METROLOGY for HYDROGEN VEHICLES 2

Deliverable D3

Report on the results of the interlaboratory comparison on hydrogen fuel including all contaminants regulated in EN 17124:2018 and ISO/FDIS 14687, with conclusions on the recommendations for future improvements to ISO 21087:2019

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Summary

This report was written as part of activity 2.3 from the EMPIR Metrology for Hydrogen Vehicles 2 (MetroHyVe2) project. The three-year European project commenced on 1st August 2020 and focused on providing solutions to four measurement challenges faced by the hydrogen industry (flow metering, quality assurance, quality control, sampling and fuel cell stack testing). For more details about this project please visit https://www.sintef.no/projectweb/metrohyve-2/.

Confidentiality Public

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Contents

1 Introduction

Several European laboratories are developing the capability to measure the contaminants specified in ISO 14687:2019 [1] and EN 17124:2022 [2] as part of European projects (i.e. EMPIR project 16ENG01 MetroHyVe [3], Horizon 2020 project HYDRAITE [4]) or of businesses (i.e. Air Liquide, Linde). The new standard ISO 21087:2019 [5] is setting uncertainty thresholds and validation procedure to be met (i.e. relative measurement uncertainty < 20 %). A lack of gas calibrants with sufficiently low uncertainty (i.e. formaldehyde and ammonia), reference materials for validation and inter-laboratory comparison are a barrier for European commercial laboratories to prove their compliance to ISO 21087:2019 requirements and their ability to measure contaminants in ISO 14687:2019.

The first inter-laboratory comparison led by EURAMET showed that several NMIs and analytical laboratories have good agreement on measurement of carbon monoxide and hydrogen sulphide in hydrogen [6]. In 16ENG01 MetroHyVe [3] an inter-laboratory comparison for four contaminants out of the 13 regulated in ISO 14687:2019 was organised. However, this study was performed at an amount fraction level for H2S 250 times higher than the ISO 14687:2019 threshold.

Traceability and robust validation (using traceable gas standards) can be obtained through a coordinated comparison of measurement capability. The aim of this intercomparison including 8 contaminants (nitrogen (N_2), carbon monoxide (CO), carbon dioxide (CO_2), propane (C_3H_8), oxygen (O_2), water (H_2O), tetrachlorohexafluorobutane ($C_4Cl_4F_6$) and hydrogen sulphide (H_2S) or carbonyl suplphide(COS)) is to provide a metrologically traceable validation of measurement methods through the use of traceable gas mixtures. This is achieved through organizing a round robin laboratory comparison aimed at hydrogen purity laboratories.

2 Contact information

Organisation:

RISE (Research Institutes of Sweden) is the Swedish National Metrology Institute and scheme coordinator (Group Chemical Problem Solving).

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NPL (National Physical Laboratory) is the National Metrology Institute of the United Kingdom and has prepared and shipped all the cylinders

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3 Assigned values

3.1 Gas mixtures preparation

One gas cylinder (10 L water volume, valve DIN 477 No.1) per participant was prepared by NPL in high-pressure cylinders (SGS, Luxfer, UK). All participant gas cylinder were prepared gravimetrically by dilution of NPL PRMs in high purity hydrogen (99.9999 %, BIP+, Air Products, US) according to ISO 6142-1 [7]. All NPL PRMs used for the preparation were initially prepared gravimetrically from pure compounds in hydrogen matrix and certified by NPL according to ISO 6142-1 [7]. The transfer of gas from the parent cylinder was done using a well purged gas transfer line. The gas transfer line used was a 1/16" (Thames Restek, UK) treated tubing with Swagelok® connections with a minimum-dead-volume (MDV) connection (developed by NPL) at each end to connect to the cylinder. All components used were treated with Silconert® passivation (Thames Restek, UK). Purging was done via cyclic pressure purging a minimum of six times at each end of the filling line (the line was pressurised with filling gas then depressurised to displace residual air from the line). The cylinder used to prepare each sample was weighed against a tare cylinder (of equal size and shape) on a top pan electronic balance of type XPE26003LC (Mettler Toledo, US) using an automated weighing facility (KRISS, SK). The sample cylinders were weighed once they had been evacuated (before gas addition) and again after each addition. The mass of the PRM transferred was calculated using the mass difference between the cylinder before and after gas transfer [8]. The cylinders were rolled for 2 hours to homogenise the gas mixture after the preparation.

The nominal composition of the mixtures in this comparison are within the following ranges:

Table 1: Nominal ranges of amount fraction

Cylinder		Amount fraction
N_2	µmol/mol	150-600
CO	µmol/mol	0.1-0.4
CO_2	µmol/mol	1-4
C_3H_8	µmol/mol	0.3 -1.3
O_2	µmol/mol	2.5 -10
H_2O	µmol/mol	2.5 -10
$C_4Cl_4F_6$	µmol/mol	0.025 – 0.1
H_2S/COS	µmol/mol	0.003 – 0.0015

The pressure is at least 60 bar in each cylinder. After measurement, the cylinders were requested to be returned to NPL for re-analysis.

During the preparation of the cylinders for the intercomparison, a large variation of behaviours for H_2S in the cylinders was observed with sometimes a significant decay. In order to not significantly delay the intercomparison, H_2S was replaced by COS (at the same levels as proposed in the protocol) for all participants except one as they didn´t have the capability to measure COS.

3.2 Stability

The stability of the gas mixtures prepared was assessed in the MetroHyVe 2 Activity 2.2.

3.3 Reference values

A reference value and associated uncertainty was established for the amount fraction of each of the component in each cylinder using accredited or validated analytical methods. The reference values and uncertainties used for the performance rating of the participants' results are given in annex B.

The sulphur amount fraction (COS and H_2S) was measured on a gas chromatograph coupled with a sulphur chemiluminescence detector (GC-SCD) (Agilent, UK). The method used a HP-1 column (60 m x 0.530 mm) with helium carrier. The sample loop size used for injection was 5 ml.

O_2 was analysed by gas chromatography (Agilent with pulsed discharge helium ionization detector (PDHID, VICI) using helium as a carrier gas. The GC/PDHID sampling loop was 1 ml. The sample was transferred onto capillary column molecular sieve 5A plot (30 m x 0.53 mm x 50 µm) and a second capillary column molecular sieve 5A plot (50 m x 0.53 mm x 50 µm). The GC oven was set at 30 degrees Celsius.

H_2O was measured using quartz crystal microbalance, QMA401 (Michell, US). Gases are sampled directly from the gas cylinder to the analyser, a valve was used to restrict the flow to 0.333 L/min for the QMA.

CO and CO_2 were measured with a gas chromatograph (Peak Laboratories, US) coupled with a flame ionization detector (GC/FID) with a methanizer. The method used a Hayesep D column (4.7 cm x 3.81 cm) with nitrogen carrier. The analysis of CO was realised with the column held at a temperature of 30 ºC. The analysis of CO_2 was realised with the column held at a temperature of 65 ºC. The loop size used for sample injection was 5 ml.

N_2 was measured using gas chromatograph with a thermal conductivity detector (GC-TCD) (Agilent Technologies, UK). The method used a HP-PLOT Q PT 15 m x 0.53 mm x 40 µm column, a HP-PLOT Molecular sieve 30 m x 0.53 mm x 50 µm column, and a section of fused silica tubing (diameter: 0.25 mm, length1.5 m) with helium as carrier gas. The loop size used for sample injection was 2 ml.

$C_3H_8$was measured using a GC-FID (Agilent, UK). The method used a DB 624 column (75 m x 0.535 mm OD with film thickness 3 µm) with helium carrier.

$C_4Cl_4F_6$was analysed using selected ion flow tube – mass spectrometry (SIFT-MS), Voice 200 Ultra (Syft, NZ). The reagent ion used was O_2^+ and the reaction product measured was at m/z 182 atomic mass unit (amu) ($CF_3CHCl_2.H_3O^+$).

The reference value was established against a reference value (NPL primary reference material or a dynamically generated reference gas). All analytical instruments were calibrated using NPL gravimetric gas standards in hydrogen matrix gas. Gravimetric standards and/or dynamic standards (prepared by dilution using mass flow controller system (Bronkhorst, NL)) were used to generate calibration curves in the range needed to cover the ISO 14687 threshold and the measured values (as long as it is above the limit of detection). The data was scrutinised however no result was discarded without a technical reason.

4 Evaluation of the participants

4.1 List of participants

To safeguard the anonymity of the participants, a laboratory code is used for identification. This code is only known to the coordinator and the participating laboratory. Table 2 lists the participant's countries and the number of participants from that country.

Table 2: List of countries and number of participants per country

Country	Number of participants
France	3
Germany	2
United Kingdom	1
Austria	1
Poland	1
Norway	1
China	2
Japan	1
USA	1

4.2 Reported results

The number of participants that signed up for participation in this comparison was 13. All participants reported measurement uncertainty for those requested amount fractions of the components they measured (participants could not measure all components present in the mixture they received). The participants used a large variety of analytical techniques as presented in Table 3.

Table 3: Summary of analytical techniques used by the participants.

Lab code	N_2	CO	CO_2	C_3H_8	O_2	H_2O	$C_4Cl_4F_6$	H_2S/COS
L01	GC-PDHID	FTIR	GC-FID	GC-FID	Electrochemical Sensor	CRDS	GC-MS	GC-PFPD
L02	GC-PDHID	GC-PDHID	GC-TCD	GC-TCD	GC-PDHID	CRDS	GC-MS	GC-SCD
L03	GC-TCD	GC-FID (MTN)	GC-FID (MTN)	GC-FID	Electrochemical Oxygen Meter	Dew point Hygrometer	/	Cryogenic-GC-SCD
L04	GC-PED	GC-PED	GC-PED	GC-FID	Portable trace oxygen analyser	Portable dew point analyser	GC-PED	GC-PED
L05	GC-TCD	GC-FID (MTN)	GC-FID (MTN)	GC-FID	GC-HPID	CRDS	TD-GC-MS	GC-FPD

L06	GC-PDHID	GC-PDHID	GC-PDHID	GC-FID	Electrochemical cell	CRDS	GC-ECD	GC-SCD
L07	µGC-TCD	OFCEAS	OFCEAS	GC-FID	OFCEAS	OFCEAS	TD-GC-XSD	TD-GC-PFPD
L08	GC-PED	GC-PED	IMR-MS	GC-PED	GC-PED	QMA	/	GC-SCD (with pre-concentrator)
L09	GC-PDHID	OFCEAS	GC-FID	GC-FID	GC-PDHID	OFCEAS	GC-PDECD	GC-FPD
L10	GC-TCD	/	GC-TCD	/	GC-TCD	/	/	*
L11	GC-TCD	GC-FID (MTN)	GC-PDHID	GC-FID	GC-PDHID	CRDS	TD-GC-MS	GC-SCD
L12	GC-PED	GC-PED	GC-PED	GC-FID	GC-PED	FTIR-OFCEAS	/	GC-PED
L13	EIS	FTIR	FTIR	IMR-MS	IMR-MS	FTIR	IMR-MS	IMR-MS

GC: Gas chromatography; PDHID: pulse discharge helium ionisation detector; FTIR: Fourier transformed infra-red spectroscopy; FID: flame ionisation detector; CRDS: cavity ringdown spectroscopy; PFPD: pulsed flame photometric detector; TCD: thermal conductivity detector; MS: mass spectrometry; SCD: sulphur chemiluminescence detector; MTN: methanizer; PED: plasma emission detector; TD: thermos-desorption; ECD: electron capture detector; OFCEAS: optical feedback cavity enhanced adsorption spectroscopy; XSD: halogen specific detector; IMR-MS: ion-molecule reaction mass spectrometry; QMA: quartz microbalance analyser; EIS: electron impact spectrometry, HPID: He Plasma Ionization Detector.*not communicated

4.3 Evaluation of participant results

The results of the participants have been evaluated by means of zeta-scores using methods from ISO 13528:2022 [9] and the procedure for calculation is described in annex A. The results of the evaluation are presented in annex B. The interpretation of the zeta-score is the following:

$\lvert\zeta\rvert \le 2$	Satisfactory result (green in table 4)
$2 < \lvert\zeta\rvert \le 3$	Questionable result (orange in table 4)
$\lvert\zeta\rvert > 3$	Unsatisfactory result (red in table 4)

Overviews of the calculated zeta -scores are given in table 4. The results are the one obtained before re-analysis of the cylinders.

Table 4: Overview of the zeta-scores. The colour coding corresponds to satisfactory zeta-score in green, questionable zeta-score in orange and unsatisfactory zeta-score in red.

Lab code	N_2	CO	CO_2	C_3H_8	O_2	H_2O	$C_4Cl_4F_6$	H_2S/COS
L01	-7.35	-7.86	-2.41	2.96	-13.15	4.92		-6.94
L02	-1.42	-0.67	-2.08	8.29	0.43	1.12	118086.98	8.76
L03	5.76	-1.13	1.97	-3.34	-2.33	8.06		-4.88
L04	5.98	0.60	-1.68	-0.86	9.58	-2.23	-6.91	
L05	-0.02	0.99	0.18	1.52	7.02	-0.15	-1.75	-1.64
L06	0.39	-8.43	1.13	0.11	-0.29	1.33	1.94	4.41
L07	0.68	-4.18	0.71	2.25	-81.21	3.12		-4.79
L08	-2.05	2.79	14.15	-6.81		-3.60		-0.39
L09	-6.74	-2.35	-0.29	0.78	-0.03	1.14		-1.63
L10	-5.57		1.90		-1.03			-11.28
L11	-0.20	-0.02	0.42	-0.63	-0.24	0.56	0.44	-0.31
L12	-1.78	-1.90	-0.44	-1.97	1.80	11.53		-0.79
L13	0.36	2.56	2.90	2.72	2.17	1.20	-1.43	-1.04

Confidentiality statement

RISE and NPL keeps all data regarding the performance of individual participants, or groups of participants, strictly confidential. Data is accordingly protected and stored in areas on networks with restricted access. The relationship between results and the laboratories that submitted them will never be disclosed. Only the laboratory is granted access to its performance through the assigned code number.

5 Comments from the participants

Several comments from participants have highlighted some of the challenges associated with the measurements of hydrogen fuel quality and challenges associated with the organisation of interlaboratory comparisons. The comments of the laboratory are reported in the table 5 with the challenges associated presented by the MetroHyVe 2 partners.

Table 5: Participants comments on the analysis and challenges associated identified by MetroHyVe 2 partners.

Participant	Comments from participants	Challenges associated
L01	Participant doesn´t have any standard for $C_4Cl_4F_6$.	Lack of commercial calibrants for halogenated compounds
L02	No uncertainty for $C_4Cl_4F_6$. The reported value was on halogen basis (10 times higher than the amount fraction)	Clear instruction to report total halogenated, sulphur and hydrocarbons
L03	The total hydrocarbon content is determined as the sum of hydrocarbons (without methane). The reported result is given as a sum of hydrocarbons compounds as on methane basis (3 times higher than propane amount fraction)	Clear instruction to report total halogenated, sulphur and hydrocarbons
L05	$C_4Cl_4F_6$ and the sulphur amount fraction were analysed by collecting in a canister. For these compounds, the calibration was not performed on the same date than the measurement. When linearity discrepancies are corrected for the analysis of O2 with HPID, the zeta-score is within the range of Satisfactory result.	Difficulty to perform analysis in short time.
L06	Participant could only perform one measurement a day for H_2O otherwise, the gas would not be sufficient.	Difficulty to perform analysis, large volume of gas required
L06	$C_4Cl_4F_6$ as SF_6 equivalent and had to dilute the sample 20 times before measurement (otherwise the concentration was too high for the analytical instrument used).	Lack of commercial calibrants for halogenated compounds
L06	Participant experienced problems with instable calibration gas for S measurement.	Lack of commercial calibrants stable for sulphur compounds
L07	No measurement uncertainty reported for CO, CO_2, $C_4Cl_4F_6$ and for S	
L07	No value reported for $C_4Cl_4F_6$ (but an interval 0.08 to 0.23 – Participant commented that they have no standard for this compound)	Lack of commercial calibrants for halogenated compounds
L08	Value reported <1.25 µmol/mol for O_2	Potential issue with cylinder stability or measurement method
L09	C_3H_8 that participant analysed total hydrocarbon expressed as methane and that the result reported is calculated using the carbon number.	Clear instruction to report total halogenated, sulphur and hydrocarbons
L09	Participant analyzed total halogenated expressed as dichloromethane (CH_2Cl_2). For this sample, participant obtained a saturated peak for C4Cl4F6.	Lack of commercial calibrants for halogenated compounds
L10	The calibration for O_2 and CO_2 was "rough"	Lack of commercial calibrants

Based on the feedback from the participants, the lack of commercial calibrants was the main issues reported especially for the halogenated or sulphur components. The lack of standard impacted the ability of the participants to perform the measurement or to determine the actual amount fraction and uncertainty. The instruction on how to report sulphur, halogens and hydrocarbons components amount fractions were not enough clear for some participants. Therefore, it may be advisable to clarify with the participants how these specific compounds representing the overall parameters have to be reported. Finally, the duration of analysis and the volume of gas were a problem for some participants, it hints as a need to improve analytical methods to reduce time and volume of gas required while ensuring accuracy of the results.

6 Discussion after reporting of the results to the participants

Following the reporting of the performance to the participants, several participants (L02, L06, L07, L08, L09 and L12) investigated their results and prepared corrective actions. The corrective actions and explanation are provided in the Table 6. Some of these participants provided a revised results which was used to recalculate their zeta-score after the corrective action (see Table 7).

Table 6: Participants investigation and corrective actions. The table presents the revised value and the issue identified. The corrective action in relation with the revised value are presented.

Participants reference	Revised results of analysis after reception of the ILC report and expanded uncertainty (k=2)	Issue identified	Corrective action taken
L02	COS 0.006944 +/- 0.001583	the wrong unit was used when transferring the result to the excel sheet	-
L02	C4Cl4F6: 0.07955 +/- 0.034	The wrong unit was used when transferring the result to the excel sheet. The result was the sum of the halides.	-
L02	C3H6: 0,6638 +/- 0,1225	The original result was calculated in relation to methane.	-
L02	CO2: 2.0900 +/- 0.2100	The uncertainty was recalculated taking into account more results that were not included in the previous calculations.	-
L06	COS: 0.0091 +/- 0.0019 and 0.0071 +/- 0.0015	Instability of the calibration gas	New calibration gas
L06	CO: 0.211 +/- 0.022	Instability of the calibration gas	New calibration gas
L07	O2: 5.2 +/- 1.3 -	Technical issue with analyser lead to biased results	Analyser repaired by manufacturer
L07	C4Cl4F6: 0.08 -0.23 µmol/mol	lack of standard, difficulty to identify and quantify the C4Cl4F6 compounds	-
L07	CO2: 2.16 +/- 0.22	Incorrect value no uncertainty provided on ILC report to coordinator	-
L07	CO: 0.203 +/- 0.022	Incorrect value and no uncertainty provided on ILC report to coordinator	-
L07	COS: 0.00635 +/- 0.00050	No uncertainty was provided on the reporting file	-
L08	CO2: No new data provided	Cross interference with propane	-
L09	N2: 297.65 +/- 29.77 and 290.93 +/- 29.09	Incorrect uncertainty provided on ILC report to coordinator	-
L12	H2O: 5.18 +/- 0.5	Issue with analyser and gas standard	Instrument fixed and new gas standard

Table 7: Improvement after the corrective actions reported by some participants. The * are new measurement reported after the participants receive the preliminary report, investigated issues and provided a revised measurement following the corrective action summarised in Table above.

Lab code	N_2	CO	CO_2	C_3H_8	O_2	H_2O	$C_4Cl_4F_6$	H_2S/COS
L01	-7.35	-7.86	-2.41	2.96	-13.15	4.92		-6.94
L02	-1.42	-0.67	-1.72*	-1.86*	0.43	1.12	1,78*	-1.06*
L03	5.76	-1.13	1.97	-3.34	-2.33	8.06		-4.88
L04	5.98	0.60	-1.68	-0.86	9.58	-2.23	-6.91	
L05	-0.02	0.99	0.18	1.52	7.02	-0.15	-1.75	-1.64
L06	0.39	-0.48*	1.13	0.11	-0.29	1.33	1.94	0.34*
L07	0.68	-0.12*	-0.21*	2.25	-0.38*	3.12		-3.74*
L08	-2.05	2.79	14.15	-6.81		-3.60		-0.39
L09	-1.03*	-2.35	-0.29	0.78	-0.03	1.14		-1.63
L10	-5.57		1.90		-1.03			-11.28
L11	-0.20	-0.02	0.42	-0.63	-0.24	0.56	0.44	-0.31
L12	-1.78	-1.90	-0.44	-1.97	1.80	1.50*		-0.79
L13	0.36	2.56	2.90	2.72	2.17	1.20	-1.43	-1.04

An additional observation may be made based on the results provided and the uncertainty variance between laboratories. The variation of uncertainties between laboratories was significant and influence the zeta-score. L01 reported the smallest uncertainty for all the compounds measured. A recommendation to L01 would be to increase their measurement uncertainties as it would significantly improve their zeta score and provide a more realistic uncertainty on their measurement.

Based on the corrective actions realised by the laboratories, the lack of reliable standards was again one of the main sources of biased results. It is important to evaluate if these standards were traceable and stable and how to feedback to the manufacturer to improve their performance. It is critical for laboratories with unsatisfactory zeta-scores to review the quality of the gas standards used for the measurement and discuss with the manufacturer to find the sources of the issues encountered.

7 General conclusions

The intercomparison was successful, as it involved a large number of participants (13), was conducted over a reasonable period of less than a year and included 8 contaminants of hydrogen fuel at level close to the ISO14687 threshold.

The performance of the laboratories was relatively good with more than 58% of the laboratory achieving satisfactory or questionable results on all the compounds tested as shown in table 8. The number of laboratories showing unsatisfactory results was higher for sulphur, nitrogen and water. These compounds are critical for hydrogen fuel quality and may require more work to support laboratory in improving their performance.

Table 8. Percentage of laboratory being satisfactory, questionable, or unsatisfactory based on zeta-score. The value in bracket corresponds to the percentage of laboratory after the corrective actions were implemented. CAP: corrective actions plan

Lab code	N_2	CO	CO_2	C_3H_8	O_2	H_2O	$C_4Cl_4F_6$	H_2S/COS
Laboratory satisfactory (after CAP)	54% (61%)	46% (62%)	69% (77%)	50% (58%)	50% (58%)	42% (58%)	67% (67%)	45% (73%)
Laboratory questionable (after CAP)	8% (8%)	23% (23%)	23% (15%)	25% (25%)	17% (17%)	17% (8%)	0% (0%)	0% (0%)
Laboratory unsatisfactory (after CAP)	38% (31%)	31% (15%)	8% (8%)	25% (17%)	33% (25%)	42% (33%)	33% (33%)	55% (27%)

The outcomes of the intercomparison highlighted the following key points:

- corrective actions significantly improved the performance of the laboratory and helped them achieving satisfactory results. The key aspect of interlaboratory comparison is to benchmark and identify what should be improved
- The lack of commercial and stable calibrants has impacted in some cases, the ability of participants to provide satisfactory results. It needs to be improved by the industry through identifying the gap and ensuring reliability, traceability, stability and affordability of gas calibrants.
- Instrument issues and delay to identify and solved the issues were other challenges encountered by participants. As analysis of hydrogen is a new application for gas analyser manufacturers, it is important for the industry to be informed of the potential problem associated with the measurement and improve the response time to solve instrument issues.
- the duration of analysis and the volume of gas were a problem for some participants, it hints to a need to improve analytical methods to reduce time and volume of gas required while maintaining accuracy of the results.

For future interlaboratory comparisons, it is recommended to improve guidance on reporting hydrocarbons, halogenated and sulphur compounds through for example, a kick-off meeting.

This report highlights the importance to perform interlaboratory comparisons and the overall good performance of laboratory on hydrogen fuel quality. Further corrective actions plan may be progressed with participants. The MetroHyVe 2 partners will support future interlaboratory comparisons on hydrogen fuel.

8 Conclusions on the recommendations for future improvements to ISO 21087:2019

For the results of the intercomparison, it appears clearly that fully complying with ISO 21087:2019 is very challenging for many participants. The biggest challenge is often on the measurement uncertainties where large variations were observed between participants. Sometimes, measurement uncertainties stated were too stringent, leading to unsatisfactory results. It would be useful to include in ISO 21087 examples to guide laboratory for the determination of uncertainties: training or annex/appendix with uncertainty determination examples.

Another challenge encountered by participants is the lack of reliable gas calibrants. ISO21087 should explicitly raise awareness on the criticality of reliable standards on analytical results.

There is lack of accreditation bodies for ISO21087 and therefore it is difficult to verify laboratory claims. The intercomparison demonstrates that there is a need for more clarity regarding accreditation and maybe more clarity between ISO17025 (which most of analysis laboratories are familiar with) and ISO21087 requirements. The goal would also to avoid duplication of information by referring to ISO 17025 when adequate in ISO 21087.

Finally, the intercomparison clearly demonstrated the needs for these types of exercises as many laboratories performed corrective actions based on their results in this intercomparison, which in turn significantly improved their performances. ISO 21087 could include a claim that participation to interlaboratory comparison is required on a regular basis (could be annually).

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[8] V. G. B. A. Milton MJT, “Gravimetric methods for the preparation of standard gas mixtures,” *Metrologia,* vol. 48, pp. R1-R9, 2011.

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Annex A: procedure for the evaluation of laboratory results

For qualification of the laboratory results, zeta-scores (standardized measure of performance, calculated using the participant result, assigned value and the combined standard uncertainties for the result and the assigned value) and E_n-scores are calculated using methods from ISO13528:2022 [9]. Both are a measure for the relative distance from the reference value. The uncertainty stated by the participant is incorporated in the calculation of the E_n-score.

The zeta-score [9] helps to evaluate a participant’s ability to provide results close to the assigned value within their claimed uncertainty and is defined as:

$$\zeta_i = \frac{x_i - x_{pt}}{\sqrt{u^2(x_i) + u^2(x_{pt})}} \qquad \text{(A1)}$$

x_i represents the result (or the average of the replicates) reported by participant i

x_{pt} represents the assigned value in the reference laboratory

$u(x_{pt})$ is the standard uncertainty of the assigned value x_{pt}

$u(x_i)$ is the participant’s own estimate of the standard uncertainty of its result x_i

Annex B: Laboratory results and evaluation

The assigned values measured according to section 2 are indicated in table B.1

Table B.1: Assigned values and associated uncertainties for N_2

Lab code	Units	Reference amount fraction	Reference uncertainty *k*=2
L01	µmol/mol	305	8
L02	µmol/mol	311	7
L03	µmol/mol	325	3
L04	µmol/mol	308	7
L05	µmol/mol	307	5
L06	µmol/mol	323	4
L07	µmol/mol	299	6
L08	µmol/mol	324	7
L09	µmol/mol	310	5
L10	µmol/mol	302	8
L11	µmol/mol	314	7
L12	µmol/mol	322	5
L13	µmol/mol	304	6

Table B.2: Assigned values and associated uncertainties for CO

Lab code	Units	Reference amount fraction	Reference uncertainty *k*=2
L01	µmol/mol	0.216	0.006
L02	µmol/mol	0.207	0.006
L03	µmol/mol	0.216	0.006
L04	µmol/mol	0.205	0.005
L05	µmol/mol	0.204	0.007
L06	µmol/mol	0.216	0.006
L07	µmol/mol	0.216	0.008
L08	µmol/mol	0.216	0.007
L09	µmol/mol	0.206	0.005
L10	µmol/mol	0.201	0.005
L11	µmol/mol	0.209	0.007
L12	µmol/mol	0.214	0.007
L13	µmol/mol	0.202	0.007

Table B.3: Assigned values and associated uncertainties for CO_2

Lab code	Units	Reference amount fraction	Reference uncertainty *k*=2
L01	µmol/mol	2.233	0.019
L02	µmol/mol	2.275	0.043
L03	µmol/mol	2.377	0.029
L04	µmol/mol	2.252	0.023
L05	µmol/mol	2.242	0.023
L06	µmol/mol	2.360	0.026
L07	µmol/mol	2.183	0.048
L08	µmol/mol	2.369	0.036
L09	µmol/mol	2.263	0.050
L10	µmol/mol	2.209	0.016
L11	µmol/mol	2.297	0.018
L12	µmol/mol	2.352	0.052
L13	µmol/mol	2.222	0.047

Table B.4: Assigned values and associated uncertainties for C_3H_8

Lab code	Units	Reference amount fraction	Reference uncertainty *k*=2
L01	µmol/mol	0.7634	0.0123
L02	µmol/mol	0.7778	0.0092
L03	µmol/mol	0.8129	0.0096
L04	µmol/mol	0.7700	0.0068
L05	µmol/mol	0.7667	0.0079
L06	µmol/mol	0.8071	0.0088
L07	µmol/mol	0.7464	0.0071
L08	µmol/mol	0.8102	0.0070
L09	µmol/mol	0.7738	0.0070
L10	µmol/mol	0.7553	0.0130
L11	µmol/mol	0.7854	0.0125
L12	µmol/mol	0.8043	0.0069
L13	µmol/mol	0.7597	0.0081

Table B.5: Assigned values and associated uncertainties for O_2

Lab code	Units	Reference amount fraction	Reference uncertainty *k*=2
L01	µmol/mol	5.45	0.08
L02	µmol/mol	5.21	0.08
L03	µmol/mol	5.45	0.10
L04	µmol/mol	5.16	0.08
L05	µmol/mol	5.14	0.12

L06	µmol/mol	5.45	0.10
L07	µmol/mol	5.45	0.13
L08	µmol/mol	5.43	0.13
L09	µmol/mol	5.19	0.11
L10	µmol/mol	5.06	0.11
L11	µmol/mol	5.26	0.08
L12	µmol/mol	5.39	0.15
L13	µmol/mol	5.09	0.11

Table B.6: Assigned values and associated uncertainties for H_2O

Lab code	Units	Reference amount fraction	Reference uncertainty *k*=2
L01	µmol/mol	4.878	0.114
L02	µmol/mol	4.786	0.119
L03	µmol/mol	4.958	0.123
L04	µmol/mol	4.685	0.115
L05	µmol/mol	4.687	0.117
L06	µmol/mol	4.725	0.097
L07	µmol/mol	4.698	0.093
L08	µmol/mol	4.518	0.086
L09	µmol/mol	4.520	0.110
L10	µmol/mol	4.751	0.110
L11	µmol/mol	4.529	0.103
L12	µmol/mol	4.788	0.118
L13	µmol/mol	4.806	0.163

Table B.7: Assigned values and associated uncertainties for $C_4Cl_4F_6$

Lab code	Units	Reference amount fraction	Reference uncertainty *k*=2
L01	µmol/mol	0.05022	0.00138
L02	µmol/mol	0.04920	0.00120
L03	µmol/mol	0.04567	0.00174
L04	µmol/mol	0.04902	0.00117
L05	µmol/mol	0.05000	0.00121
L06	µmol/mol	0.04935	0.00120
L07	µmol/mol	0.04842	0.00185
L08	µmol/mol	0.04886	0.00119
L09	µmol/mol	0.04767	0.00109
L10	µmol/mol	0.04918	0.00149
L11	µmol/mol	0.04842	0.00142

L12	µmol/mol	0.04749	0.00119
L13	µmol/mol	0.05015	0.00122

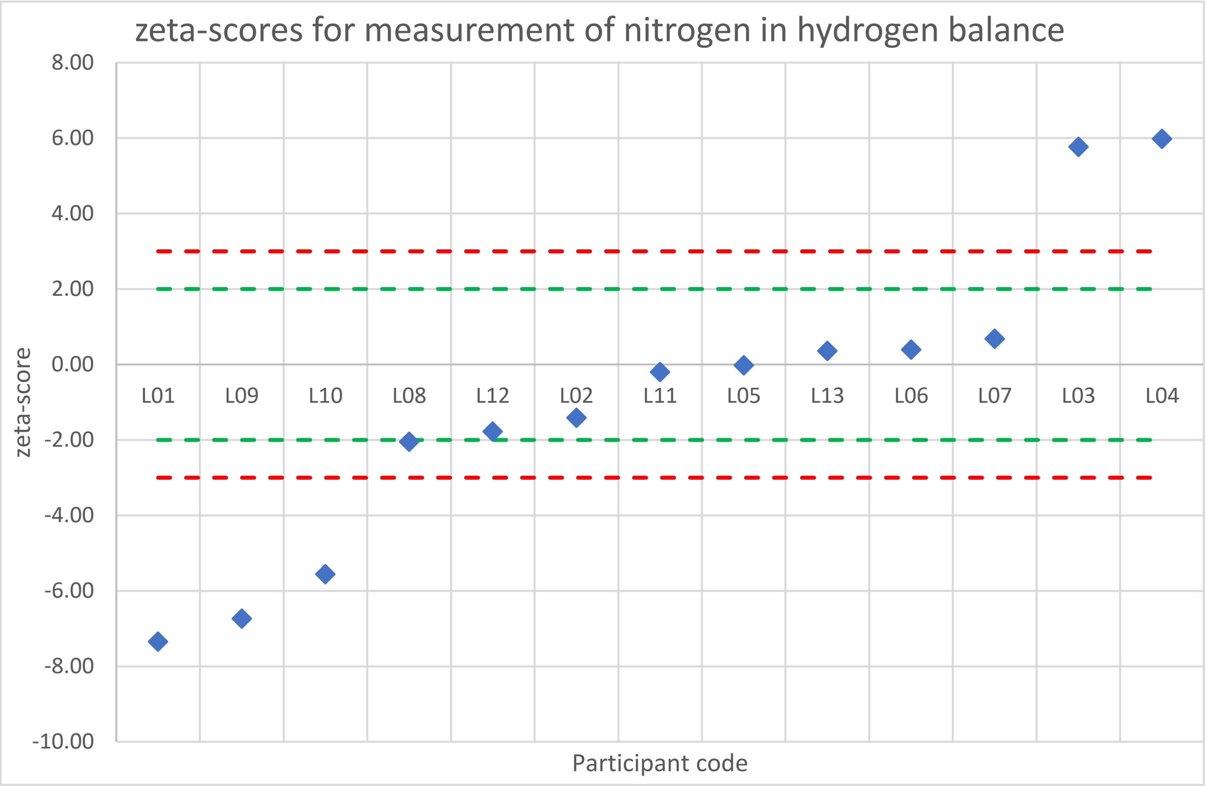
Table B.8: Assigned values and associated uncertainties for S

Lab code	Units	Reference amount fraction	Reference uncertainty *k*=2
L01	µmol/mol	0.007390	0.000602
L02	µmol/mol	0.007818	0.000436
L03	µmol/mol	0.007977	0.000363
L04	µmol/mol	0.008363	0.000418
L05	µmol/mol	0.007928	0.000375
L06	µmol/mol	0.007802	0.000477
L07	µmol/mol	0.007767	0.000571
L08	µmol/mol	0.007853	0.000510
L09	µmol/mol	0.008171	0.000373
L10	µmol/mol	0.008380	0.000770
L11	µmol/mol	0.007361	0.000727
L12	µmol/mol	0.007646	0.000433
L13	µmol/mol	0.008255	0.000354

The results for the laboratories are presented in the following figures. For each compound:

- The zeta-scores as a diagram

N_2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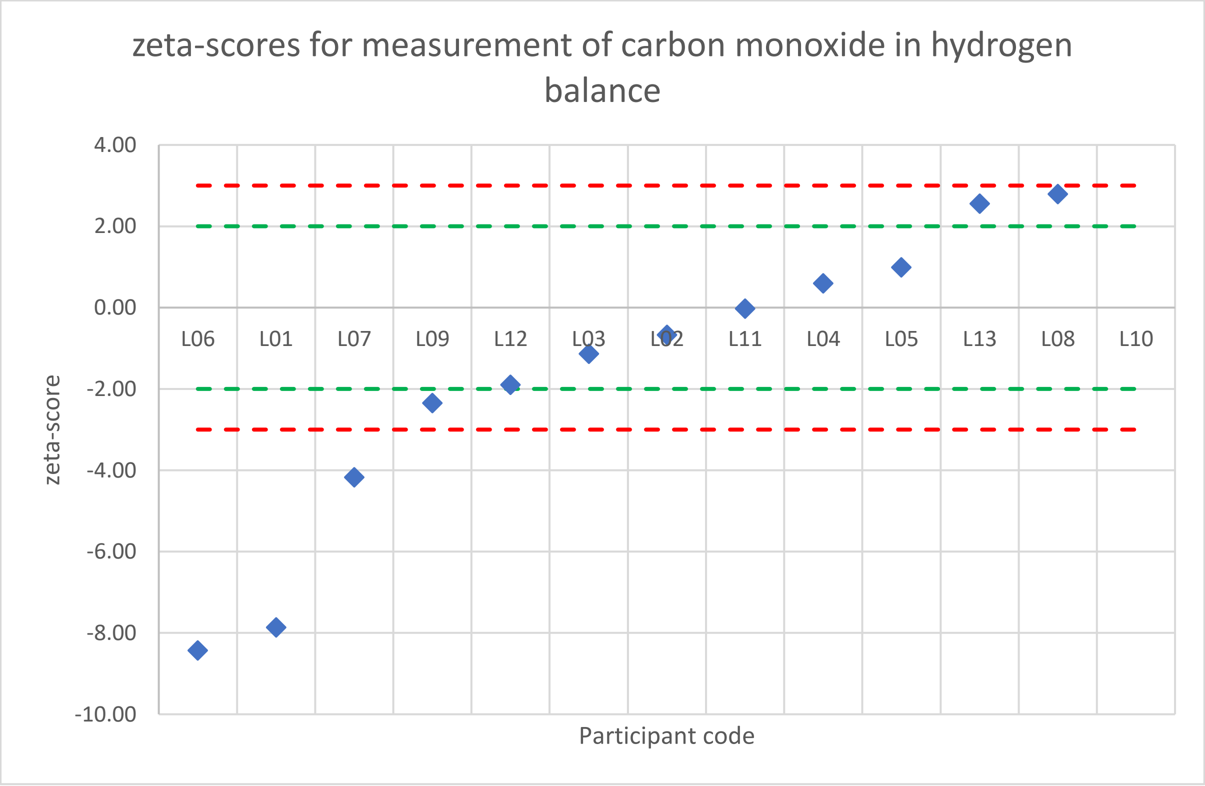
2.00
0.00
-2.00
-4.00
-6.00
-8.00
-10.00
zeta-score
L01
L09
L10
L08
L12
L02
L11
L05
L13
L06
L07
L03
L04
Participant code

CO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0.00
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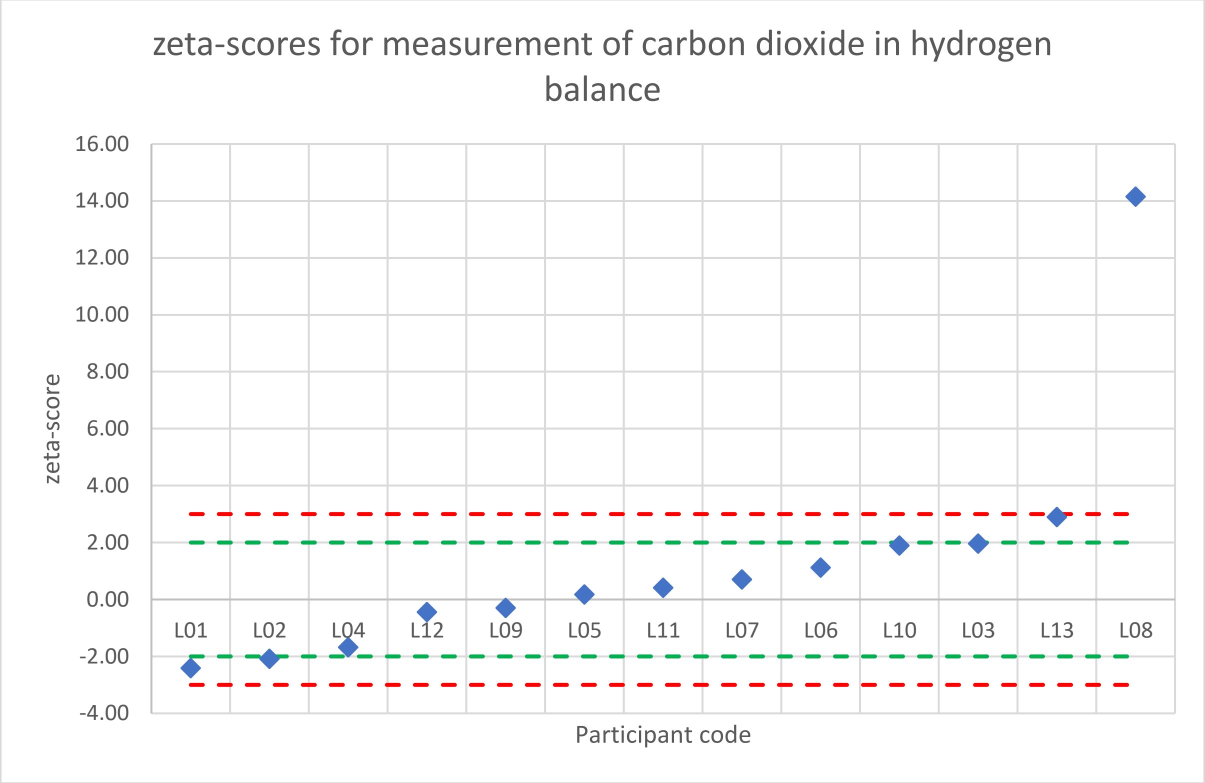
-8.00
-10.00
zeta-score
L06
L01
L07
L09
L12
L03
L02
L11
L04
L05
L13
L08
L10
Participant code

CO2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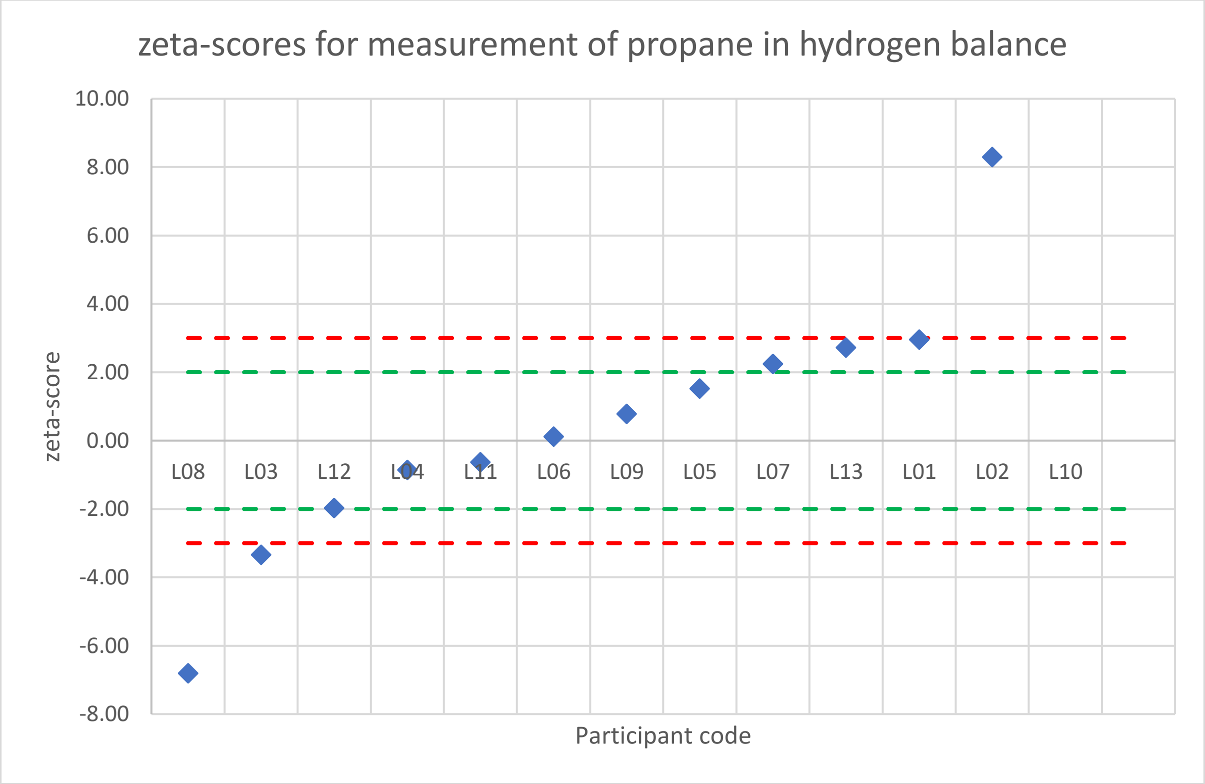
12.00
10.00
8.00
6.00
4.00
2.00
0.00
-2.00
-4.00
zeta-score
L01
L02
L04
L12
L09
L05
L11
L07
L06
L10
L03
L13
L08
Participant code

C3H8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-8.00
zeta-score
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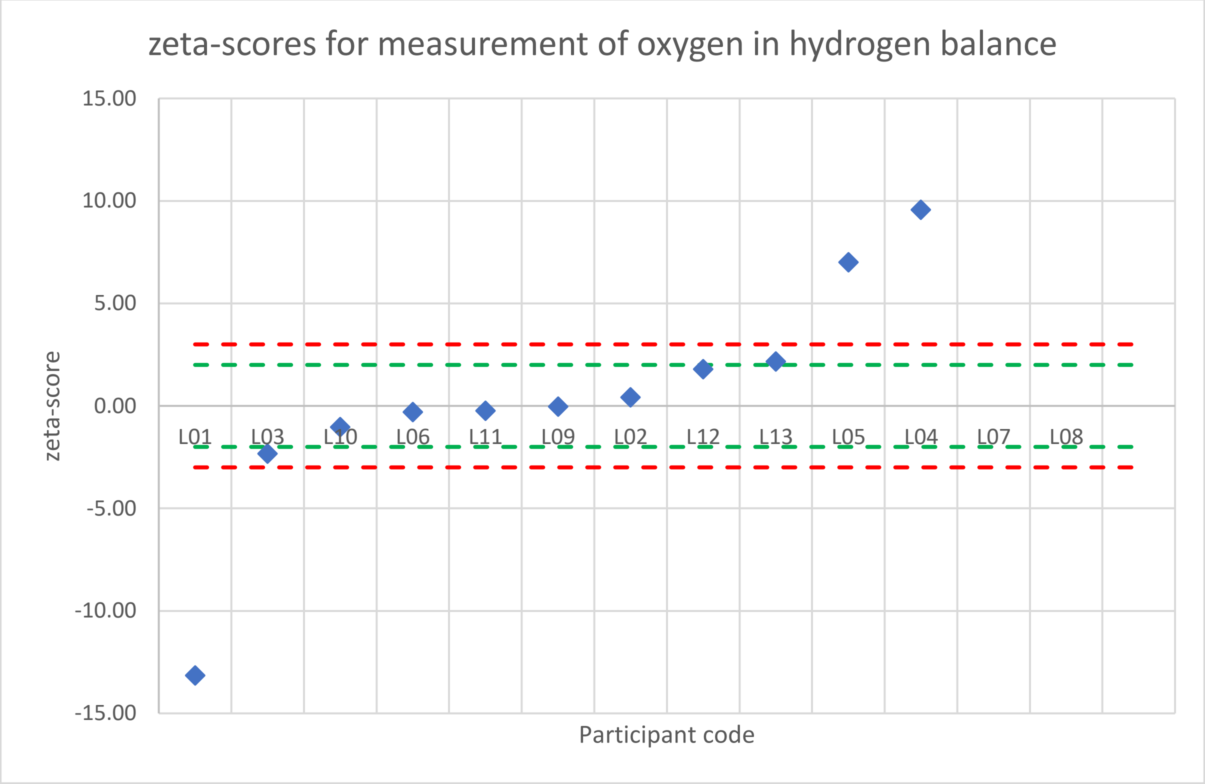
L03
L12
L04
L11
L06
L09
L05
L07
L13
L01
L02
L10
Participant code

O2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5.00
0.00
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-10.00
-15.00
zeta-score
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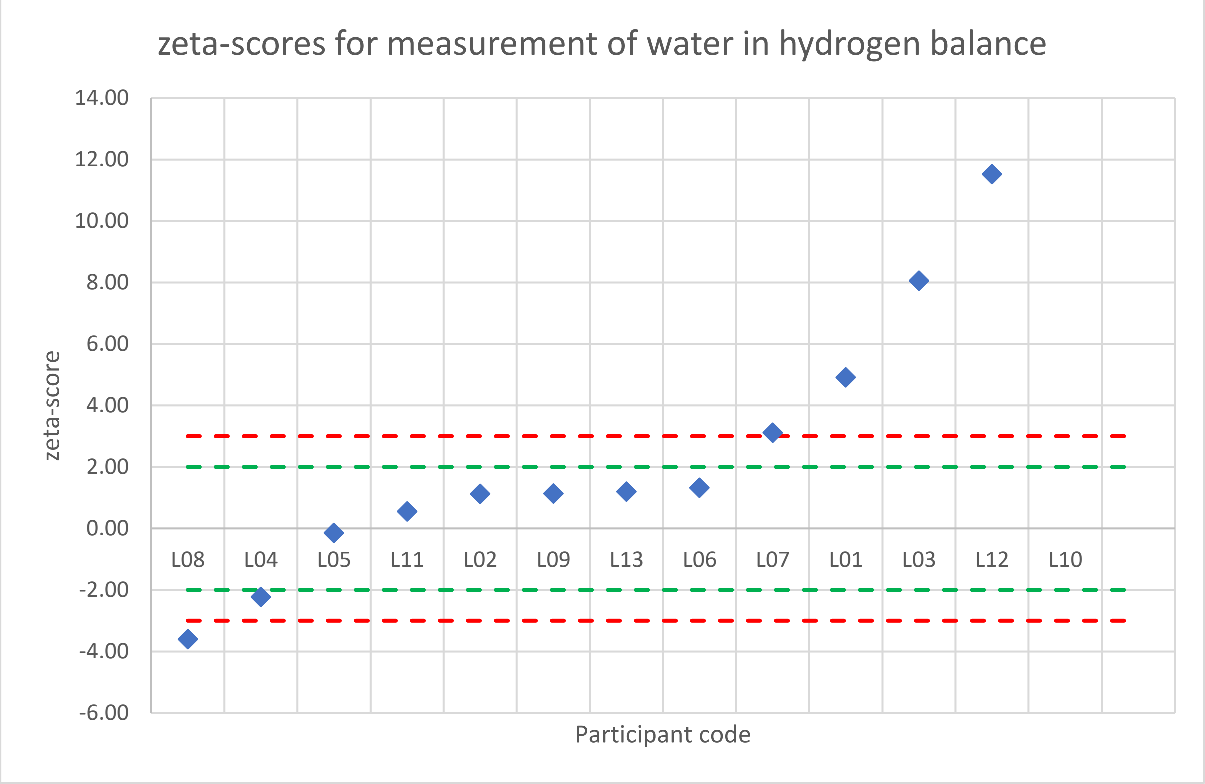
L03
L10
L06
L11
L09
L02
L12
L13
L05
L04
L07
L08
Participant code

H2O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4.00
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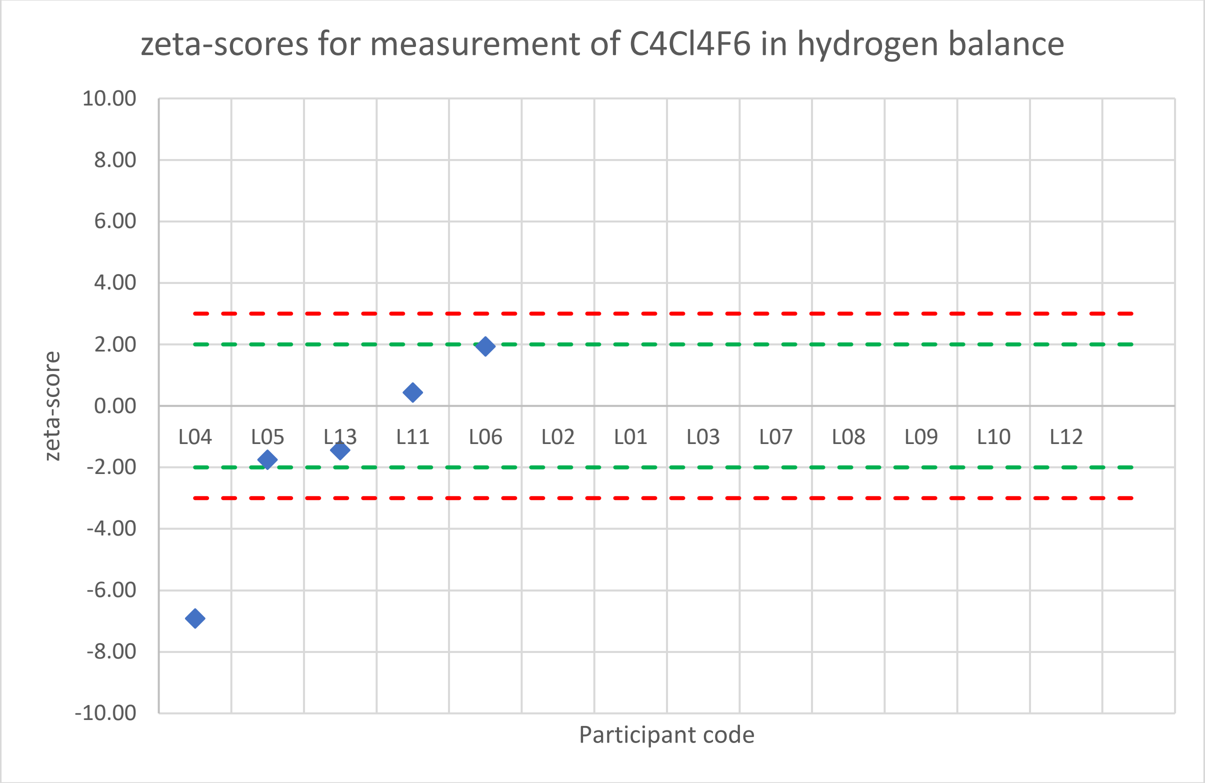
0.00
-2.00
-4.00
-6.00
zeta-score
L08
L04
L05
L11
L02
L09
L13
L06
L07
L01
L03
L12
L10
Participant code

C4Cl4F6


zeta-scores for measurement of C4Cl4F6 in hydrogen balance
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8.00
6.00
4.00
2.00
0.00
-2.00
-4.00
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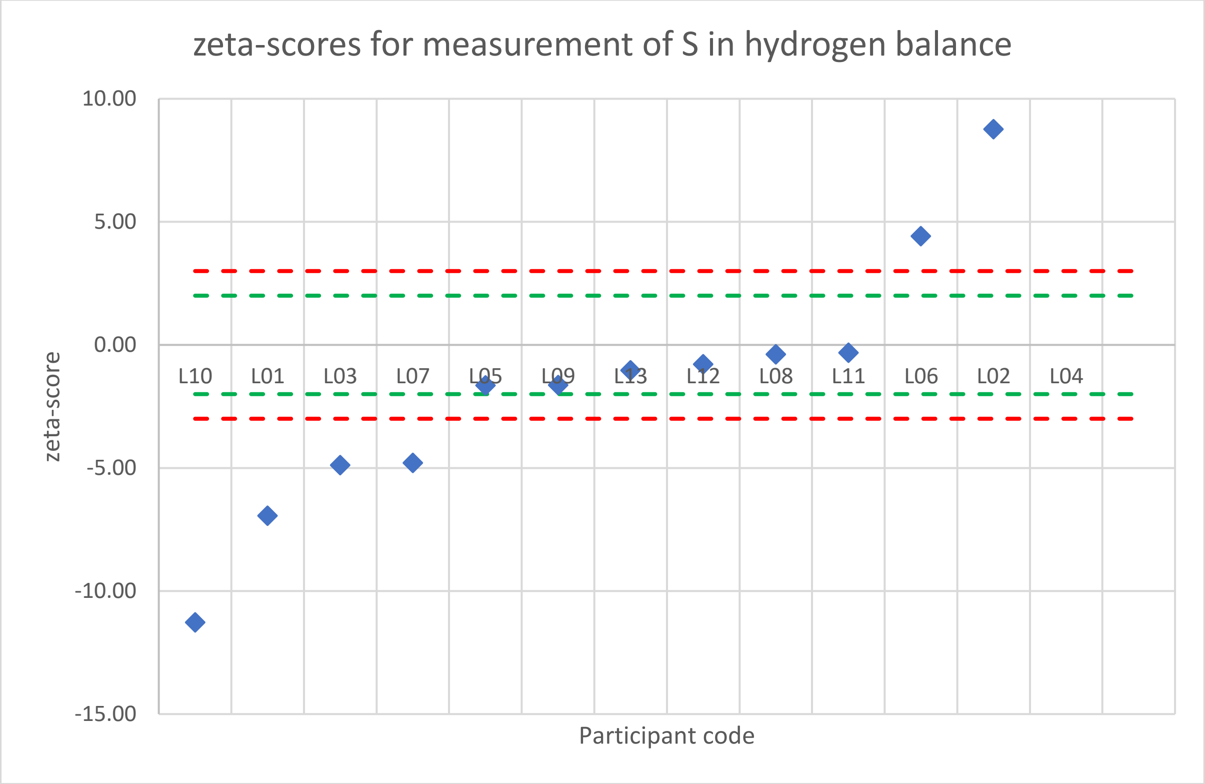
-8.00
-10.00
zeta-score
L04
L05
L13
L11
L06
L02
L01
L03
L07
L08
L09
L10
L12
Participant code

S


zeta-scores for measurement of S in hydrogen balance
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5.00
0.00
-5.00
-10.00
-15.00
zeta-score
L10
L01
L03
L07
L05
L09
L13
L12
L08
L11
L06
L02
L04
Participant code