
NMI	National metrology institute
PDHID	Pulsed discharge helium ionization detector
ppb	part per billion
ppm	part per million
OFCEAS	Optical feedback cavity-enhanced absorption spectroscopy
SCCM	standard cubic centimetres per minute
SCD	Sulphur chemiluminescence detector
TCD	Thermal conductivity detector
UPH	Ultra-pure hydrogen

PARTICIPANTS NAME / ABBREVIATED NAME

AL	Air Liquide
CEA	Commissariat à l'énergie atomique et aux énergies alternatives
KRISS	Korea Research Institute of Standards and Science
LD	Linde
NPL	National Physical Laboratory
P&E	Power and Energy
SP	SP Sveriges Tekniska Forskningsinstitut AB
SINTEF	Selskapet for INdustriell og TEknisk Forskning ved norges tekniske hoegskole
VNIIM	D.I.Mendeleyev Institute for Metrology
VSL	Van Swinden Laboratorium

1. INTRODUCTION

The use of fuel cell hydrogen as an energy vector provides many advantages as it can power vehicles without producing harmful emissions such as carbon dioxide, nitrogen oxides or sulphur oxides. We expect to see a large number of hydrogen refuelling stations to be installed across Europe and automotive manufacturers such as Hyundai, Toyota and Nissan will be rolling out their fuel cell vehicles from 2015 onwards. There are several routes for producing hydrogen, but the two most favoured are by steam methane reforming (the conventional method) and electrolysis. The advantage of electrolysis is that the electrolyser can be powered directly by renewable sources such as solar panels.

Hydrogen provided to a fuel cell vehicle must be purity analysed, this is because the presence of certain impurities can cause degradation of the fuel cell system. European Directive 2014/94/EU requires that all fuel cell hydrogen must comply with ISO 14687-2 [1] which provides maximum limits of 13 gaseous impurities. This laboratory comparison involves measurement of two impurities, carbon monoxide and hydrogen sulphide. These impurities were selected because they can cause severe degradation of the fuel cell system.

The analytical challenge of hydrogen purity analysis lies in the low amount fractions that need to be measured as specified in ISO 14687-2. Carbon monoxide and hydrogen sulphide are very reactive components that can be very detrimental to a fuel cell system. These are therefore the two key impurities that must be measured. The limits specified in ISO 14687-2 are 200 nmol mol⁻¹ and 4 nmol mol⁻¹ for carbon monoxide and total sulphur compounds, respectively [1].

Ten laboratories participated in the comparison: NPL (United Kingdom) and VSL (the Netherlands) as coordinating laboratories, SP (Sweden), VNIIM (Russia), KRISS (Korea), Air Liquide (France), Linde (Germany), CEA (France), SINTEF (Norway), and Power and Energy (United States of America).

2. PREPARATION OF THE MIXTURES

A. MIXTURE SELECTION AND DISTRIBUTION

The composition of the hydrogen mixtures were selected considering the following factors:

- The impurity amount fractions should be low enough to make the measurements challenging
- The impurity amount fractions should not be too low to cause the mixture to lose stability over the timeline of the comparison
- The laboratories preparing the mixtures must be able to provide an accurate reference value for the impurity amount fractions

For these reasons, three compositions were selected:

- 1 µmol/mol carbon monoxide in hydrogen
- 100 nmol/mol carbon monoxide in hydrogen
- 1 µmol/mol hydrogen sulphide in hydrogen

Due to the high number of participants involved in the comparison, two sets of the mixtures were provided, one set by Air Liquide and one set by Linde. The reference value assignment and the mixture stability were defined by the co-ordinating laboratories (NPL and VSL).

Each set of mixtures was analysed by different participants, mentioned here in alphabetical order:

Set 1: KRISS, Linde, NPL, SINTEF, VNIIM and VSL

Set 2: Air Liquide, CEA (2 techniques reported), Power & Energy, NPL and VSL

All participants' results will be reported using a degree of equivalence, defined as the difference with respect to the reference value and the associated expanded uncertainty.

In order to keep the report anonymous, the results of analysis will be presented in a random order with coding system for each laboratory. The results of Set 1 and Set 2 are presented jointly.

Details of the mixture preparation and determination of the assigned reference values are detailed in the next section.

B. MIXTURE PREPARATION

A summary of the mixtures is shown below in Table 1. This details the nominal amount fractions, pressure and date of preparation of the mixtures. A summary of the production methods is detailed below.

Table 1: Details of the mixtures prepared for Euramet 1220

Set	Impurity	Nominal amount fraction ($\mu\text{mol mol}^{-1}$)	Pressure (bar)	Date of preparation
1	H ₂ S	1	130	06/02/2014
1	CO	1	130	06/02/2014
1	CO	0.1	140	06/02/2014
2	H ₂ S	1	200	30/01/2014
2	CO	1	135	30/01/2014
2	CO	0.1	170	30/01/2014

i. Air Liquide mixture preparation

The mixtures were prepared in accordance with ISO 6142 [2]. The mixtures were prepared gravimetrically using pure gas and pure hydrogen (purity grade N6.0) in 10 litre aluminium cylinders with outlet in stainless steel, model NFE 25E.

ii. Linde mixture preparation

The mixtures were prepared in accordance with ISO 6142 [2]. The mixtures were prepared gravimetrically using pure gas and pure hydrogen (grade 6 purity) in 10 litre aluminium cylinders with outlet in stainless steel, model DIN 477-1 no 14. The analytical verification was performed using GC-PDHID for carbon monoxide in hydrogen and GC-SCD for hydrogen sulphide in hydrogen.

C. REFERENCE VALUES AND STABILITY EVALUATION

The duration of the comparison (almost two years) turned out to be an issue for the stability of CO and H₂S in hydrogen. Furthermore, cylinder transportation between partners is another possible source of instability (e.g. temperature, handling).

As the coordinators decided to evaluate the stability, also with respect to the reference value assignment, a minimum of four measurements were performed by NPL and VSL along the duration of the EURAMET 1220 exercise. The three mixtures prepared by both Air Liquide and Linde were analysed by VSL and NPL over the duration of the study, all against primary reference gas standards in order to provide reference values for the comparison. Out of the four measurements, at least one was performed at the start and end of the measurement campaign.

i. Measurements setup

To evaluate stability of the two sets of mixtures, NPL and VSL carried out analysis during the length of the EURAMET 1220 inter-comparison.

- For the set 1, the measurements were performed in March 2014 (VSL), April 2014 (NPL), April 2015 (VSL) and January 2016 (NPL). Remark: all the participants were performing their analysis between April 2014 and April 2015.
- For the set 2, the measurements were performed in March 2014 (NPL), June 2014 (VSL), April 2015 (NPL) and January 2016 (NPL). Remark: all the participants were performing their analysis between June 2014 and September 2015.

The analytical methods used for the reference value is detailed in the Section below (Analytical methods).

ii. Analytical methods

NPL analytical methods:

Hydrogen sulphide was measured by GC-SCD model Agilent 7890A with SCD detector 355 (Agilent, United Kingdom) with all lines Sulfinert® treated and carbon monoxide by CRDS, model CO-23r (Los Gatos Research Inc., United States of America) using NPL validated methods. In order to assign the reference values, two calibration methods were used: static gravimetric gas standards and dynamic reference gas standards. The static reference gas standards were prepared gravimetrically; this allows the composition of the mixture to be assigned with high accuracy. However, hydrogen sulphide and carbon monoxide are known to change composition within a static mixture over time due to reactions or adsorption to the cylinder walls. Therefore dynamic reference gas standards were also used to provide further validation of the EURAMET 1220 mixtures. The dynamic reference gas standards were prepared by blending high amount fraction mixtures with ultra-pure Hydrogen (purity grade BIP®+, 99.9999 % from Air Products, United Kingdom), thus producing the desired mixture at the point-of-use (preventing any issues around mixture instability).

The gravimetric reference gas standards were produced at NPL for calibration of the measurements. The purity of each parent gas (CO, H₂S and H₂) was tested to ensure that the impurity level is compliant with the objective of the measurements. The purity analysis results are CO: 99.998 % pure; H₂S: 99.69 % pure. Ultra-pure Hydrogen (purity grade BIP®+, 99.9999 % from Air Products, United Kingdom) was tested using the above mentioned methods: in both cases no impurities were detected. The values assigned for these impurities in the ultra-pure hydrogen (purity grade BIP®+, 99.9999 %) cylinders were calculated using the limit of detection of GC-SCD instrument for H₂S and GC-methaniser-FID instrument for CO. It should be mentioned that the GC-methaniser-FID has a higher LOD than the reported CRDS manufacturer LOD.

The analysis of each mixture was performed three times on at least three different days: day 1 and day 2 using static standards and day 3 using a dynamic standard. The analysis of hydrogen sulphide was performed on the GC-SCD using a switching method (A-B-A-B etc.). Using this approach 50 data points were obtained for each mixture on each day, and a ratio method was used to reduce the effects of instrument drift. The carbon monoxide analysis was performed on CRDS using the same alternate switching method (A-B-A-B etc.). Each measurement lasted 20 minutes and was repeated five times. On the third day of carbon monoxide analysis, the cylinders were compared against the dynamic reference standard. To achieve this, gas mixture cylinders with 100 and 10 µmol/mol of CO were diluted with ultra-pure Hydrogen (purity grade BIP®+, 99.9999 % from Air Products, United Kingdom) to produce flows with nominal amount fractions of 1 µmol/mol and 100 nmol/mol, respectively.

An important consideration when providing the reference value is the measurement uncertainty. This was calculated by combining the measurement repeatability, gravimetric uncertainty of the primary reference gas standard and in the case of CRDS the uncertainty from the zero measurement. Therefore for each measurement, the calculated relative expanded uncertainties ($k=2$) were defined as:

$$\frac{U(x_i)}{x_i} = 2 \times \sqrt{\left(\frac{u(g_i)}{g_i}\right)^2 + \left(\frac{u(r_i)}{\bar{r}_i}\right)^2 + \left(\frac{u(z)}{\bar{r}_i}\right)^2}$$

where U denotes the expanded uncertainty ($k = 2$) of the variable between parenthesis, u the uncertainty ($k=1$), g_i is the calculated gravimetric amount fraction of component i , r_i is the instrument reading of component i and z is the zero measurement reading of the instrument ($u(r_i)$ represents the repeatability of the instrument readings).

VSL analytical methods:

The analysis of hydrogen sulphide was performed on the GC-SCD, model Agilent 6890 (Agilent, the Netherlands) equipped with a DB-1 capillary column and He as carrier gas. The mixtures were connected to a multi position valve which is connected to an all stainless steel, low volume diaphragm reducer valve and a mass flow controller controlling the flow into the GC. No reducing valves were used for individual cylinders. All tubing and devices used were Silcosteel® passivated as was all tubing inside the GC. The responses used are the average of at least 10 injections per mixture. For the measurement 3 calibration standards were used.

The analysis of carbon monoxide at $1 \mu\text{mol mol}^{-1}$ was performed using a GC-FID, model Agilent 6890 (Agilent, the Netherlands) equipped with a Ni catalyst to convert the CO to CH₄ and a packed molsieve 5A column with He as carrier gas. The cylinders were fitted with all stainless steel, low volume diaphragm reducer valves. The responses used are the average of 9 injections per mixture. For the measurement 3 calibration standards were used.

The analysis of carbon monoxide at $0.1 \mu\text{mol mol}^{-1}$ was performed using an OPO-CRDS system built by VSL [3]. Two standards were used as brackets. For the measurements 16 and 40 scans were averaged and the resulting spectrum used as one response. The absorption was measured around 2190 cm^{-1} and the area was integrated over the whole absorption line. This absorption line was chosen because it gave sufficient sensitivity and a return to baseline at the edges of the feature.

To ensure that the mixtures were assigned values with sufficiently low uncertainties for the comparison, three primary reference gas standards were used as calibrant. The analysis of each mixture was performed three times on three different days.

All measurements were performed according to ISO 6143 [4] and a first order linear calibration curve was applied. The mixture to be analysed was added as an unknown and the value and uncertainty calculated according to ISO 6143 were used as result. All uncertainties due to purity analysis, preparation of the standards and the analytical measurement are input parameters for ISO 6143. The amount fraction calculated for the ‘unknown’ incorporates all these uncertainties. The uncertainty given on the result is the uncertainty in the average of the individual results. The standards were newly prepared for this comparison therefore no factor for stability has been added to the uncertainty budget. Only for H₂S an absolute value of 1 nmol was added to the uncertainty of the average as this is a systematic uncertainty due to purity analysis.

iii. Data treatment

The data treatment involved several steps in order to ensure the reference value for each participants and an optimal uncertainty.

As mentioned before, the EURAMET 1220 duration was considered long (almost 2 years), the stability evaluation of the amount fraction of the impurity (CO, H₂S) in the hydrogen matrix was the first step of the data treatment. After determining whether the mixtures were considered stable or unstable, the reference values and their uncertainty were assigned based on the four measurements performed by VSL and NPL over the duration of EURAMET 1220. Finally, the degree of equivalence was calculated in order to evaluate all participants against each other.

Stability evaluation

The significance of the degradation is evaluated using the significance of the slope of a linear regression (α_1) at 95% confidence level. The slope α_1 can be assessed for significance as follows:

$$|\alpha_1| < k u(\alpha_1)$$

where k has been chosen from the t -distribution with the appropriate number of degrees of freedom (df). The value of α_1 is compared to its expanded uncertainty using as coverage factor the t -value (95%; df). If the absolute value of α_1 exceeds its expanded uncertainty, the degradation is considered significant at 95% confidence level [5]. Otherwise, the degradation is considered not significant at 95% confidence level, then $\alpha_1 = 0$.

As the comparison was running for almost 2 years, some impurities levels were significantly unstable over this long period. Based on this observation the reference value and the uncertainty were determined differently depending if the compound was significantly stable or unstable in the mixture.

Reference value assignment for unstable mixtures

For unstable compounds in hydrogen mixture (Set 1 mixtures: 1 $\mu\text{mol/mol}$ CO; 0.1 $\mu\text{mol/mol}$ CO and 1 $\mu\text{mol/mol}$ H₂S), the reference value was expressed as a function of time. The equation is given below:

$$x_{ref}(t) = \alpha_0 + \alpha_1 t$$

where α_0 and α_1 denote the coefficients of a straight line fitted through the data from both reference laboratories, using ordinary least squares. The time t can be measured in a suitable chosen unit, for example the date of measurement.

Reference value assignment for stable mixtures

For stable compounds in hydrogen mixture (Set 2 mixtures: 1 $\mu\text{mol/mol}$ CO; 0.1 $\mu\text{mol/mol}$ CO and 1 $\mu\text{mol/mol}$ H₂S), the reference value was assigned as the mean of the means of VSL and NPL measurements:

$$x_{ref}(t) = \frac{\sum x_i}{n}$$

where x_i represent the mean of measurements performed by VSL and NPL, i represents the measurements order and n the total number of measurements performed by VSL and NPL ($n = 4$).

Uncertainty of reference value

In principle, the uncertainty evaluation of the reference value can be done using the law of propagation of uncertainty from the GUM (*Guide to the expression of Uncertainty in Measurement*) [6], had the underlying data used for calculating the reference value be consistent. As this is not the case, the datasets do not pass the χ^2 -test, as required [7], the Monte Carlo method of GUM-S1 [8] has been used instead to propagate the uncertainties. This procedure is known as procedure B [7] for the evaluation of key comparison data.

Procedure B has been implemented with a sample size of $M = 100000$, which suffices to produce the output (reference value, standard uncertainty, and expanded uncertainty at 95 % level of coverage) with sufficient accuracy. The reference value has been computed for each sample using either the time-dependent model (for the unstable mixtures) or the time-independent average (for the stable mixtures).

Degrees-of-equivalence

The evaluation of the comparison has been done using degrees-of-equivalence. A degree-of-equivalence is defined as the difference between a laboratory's result and the reference value, i.e.

$$d_i = x_i - x_{ref}$$

and its associated standard uncertainty at the 95% coverage level [7]. In the same run of the Monte Carlo method based on procedure B [7] as described previously for the computation of the reference value and its associated standard uncertainty, the differences between the laboratory result and the reference value are obtained. From these M differences, the average is calculated as d_i and the standard deviation as its associated standard uncertainty $u(d_i)$. Using $k = 2$, the standard uncertainty is converted into an expanded uncertainty.

This implementation of the Monte Carlo method ensures that the relevant correlations are taken into account, in particular those arising in the differences calculated for the coordinating laboratories (the reference value is correlated with the results from the coordinating laboratories).

iv. Set (1) - data evaluation

The evaluation of the data from Set (1) showed significant degradation (95 % confidence level) of CO and H₂S amount fractions during the EURAMET 1220 intercomparison. The reference value was then considered time-dependent and fitted using a straight line. The equation used to determine the reference value for each participant is given in Table 2.

Table 2: Results of the statistical test for the significance of the degradation of CO and H₂S compounds in the set (1) of cylinder during the entire comparison exercise using t-value (95 %, df).

	Cylinder reference	Set 1	Reference value equation with $x_{ref,t}$ in [$\mu\text{mol/mol}$] and t in [days]
CO – 1 $\mu\text{mol mol}^{-1}$	9392266	Significant degradation at 95 % confidence level	$x_{ref,t} = -0.00006462*t + 1.000$
CO - 0.1 $\mu\text{mol mol}^{-1}$	9392300	Significant degradation at 95 % confidence level	$x_{ref,t} = -0.00002896*t + 0.08548$
H ₂ S – 1 $\mu\text{mol mol}^{-1}$	9392267	Significant degradation at 95 % confidence level	$x_{ref,t} = -0.0001231*t + 0.6611$

v. Set (2) - data evaluation

The evaluation of the data from Set (2) showed no significant degradation (95 % confidence level) of H₂S amount fraction and CO amount fraction during the EURAMET 1220 inter-comparison. The reference value was not considered time dependent. The reference value was assigned as the mean of the means of VSL and NPL measurements.

Table 3: Results of the statistical test for the significance of the degradation of CO and H₂S compounds in the set (2) of cylinder during the entire comparison exercise using t-value (95 %, df). No significant degradation was observed, the reference values were reported.

	Cylinder reference	Set 2	Reference value [$\mu\text{mol/mol}$]
CO – 1 $\mu\text{mol mol}^{-1}$	3904132	No significant degradation at 95 % confidence level	0.985
CO - 0.1 $\mu\text{mol mol}^{-1}$	4360955	No significant degradation at 95 % confidence level	0.099
H ₂ S – 1 $\mu\text{mol mol}^{-1}$	4361338	No significant degradation at 95 % confidence level	0.949

3. METHODS

A range of analytical methods were used to perform analysis of hydrogen sulphide and carbon monoxide for this comparison. This section summarises these methods. A detailed description of the measurements is given in Annex B.

Table 4: Summary of the methods used by the participants for the determination of H₂S amount fraction in hydrogen

Participant code	Technique	Calibration
NPL	GC-SCD	Primary standard gas mixtures were prepared (in accordance with ISO 6142) in 10 litre BOC Spectraseal cylinders with a proprietary pre-treatment. All mixtures were validated against existing NMI standard gas mixtures (either directly, or using dynamic dilution) before use.
VSL	GC-SCD	Static calibration gas mixture
A	n.a.*	n.a.*
B	OFCEAS	Primary Standard Gas Mixtures from NPL (UK) and Primary standards from Air Liquide
C	ED-GC-TCO	Dilution of static standard from Matheson TriGas
D	GC-MS	Dilution of static standard
E	GC-SCD	Primary Standard Gas Mixtures, prepared by the gravimetric method from pure substances, according to ISO 6142:2001 "Gas analysis - Preparation of calibration gas mixtures - Gravimetric method" were used as calibration standards.
F	GC-MS	Primary standards dynamically diluted with pure hydrogen
G	UV absorption spectroscopy	Primary Standard Gas Mixtures, prepared by the gravimetric method from pure substances, according to ISO 6142:2001 "Gas analysis - Preparation of calibration gas mixtures - Gravimetric method" were used as calibration standards.
H	OFCEAS	Static Standard procured from Praxair Calibration realised by the producer of the instrument, AP2E (France)
I	IMR-MS	n.a.*

* n.a. means not available

Table 5: Summary of the methods used by the participants for the determination of 0.1 $\mu\text{mol/mol}$ CO amount fraction in hydrogen

Participant code	Technique	Calibration
NPL	CRDS	Primary standard gas mixtures were prepared (in accordance with ISO 6142) in 10 litre BOC Spectraseal cylinders with a proprietary pre-treatment. All mixtures were validated against existing NMI standard gas mixtures (either directly, or using dynamic dilution) before use.
VSL	CRDS	Static calibration gas mixture
A	GC-FID	The primary reference materials for conducting EURAMET 1220 were prepared by gravimetric method in accordance with ISO6142:2001.
B	GC-TCD	Primary Standard Gas Mixtures from NPL (UK) and Primary standards from Air Liquide
C	ED-GC-TCD	Dilution of static standard from Matheson TriGas
D	FTIR	Dilution of static standard
E	GC-PDHID	Primary Standard Gas Mixtures, prepared by the gravimetric method from pure substances, according to ISO 6142:2001 "Gas analysis - Preparation of calibration gas mixtures - Gravimetric method" were used as calibration standards.
F	GC-PDHID	Primary standards dynamically diluted with pure hydrogen
G	GC-FID (methaniser)	Primary Standard Gas Mixtures, prepared by the gravimetric method from pure substances, according to ISO 6142:2001 "Gas analysis - Preparation of calibration gas mixtures - Gravimetric method" were used as calibration standards.
H	OFCEAS	Standard procured from Praxair Calibration realised by the producer of the instrument, AP2E (France)
I	IMR-MS	n.a.*

* n.a. means not available

Table 6 : Summary of the methods used by the participants for the determination of 1.0 $\mu\text{mol/mol}$ CO amount fraction in hydrogen

Participant code	Technique	Calibration
NPL	CRDS	Primary standard gas mixtures were prepared (in accordance with ISO 6142) in 10 litre BOC Spectraseal cylinders with a proprietary pre-treatment. All mixtures were validated against existing NMI standard gas mixtures (either directly, or using dynamic dilution) before use.
VSL	CRDS	Static calibration gas mixture
A	GC-FID	The primary reference materials for conducting EURAMET 1220 were prepared by gravimetric method in accordance with ISO6142:2001.
B	n.a.*	n.a.*
C	ED-GC-TCD	Dilution of static standard from Matheson TriGas
D	FTIR	Dilution of static standard
E	GC-PDHID	Primary Standard Gas Mixtures, prepared by the gravimetric method from pure substances, according to ISO 6142:2001 "Gas analysis - Preparation of calibration gas mixtures - Gravimetric method" were used as calibration standards.
F	GC-PDHID	Primary standards dynamically diluted with pure hydrogen
G	GC-FID (methaniser)	Primary Standard Gas Mixtures, prepared by the gravimetric method from pure substances, according to ISO 6142:2001 "Gas analysis - Preparation of calibration gas mixtures - Gravimetric method" were used as calibration standards.
H	OFCEAS	Standard procured from Praxair Calibration realised by the producer of the instrument, AP2E (France)
I	IMR-MS	Standard procured from Air Products

* n.a. means not available

4. RESULTS

Measurement reports were provided by each of the participants of the comparison, these can be found in Appendix C. Below are the results of the comparison, each participant provided an overall result with an assigned uncertainty for each of the mixtures analysed. The results of the comparison are shown below in Figures 1-3. The results of the participants are represented by their degree of equivalence.

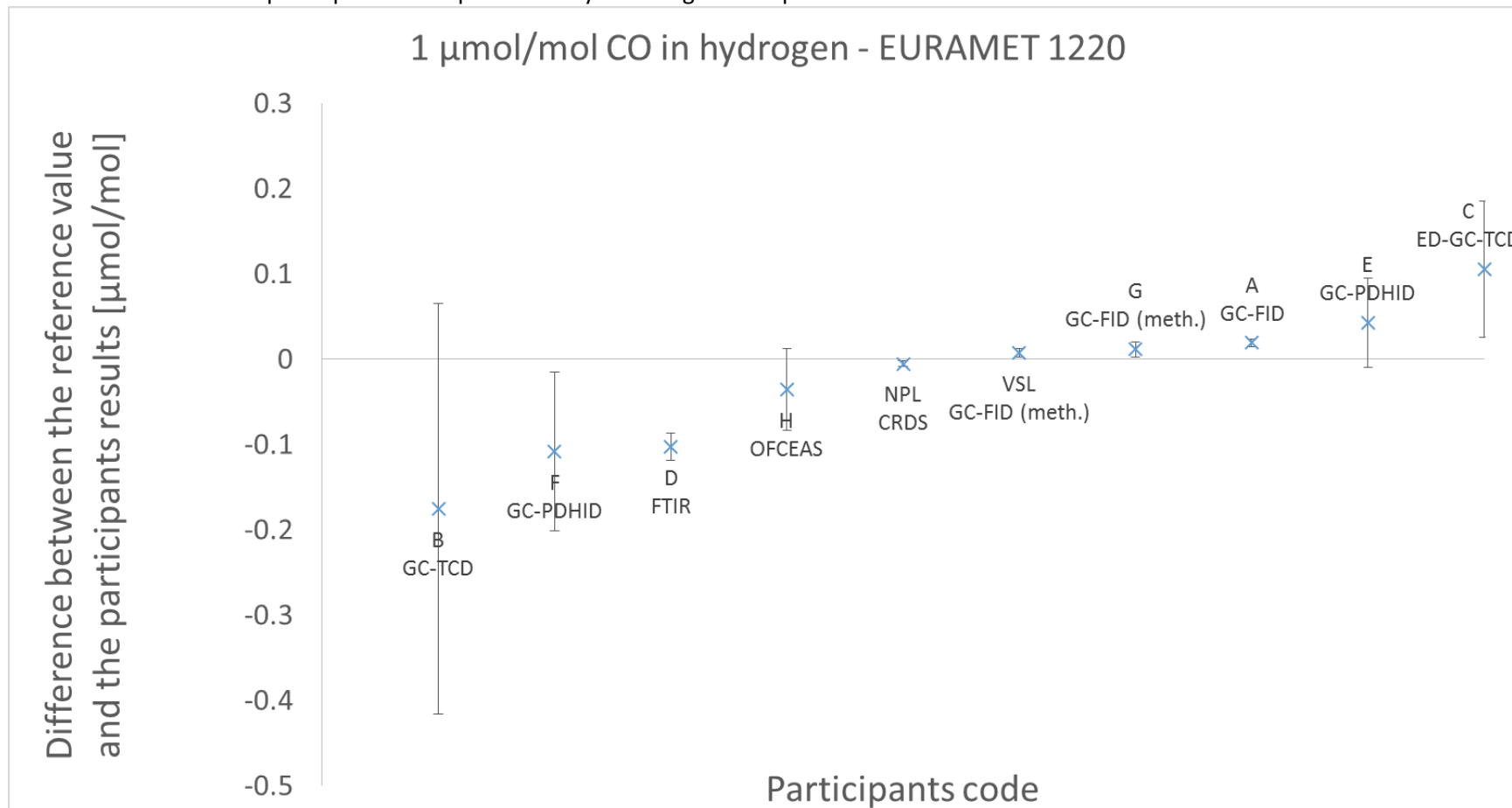


Figure 1. Degree of equivalence for 1 $\mu\text{mol/mol}$ of CO in hydrogen for each participant. The expanded uncertainty is represented with a coverage factor $k = 2$.

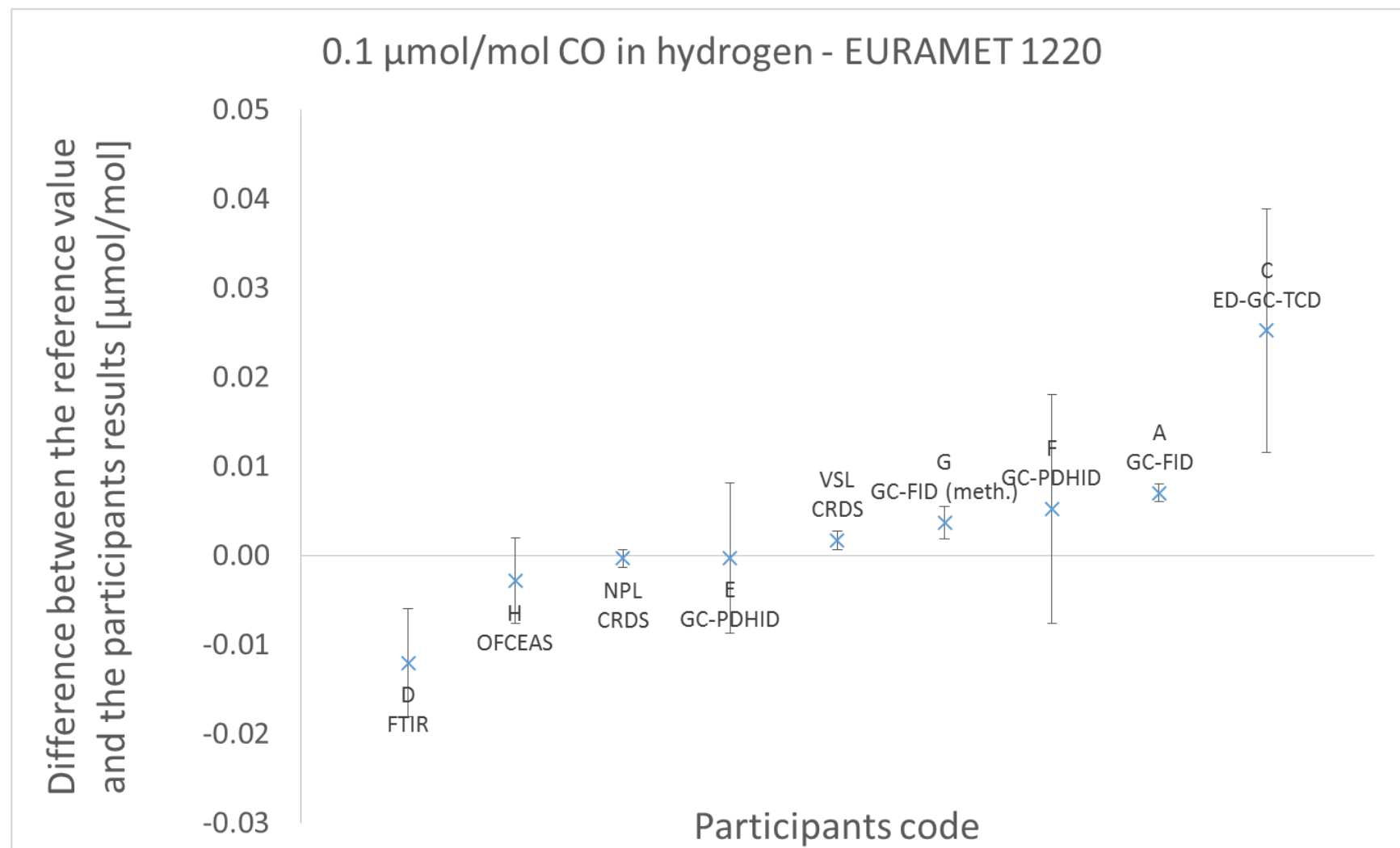


Figure 2. Degree of equivalence for 0.1 $\mu\text{mol/mol}$ of CO in hydrogen for each participant. The expanded uncertainty is represented with a coverage factor $k = 2$.

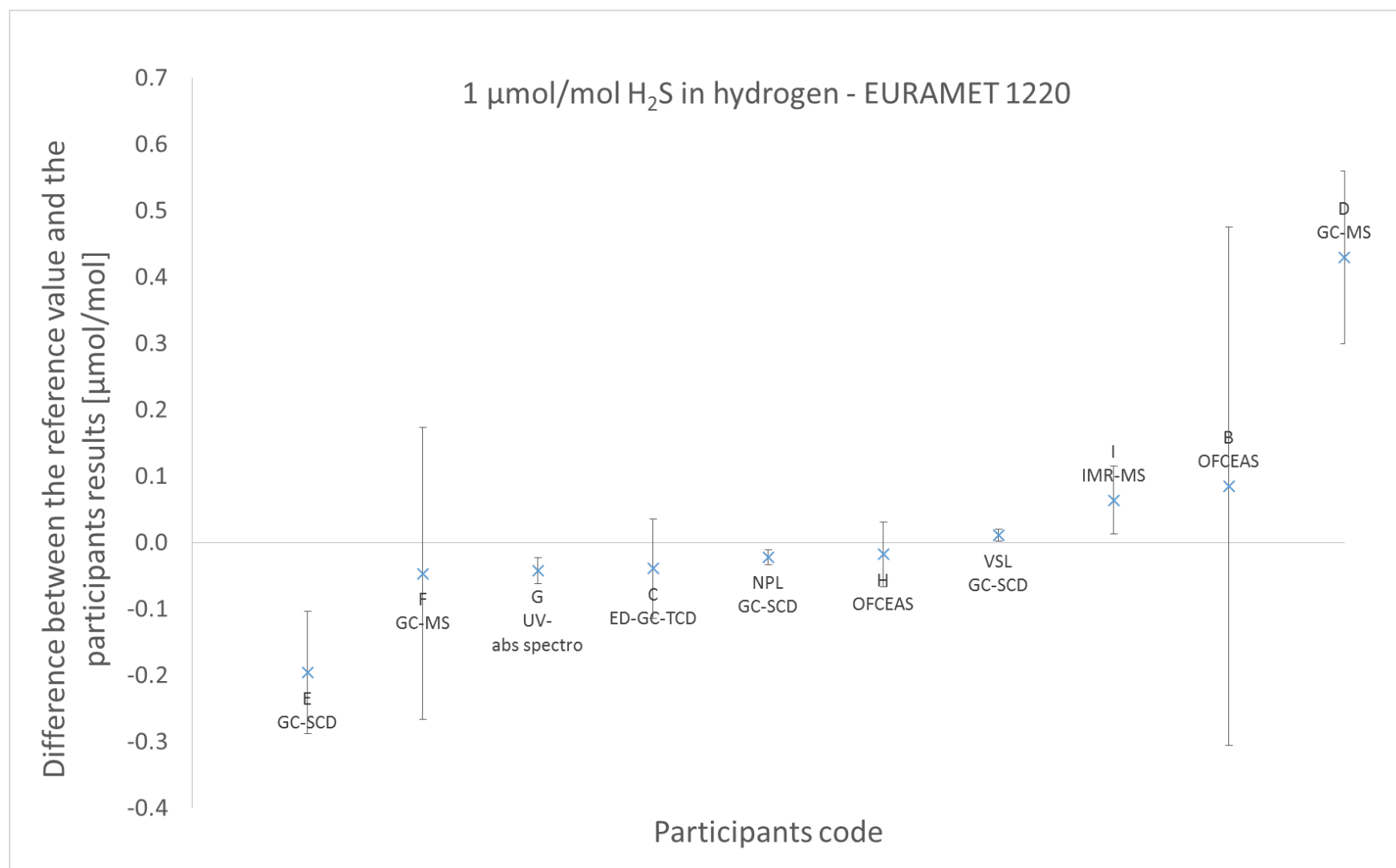


Figure 3. Degree of equivalence for 1 $\mu\text{mol/mol}$ of H₂S in hydrogen for each participant. The expanded uncertainty is represented with a coverage factor $k = 2$.

5. ANNEX

ANNEX A. KEY COMPARISON REFERENCE VALUE DETERMINATION AND STABILITY ASSESSMENT.

The raw data are reported based on the time of measurements and the laboratory which performed the measurements. The time 0 was considered on the first measurement occasion. The time reported is an average for each laboratory sequence.

Table A.1. Results of stability measurements for carbon monoxide in hydrogen in set 2 cylinders.

Sequence	Laboratory performing the analysis	Time [days]	Results set 2 for 1 $\mu\text{mol/mol CO}$ [$\mu\text{mol/mol}$]	Results set 2 for 0.1 $\mu\text{mol/mol CO}$ [nmol/mol]
1	NPL	0	0.9823	98.07
1	NPL	0	0.9831	98.53
1	NPL	0	0.9830	98.53
2	VSL	93	0.9954	101.50
2	VSL	93	0.9865	100.60
2	VSL	93	0.9964	99.50
3	NPL	401	0.9829	98.57
3	NPL	401	0.9830	98.59
3	NPL	401	0.9829	98.57
4	NPL	681	0.9824	97.80
4	NPL	681	0.9825	97.86
4	NPL	681	0.9825	97.86

Table A.2. Results of stability measurements for H₂S in hydrogen in set 2 cylinders.

Sequence	Laboratory performing the analysis	Time [days]	Results set 2 for 1 $\mu\text{mol/mol H}_2\text{S}$ in hydrogen [$\mu\text{mol/mol}$]
1	NPL	0	0.9367
1	NPL	0	0.9593
1	NPL	0	0.9695
1	NPL	0	0.9468
2	VSL	93	0.9609
2	VSL	93	0.9456
2	VSL	93	0.9728
2	VSL	93	0.9642
2	VSL	93	0.9880
2	VSL	93	0.9546
2	VSL	93	0.9731
3	NPL	401	0.9265
3	NPL	401	0.9376
3	NPL	401	0.9330
4	NPL	641	0.9402
4	NPL	641	0.9451
4	NPL	641	0.9459

Table A.3. Results of stability measurements for H₂S and carbon monoxide in hydrogen in set 1 cylinders.

Laboratory performing the analysis	Time [days]	Results set 1 for 1 $\mu\text{mol/mol}$ CO [$\mu\text{mol/mol}$]	Results set 1 for 0.1 $\mu\text{mol/mol}$ CO [nmol/mol]	Results set 1 for 1 $\mu\text{mol/mol}$ H ₂ S in hydrogen [$\mu\text{mol/mol}$]
VSL	0	1.0095	87.50	0.6668
VSL	0	1.0049	87.00	0.6961
VSL	0	1.0042	-	0.6859
NPL	32	0.9913	84.36	0.6331
NPL	32	0.9933	84.16	0.6401
NPL	32	0.9933	84.11	0.6321
VSL	401	0.9585	70.50	0.6440
VSL	401	0.9778	-	0.5996
VSL	401	0.9684	-	0.5945
VSL	401	0.9774	-	0.5978
VSL	401	0.9755	-	0.6080
VSL	401	-	-	0.6134
NPL	681	0.9577	67.68	0.5727
NPL	681	0.9579	67.77	0.5795
NPL	681	0.9579	67.84	0.5862

ANNEX B. SUMMARY OF PARTICIPANTS ANALYTICAL METHODS

Table B.1: Summary of the analytical methods used for the determination of 1 $\mu\text{mol/mol}$ H_2S in hydrogen by the participant of EURAMET 1220

Participant code	Methods	Technique	Instruments	Calibration	Uncertainty calculation
NPL	Internal method Column: HP-1 (60 m length x 0.53 mm outside diameter x 0.25 μm film thickness) He: carrier gas All tubing between gas standards and GC system was Sulfinert® treated stainless steel	GC-SCD	Agilent, 7890A	Primary standard gas mixtures were prepared (in accordance with ISO 6142) in 10 litre BOC Spectraseal cylinders with a proprietary pre-treatment. All mixtures were validated against existing NMI standard gas mixtures (either directly, or using dynamic dilution) before use. The primary standard gas mixtures were prepared from dilutions of 'parent mixtures' of higher amount fractions. These parent mixtures were prepared at nominal amount fractions of 100 $\mu\text{mol mol}^{-1}$ by first adding the CO or H_2S into the cylinder via an intermediate vessel, then adding the H_2 directly into the cylinder. Purity analysis was performed on the source gases used in the comparison. The purity analysis results are CO: 99.998 % pure; H_2S : 99.69 % pure and H_2 > 99.9999 % pure.	Type A uncertainty evaluation using normal distribution
VSL	Internal method Column: DB-1 capillary column He: carrier gas. All tubing between gas standards and GC system was Sulfinert® treated stainless steel	GC-SCD	Agilent 6890, United States of America	For the measurement 3 calibration standards were used. The standards were newly prepared for this comparison therefore no factor for stability has been added to the uncertainty budget. Only for H_2S an absolute value of 1 nmol was added to the uncertainty of the average as this is a systematic uncertainty due to purity analysis.	All uncertainties due to purity analysis, preparation of the standards and the analytical measurement are input parameters for ISO 6143. The amount fraction calculated for the 'unknown' incorporates all these uncertainties. For the analysis of the CO high value one new standard was prepared starting from 300 $\mu\text{mol/mol}$ CO in N_2 and no instability was found by comparison with the older mixtures used in 2014. Therefore, two of the standards prepared in 2014 were used together with this new standard. For the analysis of CO low value and for H_2S only newly prepared standards were used. The uncertainty given on the result is the uncertainty in the average of the individual results (5, 2 and 6). The standards were newly prepared for this comparison therefore no factor for stability has been added to the uncertainty budget. Only for H_2S an absolute value of 1 nmol was added to the uncertainty of the average as this is a systematic uncertainty due to purity analysis.
A	No participation	n.a.*	n.a.*	n.a.*	n.a.*
B	Internal method	OFCEAS	n.a.*	Primary Standard Gas Mixtures from NPL (UK) and Primary standards from Air Liquide	The uncertainty reported is two times the standard deviation of the measurements.

Participant code	Methods	Technique	Instruments	Calibration	Uncertainty calculation
C	Internal method Concentration of impurities in a small volume typically less than 200uL using a cold trap. The impurity levels is then suitable for quantifying with a TCD. 1- For H₂S, cold trap (-60°C) using short section of RT-U bond 2- For CO, cold trap (-60°C) using short section of molsieve Collection during 5 min on the cold trap Heating at 100 °C / sec for 2 seconds Ultra pure hydrogen (10 sccm flow) carry the desorbed impurities to TCD detector. Compounds are identified according to their retention times.	ED-GC-TCD	Power+Energy HEMSTM, United States of America	Reference gas from 5.6 ppm ($U = 5\%$; $k = 2$) of H₂S in 99.999 % hydrogen and prepared by Matheson TriGas. This gas mix was diluted with ultra-pure hydrogen (better than 99.999999 %). Two MFCs each rated at 1000 sccm and 0.1% FS error, were used to blend 920 sccm of UPH hydrogen with 200 sccm of the reference gas. This resulted a purity level of 1.00 ppm of H₂S in hydrogen with $\pm 8\%$ accuracy. The confidence level of this number is estimated at 95 % confidence. Residual H₂S in the mixing station is estimated to add less than 0.2ppb to the analysis of the measured H₂S. As it is undetectable even when the sample size is increased to 10 liters when using the enrichment concentration processing technology. The calibration method used was to compare areas under signals with reference measurements using UPH to the reference gas obtained from Matheson Gas and using precision MFC's. These Matheson Gas reference sample gases were diluted with UPH generated by using a Hydrogen permeation stream from a Pd cell built to supply 9-9's hydrogen (UPH). The resulting signals from the TCD using the calibrated reference gas described above were compared to the signals generated by use the EURAMET bottles to supply the test gas stream at a flowrate of 150 sccm thru the cold trap for 5 minutes.	The uncertainty in this report we think should be two Standard Deviation of the calculated impurity plus the uncertainty of the calibration gas plus 1% for the MFC's used to generate the calibration TCD signals.
D	Internal method	GC-MS	Agilent 5975T	Concentrated calibration gas (+/5 %) that was dynamically diluted from 1 to 5 ppm. Averages were established from 5 injections at each concentration levels, outliers excluded. The linearity of the response were evaluated before the sample were injected 5 times. One calibration curve per sample were recorded due to MS signal drift.	The uncertainty was reported as the standard deviation of the measurements.
E	Internal method	GC-SCD	n.a.*	Primary Standard Gas Mixtures, prepared by the gravimetric method from pure substances, according to ISO 6142:2001 "Gas analysis - Preparation of calibration gas mixtures - Gravimetric method" were used as calibration standards.	n.a.*
F	Internal method Purified helium: carrier gas Column: Porabond-Q All tubing between gas standards and GC system was Sulfinert® treated stainless steel	GC-MS	GC Perkin Elmer Clarus 580 coupled to a Perkin Elmer Clarus SQ8S Mass Spectrometer	Primary standards (4.9% CO and 51% H₂S) were dynamically diluted with pure hydrogen to prepare test gases and automatically injected in the analytical instrument using a dilution device (Alytech GasMix™ unit, Sulfinert®-treated, France). To ensure the purity of hydrogen used for the dynamic dilution and avoid pollution from the balance gas, a gas purifier was used (SAES, model PS4-MT3-H-2) prior the dilution of the primary standards.	The estimated value of the uncertainty included the various systematic errors (trueness), the random errors (precision), and the uncertainty associated with the preparation of the gas standards (u_{std}). The uncertainty of the standard gases (u_{std}) was obtained from the uncertainty certified by the manufacturer of the standard gas mixtures (not indicated herein). The uncertainty of the precision ($u_{precision}$) corresponded to the relative standard deviation of the n replicates at one concentration. The uncertainty of trueness was calculated from % of bias

Participant code	Methods	Technique	Instruments	Calibration	Uncertainty calculation
					obtained in the recovery of the reference material. The equation proposed to obtain the overall uncertainty is the sum of trueness, precision and standards uncertainty. The obtained value of uncertainty was multiplied by a coverage factor to obtain the expanded uncertainty. A factor of 2 was used to obtain a confidence level of 95 %. As the results were proportional to the analyte concentration, the expanded uncertainties were calculated on a given sample concentration.
G	Internal method with the following instrument parameters: Wavelength: 200.2 nm (SBW: 1 nm); Optical path length of the gas cell: 122.4 mm Flushing time: 2 min; Integration time: 1 s	UV absorption spectroscopy	Agilent Cary 5000, United State of America	Primary Standard Gas Mixtures, prepared by the gravimetric method from pure substances, according to ISO 6142:2001 "Gas analysis - Preparation of calibration gas mixtures - Gravimetric method" were used as calibration standards. Verification for calibration gas mixtures and pre-mixtures on the level of 84 $\mu\text{mol/mol}$, 9 $\mu\text{mol/mol}$, 1 $\mu\text{mol/mol}$ were carried out by the same instrument and the same parameters. Verification for 9 $\mu\text{mol/mol}$ and 1 $\mu\text{mol/mol}$ mixtures were additionally performed by GC-MS (Agilent 7890, United State of America). Verification measurements for high concentration pre-mixtures (0.7 %, 772 $\mu\text{mol/mol}$) were performed by the same instrument and the gas cell with optical path length 9.7 mm	The uncertainty contribution considered were the uncertainty of calibration standards (weighing + purity), the uncertainty due to standards verification and the uncertainty within and between day measurements. A coverage factor of 2 was used to report the expanded uncertainty.
H	Internal method	OFCEAS	PROCEAS, France	Standard procured from Praxair Calibration realised by the producer of the instrument, AP2E (France)	The final standard deviation expressed in % results from the higher standard deviation of measurements added with the standard deviation of the calibration standard. The reported value was expanded by k factor: 2.
I	No participation	n.a.*	n.a.*	n.a.*	n.a.*

* n.a. means not available

Table B.2 : Summary of the analytical methods used for the determination of 1 $\mu\text{mol/mol}$ CO in hydrogen by the participant of EURAMET 1220

Participant code	Methods	Technique	Instruments	Calibration	Uncertainty calculation
NPL	Internal method Cavity ring-down spectroscopy (CRDS). LGR off-axis ICOS CO-23r Analyser.	CRDS	off-axis ICOS CO-23r Analyser (Los Gatos Research, United States of America)	Primary standard gas mixtures were prepared (in accordance with ISO 6142) in 10 litre BOC Spectraseal cylinders with a proprietary pre-treatment. All mixtures were validated against existing NMI standard gas mixtures (either directly, or using dynamic dilution) before use. The primary standard gas mixtures were prepared from dilutions of 'parent mixtures' of higher amount fractions. These parent mixtures were prepared at nominal amount fractions of 100 $\mu\text{mol/mol}$ by first adding the CO into the cylinder via an intermediate vessel, then adding the H ₂ directly into the cylinder. Purity analysis was performed on the source gases used in the comparison. The purity analysis results are CO: 99.998 % pure and H ₂ > 99.9999 % pure.	Type A uncertainty evaluation using normal distribution
VSL	Internal method Column: Molsieve 5A He: carrier gas. Ni catalyst to convert the CO to CH ₄ The mixtures were connected to a multi-position valve with one inlet to the GC. The cylinders were fitted with all stainless steel, low volume diaphragm reducer valves. The responses used are the average of 9 injections per mixture.	GC-FID (methaniser)	Agilent 6890, United States of America	For the measurement 3 calibration standards were used. The standards were newly prepared for this comparison therefore no factor for stability has been added to the uncertainty budget.	All uncertainties due to purity analysis, preparation of the standards and the analytical measurement are input parameters for ISO 6143. The amount fraction calculated for the 'unknown' incorporates all these uncertainties. For the analysis of the CO high value one new standard was prepared starting from 300 $\mu\text{mol/mol}$ CO in N ₂ and no instability was found by comparison with the older mixtures used in 2014. Therefore, two of the standards prepared in 2014 were used together with this new standard. The uncertainty given on the result is the uncertainty in the average of the individual results. The standards were newly prepared for this comparison therefore no factor for stability has been added to the uncertainty budget.
A	Internal methods Column: 9 ft. long stainless steel packed column containing 80/100 molecular Sieve 5A Carrier: Nitrogen (99.999 %) Oven temperature: 95 °C Sample loop 10 ml	GC-FID	Agilent 6890, Korea	The primary reference materials for conducting EURAMET 1220 were prepared by gravimetric method in accordance with ISO6142:2001. Impurity-assessed raw gases of CO and H ₂ were preliminary mixed and then total 6-step dilutions by H ₂ , 3 %mol/mol → 0.3 %mol/mol → 380 $\mu\text{mol/mol}$ → 50 $\mu\text{mol/mol}$ → 7 $\mu\text{mol/mol}$ → 1 $\mu\text{mol/mol}$, were followed to yield calibration standards at the nominal concentration of 1 $\mu\text{mol/mol}$.	Type A uncertainty evaluation using normal distribution
B	Internal method	GC-TCD	n.a.*	Primary Standard Gas Mixtures from NPL (UK) and Primary standards from Air Liquide	The uncertainty reported is two times the standard deviation of the measurements.

Participant code	Methods	Technique	Instruments	Calibration	Uncertainty calculation
C	Internal method Concentration of impurities in a small volume typically less than 200 μL using a cold trap. The impurity levels is then suitable for quantifying with a TCD. 1- For H₂S, cold trap (-60°C) using short section of RT-U bond 2- For CO, cold trap (-60°C) using short section of molsieve Collection during 5 min on the cold trap Heating at 100 °C / sec for 2 seconds Ultra-pure hydrogen (10 sccm flow) carry the desorbed impurities to TCD detector. Compounds are identified according to their retention times.	ED-GC-TCD	Power+Energy HEMS™, USA	Reference gas from 5.6 ppm ($U = 5\%$; $k = 2$) of H₂S in 99.999 % hydrogen and prepared by Matheson TriGas. This gas mix was diluted with UPH, with purity better than 99.999999 %. Two MFCs each rated at 1000 sccm and 0.1 % FS error, were used to blend 920 sccm of UPH hydrogen with 200 sccm of the reference gas. This resulted a purity level of 1.00 ppm of H₂S in hydrogen with $\pm 8\%$ accuracy. The confidence level of this number is estimated at 95 % confidence. Residual H₂S in the mixing station is estimated to add less than 0.2 ppb to the analysis of the measured H₂S. As it is undetectable even when the sample size is increased to 10 liters when using the enrichment concentration processing technology. The calibration method used was to compare areas under signals with reference measurements using UPH to the reference gas obtained from Matheson Gas and using precision MFC's. These Matheson Gas reference sample gases were diluted with UPH generated by using a Hydrogen permeation stream from a Pd cell built to supply 9-9's hydrogen (UPH). The resulting signals from the TCD using the calibrated reference gas described above were compared to the signals generated by use the Euramet bottles to supply the test gas stream at a flowrate of 150 sccm thru the cold trap for 5 minutes.	The uncertainty in this report we think should be two Standard Deviation of the calculated impurity plus the uncertainty of the calibration gas plus 1 % for the MFC's used to generate the calibration TCD signals.
D	Internal method FTIR (35 m path)	FTIR	Bruker Vertex 70	A 913 ppb CO calibration gas (HiQ, +/- 5 %) was used. A one point calibration were used directly for repeated scans of the sample at 1 μ mol/mol level.	The uncertainty was reported as the standard deviation of the measurements.
E	Internal method	GC-PDHID	n.a.*	Primary Standard Gas Mixtures, prepared by the gravimetric method from pure substances, according to ISO 6142:2001 "Gas analysis - Preparation of calibration gas mixtures - Gravimetric method" were used as calibration standards.	n.a.*

Participant code	Methods	Technique	Instruments	Calibration	Uncertainty calculation
F	Internal method Purified helium: carrier gas Column: Molsieve 5A All tubing between gas standards and GC system was Sulfinert® treated stainless steel	GC-PDHID	GC Perkin Elmer Clarus 580 coupled to a PDHID system (Valco Instruments, Model D-4-I)	Primary standards (4.9% CO and 51% H ₂ S) were dynamically diluted with pure hydrogen to prepare test gases and automatically injected in the analytical instrument using a dilution device (Alytech GasMix™ unit, Sulfinert®-treated, France). To ensure the purity of hydrogen used for the dynamic dilution and avoid pollution from the balance gas, a gas purifier was used (SAES, model PS4-MT3-H-2) prior the dilution of the primary standards.	The uncertainty (u) associated with the results included various components related to the sources of error that determined the precision and trueness of the measurement. The estimated value of the uncertainty included the various systematic errors (trueness), the random errors (precision), and the uncertainty associated with the preparation of the gas standards (u _{std}). The uncertainty of the standard gases (u _{std}) was obtained from the uncertainty certified by the manufacturer of the standard gas mixtures (not indicated herein). The uncertainty of the precision corresponded to the relative standard deviation of the n replicates at one concentration. The uncertainty of trueness was calculated from % of bias obtained in the recovery of the reference material. The equation proposed to obtain the overall uncertainty is the sum of trueness, precision and standards uncertainty. The obtained value of uncertainty was multiplied by a coverage factor to obtain the expanded uncertainty. A factor of 2 was used to obtain a confidence level of 95%. As the results were proportional to the analyte concentration, the expanded uncertainties were calculated on a given sample concentration.
G	Internal method with the following instrument parameters: Column: packing – Carbosphere, l= 1.8 m, d _{int} =0.032 m. t = 40 °C V _{dose} =5 cm ³ ; Data collection: Software "ChemStation" version A.10.02.	GC-FID (methaniser)	Agilent 6890N, United States of America	Primary Standard Gas Mixtures, prepared by the gravimetric method from pure substances, according to ISO 6142:2001 "Gas analysis - Preparation of calibration gas mixtures - Gravimetric method" were used as calibration standards. Target CO/H ₂ calibration gas mixtures were prepared in aluminum cylinders (Luxfer), V= 5 dm ³ without treatment. Verification of 76 µmol/mol, 6 µmol/mol, 1 µmol/mol, 0.1 µmol/mol calibration gas mixtures and pre-mixtures were carried out by the same instrument and with the same parameters. Verification measurements for high concentration pre-mixtures (1.16 %; 0.094 %) were performed by gas chromatography (Varian model 2860, United States of America) with thermal conductivity detector.	The uncertainty contribution considered were the uncertainty of calibration standards (weighing plus purity), the uncertainty due to standards verification and the uncertainty within and between day measurements. A coverage factor of two was used to report the expanded uncertainty.
H	Internal method	OFCEAS	PROCEAS, France	Standard procured from Praxair Calibration realised by the producer of the instrument, AP2E	The final standard deviation expressed in % results from the higher standard deviation of measurements added with the standard deviation of the calibration standard. The reported value was expanded by k factor: 2.

Participant code	Methods	Technique	Instruments	Calibration	Uncertainty calculation
I	No participation	n.a.*	n.a.*	n.a.*	n.a.*

* n.a. means not available

Table B.3: Summary of the analytical methods used for the determination of 0.1 $\mu\text{mol/mol}$ CO in hydrogen by the participants of EURAMET 1220

Participant code	Methods	Technique	Instruments	Calibration	Uncertainty calculation
NPL	Internal method Cavity ring-down spectroscopy (CRDS). LGR off-axis ICOS CO-23r Analyser.	CRDS	off-axis ICOS CO-23r Analyser (Los Gatos Research, United States of America)	Primary standard gas mixtures were prepared (in accordance with ISO 6142) in 10 litre BOC Spectraseal cylinders with a proprietary pre-treatment. All mixtures were validated against existing NMI standard gas mixtures (either directly, or using dynamic dilution) before use. The primary standard gas mixtures were prepared from dilutions of 'parent mixtures' of higher amount fractions. These parent mixtures were prepared at nominal amount fractions of 100 $\mu\text{mol mol}^{-1}$ by first adding the CO into the cylinder via an intermediate vessel, then adding the H ₂ directly into the cylinder. Purity analysis was performed on the source gases used in the comparison. The purity analysis results are CO: 99.998 % pure and H ₂ > 99.9999 % pure.	Type A uncertainty evaluation using normal distribution
VSL	Internal method For the measurements 16 and 40 scans were averaged and the resulting spectrum used as one response. The absorption was measured around 2190 cm^{-1} and the area was integrated over the whole absorption line. This absorption line was chosen because it gave sufficient sensitivity and a return to baseline at the edges of the feature.	CRDS	OPO-CRDS (VSL, the Netherlands)	Two standards were used as brackets. The standards were newly prepared for this comparison therefore no factor for stability has been added to the uncertainty budget.	All uncertainties due to purity analysis, preparation of the standards and the analytical measurement are input parameters for ISO 6143. The amount fraction calculated for the 'unknown' incorporates all these uncertainties. For the analysis of the CO high value one new standard was prepared starting from 300 $\mu\text{mol/mol}$ CO in N ₂ and no instability was found by comparison with the older mixtures used in 2014. Therefore 2 of the standards prepared in 2014 were used together with this new standard. The uncertainty given on the result is the uncertainty in the average of the individual results. The standards were newly prepared for this comparison therefore no factor for stability has been added to the uncertainty budget.
A	Internal methods Column: 6 ft. long stainless steel packed column containing a Molecular Sieve 13X extended by the 9 ft. long Molecular Sieve 5A column Carrier: Nitrogen (99.999 %) Oven temperature: 50 °C Sample loop 10 ml	GC-FID	Agilent 6890, Korea	The primary reference materials for conducting EURAMET 1220 were prepared by gravimetric method in accordance with ISO6142:2001. Impurity-assessed raw gases of CO and H ₂ were preliminary mixed and then total 6-step dilutions by H ₂ , 3 %mol/mol $\rightarrow$ 0.3 % mol/mol $\rightarrow$ 380 $\mu\text{mol/mol}$ $\rightarrow$ 50 $\mu\text{mol/mol}$ $\rightarrow$ 7 $\mu\text{mol/mol}$ $\rightarrow$ 1 $\mu\text{mol/mol}$, were followed to yield calibration standards at the nominal concentration of 1 $\mu\text{mol/mol}$.	Type A uncertainty evaluation using normal distribution
B	n.a.*	n.a.*	n.a.*	n.a.*	n.a.*
C	Internal method Concentration of impurities in a small	ED-GC-TCD	Power+Energy HEMS™, USA	Reference gas from 5.6 ppm ($U = 5\%$; $k = 2$) of H ₂ S in 99.999 % hydrogen and prepared by Matheson TriGas. This gas mix	The uncertainty in this report we think should be two Standard Deviation of the calculated impurity plus the

Participant code	Methods	Technique	Instruments	Calibration	Uncertainty calculation
	volume typically less than 200 μL using a cold trap. The impurity levels is then suitable for quantifying with a TCD. 1- For H₂S, cold trap (-60°C) using short section of RT-U bond 2- For CO, cold trap (-60°C) using short section of molsieve Collection during 5 min on the cold trap Heating at 100 °C / sec for 2 seconds Ultra pure hydrogen (10 sccm flow) carry the desorbed impurities to TCD detector. Compounds are identified according to their retention times.			was diluted with UPH, with purity better than 99.999999 %. Two MFCs each rated at 1000 sccm and 0.1 % FS error, were used to blend 920 sccm of UPH hydrogen with 200 sccm of the reference gas. This resulted a purity level of 1.00 ppm of H₂S in hydrogen with $\pm$ 8% accuracy. The confidence level of this number is estimated at 95 % confidence. Residual H₂S in the mixing station is estimated to add less than 0.2ppb to the analysis of the measured H₂S. As it is undetectable even when the sample size is increased to 10 liters when using the enrichment concentration processing technology. The calibration method used was to compare areas under signals with reference measurements using UPH to the reference gas obtained from Matheson Gas and using precision MFC's. These Matheson Gas reference sample gases were diluted with UPH generated by using a Hydrogen permeation stream from a Pd cell built to supply 9-9's hydrogen (UPH). The resulting signals from the TCD using the calibrated reference gas described above were compared to the signals generated by use the EURAMET bottles to supply the test gas stream at a flowrate of 150 sccm thru the cold trap for 5 minutes.	uncertainty of the calibration gas plus 1 % for the MFC's used to generate the calibration TCD signals.
D	Internal method FTIR (35 m path)	FTIR	Bruker Vertex 70	A 913 ppb CO calibration gas (HiQ, +/- 5 %) was used. A one point calibration were used directly for repeated scans of the sample at 1 ppm mol level. For the 0.1 ppm mol level, the same calibration gas was diluted by pressure reading in the FTIR measurement cell to 1/10 of the original concentration by pressure reading. The dilution were performed with Nitrogen (5.0 quality).	The uncertainty was reported as the standard deviation of the measurements.
E	Internal method	GC-PDHID	n.a.*	Primary Standard Gas Mixtures, prepared by the gravimetric method from pure substances, according to ISO 6142:2001 "Gas analysis - Preparation of calibration gas mixtures - Gravimetric method" were used as calibration standards.	n.a.*

Participant code	Methods	Technique	Instruments	Calibration	Uncertainty calculation
F	Internal method Purified helium: carrier gas Column: Molsieve 5A All tubing between gas standards and GC system was Sulfinert® treated stainless steel	GC-PDHID	GC Perkin Elmer Clarus 580 coupled to a PDHID system (Valco Instruments, Model D-4-I)	Primary standards (4.9% CO and 51% H ₂ S) were dynamically diluted with pure hydrogen to prepare test gases and automatically injected in the analytical instrument using a dilution device (Alytech GasMix™ unit, Sulfinert®-treated, France). To ensure the purity of hydrogen used for the dynamic dilution and avoid pollution from the balance gas, a gas purifier was used (SAES, model PS4-MT3-H-2) prior the dilution of the primary standards.	The uncertainty (u) associated with the results included various components related to the sources of error that determined the precision and trueness of the measurement. The estimated value of the uncertainty included the various systematic errors (trueness), the random errors (precision), and the uncertainty associated with the preparation of the gas standards (u_{std}). The uncertainty of the standard gases (u_{std}) was obtained from the uncertainty certified by the manufacturer of the standard gas mixtures (not indicated herein). The uncertainty of the precision ($u_{precision}$) corresponded to the relative standard deviation of the n replicates at one concentration. The uncertainty of trueness was calculated from % of bias obtained in the recovery of the reference material. The equation proposed to obtain the overall uncertainty is the sum of trueness, precision and standards uncertainty. The obtained value of uncertainty was multiplied by a coverage factor to obtain the expanded uncertainty. A factor of 2 was used to obtain a confidence level of 95 %. As the results were proportional to the analyte concentration, the expanded uncertainties were calculated on a given sample concentration.
G	Internal method with the following instrument parameters: Column: packing – Carbosphere, 80/100 mesh; l= 1.8 m, dint=0.032 m. t = 40 °C V_{dose} =5 cm ³ ; Data collection: Software "ChemStation" version A.10.02.	GC-FID (methaniser)	Agilent 6890N, United States of America	Primary Standard Gas Mixtures, prepared by the gravimetric method from pure substances, according to ISO 6142:2001 "Gas analysis - Preparation of calibration gas mixtures - Gravimetric method" were used as calibration standards. Target CO/H ₂ calibration gas mixtures were prepared in aluminum cylinders (Luxfer), V= 5 dm ³ without treatment. Verification of 76 µmol/mol, 6 µmol/mol, 1 µmol/mol, 0.1 µmol/mol calibration gas mixtures and pre-mixtures were carried out by the same instrument and with the same parameters. Verification measurements for high concentration pre-mixtures (1.16 %; 0,094 %) were performed by gas chromatography (Varian model 2860, United States of America) with thermal conductivity detector.	The uncertainty contribution considered were the uncertainty of calibration standards (weighing + purity), the uncertainty due to standards verification and the uncertainty within and between day measurements. A coverage factor of 2 was used to report the expanded uncertainty.
H	Internal method	OFCEAS	PROCEAS, France	Standard procured from Praxair Calibration realised by the producer of the instrument, AP2E	the final standard deviation expressed in % results from the higher standard deviation of measurement 1 and 2 added with the standard deviation of the calibration standard with the following formulae The reported value was expanded by k factor: 2.

Participant code	Methods	Technique	Instruments	Calibration	Uncertainty calculation
I	Internal method	IMR-MS	V&F Analyse und Messtechnik GmbH, Austria	Standard procured from Air Products	the final standard deviation expressed in % results from the higher standard deviation of measurements added with the standard deviation of the calibration standard. The reported value was expanded by k factor: 2.

* n.a. means not available

ANNEX C. PARTICIPANT'S RESULTS.

The results are reported as given by the participants. No rounding was performed.

Laboratory name: NPL

Measurement 1:

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation ($\mu\text{mol/mol}$)	No. of replicates
CO (high)	08/04/14	0.9913	0.0004	10
CO (low)	07/04/14	0.08436	0.00002	8
H ₂ S	07/04/14	0.6331	0.0121	40

Measurement 2:

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation ($\mu\text{mol/mol}$)	No. of replicates
CO (high)	08/04/14	0.9933	0.0001	8
CO (low)	11/04/14	0.08416	0.00001	8
H ₂ S	08/04/14	0.6401	0.0150	40

Measurement 3:

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation ($\mu\text{mol/mol}$)	No. of replicates
CO (high)	11/04/14	0.9933	0.0001	8
CO (low)	14/04/14	0.08411	0.00001	8
H ₂ S	09/04/14	0.6321	0.0193	40

Final results:

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Expanded uncertainty ($\mu\text{mol/mol}$) *	No. of replicates
CO (high)	-	0.9926	0.0052	3
CO (low)	-	0.0842	0.0010	3
H ₂ S	-	0.6351	0.0112	3

Laboratory name: VSL

Measurement #1

Component	Date (yyyy/mm/dd)	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
CO high value	2015-04-14	0.9585 10^{-6}	1.4	1
CO low value	2015-04-15	70.5 10^{-9}	0.9	2
H ₂ S	2015-04-20	0.644 10^{-6}	0.9	1

Measurement #2

Component	Date (yyyy/mm/dd)	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
CO high value	2015-04-14	0.9778 10^{-6}	1.1	1
CO low value	-	-	-	-
H ₂ S	2015-04-22	0.5996 10^{-6}	0.7	1

Measurement #31

Component	Date (yyyy/mm/dd)	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
CO high value	2015-04-15	0.9684 10^{-6}	0.8	1
CO low value	-	-	-	-
H ₂ S	2015-04-22	0.5945 10^{-6}	0.7	1

Measurement #4

Component	Date (yyyy/mm/dd)	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
CO high value	2015-04-15	0.9774 10^{-6}	0.5	1
CO low value	-	-	-	-
H ₂ S	2015-04-23	0.5978 10^{-6}	0.8	1

Measurement #5 and also 6 for H₂S

Component	Date (yyyy/mm/dd)	Result (mol/mol)	Standard deviation (% relative)	Number of replicates
CO high value	2015-04-15	0.9755 10^{-6}	0.9	1
CO low value	-	-	-	-
H ₂ S	2015-04-23	0.6080 10^{-6}	0.6	1
H ₂ S	2015-04-24	0.6134 10^{-6}	0.9	1

Results

Component	Date (yyyy/mm/dd)	Result (mol/mol)	Standard deviation (% relative; k=1)	Number of replicates
CO high value	2015-04-15	0.9715 10^{-6}	0.38	5
CO low value	2014-04-15	70.5 10^{-9}	0.9	2
H ₂ S	2015-04-24	0.6096 10^{-6}	1.4	6

Laboratory code: A

Measurement #1

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation (% relative)	Number of replicates
CO high value	15/10/14	1.0032	0.037	4
CO low value	21/10/14	0.0854	0.25	4
H ₂ S	-			

Measurement #2

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation (% relative)	Number of replicates
CO high value	05/11/14	1.0038	0.017	3
CO low value	04/11/14	0.0857	0.33	4
H ₂ S	-			

Measurement #3

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation (% relative)	Number of replicates
CO high value	06/11/14	1.0042	0.012	3
CO low value	07/11/14	0.0855	0.22	3
H ₂ S	-			

Results

Component	Result ($\mu\text{mol/mol}$)	Expanded uncertainty [k=2] (% relative)
CO high value	1.0036	0.33
CO low value	0.0855	0.89
H ₂ S		

Laboratory code: B

Measurement #1

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation (% relative)	Number of replicates
CO high value	11/03/15	0.8	13	3
CO low value	-	-	-	-
H ₂ S	11/03/15	0.8	25	2

Measurement #2

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation (% relative)	Number of replicates
CO high value	12/03/15	0.8	15	3
CO low value	-	-	-	-
H ₂ S	12/03/15	0.65	31	2

Measurement #32

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation (% relative)	Number of replicates
CO high value	13/03/15	0.8	14	3
CO low value	-	-	-	-
H ₂ S	13/03/15	0.7	28	2

Results

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation (% relative)	Number of replicates
CO high value	13/03/15	0.8	15	3
CO low value	-	-	-	-
H ₂ S	13/03/15	0.7	28	2

Laboratory code: C

Measurement #1

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation (% relative)	Number of replicates
CO high value	26 -09-2015	1.0909	6.34E-03	4
CO low value	26 -09-2015	0.127	1.53E-03	3
H ₂ S	24 -09-2015	0.8908	1.43E-02	4

Measurement #2

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation (% relative)	Number of replicates
CO high value	26 -09-2015	1.0884	9.37E-03	4
CO low value	26 -09-2015	0.126	1.53E-03	3
H ₂ S	28 -09-2015	0.9052	5.0E-02	4

Measurement #3

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation (% relative)	Number of replicates
CO high value	26 -09-2015	1.0927	7.58E-03	4
CO low value	26 -09-2015	0.120	5.62E-03	4
H ₂ S	28 -09-2015	0.8983	3.0E-02	4

Results

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation (% relative)	Number of replicates
CO high value	26 -09-2015	1.091	4.1E-3	12
CO low value	26 -09-2015	0.124	5.1E-3	10
H ₂ S	28 -09-2015	0.90	2.4E-3	12

Laboratory code: D

Results

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Expanded uncertainty (% relative)	Number of replicates
CO high value	30/01/2015	0.876	0.9	4
CO low value	30/01/2015	0.064	4.7	4
H ₂ S	30/01/2015	1.05	6.2	5

Laboratory code: E

Results

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Expanded uncertainty (% relative)	Number of replicates
CO high value	16/05/2014	1.04	5	n.a.
CO low value	16/05/2014	0.084	10	n.a.
H ₂ S	26/05/2014	0.46	20	n.a.

Laboratory code: F

Measurement #1

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation (% relative)	Number of replicates
CO high value	11/07/14	0.805	1.1	5
CO low value	11/07/14	0.106	1.5	5
H ₂ S	11/07/14	0.923	11.8	7

Measurement #2

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation (% relative)	Number of replicates
CO high value	16/09/14	0.949	0.5	5
CO low value	16/09/14	0.102	2.1	5
H ₂ S	24/09/14	0.890	2.2	7

Results

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Expanded uncertainty (% relative)	Number of replicates
CO high value		0.877	10.7	2
CO low value		0.104	12.3	2
H ₂ S		0.907	24.3	2

Laboratory code: G

Measurement #1

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation (% relative)	Number of replicates
CO high value	17/07/2014	0.99932	0.23	6
CO low value	22/07/2014	0.08422	0.82	5
H ₂ S	18/08/2014	0.608286	1.3	4

Measurement #2

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation (% relative)	Number of replicates
CO high value	18/07/2014	1.00380	0.17	6
CO low value	22/07/2014	0.08531	0.63	5
H ₂ S	19/08/2014	0.593722	1.2	4

Measurement #3

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation (% relative)	Number of replicates
CO high value	18/07/2014	1.00531	0.17	6
CO low value	22/07/2014	0.08527	0.84	5
H ₂ S	21/08/2014	0.601043	1.2	4

Measurement #4

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation (% relative)	Number of replicates
CO low value	23/07/2014	0.08521	1.05	5
CO low value	23/07/2014	0.08517	0.94	5

Results

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Expanded uncertainty [k=2] ($\mu\text{mol/mol}$)
CO high value	29/07/2014	1.0028	0.0084
CO low value	29/07/2014	0.08504	0.0016
H ₂ S	01/09/2014	0.601	0.018

Laboratory name: H

Measurement #1

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation (% relative)	Number of replicates
CO high value	26/11/2014	0.951	0.1	~ 45 min 2450 points
CO low value	26/11/2014	0.096	0.6	~ 10 min 690 points
H ₂ S	19/11/2014	0.920	1.2	~ 45 min 2734 points

Measurement #2

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation (% relative)	Number of replicates
CO high value	28/11/2014	0.949	0.1	6 min 429 points
CO low value	28/11/2014	0.096	0.8	~ 1 hour 3510 points
H ₂ S	25/11/2014	0.919	0.3	~ 50min 3077 points

Measurement #3

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation (% relative)	Number of replicates
CO high value				
CO low value				
H ₂ S	26/11/2014	0.955	0.4	~ 1 hour 3659 points

Measurement #4

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation (% relative)	Number of replicates
CO high value				
CO low value				
H ₂ S	28/11/2014	0.929	1.5	~ 40 min 2383 points

Results

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation (% relative)	Number of replicates
CO high value	Average of the 2 above values	0.950	5	2
CO low value	Average of the 2 above values	0.096	5	2
H ₂ S	Average of the 4 above values	0.931	5.2	4

Laboratory code: I

Measurement #1

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation (% relative)	Number of replicates
CO high value	-	Failure	-	-
CO low value	-	Failure	-	-
H ₂ S	28/11/2014	1.016	0.8	~30 min 617 points

Measurement #2

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation (% relative)	Number of replicates
CO high value	-	Failure	-	-
CO low value	-	Failure	-	-
H ₂ S	28/11/2014	1.014	0.9	~30 min 932 points

Measurement #3

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Standard deviation (% relative)	Number of replicates
CO high value	-	Failure	-	-
CO low value	-	Failure	-	-
H ₂ S	28/11/2014	1.010	0.8	~20 min 582 points

Results

Component	Date (dd/mm/yy)	Result ($\mu\text{mol/mol}$)	Expanded uncertainty (% relative)	Number of replicates
CO high value	Average of the	Failure	-	-
CO low value	three	Failure	-	-
H ₂ S	measurements	1.013	5.08	3

ANNEX D. DEGREE OF EQUIVALENCE RESULTS.

Table D.1. Participants results for the analysis of 1.0 $\mu\text{mol/mol}$ of CO in hydrogen and the corresponding degree of equivalence. The uncertainties were rounded up to two significant digits, the mean and degree of equivalence were rounded accordingly.

Laboratory code and techniques	Mean value [$\mu\text{mol/mol}$]	Uncertainty ($k = 2$) [$\mu\text{mol/mol}$]	Degree of equivalence [$\mu\text{mol/mol}$]	Uncertainty of the degree of equivalence ($k = 2$) [$\mu\text{mol/mol}$]
B / GC-TCD	0.80	0.24	-0.18	0.25
F / GC-PDHID	0.877	0.094	-0.108	0.094
D / FTIR	0.876	0.016	-0.103	0.017
H / OFCEAS	0.950	0.048	-0.035	0.048
NPL / CRDS	0.9926	0.0052	-0.0054	0.0036
VSL / GC-FID (meth.)	0.9928	0.0064	0.0076	0.0053
G / GC-FID (meth.)	1.0028	0.0084	0.0119	0.0089
A / GC-FID	1.0036	0.0034	0.0192	0.0043
E / GC-PDHID	1.04	0.052	0.043	0.052
C / ED-GC-TCD	1.091	0.080	0.106	0.080

Table D.2. Participants results for the analysis of 0.1 $\mu\text{mol/mol}$ of CO in hydrogen and the corresponding degree of equivalence. The uncertainties were rounded up to two significant digits, the mean and degree of equivalence were rounded accordingly.

Laboratory code and techniques	Mean value [$\mu\text{mol/mol}$]	Uncertainty ($k = 2$) [$\mu\text{mol/mol}$]	Degree of equivalence [$\mu\text{mol/mol}$]	Uncertainty of the degree of equivalence ($k = 2$) [$\mu\text{mol/mol}$]
D / FTIR	0.064	0.006	-0.0120	0.0060
H / OFCEAS	0.096	0.005	-0.0028	0.0048
NPL / CRDS	0.0842	0.0010	-0.0004	0.0010
E / GC-PDHID	0.084	0.008	-0.0003	0.0084
VSL / CRDS	0.1005	0.0012	0.0017	0.0010
G / GC-FID (meth.)	0.0850	0.0016	0.0036	0.0018
F / GC-PDHID	0.104	0.013	0.005	0.013
A / GC-FID	0.0855	0.0008	0.0070	0.0010
C / ED-GC-TCD	0.124	0.014	0.025	0.014

Table D.3. Participants results for the analysis of 1 $\mu\text{mol/mol}$ of H_2S in hydrogen and the corresponding degree of equivalence. The uncertainties were rounded up to two significant digits, the mean and degree of equivalence were rounded accordingly.

Laboratory code and techniques	Mean value [$\mu\text{mol/mol}$]	Uncertainty ($k = 2$) [$\mu\text{mol/mol}$]	Degree of equivalence [$\mu\text{mol/mol}$]	Uncertainty of the degree of equivalence ($k = 2$) [$\mu\text{mol/mol}$]
E / GC-SCD	0.460	0.092	-0.196	0.092
F / GC-MS	0.91	0.22	-0.05	0.22
G / UV- abs spectro	0.601	0.018	-0.043	0.020
C / ED-GC-TCD	0.900	0.075	-0.040	0.075
NPL /GC-SCD	0.635	0.012	-0.022	0.011
H / OFCEAS	0.931	0.049	-0.018	0.049
VSL / GC-SCD	0.966	0.014	0.011	0.009
I / IMR-MS	1.013	0.052	0.064	0.052
B / OFCEAS	0.70	0.40	0.08	0.39
D / FTIR	1.05	0.14	0.43	0.13

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