# International comparison CCQM-K93.2023: Ethanol in nitrogen 105 to 135 µmol mol$^{-1}$

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Annex I - XLGenLine output – comparison between linear and quadratic fit

Annex II – Participants Report form part B

# 1. Rationale for comparison and study overview

The CCQM-K93.2023 comparison was designed to assess the comparability of laboratories' capabilities to prepare ethanol ($C_2H_5OH$) in nitrogen ($N_2$) gas mixtures. The key comparison covered ethanol amount fractions from 105 µmol mol$^{-1}$ to 135 µmol mol$^{-1}$. All measurements were conducted at NPL and involved the simultaneous comparison of 32 primary travelling standards with two travelling standards provided by each of the 16 participating laboratories.

NPL used gas chromatography with flame ionisation detection (GC-FID) to determine the ethanol amount fraction in nitrogen. Each travelling standard was prepared in dry $N_2$ following compositional constraints described in section 3. Participants calculated the ethanol amount fraction using their preferred procedures. Corrections to the submitted values were permitted, after the cylinders were returned, to account for ethanol degradation. When a correction was applied, participants were required to provide details of the decay function used and the resulting corrected amount fraction. Participants who prepared additional travelling standards to characterise decay were asked to supply full information on their composition and measurements to support comparability. On one occasion, a participant submitted a substantial correction to their initially reported amount fraction due to an error in the gravimetric value rather than mixture degradation.

The CCQM-K93.2023 comparison is classified as a Model 2, Track C comparison according to CCQM nomenclature (ref. *"CCQM-GAWG strategy for comparisons and CMC claims,"* GAWG/19-41).

# 2. Measurand, quantities and units

The measurand is the amount fraction of $C_2H_5OH$ in $N_2$, with measurement results being expressed in µmol mol$^{-1}$.

# 3. Preparation of travelling standards by participants

The travelling standards were to be prepared and analysed by participants using their usual procedures, with the constraints detailed below.

## 3.1. Nominal $C_2H_5OH$ amount fractions

Each participant was required to provide two travelling standards containing $C_2H_5OH$ in $N_2$ at two different amount fractions. The nominal intervals of the values were provided by the coordinating laboratory to each participant upon registration to the comparison and fell within the interval 105 µmol mol$^{-1}$to 135 µmol mol$^{-1}$. Table 1 below contains the distribution of the amount fractions into six sub-ranges (bins) of 5 µmol mol$^{-1}$ each and allowing for a uniform spread of approximately ± 8 %

around the nominal amount fraction of 120 µmol mol$^{-1}$. The prepared two travelling standards by a single participant were separated by more than 5 µmol mol$^{-1}$, i.e. skipping at least one sub-range. The analyses at the coordinating laboratory confirmed that the estimated amount fraction of ethanol in each travelling standard was within the assigned sub-interval, except for one laboratory who calculated a gravimetric value within the correct sub-interval, but upon analysis determined that the amount fraction fell into another. It should be noted that the gravimetric amount fraction of that standard was still in the required sub-interval. However, the laboratory decided to declare their amount fraction based on analytical validation data. The aim of equally populated sub-intervals was to obtain a uniform spread of measurements allowing a good data fit to be produced. Previous tests at NPL have proven that the GC-FID analyser provides a linear response within narrow range, but a second order polynomial function was also considered in this comparison. The repartition of participants was organised such as to reach relatively equal weights in the regression analysis. The provided sub-intervals were from 105 µmol mol$^{-1}$ to 135 µmol mol$^{-1}$.

**Table 1. Repartition of participants nominal values in six sub-intervals of $C_2H_5OH$ amount fractions.**

| Lab ID | Nominal amount fraction [µmol mol$^{-1}$] |
|---|---|
| CERI | 105-110 (Range A) |
| CMI | 105-110 (Range A) |
| IPQ | 105-110 (Range A) |
| NIST | 105-110 (Range A) |
| NMISA | 105-110 (Range A) |
| UME | 105-110 (Range A) |
| BFKH | 110-115 (Range B) |
| INMETRO | 110-115 (Range B) |
| LNE | 110-115 (Range B) |
| NIMT | 110-115 (Range B) |
| VSL | 110-115 (Range B) |
| KRISS | 115-120 (Range C) |
| NIM | 115-120 (Range C) |
| NPL | 115-120 (Range C) |
| SMU | 115-120 (Range C) |
| Ukrmetrteststandard | 115-120 (Range C) |
| CERI | 120-125 (Range D) |
| CMI | 120-125 (Range D) |
| IPQ | 120-125 (Range D) |
| NIST | 120-125 (Range D) |
| NMISA | 120-125 (Range D) |
| UME | 120-125 (Range D) |
| BFKH | 125-130 (Range E) |
| INMETRO | 125-130 (Range E) |
| LNE | 125-130 (Range E) |
| NIMT | 125-130 (Range E) |
| VSL | 125-130 (Range E) |
| KRISS | 125-130 (Range E) |

| | |
|---|---|
| NIM | 130-135 (Range F) |
| NPL | 130-135 (Range F) |
| SMU | 130-135 (Range F) |
| Ukrmetrteststandard | 130-135 (Range F) |

## 3.2. Cylinder characteristics

Travelling standards were to be prepared in cylinders with a nominal volume equal to or greater than 5 $dm^3$, with a pressure between 10 MPa and 15 MPa. Participants were encouraged to use their optimal cylinder coating and surface polishing.

## 3.3. Cylinder valves

Cylinders were mostly fitted with DIN and BS valves. Alternatively, valves conforming to one of the standards AFNOR, CGA or JIS were also used. Participants were required to provide the stem connectors along with the cylinders in the latter case. Participants informed NPL of the exact type of valve they had used at the time of the mixture preparation or shipping.

# 4. Travelling standard verification

Participants were allowed to perform a verification of their travelling standards before shipment to the coordinating lab and after return

## 4.1. Before shipment

The verification of the travelling standards was performed before shipment to the coordinating laboratory by all participants. The travelling standards were intended to be held at NPL for a maximum period of four months. However, due to unplanned delays, the hold time was significantly increased (revised schedule, Table 2, below).

## 4.2. After return

After measurements at NPL and prior to the preparation of this Draft A report, the laboratories had the opportunity to perform another verification of their travelling standards. The final results were submitted to the coordinating laboratory before 31 Aug 2024 for inclusion in Draft A report.

# 5. Transport of cylinders to and from NPL

Cylinders were to arrive at NPL no later than 20 December 2023. However, due to transport delays, the deadline was extended to April 2024. It was the responsibility of the participating laboratories to organise transport of their cylinders to NPL, and to ensure that proper arrangements were made for local customs formalities. NPL assisted the participants with this, when possible.
Participants were encouraged to inform NPL of their transport and customs arrangements prior to the cylinders leaving their laboratory. Additional fees associated with customs clearance, storage or other costs as part of the shipping process were charged to the participant. At the end of the comparison,

the participants were responsible for the arrangements and costs of shipping the cylinders from NPL back to their laboratories.

# 6. Comparison measurement procedures

## 6.1. Preparation for analysis

On receipt by NPL, all cylinders were allowed to equilibrate at laboratory temperature for at least 24 hours. After that period, the cylinders were homogenised by rolling for at least one hour. Whenever a cylinder connector appropriate to the cylinder valve was provided by a participant (AFNOR, CGA, JIS or other connectors), it was utilised for the measurement. Alternatively, one of NPL's BS and DIN connectors available for the study was used. Restrictor valves were used as pressure reducers, when possible, to minimise dead volume of the sampling inlet and achieve quicker equilibration. Each cylinder was connected from the pressure reducer to one inlet of an automatic gas sampler of a GC−FID analyser. The pressure reducer of each cylinder was purged ten times with the participant's mixture. The cylinder valve was then closed leaving the restrictor valve or regulator pressurised. The cylinders were then left for a short time before the analysis of the travelling standard was performed by GC−FID, as described in section 6.2.

## 6.2. Analysis of travelling standards

Immediately prior to the analysis, each cylinder valve was re-opened and the pressure reducer purged three times. The suite of cylinders from participants was analysed randomly, together with one control cylinder (D180650 reference standard mixture of $C_2H_5OH$ in $N_2$ with amount fraction of 121.35 ± 0.10 µmol $mol^{-1}$ ($k$=1)) to correct for within-run and between-run drifts in the analyser and to facilitate the calculation of the ratio to the reference standard. Initially, it was planned to use an analytical method in which thirteen consistent samples (seven controls and six participants') were injected in an ABABA… configuration. The three initial runs were to be used for system conditioning and data from them discarded. Due to long equilibration times and difficulty in achieving relative measurement uncertainty below 0.05 % ($k$=1), the equilibration time was set to ten hours, which is approximately 12 equilibration runs. The number of ratios to the reference standard was also increased from 13 to 18.

# 7. Travelling standard shipment, results submission, and reports

It was participants' responsibility to send their travelling standard and their estimates for the amount fractions and standard uncertainties in full and in compliance with the comparison schedule and deadlines, as per Table 2 (below).

NPL is responsible for the preparation of the final reports of the comparisons. The first draft of the Draft A report, was prepared as soon as the analyses of the travelling standards were completed. It included the results submitted by the participants, identified by lab ID. The results were presented at the subsequent GAWG meeting.

# 8. Comparison schedule

The comparison was organised by NPL and followed the revised schedule, presented in the table below.

**Table 2. Comparison schedule with deadlines.**

| Due Date | Event |
|---|---|
| 30 June 2023 | Registration |
| 31 May 2024 | Deadline for arrival of cylinders and report form part A at NPL |
| 31 Jan 2025 | Measurements at NPL completed |
| 31 Aug 2025 | Participant's second analysis completed (optional) and submission of report form part B |
| 15 Dec 2025 | Draft A report distributed to participants |

In more detail, the comparison procedure and timelines were as follows:

- The participants had to send their two travelling standards to NPL before 20 December 2023. Although it was important to meet the deadline, so that their travelling standards could be analysed at the same time as those of the others, the deadline was extended to May 2024 due to customs delays. The extended deadline was respected by all participants and report forms Part A were received on time.
- On examination of the information submitted by the participants, NPL did not find information that appeared to be anomalous compared to the other participants; no participant was invited to check the submitted data. It was communicated that once all participants had been informed of the results, individual values and uncertainties could only be changed, removed, or the complete comparison abandoned, if there was full agreement between all participants and on the basis of a clear corruption of a mixture during its transport or some other phenomenon rendered the comparison (or part of it) invalid.
- Draft A of the report was circulated to all participants following completion of the comparison, inviting comments and feedback. Participants were given a deadline of one month to submit their responses.
- Following approval of the Key Comparison Reference Values (KCRVs) by the GAWG, Draft B of the report was prepared. At this stage, the participant results were no longer considered confidential, and the report could be used to support Calibration and Measurement Capabilities (CMCs), presentations, and publications. However, the KCRVs and the Degrees of Equivalence (DOEs) remained confidential until their approval by the CCQM and subsequent publication in the Key Comparison Database (KCDB). The first publication arising from this comparison will be led by NPL. Other participants may publish results from CCQM-K93.2023, subject to agreement from NPL. Draft B becomes the final report once it has been presented to the CCQM as the final version.

# 9. Data analysis

## 9.1. Parameters considered for calculations

Upon completion of the analysis, the obtained peak area ratios of the participants' standards against the reference standard (NPL's D180650) were tabulated along with the associated measurement uncertainty (i.e. the repeatability uncertainty). The uncertainties were combined with the peak integration uncertainty, and stability and reproducibility uncertainty. The peak integration uncertainty was evaluated by comparing the outputs of independent integrations performed by two scientists on the same data sets. Later, the same two scientists performed all the peak integrations for the comparison. Three sets of data, containing 12 peak areas (six calibrants, six samples) from analysis of three different reference materials with amount fractions of ethanol close to the data centroid of 120 µmol mol$^{-1}$ were used for this purpose. Peak ratios were then calculated. Their maximum relative uncertainty of the mean, using pooled data for each set, was used as an indication of integration uncertainty (0.06 %). Reproducibility uncertainty was evaluated by analysing a randomly selected travelling standard against the reference standard at the beginning of the measurements (April 2024) and at their end (January 2025). It was calculated by combining the repeatability uncertainties of the ratios for each of the two batches (0.03 % in April'24 and 0.02 % in January'25) with the relative to the mean difference of these ratios (0.11 %), which resulted in a combined uncertainty of 0.12 %. It has to be acknowledged that the reproducibility uncertainty also includes the drifts of both the travelling standard and the reference standard, which might be different. However, this cannot be evaluated with existing data. The peak integration uncertainty component is also included in this value, although an effort was made to minimise it by asking the same person to perform the integration of both data sets. An additional uncertainty contribution associated with the stability of the reference standard, accounting for possible decay between measurements of the first and last travelling standards in this comparison, has not been included because it was too small to estimate reliably over the 8.5-month analytical measurement period. Based on longer-term monitoring of ethanol reference materials, the coordinator established that the total drift over 8.5 months was below 0.03 µmol mol$^{-1}$, which is smaller than the uncertainty associated with peak integration. Considering all these uncertainty components, for the analysed travelling standards the minimum combined relative uncertainty of the ratios was 0.13 % and the maximum was 0.14 %. The relevance of this value was further confirmed by analysing two travelling standards against each other approximately one year apart. The difference in the obtained ratios was 0.21 %, which is within the expanded ratios uncertainty (0.28 %).

## 9.2. Regression analysis

The regression function was constructed with the independent variable (x-axis) being the $C_2H_5OH$ amount fractions as reported by participants, along with the reported standard uncertainties, and the dependent variable (y-axis) being the analyser response ratio (participant's/reference standard) along with the calculated standard uncertainties, as described in section 9.1. The $C_2H_5OH$ amount fraction regression analyses were performed using the Generalised Least Squares approach described in ISO 6143:2001 ("Gas analysis – Comparison methods for determining and checking the composition of travelling standard"), realised in the in-house software (XLGenLine 2.0). A linear fit was used for regression. Higher order regressions (e.g. second order polynomial) were tested but no additional benefit could be found and therefore the suggested fitting model was linear.

# 10. Comparison results

Measurements were performed at the coordinating laboratory (NPL) from April 2024 to January 2025. Table 3 lists the participant's name, travelling standard identifier (T. Standard ID), as supplied by the participant, and the date they were analysed at NPL. The cylinder with ID D170283 has no recorded analysis date, as it was inadvertently vented during the analysis before measurements could be completed, leaving insufficient pressure for re-analysis. The value assignment of each cylinder was performed following the methods outlined in section 9.2. After the completion of the analyses of all the travelling standards, the information submitted by the participants for the nominal amount fraction of ethanol in their travelling standards (Table 4) was analysed to confirm whether it appeared to be anomalous compared to the other participants. Anomalous data were defined as relative residual from expected regression value ± the analytical uncertainty exceeding 5 % on either end. At this point the participants were not required to submit their final amount fraction values and uncertainties. Based on the submitted nominal amount fractions, no data appeared to be anomalous and all the results were considered for further evaluation.

Upon completion of the travelling standard measurements, the dates of analysis of the travelling standards were revealed to the participants and cylinders were sent back to them for optional reanalysis and correction for analyte decay. Participants were requested to complete and submit Report Form B (Annex II), which was used for final data analysis and performance evaluation. A summary of the submitted amount fractions from Report Form B and the results from the analytical evaluation following the approach described in section 9.2 are shown in Table 5. The uncertainty from the analytical evaluation was similar for all participants' travelling standard analyses, equal to approximately 0.1 %.

**Table 3. Travelling Standards date of analysis.**

| Participant Name | T. Standard ID | Date of analysis |
|---|---|---|
| KRISS | D170283 | |
| UME | D206683 | 25/04/2024 |
| VSL | D153312 | 01/05/2024 |
| NIMT | D094486 | 08/05/2024 |
| KRISS | D170152 | 09/05/2024 |
| INMETRO | M692271 | 14/05/2024 |
| NMISA | D626508 | 15/05/2024 |
| IPQ | PRM208984 | 16/05/2024 |
| CERI | CPD-00087 | 17/05/2024 |
| NPL | 3018-R1 | 21/05/2024 |
| NPL | A668-R1 | 22/05/2024 |
| NIMT | D094484 | 23/05/2024 |
| CMI | D161473 | 29/05/2024 |
| Ukrmetrteststandard | D340116 | 31/05/2024 |
| LNE | APE1279837 | 05/06/2024 |
| CMI | D466362 | 09/08/2024 |
| INMETRO | M692275 | 20/08/2024 |
| Ukrmetrteststandard | D340107 | 21/08/2024 |
| VSL | D153425 | 22/08/2024 |
| SMU | 0695E_13 | 24/08/2024 |
| UME | D206680 | 28/08/2024 |
| BFKH | D412828 | 29/08/2024 |
| IPQ | PRM203396 | 02/09/2024 |
| NIST | CC750296 | 04/09/2024 |
| SMU | 0072F_11 | 05/09/2024 |
| LNE | APE1516246 | 06/09/2024 |
| NIM | 200226018007 | 10/09/2024 |
| CERI | CPD-00088 | 11/09/2024 |
| BFKH | D412846 | 12/09/2024 |
| NIST | CC750302 | 13/09/2024 |
| NMISA | M395423 | 09/01/2025 |
| NIM | 200226018058 | 10/01/2025 |

**Table 4. Nominal amount fractions as reported by the participants before re-analysis (data summary Report Form A).**

| Participant ID | Nominal value [µmol mol$^{-1}$] |
|---|---|
| NMISA | 108.05 |
| NMISA | 122.898 |
| VSL | 112.5 |
| VSL | 127.5 |
| KRISS | 117.77 |
| KRISS | 132.81 |
| IPQ | 110.9 |

| | |
|---|---|
| IPQ | 120.3 |
| NIMT | 112.46 |
| NIMT | 127.45 |
| SMU | 116.77 |
| SMU | 131.68 |
| CERI | 107.47 |
| CERI | 122.51 |
| LNE | 112.7 |
| LNE | 127.49 |
| Ukrmetrteststandard | 117.5 |
| Ukrmetrteststandard | 133 |
| UME | 107.5 |
| UME | 122.5 |
| BFKH | 112.47 |
| BFKH | 127.47 |
| NIM | 118.850 |
| NIM | 133.261 |
| NIST | 108.0 |
| NIST | 121.1 |
| INMETRO | 113.63 |
| INMETRO | 128.89 |
| NPL | 115.91 |
| NPL | 132.63 |
| CMI | 107.00 |
| CMI | 123.10 |

**Table 5. Final travelling standards amount fractions and uncertainties as submitted by the participant in Report Form B, and peak area ratios from the analytical determination along with combined analytical measurement uncertainty.**

| Participant ID | Cylinder ID | Reported value [µmol mol$^{-1}$] | Reported expanded uncertainty [µmol mol$^{-1}$] | Measured ratio []* | u []* |
|---|---|---|---|---|---|
| NMISA | M395423 | 108.05 | 0.16 | 0.8914 | 0.0012 |
| NMISA | D626508 | 122.898 | 0.073 | 1.0119 | 0.0014 |
| VSL | D153312 | 111.565 | 0.462 | 0.9188 | 0.0012 |
| VSL | D153425 | 127.976 | 0.513 | 1.0510 | 0.0014 |
| KRISS | D170152 | 117.77 | 0.35 | 0.9708 | 0.0013 |
| KRISS | D170283 | 132.81 | 0.39 | N/A | N/A |
| IPQ | PRM208984 | 115.5 | 1.4 | 0.9361 | 0.0013 |
| IPQ | PRM203396 | 123.6 | 2.2 | 1.0154 | 0.0014 |
| NIMT | D094484 | 112.43 | 0.27 | 0.9273 | 0.0013 |
| NIMT | D094486 | 127.42 | 0.28 | 1.0481 | 0.0014 |
| SMU | 0695E_13 | 116.77 | 0.82 | 0.9487 | 0.0013 |
| SMU | 0072F_11 | 131.68 | 0.97 | 1.0626 | 0.0014 |
| CERI | CPD-00087 | 107.36 | 0.26 | 0.8852 | 0.0012 |

| | | | | | |
|---|---|---|---|---|---|
| CERI | CPD-00088 | 122.39 | 0.24 | 1.0075 | 0.0014 |
| LNE | APE1279837 | 112.7 | 0.4 | 0.9258 | 0.0013 |
| LNE | APE1516246 | 127.49 | 0.35 | 1.0468 | 0.0014 |
| Ukrmetrtests tandard | D340107 | 117.5 | 1.2 | 0.9421 | 0.0013 |
| Ukrmetrtests tandard | D340116 | 133 | 1.4 | 1.0675 | 0.0015 |
| UME | D206680 | 107.5 | 2.0 | 0.8717 | 0.0012 |
| UME | D206683 | 122.5 | 2.3 | 0.9793 | 0.0013 |
| BFKH | D412828 | 112.47 | 0.3 | 0.9267 | 0.0012 |
| BFKH | D412846 | 127.47 | 0.34 | 1.0422 | 0.0014 |
| NIM | 200226018007 | 118.915 | 0.262 | 0.9776 | 0.0013 |
| NIM | 200226018058 | 133.304 | 0.293 | 1.0990 | 0.0015 |
| NIST | CC750302 | 107.92 | 0.65 | 0.8888 | 0.0012 |
| NIST | CC750296 | 121.8 | 1.37 | 0.9887 | 0.0013 |
| INMETRO | M692271 | 113.63 | 0.76 | 0.9230 | 0.0013 |
| INMETRO | M692275 | 128.89 | 0.67 | 1.0510 | 0.0014 |
| NPL | 3018-R1 | 115.91 | 0.37 | 0.9502 | 0.0013 |
| NPL | A668-R1 | 132.63 | 0.51 | 1.0857 | 0.0015 |
| CMI | D466362 | 107.5 | 1 | 0.8795 | 0.0012 |
| CMI | D161473 | 123.4 | 1.2 | 1.0101 | 0.0014 |

[*] ***Please, note the ratios and associated uncertainties are dimensionless.***

The information from Table 5 was then used for regression analysis. As detailed in section 9.2, XLgenline[i] software was used to construct the regression line, initially with all participants' data considered. Both the uncertainties of the amount fractions and ratios were included, and the Generalised Distance Regression (GDR) model was applied, as default except when otherwise stated (e.g. with WLS or non-weighted regression, see below). In summary, the GDR model performs weighted data regression, considering the uncertainties of both the independent and dependent variables. The reference value calculation approach for each participant is shown in Equation 1 and Equation 2. Further, the Equation 3 function was used to construct the regression line, presented in Figure 1. For comparison, the non-weighted regression (in regard to participants' declared uncertainty) is shown in Figure 2. The regression parameters (slope and intercept for weighted or non-weighted regression) were then used to calculate the residuals (Equation 4).

**Equation 1. Individual reference ratio**

$$R_i^{ref} = \frac{A_i}{A_j^{ref}}$$

**Equation 2. Average reference ratio for single travelling standards**

$$\overline{R_i^{ref}} = \sum_1^n \frac{R_i^{ref}}{n}$$

**Equation 3. Regression function – reference ratio versus amount fraction**

$$\overline{R_i^{ref}} = f(AF_i)$$

**Equation 4. Relative residual from the individual travelling standards**

$$\Delta_i = \frac{AF_i - \widehat{AF_i}}{\widehat{AF_i}}$$

**Legend:**

$R_i^{ref}$ - reference ratio for the *i*-th travel standard obtained from:

$A_i$ - peak area of the *i*-th travel standard,

$A_j^{ref}$ - averaged peak areas of the *j* – 1 and *j*-th ref. std. measurement (bracketing standards).

$\overline{R_i^{ref}}$ - average reference ratio for the i-th travel standard, measured n-times.

$f(AF_i)$ - linear regression function of the reference ratio (dependent) *vs.* reported amount fraction $AF_i$ (independent variable).

$\Delta_i$ - Normalised residual of the reported amount fraction $AF_i$ *vs.* calculated amount fraction from the regression model $\widehat{AF_i}$.

The calculated amount fractions from the regression model ($\widehat{AF_i}$) are suggested as individual KCRV (Equation 5).

**Equation 5. Proposed individual KCRV**

$$\widehat{AF_i} = KCRV_i$$

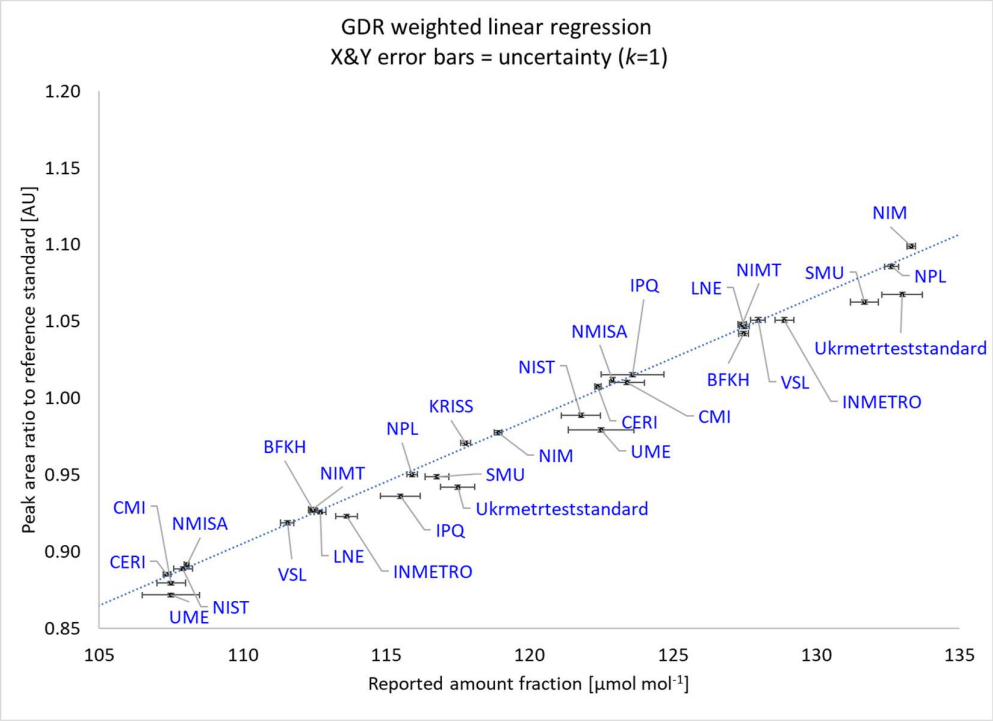



**Figure 1. Reported amount fraction *vs.* calculated peak area ratio with data from all participants (GDR weighted regression).**

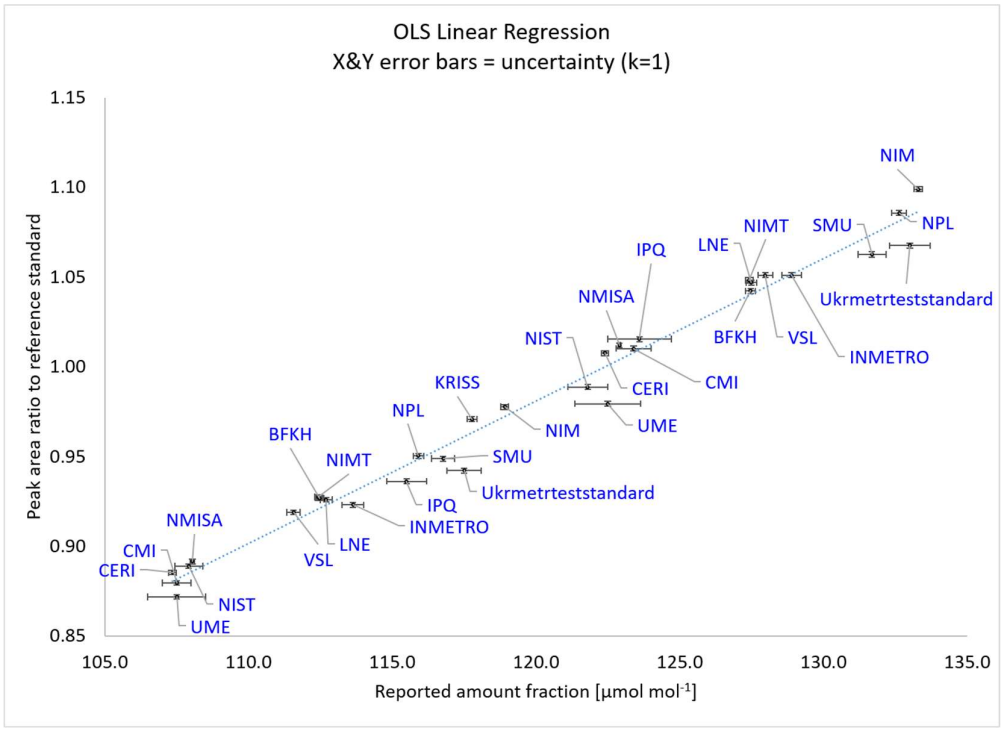



**Figure 2. Reported amount fraction vs. calculated peak area ratio with data from all participants (non-weighted regression).**

The normalised residuals were then arithmetically sorted and plotted. The data are presented in Figure 3 for weighted regression and in Figure 4 for non-weighted regression.

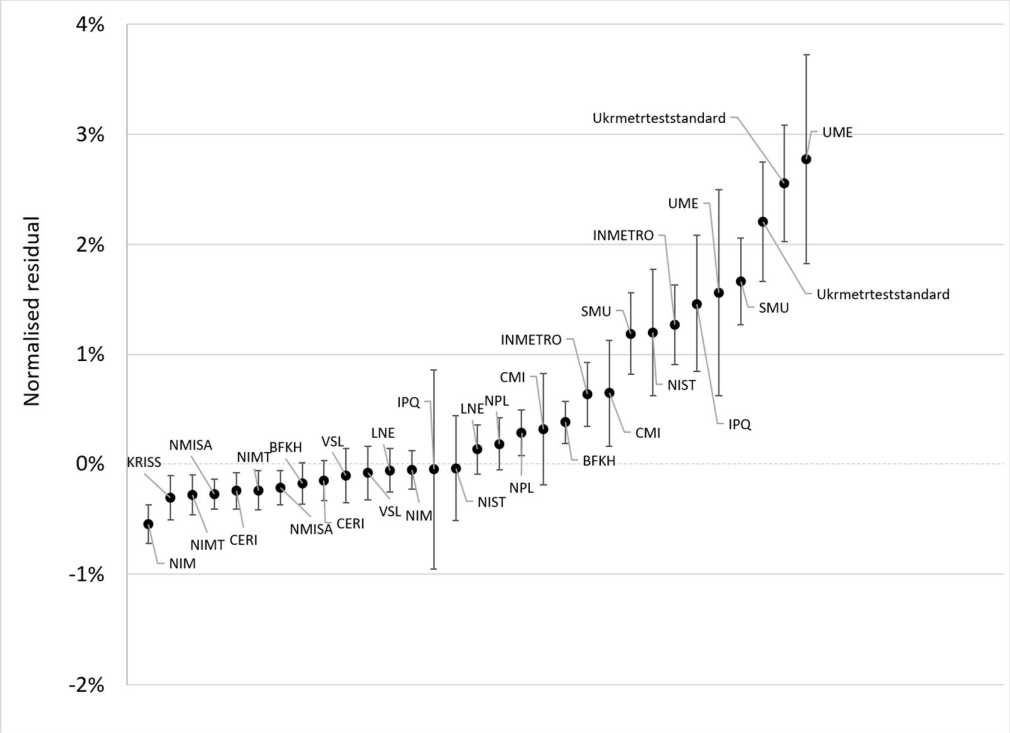


**Figure 3. Normalised residuals plot (GDR weighted regression).**

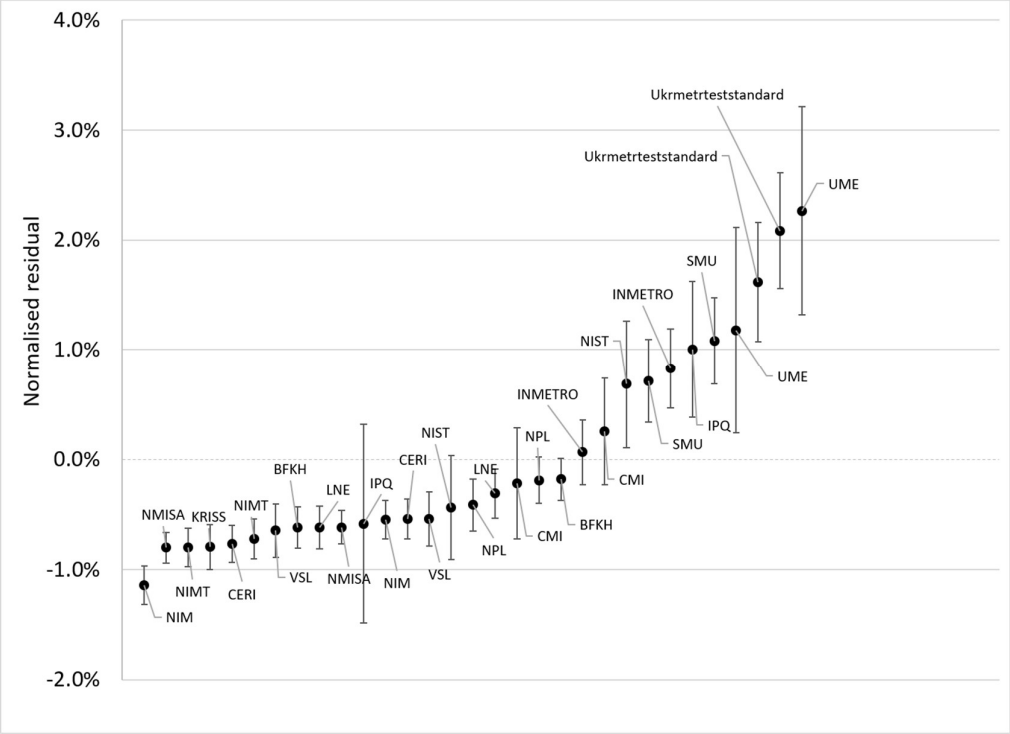



**Figure 4. Normalised residuals plot (non-weighted regression).**

To check for data consistency, Youden plots were constructed (Figure 5 and Figure 6 – weighted and non-weighted regression, respectively; error bars show combined uncertainty). The plot shows that for the majority of the cases when using weighted regression, the data points were either randomly scattered around ± 1 % of the reference value (coordinates 0:0), or along the main diagonal in quadrant 1 (that is +, + residuals plane). An exception from this trend is evident for IPQ and NIST data points. These two participants (and only them) decided to submit analytically determined amount fractions, or mathematical functions of them, for at least one of their travelling standards.

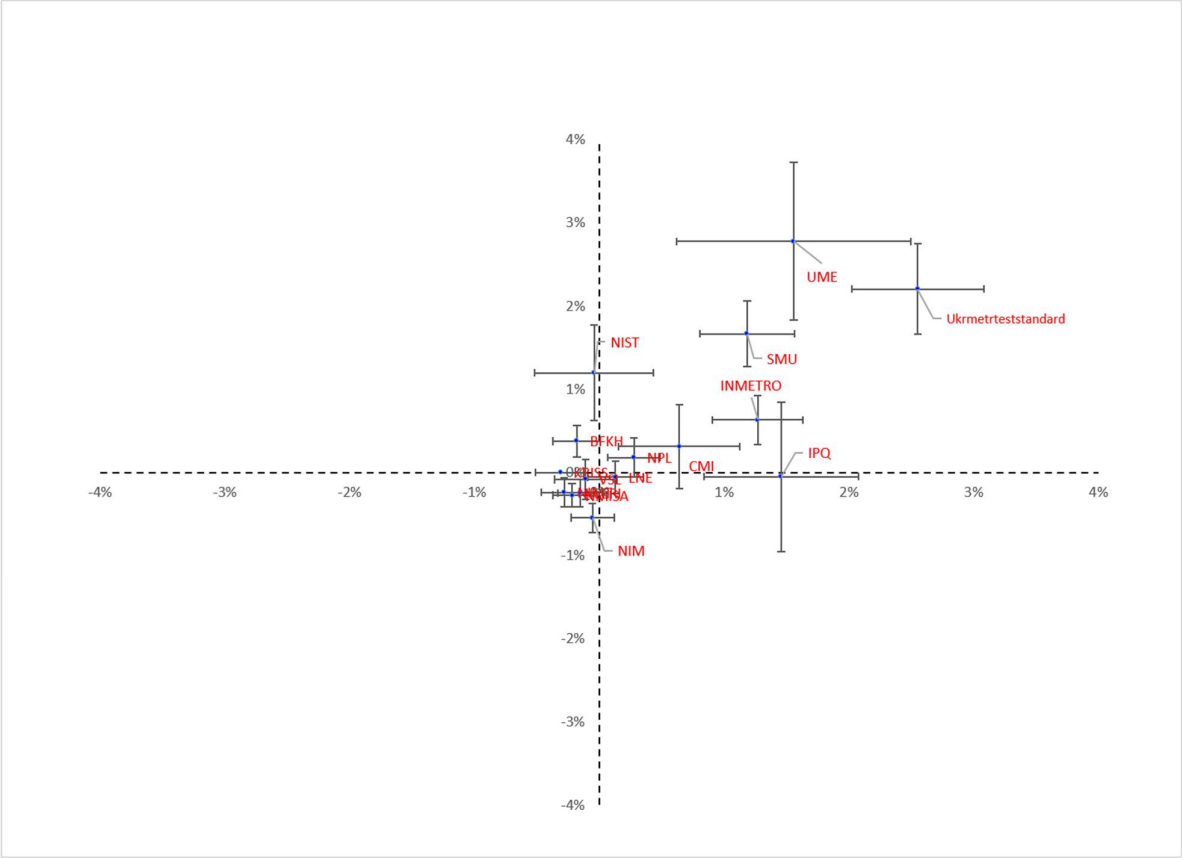



**Figure 5. Youden plot of relative residuals (GDR weighted regression).**

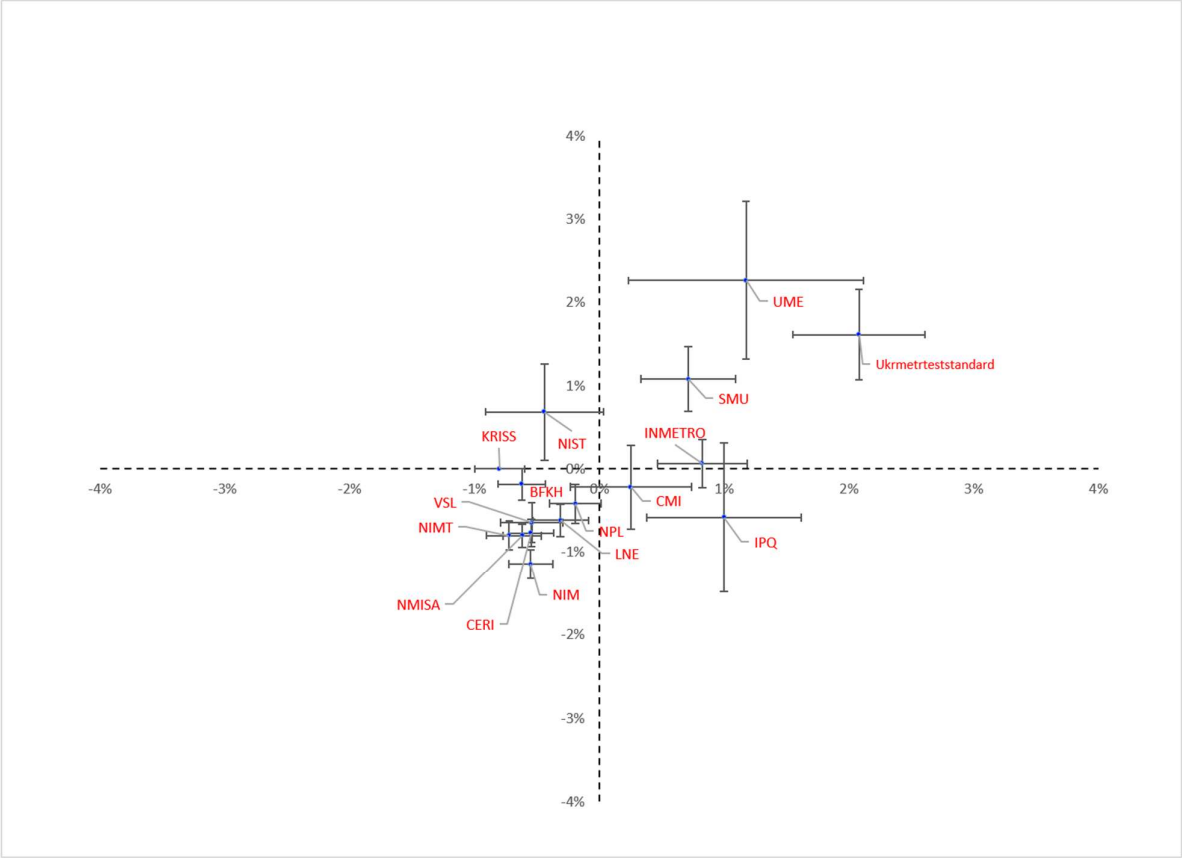



**Figure 6. Youden plot of relative residuals (non-weighted regression).**

For better visualisation, data filtered to ± 1 % relative residuals were used. Figure 7 and Figure 8 – weighted and non-weighted regression, respectively, were made (no error bars). As can be seen from Figure 8, the data are biased to negative residuals (effectively implying participants overestimated the ethanol amount fractions, or overlooked losses). In contrast, weighted regression data (Figure 7) show a more uniform spread around the 0:0 coordinates.

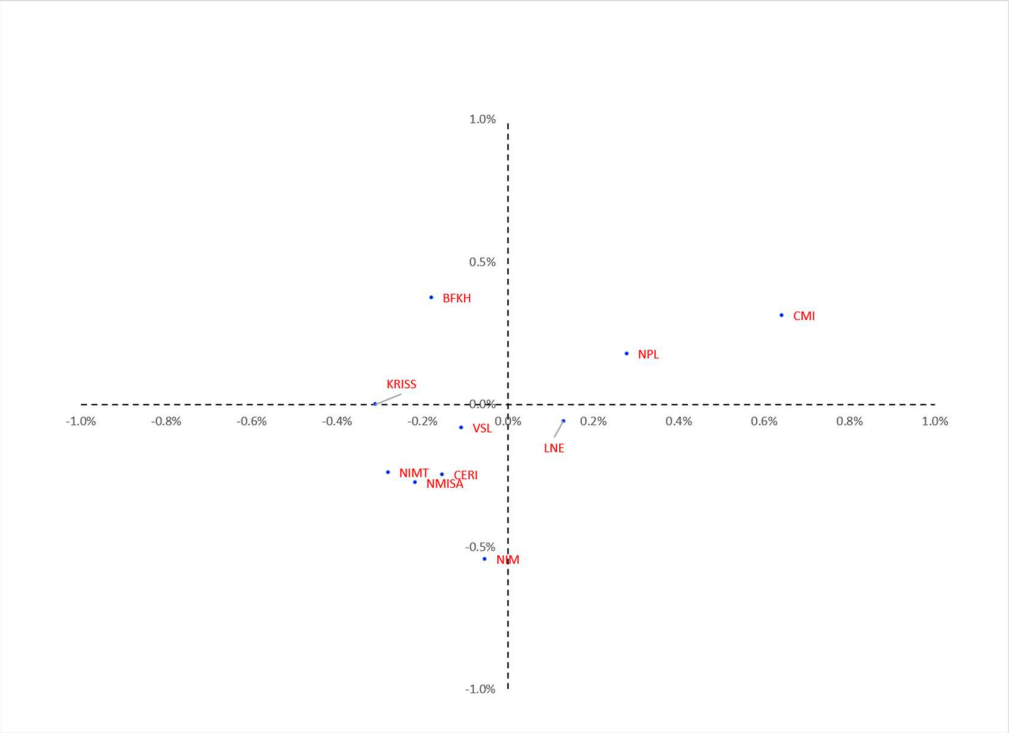



**Figure 7. Youden plot of relative residuals, limited to ± 1 % (GDR weighted regression).**

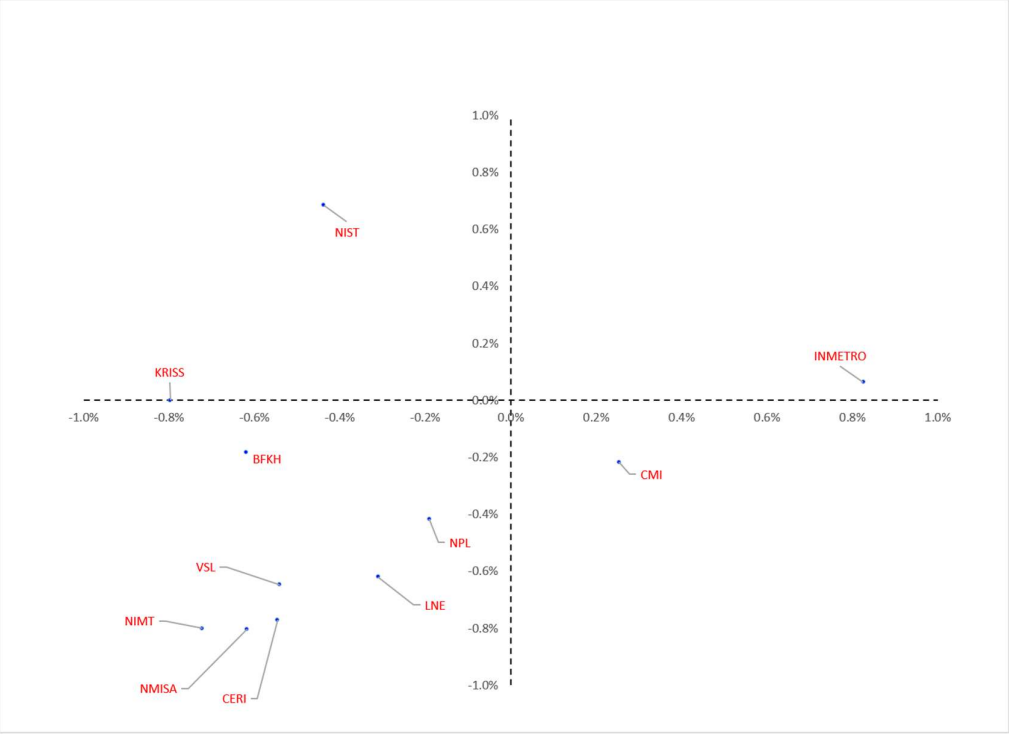



**Figure 8. Youden plot of relative residuals, limited to ± 1 % (non-weighted regression).**

These plots (Figure 7, Figure 8) can be used to select a self-consistent set of data. However, this approach might filter partially good data, e.g. when only one of the two participant's standards had a relative residual higher than the defined threshold. In that case a better decision on data consistency can be made with the help of kernel density functions against the regression residuals. A graphical representation of the Kernel density function using Scott's rule[ii] for bin size determination is presented in Figure 9 for weighted, and Figure 10 for non-weighted, regression.

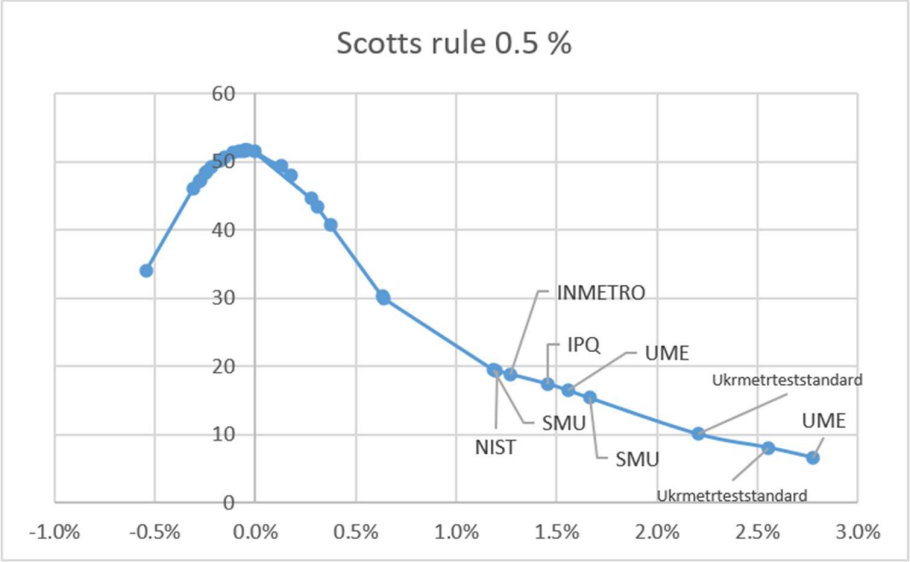



**Figure 9. Kernel density plot (Scott's rule; bandwidth 0.5 %, GDR weighted regression)**

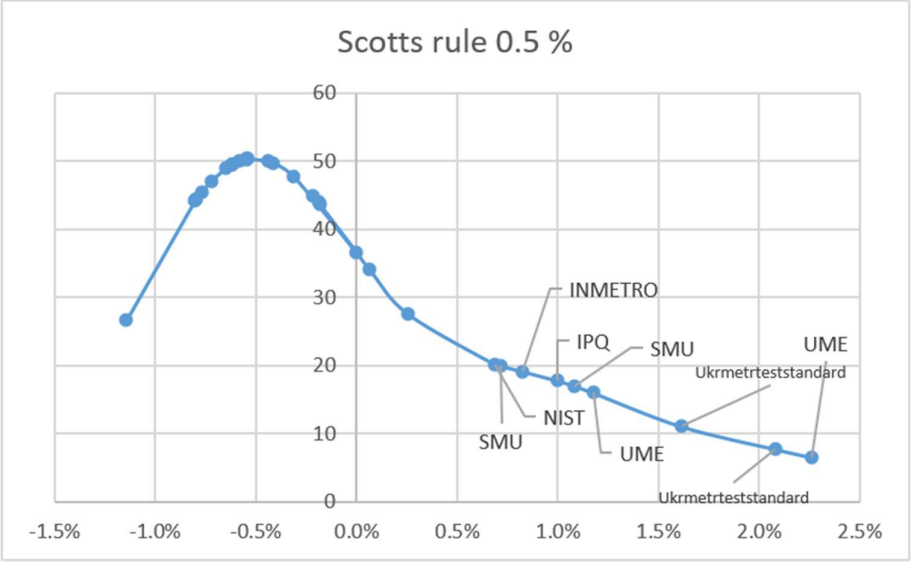



**Figure 10. Kernel density plot (Scott's rule; bandwidth 0.5 %, non-weighted regression)**

Both kernel plots based on weighted and non-weighted regression residuals identified the same travelling standards as outliers. A self-consistent data set (set of travelling standards) was then selected by excluding the identified outlier standards (Table 6, GDR regression residuals) and including all the others. Linear and quadratic fits were then tested for adequacy on the consistent data set (Annex I). Since no improvement could be demonstrated with quadratic fit, linear fit (linear regression) was chosen for data reporting.

Table 6. Outliers as identified by Kernel density plot (Figure 9).

| Participant ID | Cylinder ID | Relative residual |
|---|---|---|
| UME | D206680 | 2.78 % |
| Ukrmetrteststandard | D340107 | 2.55 % |
| Ukrmetrteststandard | D340116 | 2.20 % |
| SMU | 0695E_13 | 1.66 % |
| UME | D206683 | 1.56 % |
| IPQ | PRM208984 | 1.46 % |
| INMETRO | M692271 | 1.27 % |
| NIST | CC750296 | 1.20 % |
| SMU | 0072F_11 | 1.19 % |

The data from the set of self-consistent standards was further evaluated, using the LOO (Leave-One-Out) approach (previously applied in CCQM-K150/P189), which consists of performing weighted linear regression with all the self-consistent data set, except the data for which the reference value ($KCRV_i$) is being calculated. For a consistent dataset, removing a single result to avoid autocorrelation would have a minimal effect, as clearly illustrated in Figure 11. Based on this evidence, the participants agreed not to include a covariance term when calculating the expanded uncertainties of the degrees of equivalence, as its contribution would be negligible compared with the other uncertainty contributions (Draft A1 discussion meeting Part 2, 16 March 2026).

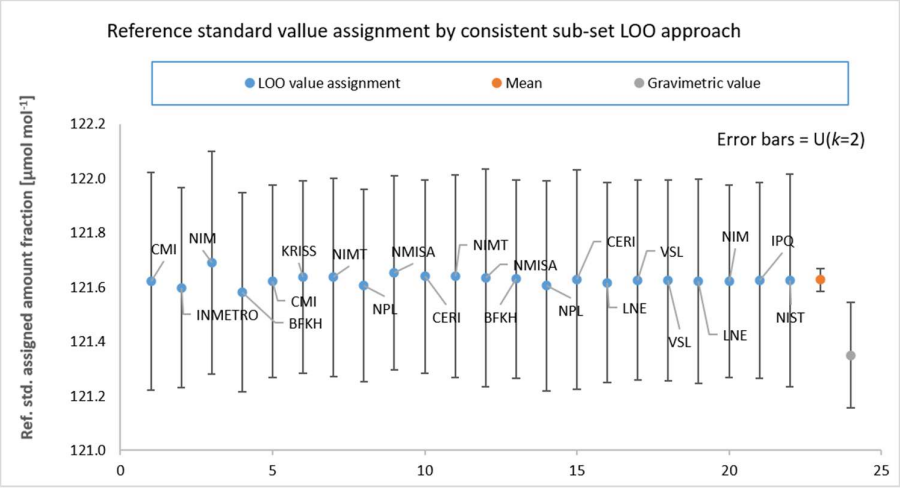



**Figure 11. Evaluation of LOO approach – Reference Standard value assignment. Each data label represents excluded standard.**

Further comparison among the regression approaches is presented on Figure 12, where the relative uncertainties of the $KCRV_i$ are shown on two scales – left ordinate: all data considered GDR regression

(yellow markers), kernel-filtered data with GDR regression (green markers), and finally kernel-filtered data with GDR regression using LOO approach (blue markers); right ordinate: all data considered, ordinary least squares regression.

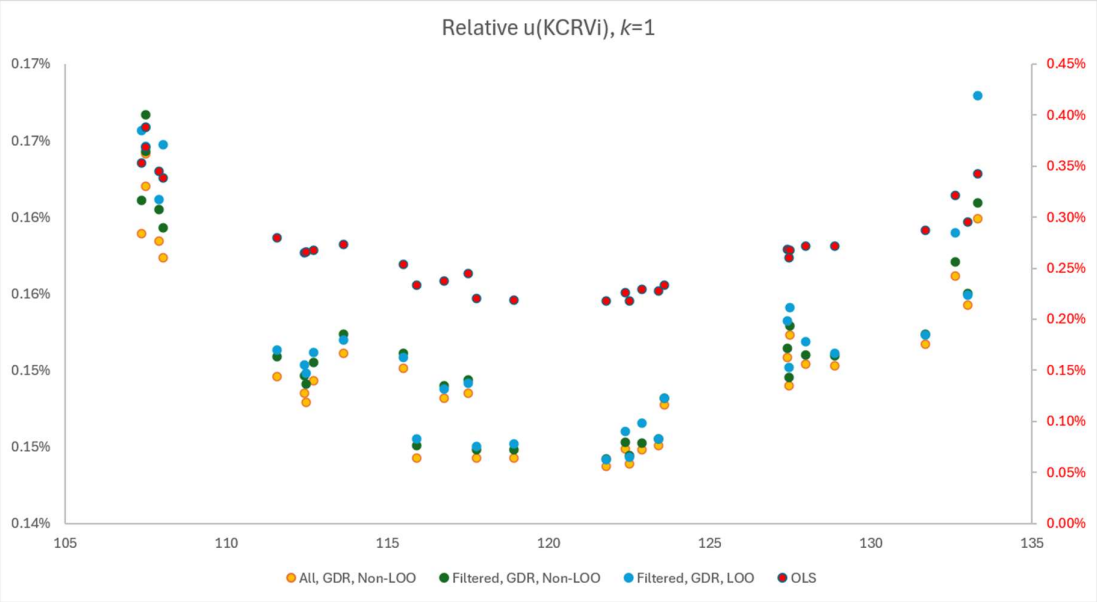



**Figure 12. KCRV$_i$ uncertainty variation with the regression approach.**

Considering the information presented in Figure 5, Figure 9, Figure 11 and Figure 12, it was decided at the Draft A1 discussion meeting Part 2 (16 March 2026) that the most appropriate approach for calculating KCRV$_i$ was to use the kernel-filtered dataset with traditional GDR regression, without applying the leave-one-out (LOO) approach. The KCRV$_i$ values, together with their respective uncertainties and relative uncertainties, calculated using this approach, are listed in

Table **7**, along with the degrees of equivalence (δ) and their respective uncertainties. A visual comparison of δ and U(δ) is given in Figure 13.

**Table 7. Individual KCRV values, obtained by GDR regression of self-consistent dataset, and Degree of Equivalence (δ).**

| Lab ID* | Cylinder ID | KCRV$_i$ [µmol mol$^{-1}$] | u(KCRV$_i$), [µmol mol$^{-1}$] | u(KCRV$_i$) % | $\delta(x_{lab}$-KCRV$_i$) | U(δ) (k=2) |
|---|---|---|---|---|---|---|
| INMETRO | M395423 | 112.08 | 0.17 | 0.15% | 1.55 | 0.83 |
| IPQ | D626508 | 113.71 | 0.17 | 0.15% | 1.79 | 1.44 |
| NIST | D153312 | 120.23 | 0.17 | 0.14% | 1.57 | 1.41 |
| SMU | D153425 | 115.27 | 0.17 | 0.15% | 1.50 | 0.89 |
| SMU | D170152 | 129.39 | 0.20 | 0.15% | 2.29 | 1.05 |
| Ukrmetrteststandard | PRM208984 | 114.45 | 0.17 | 0.15% | 3.05 | 1.25 |
| Ukrmetrteststandard | PRM203396 | 129.99 | 0.20 | 0.15% | 3.01 | 1.46 |
| UME | D094484 | 105.73 | 0.18 | 0.17% | 1.77 | 2.03 |
| UME | D094486 | 119.06 | 0.17 | 0.14% | 3.44 | 2.33 |

| | | | | | | |
|---|---|---|---|---|---|---|
| BFKH | 0695E_13 | 112.55 | 0.17 | 0.15% | -0.08 | 0.45 |
| BFKH | 0072F_11 | 126.86 | 0.19 | 0.15% | 0.61 | 0.51 |
| CERI | CPD-00087 | 107.40 | 0.17 | 0.16% | -0.04 | 0.43 |
| CERI | CPD-00088 | 122.56 | 0.18 | 0.15% | -0.17 | 0.43 |
| CMI | APE1279837 | 106.69 | 0.18 | 0.16% | 0.81 | 1.06 |
| CMI | APE1516246 | 122.88 | 0.18 | 0.15% | 0.52 | 1.25 |
| INMETRO | D340107 | 127.94 | 0.19 | 0.15% | 0.95 | 0.77 |
| IPQ | D340116 | 123.53 | 0.18 | 0.15% | 0.07 | 2.23 |
| KRISS | D206680 | 118.01 | 0.17 | 0.14% | -0.24 | 0.49 |
| LNE | D206683 | 112.43 | 0.17 | 0.15% | 0.27 | 0.52 |
| LNE | D412828 | 127.43 | 0.19 | 0.15% | 0.06 | 0.52 |
| NIM | D412846 | 118.85 | 0.17 | 0.14% | 0.07 | 0.43 |
| NIM | 200226018007 | 133.89 | 0.22 | 0.16% | -0.59 | 0.52 |
| NIMT | 200226018058 | 112.62 | 0.17 | 0.15% | -0.19 | 0.43 |
| NIMT | CC750302 | 127.59 | 0.19 | 0.15% | -0.17 | 0.48 |
| NIST | CC750296 | 107.84 | 0.17 | 0.16% | 0.08 | 1.04 |
| NMISA | M692271 | 108.16 | 0.17 | 0.16% | -0.11 | 0.38 |
| NMISA | M692275 | 123.10 | 0.18 | 0.15% | -0.21 | 0.37 |
| NPL | 3018-R1 | 115.46 | 0.17 | 0.15% | 0.45 | 0.50 |
| NPL | A668-R1 | 132.25 | 0.21 | 0.16% | 0.38 | 0.66 |
| VSL | D466362 | 111.56 | 0.17 | 0.15% | 0.00 | 0.57 |
| VSL | D161473 | 127.94 | 0.19 | 0.15% | 0.03 | 0.64 |

**** Greyed background fields are representing data for inconsistent data set of standards.***

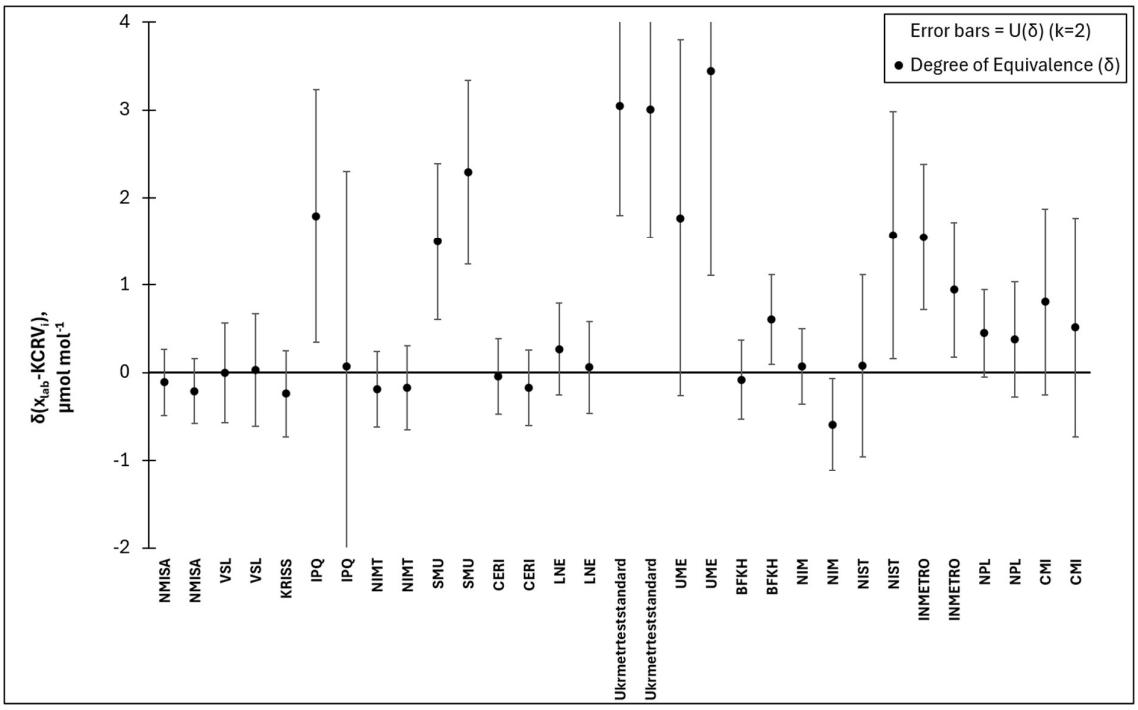



**Figure 13. A visual comparison between Degree of Equivalence (δ) and its uncertainty**

# 11. Statement "How far the light shines"

The key comparison CCQM-K93.2023 is a Track C comparison. The Comparison will underpin CMC claims for:

- Ethanol in nitrogen for travelling standards and calibrations services, over the amount fraction interval from 50 µmol mol$^{-1}$ to 1000 µmol mol$^{-1}$.
- Ethanol in synthetic air for travelling standards and calibrations services, over the amount fraction interval from 50 µmol mol$^{-1}$ to 1000 µmol mol$^{-1}$.

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# Annex I

XLGenLine output – comparison between linear and quadratic fit demonstrating no improvement with the later, comparing root mean square residual errors.

**MEASUREMENT DATA**

| x-values | u(x)-values | y-values | u(y)-values |
|---|---|---|---|
| 107.5 | 0.5 | 0.879506238 | 0.001193936 |
| 128.89 | 0.335 | 1.050976301 | 0.001417774 |
| 133.304 | 0.1465 | 1.098960228 | 0.00148554 |
| 127.47 | 0.17 | 1.042202796 | 0.001406014 |
| 123.4 | 0.6 | 1.010138983 | 0.001360675 |
| 117.77 | 0.175 | 0.970792404 | 0.001311118 |
| 112.43 | 0.135 | 0.927337726 | 0.001251876 |
| 115.91 | 0.185 | 0.95024847 | 0.00127166 |
| 122.898 | 0.0365 | 1.011919249 | 0.00135891 |
| 122.39 | 0.12 | 1.007524762 | 0.001357011 |
| 127.42 | 0.14 | 1.048115342 | 0.001424833 |
| 108.05 | 0.08 | 0.891369292 | 0.001203352 |
| 112.47 | 0.15 | 0.926732114 | 0.001244205 |
| 132.63 | 0.255 | 1.085740427 | 0.001456892 |
| 107.36 | 0.13 | 0.885234114 | 0.001191051 |
| 112.7 | 0.2 | 0.925775185 | 0.001255299 |
| 111.565 | 0.231 | 0.918787991 | 0.001234642 |
| 127.976 | 0.2565 | 1.050980853 | 0.001418679 |
| 127.49 | 0.175 | 1.046815131 | 0.001441956 |
| 118.915 | 0.131 | 0.977580902 | 0.001321789 |
| 123.6 | 1.1 | 1.015366396 | 0.001390984 |
| 107.92 | 0.325 | 0.888778313 | 0.001202811 |

**DATA FOR INVERSE EVALUATION**

| y-values | u(y)-values |
|---|---|
| 0.979301697 | 0.001320286 |
| 0.942070141 | 0.001293277 |
| 1.067500943 | 0.001452525 |
| 1.062613298 | 0.001426195 |
| 0.871736418 | 0.001175035 |
| 0.936145533 | 0.001293291 |
| 0.922974055 | 0.00126383 |
| 0.988712027 | 0.001329891 |
| 0.948747152 | 0.001306308 |

**FITTING OPTIONS**

| | |
|---|---|
| Polynomial degree(s): | 1 & 2 |
| Type of fit: | GDR |
| xmin: | |
| xmax: | |
| Tolerances | |
| Parameter values: | |
| Function values: | |
| Polynomial to pass through origin? | NO |

**RESULTS**

**POLYNOMIAL FIT: GDR, DEGREE 1**

| Results of polynomial fitting | | Results of inverse evaluation | | | |
|---|---|---|---|---|---|
| Parameter | Value | x-values | u(x)-values | y-values | u(y)-values |
| xmin: | 104.7656 | 119.0619437 | 0.171857241 | 0.979301697 | 0.001320286 |
| xmax: | 135.8984 | 114.4487134 | 0.170695539 | 0.942070141 | 0.001293277 |
| | | 129.9903995 | 0.201391885 | 1.067500943 | 0.001452525 |
| Root mean square residual error: | 1.290127359 | 129.3847887 | 0.197072908 | 1.062613298 | 0.001426195 |
| Maximum absolute weighted residual: | 2.217429248 | 105.7339113 | 0.175361615 | 0.871736418 | 0.001175035 |
| | | 113.7146163 | 0.171490202 | 0.936145533 | 0.001293291 |
| Gradient m: | 0.008070605 | 112.0825852 | 0.170338258 | 0.922974055 | 0.00126383 |
| Uncertainty associated with m: | 5.18818E-05 | 120.2279442 | 0.173294056 | 0.988712027 | 0.001329891 |
| Intercept with y-axis c: | 0.018399832 | 115.2760383 | 0.171477786 | 0.948747152 | 0.001306308 |
| Uncertainty associated with c: | 0.006165402 | | | | |
| Covariance associated with m and c: | -3.19114E-07 | | | | |
| Intercept with x-axis x0: | -2.279858016 | | | | |
| Uncertainty associated with x0 | 0.77855513 | | | | |

**POLYNOMIAL FIT: GDR, DEGREE 2**

| Results of polynomial fitting | | Results of inverse evaluation | | | |
|---|---|---|---|---|---|
| Parameter | Value | x-values | u(x)-values | y-values | u(y)-values |
| xmin: | 104.7656 | 119.1001409 | 0.182454587 | 0.979301697 | 0.001320286 |
| xmax: | 135.8984 | 114.4743102 | 0.176385824 | 0.942070141 | 0.001293277 |
| | | 129.9623478 | 0.203863493 | 1.067500943 | 0.001452525 |
| Root mean square residual error: | 1.315718935 | 129.3638862 | 0.197665755 | 1.062613298 | 0.001426195 |
| Maximum absolute weighted residual: | 2.239983445 | 105.6681379 | 0.207820955 | 0.871736418 | 0.001175035 |
| | | 113.7359455 | 0.175830103 | 0.936145533 | 0.001293291 |
| | | 112.0921833 | 0.172290263 | 0.922974055 | 0.00126383 |
| | | 120.2654713 | 0.183249287 | 0.988712027 | 0.001329891 |
| | | 115.3056968 | 0.178631437 | 0.948747152 | 0.001306308 |

# Annex II

Report form part B, as submitted by the participants. The reports below are alphabetically sorted.

# BFKH



## Participants report form, Part B

### Measurement results

| Measurements results for $C_2H_5OH$ in $N_2$ | | |
|---|---|---|
| | **Reference material 1** | **Reference material 2** |
| **Nominal amount fraction [µmol mol$^{-1}$]** | 110-115 | 125-130 |
| **Final amount fraction $\chi_{C_2H_5OH}$ [µmol mol$^{-1}$]** | 112.47 | 127.47 |
| **Expanded uncertainty $U_{\chi_{C_2H_5OH}}$ [µmol mol$^{-1}$]** | 0.30 | 0.34 |
| **Coverage factor** | 2 | 2 |

## Uncertainty budget

**Uncertainty budget of gravimetric preparation of gas mixtures**

**Cylinder number: D412828**

| Uncertainty source | Estimate $x_i$ | Standard uncertainty $u(x_i)$ |
|---|---|---|
| Purity of ethanol | 99.95 % (mol/mol) | 0.03 % (mol/mol) |
| Mass of the loop | 15.38064 g | 0.000035 g |
| Ethanol + mass of the loop | 15.531895 g | 0.000035 g |
| Mass of the cylinder, before filling | 8277,515 g | 0.0111 g |
| Mass of the cylinder, after filling | 9095.8461 g | 0.0111 g |
| u | | 0.050 µmol/mol |

**Uncertainty of measurement**

| Uncertainty source | Estimate $x_i$ | Contribution to standard uncertainty $u(x_i)$ | Standard uncertainty $u(x_i)$ |
|---|---|---|---|
| Calibration gas | 119.487 µmol/mol | 0.0005105 | 0.061 µmol/mol |
| GC measurement* | 112.466 µmol/mol | 0.0011381 | 0.128 µmol/mol |
| u | | | 0.142 µmol/mol |

*GC measurement: During the measurement, the calibration gas and the measured gas were measured alternately A-B-A-B-... During each measurement A or B, 11 samples were taken.
The baseline was continuously monotonically decreasing during the measurement. Separate linear curves were fitted to the areas of sample A and B and the areas calculated for the same time points were divided. The resulting area ratios were used to calculate standard deviations.

**Cylinder number: D412846**

| Uncertainty source | Estimate $x_i$ | Standard uncertainty $u(x_i)$ |
|---|---|---|
| Purity of ethanol | 99.95 % (mol/mol) | 0,03 % (mol/mol) |
| Mass of the loop | 15.38058 g | 0.000035 g |
| Ethanol + mass of the loop | 15.541012 g | 0.000035 g |
| Mass of the cylinder, before filling | 8264.601 g | 0.0111 g |
| Mass of the cylinder, after filling | 9030.4838 g | 0.0111 g |
| u | | 0.055 µmol/mol |

**Uncertainty of measurement**

| Uncertainty source | Estimate $x_i$ | Contribution to standard uncertainty $u(x_i)$ | Standard uncertainty $u(x_i)$ |
|---|---|---|---|
| Calibration gas | 119.487 µmol/mol | 0.0005775 | 0.069 µmol/mol |
| GC measurement* | 127.465 µmol/mol | 0.0011454 | 0.146 µmol/mol |
| u | | | 0.161 µmol/mol |

*GC measurement: During the measurement, the calibration gas and the measured gas were measured alternately A-B-A-B-... During each measurement A or B, 11 samples were taken.
The baseline was continuously monotonically decreasing during the measurement. Separate linear curves were fitted to the areas of sample A and B and the areas calculated for the same time points were divided. The resulting area ratios were used to calculate standard deviations.

## Uncertainty budget

**Please provide below the uncertainty budget used to calculate the uncertainty associated with the measurement of the ethanol amount fraction.**

**Final Results**

**The results are presented in following table with date:**

$x_{prep}$ **amount of substance fraction, from preparation**

$u_{prep}$ **uncertainty of $x_{prep}$**

$x_{ver}$ **result from verification**

$u_{ver}$ **uncertainty from verification**

**x final result**

$u_{cert}$ **final uncertainty of x**

**U(k=2) stated uncertainty of x**

| Cylinder number | $x_{prep}$ µmol/mol | $u_{prep}$ µmol/mol | $x_{ver}$ µmol/mol | $u_{ver}$ µmol/mol | $u_{cert}$ µmol/mol | $x_{ver}$- $x_{prep}$ µmol/mol | X µmol/mol | U(k=2) µmol/mol |
|---|---|---|---|---|---|---|---|---|
| D412828 | 112.47 | 0.050 | 112.466 | 0.142 | 0.150 | 0.00 | 112.47 | 0.30 |
| D412846 | 127.47 | 0.055 | 127.465 | 0.161 | 0.170 | 0.01 | 127.47 | 0.34 |

## Measurement procedure

**Please provide below a description of the measurements performed for the validation of the submitted gravimetric values obtained from the preparation, and calibrants and analysers details.**

**Verification analysis**
**Comparison method used for verification.**
**The prepared reference gas mixtures were measured against BFKH's standard.**
**BFKH's standard: Ethanol: 119.487 ± 0,130 ppm(mol/mol), measured NPL in 2011.**
**Cylinder number: OMH 138 (MKEH).**
**The verification was done using GC-FID.**

**The method used an Agilent 7890B x**

**GC measurement: During the measurement, the calibration gas and the gas to be measured were measured alternately A-B-A-B-... During each measurement A or B, 11 samples were taken.**
**The baseline was continuously monotonically decreasing during the measurement. Separate lines were fitted to the areas of sample A and B and the areas calculated for the same time points were divided. The resulting area ratios were used to calculate standard deviations.**

## Additional information

Please include in this section the following information:

- **Purity table** with uncertainties for all the parent gases, including < LOQ flags with the respective LOQ values for the impurities. Specify uncertainty distribution (Gaussian, rectangular etc.)
- Brief outline of the **dilution series** undertaken to produce the final mixtures
- Purity table for each of the final mixtures, including uncertainties, as above
- Brief outline of the validation **procedure applied to the final mixtures**
- Brief outline of any stability testing and correction procedures for the two reference materials between the time they were prepared and the time they were measured at NPL (NPL will provide the date of measurement to each participant for each reference material on measurement completion).

1. Source of EtOH

   Supelco, 1.00983, Ethanol absolute for analysis EMSURE ACS,ISO,Reag. Ph Eur

   Purity table for nominally pure EtOH

| Component | Method | Mole fraction (mol/mol) | Distribution | Uncertainty (mol/mol) |
|---|---|---|---|---|
| $C_2H_5OH$ | Specification | 0.9995 | Rectangular | 0.0006 |
| $H_2O$ | Specification | 0.0005 | Rectangular | 0.00058 |

2. Source of $N_2$ (4.5), Messer

   Purity table for nominally pure $N_2$

| Component | Method | Mole fraction (mol/mol) | Distribution | Uncertainty (mol/mol) |
|---|---|---|---|---|
| $N_2$ | Specification | 0.999975 | Rectangular | 0.000029 |
| $O_2$ | Specification | 0.000005 | Rectangular | 0.000006 |
| $H_2O$ | Specification | 0.000005 | Rectangular | 0.000006 |
| $C_nH_m + CO_2$ | Specification | 0.0000025 | Rectangular | 0.0000029 |
| CO | Specification | 0.0000005 | Rectangular | 0.0000006 |

3. Preparation method - Following evacuation of the cylinder, ethanol was added from a glass loop. Nitrogen was then added directly to the cylinder.

Gravimetric preparation

The gas standards were prepared gravimetrically through one step dilution. We used two balances. One was used for weighing of aluminium alloy cylinder, the other was used for weighing of glass loop.

Specification of balance for cylinder

Mettler Toledo, XP26003L, Capacity: 26.1 kg, Uncertainty (k=2): 0.022 g,

Specification of balance for glass loop

Mettler Toledo, AE 163, Capacity: 30 g, Uncertainty (k=2): 0.00007 g,

Weighing method for cylinders

A-B-A-B substitution method was used for cylinders. A is a tare cylinder and B is K93 cylinder.

Weighing method for glass loop

A-B-A-B substitution method was used for glass loop. A is a tare glass and B is glass loop.

## Additional information

**Please include in this section the following information:**

- **Purity table with uncertainties for all the parent gases, including < LOQ flags with the respective LOQ values for the impurities. Specify uncertainty distribution (Gaussian, rectangular etc.)**
- **Brief outline of the dilution series undertaken to produce the final mixtures**
- **Purity table for each of the final mixtures, including uncertainties, as above**
- **Brief outline of the validation procedure applied to the final mixtures**
- **Brief outline of any stability testing and correction procedures for the two reference materials between the time they were prepared and the time they were measured at NPL (NPL will provide the date of measurement to each participant for each reference material on measurement completion).**

4. **Purity table for final mixtures**

**Cylinder number: D412828**

| Component | Mole fraction (mol/mol) | Distribution | Uncertainty (mol/mol) |
|---|---|---|---|
| $C_2H_5OH$ | 0.00011247 | Rectangular | 0.00000010 |
| $N_2$ | 0.999875 | Rectangular | 0.000029 |
| $O_2$ | 0.000005 | Rectangular | 0.000006 |
| $H_2O$ | 0.000005 | Rectangular | 0.000006 |
| $C_nH_m + CO_2$ | 0.0000025 | Rectangular | 0.0000029 |
| CO | 0.0000005 | Rectangular | 0.0000006 |

**Cylinder number: D412846**

| Component | Mole fraction (mol/mol) | Distribution | Uncertainty (mol/mol) |
|---|---|---|---|
| $C_2H_5OH$ | 0.00012747 | Rectangular | 0.00000011 |
| $N_2$ | 0.999859 | Rectangular | 0.000029 |
| $O_2$ | 0.000005 | Rectangular | 0.000006 |
| $H_2O$ | 0.000005 | Rectangular | 0.000006 |
| $C_nH_m + CO_2$ | 0.0000025 | Rectangular | 0.0000029 |
| CO | 0.0000005 | Rectangular | 0.0000006 |

## Shipping instructions for CCQM-K93.2023 comparison

**TBC**

**BFKH contact:** **Judit Fuko**
**Tel:** **+3614585988**
**Email:** **fuko.judit@bfkh.gov.hu**

**BFKH Address:** **BFKH MMFF SKMO**
**Nemetvolgyi ut 37-39. C/107.**
**XII. Budapest**
**1124 Hungary**

CERI

# Participants report form, Part B

## Measurement results

**Please indicate below the final value and associated expanded uncertainty of the $C_2H_5OH$ amount fraction in each of the two reference materials.**

| **Measurements results for $C_2H_5OH$ in $N_2$** | | |
|---|---|---|
| | **Travelling standard 1** | **Travelling standard 2** |
| **Nominal amount fraction [µmol mol$^{-1}$]** | 107.36 µmol mol$^{-1}$ | 122.39 µmol mol$^{-1}$ |
| **Final amount fraction $\chi_{C_2H_5OH}$ [µmol mol$^{-1}$]** | 107.36 µmol mol$^{-1}$ | 122.39 µmol mol$^{-1}$ |
| **Expanded uncertainty $U_{\chi_{C_2H_5OH}}$ [µmol mol$^{-1}$]** | 0.26 µmol mol$^{-1}$ | 0.24 µmol mol$^{-1}$ |
| **Coverage factor** | $k$=2 | $k$=2 |

## Gravimetric preparation and purity

- **Statement whether the reported values are true gravimetric values, based on the masses and purities of the components added, or they have been determined and/or corrected by analysis.**

Our report values are true gravimetric values, based on the masses and purities of the components added.

- **Purity table with uncertainties for all the parent gases, including < LOQ flags with the respective LOQ values for the impurities. Specify uncertainty distribution (Gaussian, rectangular etc.)**

Nitrogen

Purity of nitrogen: 0.9999993 mol/mol

Impurities in nitrogen:

| Component | Amount fraction µmol/mol | Uncertainty µmol/mol | Assumed distribution |
|---|---|---|---|
| Carbon monoxide[1)] | Under 0.003 | 0.0017 | Rectangle |
| Carbon dioxide[1)] | Under 0.003 | 0.0017 | Rectangle |
| Methane[1)] | Under 0.004 | 0.0023 | Rectangle |
| Nitrogen oxide[1)] | Under 0.002 | 0.0012 | Rectangle |
| Sulfur Dioxide[1)] | Under 0.002 | 0.0012 | Rectangle |
| Hydrogen[2)] | Under 0.05 | 0.0029 | Rectangle |
| Oxygen[2)] | Under 0.05 | 0.0029 | Rectangle |
| Total Hydrocarbon[2)] | Under 0.05 | 0.0029 | Rectangle |
| Water[2)] | Under 0.5 | 0.29 | Rectangle |

1): These components were measured by CERI.

2): These components were measured by a gas manufacture.

Ethanol

CERI used a NMIJ CRM.

| Component | Amount fraction | Uncertainty ($k$=2) | Assumed distribution |
|---|---|---|---|
| Ethanol | 0.999 mol/mol | 0.001 mol/mol | Normal |

Impurities in the ethanol were water 108 µg/g and acetaldehyde 2 µg/g.

- **Brief outline of the dilution series undertaken to produce the final traveling standard**

The gas standards were prepared gravimetrically through one step dilution according to ISO6142-1. CERI used two balances. One was used for weighing of 10L aluminium alloy cylinder, the other was used for weighing of 250mL stainless steel vessel which contained ethanol. The mass of the ethanol filled into the cylinder was calculated from the mass of the vessel before and after the preparation of gas standard.

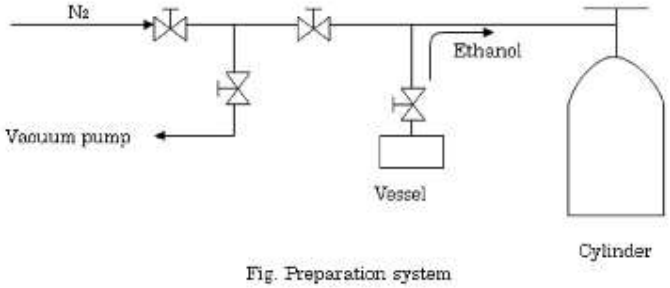



Fig. Preparation system

Specification of Balance for cylinders

Model No.: Chyo Balance Corporation

Resolution: 1 mg, Capacity: 30 kg

Uncertainty ($k$=2): 0.004022 g

Specification of Balance for stainless steel vessels

Model No.: Mettler-Toledo Model AX1005 comparator

Resolution: 0.01 mg, Capacity: 1 kg

Uncertainty ($k$=2): $6.914\times10^{-5}$ g

Weighing method for cylinders

A-B-A-B substitution method was used for cylinders. A is a K93 cylinder and B is a tare cylinder.

Weighing method for vessels

A'-B'-A'-B'-A'-B'-A'-B' substitution method was used for vessels. A' is a vessel contained ethanol and B' is a tare vessel.

Difference mass between the K93 cylinder and the tare cylinder before preparation: 5.392 g

Difference mass between the K93 cylinder and the tare cylinder after preparation: 1176.810 g

Difference mass between the vessel and the tare vessel before preparation: 20.0413583 g

Difference mass between the vessel and the tare vessel after preparation: 19.8053705 g

- **Purity table for each of the final travelling standard, including uncertainties, as above**

Amount fractions range 105-110 µmol mol$^{-1}$

**Travelling standard 1**

CPD-00087

| Component | Amount fraction µmol mol$^{-1}$ | Uncertainty µmol mol$^{-1}$ | Assumed distribution |
|---|---|---|---|
| Carbon monoxide | Under 0.003 | 0.0017 | Rectangle |
| Carbon dioxide | Under 0.003 | 0.0017 | Rectangle |
| Methane | Under 0.004 | 0.0023 | Rectangle |
| Nitrogen oxide | Under 0.002 | 0.0012 | Rectangle |
| Sulfur Dioxide | Under 0.002 | 0.0012 | Rectangle |
| Hydrogen | Under 0.05 | 0.0029 | Rectangle |
| Oxygen | Under 0.05 | 0.0029 | Rectangle |
| Total Hydrocarbon | Under 0.05 | 0.0029 | Rectangle |
| Water | Under 0.5 | 0.29 | Rectangle |
| Ethanol | 107.36 | 0.26 | Normal |
| Nitrogen | Balance | - | - |

Amount fractions range 120-125 µmol mol$^{-1}$

**Travelling standard 2**

CPD-00088

| Component | Amount fraction µmol mol$^{-1}$ | Uncertainty µmol mol$^{-1}$ | Assumed distribution |
|---|---|---|---|
| Carbon monoxide | Under 0.003 | 0.0017 | Rectangle |
| Carbon dioxide | Under 0.003 | 0.0017 | Rectangle |
| Methane | Under 0.004 | 0.0023 | Rectangle |
| Nitrogen oxide | Under 0.002 | 0.0012 | Rectangle |
| Sulfur Dioxide | Under 0.002 | 0.0012 | Rectangle |
| Hydrogen | Under 0.05 | 0.0029 | Rectangle |
| Oxygen | Under 0.05 | 0.0029 | Rectangle |
| Total Hydrocarbon | Under 0.05 | 0.0029 | Rectangle |
| Water | Under 0.5 | 0.29 | Rectangle |
| Ethanol | 122.39 | 0.24 | Normal |
| Nitroegn | Balance | - | - |

## Measurement procedure

- **Description of the measurements performed for the validation of the submitted gravimetric values, obtained from the preparation**
- **Calibrants and analysers details.**

Analyser: MeXA-1170HFID (Heated Type THC Analyzer) made by HORIBA

Gas standards, approximately 105 µmol mol$^{-1}$ and 125 µmol mol$^{-1}$, for calibration were prepared with the same procedure as shipped gas standards for NPL at the same time. The analyser was calibrated with these gas standards.

The shipped gas standards were evaluated with 11 set of measurement for 3-days before shipped for NPL.

1 set of measurement is shown below.

Gas standard 125 µmol mol$^{-1}$→CPD-00088→CPD-00087→Gas standard 105 µmol mol$^{-1}$

After cylinders were shipped back to CERI, we evaluated them with re-prepared(fresh) gas standards, approximately 105 µmol mol$^{-1}$ and 125 µmol mol$^{-1}$. The shipped backed cylinders were evaluated with 11 set of measurement in 3-days. 1 set of measurement is same as shown previously.

Uncertainty of repeatability (11 set of measurement) is 0.02945 µmol mol$^{-1}$.

## Uncertainty budget

**Please provide below the uncertainty budget used to calculate the uncertainty associated with the measurement of the ethanol amount fraction.**

**Gravimetric value**

| Uncertainty source | Standard uncertainty | | Assumed distribution | Divisor | Standard uncertainty | | Sensitivity factor | | Contribution to standard uncertaintv | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | U(x$_i$) | | \|c$_i$\| | | U(x$_i$)×\|c$_i$\| = u(y$_i$) | |
| Purity of ethanol | 0.001 | mol mol$^{-1}$ | Normal | 2 | 0.0005 | mol mol$^{-1}$ | 0.0001225 | | 6.125E-08 | |
| Mass of the vessel, before filling | 6.914E-05 | g | Normal | 2 | 3.457E-05 | g | 0.0005187 | g$^{-1}$ | 1.793E-08 | |
| Mass of the cylinder, after filling | 6.914E-05 | g | Normal | 2 | 3.457E-05 | g | 0.0005187 | g$^{-1}$ | 1.793E-08 | |
| Mass of the cylinder, before filling | 0.007194 | g | Normal | 2 | 0.003597 | g | 1.045E-07 | g$^{-1}$ | 3.759E-10 | |
| Mass of the cylinder, after filling | 0.06142 | g | Normal | 2 | 0.03071 | g | 1.045E-07 | g$^{-1}$ | 3.209E-09 | |
| Molar mass of ethanol | 0.00118 | g mol$^{-1}$ | Normal | 2 | 0.00059 | g mol$^{-1}$ | 2.656E-06 | mol g$^{-1}$ | 1.567E-09 | |
| Molar mass of nitrogen | 0.00028 | g mol$^{-1}$ | Normal | 2 | 0.00014 | g mol$^{-1}$ | 4.368E-06 | mol g$^{-1}$ | 6.115E-10 | |
| Impurities in nitrogen | 2.9E-07 | mol mol$^{-1}$ | Normal | 2 | 1.45E-07 | mol mol$^{-1}$ | 0.0001224 | mol mol$^{-1}$ | 1.775E-11 | |
| | | | | | | | Combined uncertainty | | 6.639E-08 | mol mol$^{-1}$ |
| | | | | | | | | | 0.06639 | µmol mol$^{-1}$ |

**Travelling standard 1**

CPD-00087

| Uncertainty source | Standard uncertainty | | Assumed distribution | Divisor | Standard uncertainty U(x$_i$) | |
|---|---|---|---|---|---|---|
| Gravimetoric value | 0.06639 | µmol mol$^{-1}$ | - | 1 | 0.06639 | µmol mol$^{-1}$ |
| Stability | 0.05 | µmol mol$^{-1}$ | - | 1 | 0.05 | µmol mol$^{-1}$ |
| Verification (repeatability) | 0.02945 | µmol mol$^{-1}$ | - | 1 | 0.02945 | µmol mol$^{-1}$ |
| Verification (gas standard1) | 0.06639 | µmol mol$^{-1}$ | - | 1 | 0.06639 | µmol mol$^{-1}$ |
| Verification (gas standard2) | 0.06639 | µmol mol$^{-1}$ | - | 1 | 0.06639 | µmol mol$^{-1}$ |

Final amount fraction: 107.36 µmol mol$^{-1}$

Combined uncertainty: 0.1288 µmol mol$^{-1}$

Expanded uncertainty: 0.26 µmol mol$^{-1}$

**Travelling standard 2**

CPD-00088

| Uncertainty source | Standard uncertainty | | Assumed distribution | Divisor | Standard uncertainty U(x$_i$) | |
|---|---|---|---|---|---|---|
| Gravimetoric value | 0.06639 | µmol mol$^{-1}$ | - | 1 | 0.06639 | µmol mol$^{-1}$ |
| Stability | 0.02 | µmol mol$^{-1}$ | - | 1 | 0.02 | µmol mol$^{-1}$ |
| Verification (repeatability) | 0.02945 | µmol mol$^{-1}$ | - | 1 | 0.02945 | µmol mol$^{-1}$ |
| Verification (gas standard1) | 0.06639 | µmol mol$^{-1}$ | - | 1 | 0.06639 | µmol mol$^{-1}$ |
| Verification (gas standard2) | 0.06639 | µmol mol$^{-1}$ | - | 1 | 0.06639 | µmol mol$^{-1}$ |

Final amount fraction: 122.39 µmol mol$^{-1}$

Combined uncertainty: 0.1204 µmol mol$^{-1}$

Expanded uncertainty: 0.24 µmol mol$^{-1}$

## Additional information

**Please include in this section a brief outline of any stability testing (including sorption effects investigation, if performed) and correction procedures for the two travelling standards between the time they were prepared and the time they were measured at NPL (NPL will provide the date of measurement to each participant for each travelling standard on measurement completion)**

Gas standards, approximately 105 µmol mol$^{-1}$ and 125 µmol mol$^{-1}$, for calibration were prepared with the same procedure as shipped gas standards for NPL at the same time. The analyser is calibrated with these gas standards.

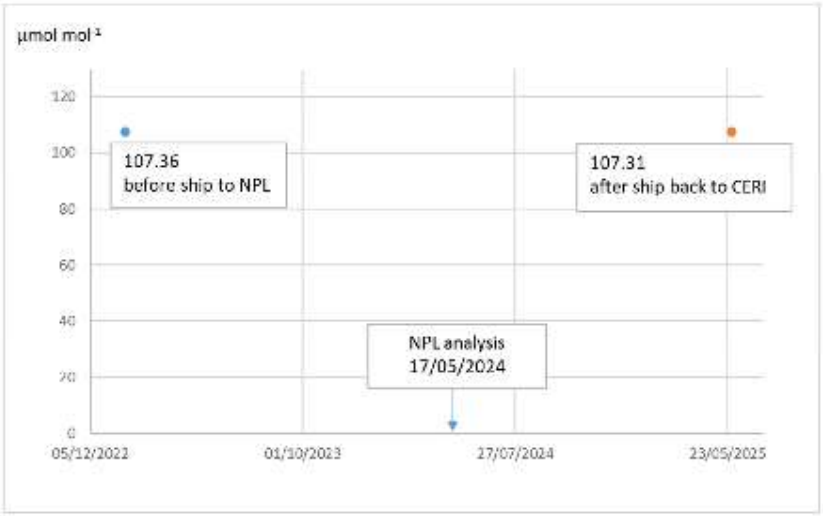
The shipped gas standards were evaluated with 11 set of measurement in 3days before shipped for NPL.

1 set of measurement is shown below.

Gas standard 125 µmol mol$^{-1}$→CPD-00088→CPD-00087→Gas standard 105 µmol mol$^{-1}$

After the cylinders were shipped back to CERI, we evaluated them with re-prepared(fresh) gas standards, about 105 µmol mol-1 and 125 µmol mol$^{-1}$. The shipped backed cylinders were evaluated with 11 set of measurement in 3-days. 1 set of measurement is same as shown previously.

| Nominal mole fraction / µmol mol$^{-1}$ | Gravimetric value $x$(C2H5OH) / µmol mol$^{-1}$ (18-19/12/2023) | Measured value before ship to NPL $x$(C2H5OH) / µmol mol$^{-1}$ (20/12/2023～24/01/2024) | Measured value after ship back to CERI x(C2H5OH) / µmol mol-1 (26-28/05/2025) |
|---|---|---|---|
| 105-110 | 107.36 | 107.36 | 107.31 |
| 120-125 | 122.39 | 122.37 | 122.37 |







**The evaluation for before shipment has done with immediately after preparation and just before shipped for NPL in case of poor stability of the cylinders. But in the end, any obvious concentration change of the shipped gas standards haven't observed. Then we decided not to correct gravimetric values. Then, our report values are true gravimetric values, based on the masses and purities of the components added.**

CCQM-K93.2023 19/12/2022

The difference of the gravimetric value and measured value after ship back to CERI was estimated as uncertainty of stability.

CERI Participants List:

Mr. Dai Akima, Ms. Tomoe Nishino and Mr. Shuhei Nakajima

# Participants report form, Part B

## Measurement results

**Please indicate below the final value and associated expanded uncertainty of the $C_2H_5OH$ amount fraction in each of the two travelling standards.**

| **Measurements results for $C_2H_5OH$ in $N_2$** | | |
|---|---|---|
| | **Travelling standard 1** | **Travelling standard 2** |
| **Nominal amount fraction [µmol mol$^{-1}$]** | **107** | **123** |
| **Final amount fraction $\chi_{C_2H_5OH}$ [µmol mol$^{-1}$]** | **107,5** | **123,4** |
| **Expanded uncertainty $U_{\chi_{C_2H_5OH}}$ [µmol mol$^{-1}$]** | **1,0** | **1,2** |
| **Coverage factor** | **2** | **2** |

## Gravimetric preparation and purity

Please provide below the following information:

- Statement whether the reported values are true gravimetric values, based on the masses and purities of the components added, or they have been determined and/or corrected by analysis.
- Details on the correction procedure, if applicable.
- Purity table with uncertainties for all the parent gases, including < LOQ flags with the respective LOQ values for the impurities. Specify uncertainty distribution (Gaussian, rectangular etc.)
- Brief outline of the dilution series undertaken to produce the final travelling standard
- Purity table for each of the final travelling standard, including uncertainties, as above

- The reported values are true gravimetric values, based on the masses of components added.
- Purity table for parent gases (liquid):

| | Purity (%) | Uncertainty (%) |
|---|---|---|
| Ethanol | 99,8 | 0,001 |
| Nitrogen | 99,996 | 2,5E-5 |

The liquid ethanol was injected directly to the cylinders a then diluted by nitrogen. There was no further dilution needed.

True concertation based on gravimetric:

| Serial number of cylinder | Concentration [µmol/mol] | Uncertainty [µmol/mol] |
|---|---|---|
| D466362 | 107,0 | 0,2 |
| D161473 | 123,1 | 0,2 |

## Measurement procedure

Please provide below:

- Description of the measurements performed for the validation of the submitted gravimetric values, obtained from the preparation
- Calibrants and analysers details.

The analysis of gas mixture was carried out by GC-FID. The column was Rt-U-BOND (Restek) 30 m, 0,53 mm ID, 20 µm df (polar column incorporating DVB ethylene glycol-dimethylacrylate polymer). Injection to column was done by 1 ml loop through gas liner (1 mm inner diameter). All sampling lines in GC were heated at 100 °C. Owen temperature program was isotherm at 150 °C. Whole temperature program took 1,8 min.

Calibration method and value assignment

Four points calibration curves were prepared for each compound. Used formulae for calculation of compositions of PRM.

$$y_k = \frac{\sum_{j=1}^{r}\left(\frac{x_{k,j}\cdot m_j}{\sum_{i=1}^{q} x_{i,j}\cdot M_i}\right)}{\sum_{j=1}^{r}\left(\frac{m_j}{\sum_{i=1}^{q} x_{i,j}\cdot M_i}\right)}$$

Where:

- $y_k$ is amount of substance fraction of component $k$ in the prepared mixture
- $x_{k,j}$ is amount of substance fraction of component $k$ in parent gas or liquid $j$
- $m_j$ is mass added of parent gas or liquid $j$
- $x_{i,j}$ is amount of substance fraction of component $i$ in parent gas or liquid $j$
- $M_i$ is the molar mass of the component $i$

**Calibration standards**:

55 [µmol/mol].....uncertainty 0,1 [µmol/mol]

265 [µmol/mol]..... Uncertainty 0,2 [µmol/mol]

490 [µmol/mol]..... Uncertainty 1 [µmol/mol]

762 [µmol/mol]..... Uncertainty 1,5 [µmol/mol]

## Uncertainty budget

**Please provide below the uncertainty budget used to calculate the uncertainty associated with the measurement of the ethanol amount fraction.**

Standard uncertainty $u^2(y_{k,grav})$

$$u^2(y_{k,grav}) = \sum_{i=1}^{q}\left(\frac{\partial y_k}{\partial M_i}\right)^2 \cdot u^2(M_i) + \sum_{j=1}^{r}\left(\frac{\partial y_k}{\partial m_j}\right)^2 \cdot u^2(m_j) + \sum_{j=1}^{r}\sum_{i=1}^{q}\left(\frac{\partial y_k}{\partial x_{i,j}}\right)^2 \cdot u^2(x_{i,j})$$

Where:

- $y_k$ amount of substance fraction of component $k$ in the prepared mixture
- $m_j$ weight of compound j
- $M_i$ molar mass of compound i
- $x_{ij}$ amount of substance fraction of component i in the parent gas or liquid j
- $m_j$ weight of compound j

Expressions for sensitivity coefficients appiring in previous formula follows:

$$\frac{\partial y_k}{\partial m_j} = \frac{1}{n_\Omega}\frac{x_{kj}}{M_j} - \frac{n_k}{n_\Omega^2}\frac{1}{M_j}$$

$$\frac{\partial y_k}{\partial M_i} = -\frac{1}{n_\Omega}\sum_{j=1}^{p}\frac{x_{kj}m_j}{M_j^2}x_{ij} + \frac{n_k}{n_\Omega}\sum_{j=1}^{p}\frac{m_j}{M_j^2}x_{ij}$$

$$\frac{\partial y_k}{\partial x_{ij}} = -\frac{1}{n_\Omega}\frac{x_{kj}m_j}{M_j^2}M_i + \frac{n_k}{n_\Omega^2}\frac{m_j}{M_j^2}M_i \ (for\ i \neq k)$$

$$\frac{\partial y_k}{\partial x_{kj}} = \frac{1}{n_\Omega}\left(-\frac{x_{kj}m_j}{M_j^2}M_k + \frac{m_j}{M_j}\right) + \frac{n_k}{n_\Omega^2}\frac{m_j}{M_j^2}M_i$$

## Additional information

**Please include in this section a brief outline of any stability testing (including sorption effects investigation, if performed) and correction procedures for the two travelling standards between the time they were prepared and the time they were measured at NPL (NPL will provide the date of measurement to each participant for each travelling standard on measurement completion).**

We performed a three years stability study.

# INMETRO



## Participants report form, Part B

### Measurement results

**Please indicate below the final value and associated expanded uncertainty of the $C_2H_5OH$ amount fraction in each of the two travelling standards.**

| **Measurements results for $C_2H_5OH$ in $N_2$** | | |
|---|---|---|
| | **Travelling standard 1** | **Travelling standard 2** |
| **Nominal amount fraction [µmol mol$^{-1}$]** | **114** | **128** |
| **Final amount fraction $\chi_{C_2H_5OH}$ [µmol mol$^{-1}$]** | **113.63 (PSM1)** | **128.89 (PSM2)** |
| **Expanded uncertainty $U_{\chi_{C_2H_5OH}}$ [µmol mol$^{-1}$]** | **0.76** | **0.67** |
| **Coverage factor** | **2** | **2** |

## Gravimetric preparation and purity

**Please provide below the following information:**

- **Statement whether the reported values are true gravimetric values, based on the masses and purities of the components added, or they have been determined and/or corrected by analysis.**
- **Details on the correction procedure, if applicable.**
- **Purity table with uncertainties for all the parent gases, including < LOQ flags with the respective LOQ values for the impurities. Specify uncertainty distribution (Gaussian, rectangular etc.)**
- **Brief outline of the dilution series undertaken to produce the final travelling standard**

- **Purity table for each of the final travelling standard, including uncertainties, as above**

The gas standards for CCQM-K93 were prepared gravimetrically through one step dilution according to ISO6142:2015. Inmetro used two balances. One was used for weighing of aluminium alloy cylinders (Mettler Toledo, SB12001), the other balance (Sartorius, CP224S) was used for weighing of syringes (Vici series 2, volumes of 500 microL for PSM1 and 300microL for PSM2) with ethanol. It was used 2 new cylinders of 5 L aluminum cylinder (Scott gases) with internal surface treatment Aculife (Luxfer). The pure ethanol was a Lichrosolv (lot K49937627 from Merk), with analysis of water content by Karl-Fisher and total organic compounds by 2 GC-FID methods, with purity results according to Table 1. The matrix used was nitrogen 99,9999% from White Martins, with purity results derived from ISO6142 estimation from supplier, presented at Table 2. The Gas Laboratory from Inmetro is developing the criogenic method to analyse the nitrogen impurities by GC PDHID, but the results are still being evaluated.

The gravimetric results of amount-of-substance fraction and its respective uncertainty were obtained by the software ISO6142 (VSL) and the results are presented in Tables 3, 4 and 5.

Table 1 – Ethanol purity table

| Component | Method | Amount Fraction (mol/mol) | Standard uncertainty (mol/mol) |
|---|---|---|---|
| $C_2H_5OH$ | Balance | 0.99892 | 0.00002 |
| $H_2O$ | Karl Fischer | 0.001067 | 0.000014 |
| THC | GC-FID | 0.00002 | 0.000006 |

Table 2 – Nitrogen purity table

| Component | Method | Amount Fraction (mol/mol) | Standard uncertainty (mol/mol) |
|---|---|---|---|
| $N_2$ | Balance | 0.9999994 | 0.0000002 |
| CO | ISO 6142 estimation from supplier info | 0.00000005 | 0.00000029 |
| $H_2O$ | ISO 6142 purity estimation from supplier info | 0.00000025 | 0.00000014 |
| $O_2$ | ISO 6142 purity estimation from supplier info | 0.00000025 | 0.00000014 |
| THC | ISO 6142 purity estimation from supplier info | 0.00000005 | 0.000000029 |

Table 3 – Weighing results table

| | Result (g) | Standard uncertainty (g) | Result (g) | Standard uncertainty (g) |
|---|---|---|---|---|
| | PSM 1: M692271 | | PSM 2: M692275 | |
| Evacuated cylinder | -203.48 | 0.0020 | -211.96 | 0.0016 |
| Full syringe | 0.1676 | 0.0001 | 0.1841 | 0.0001 |
| Empty syringe | 0.0479 | 0.0001 | 0.0484 | 0.0001 |
| Full cylinder | 436.93 | 0.0022 | 428.11 | 0.0012 |
| **Mass transferred of Ethanol** | **0.1197** | **0.0001** | **0.1357** | **0.0001** |
| **Mass transferred of Nitrogen** | **640.29** | **0.0030** | **639.93** | **0.0020** |

Table 4 – Gravimetric results of final mixtures table

| Component | Amount fraction (mol/mol) | Standard uncertainty (mol/mol) | Amount fraction (mol/mol) | Standard uncertainty (mol/mol) |
|---|---|---|---|---|
| | PSM 1: M692271 | | PSM 2: M692275 | |
| $C_2H_5OH$ | $113.63 \times 10^{-6}$ | $0.003 \times 10^{-6}$ | $128.89 \times 10^{-6}$ | $0.004 \times 10^{-6}$ |
| $N_2$ | 0.9998795 | 0.0000002 | 0.9998704 | 0.0000002 |

Table 5 – Gravimetric results of purity table

| Component | Amount fraction (mol/mol) | Standard uncertainty (mol/mol) | Amount fraction (mol/mol) | Standard uncertainty (mol/mol) |
|---|---|---|---|---|
| | PSM 1: M692271 | | PSM 2: M692275 | |
| CO | 0.00000005 | 0.00000003 | 0.00000005 | 0.00000003 |
| $H_2O$ | 0.00000043 | 0.00000014 | 0.00000039 | 0.00000014 |
| $O_2$ | 0.00000025 | 0.00000014 | 0.00000025 | 0.00000014 |
| THC | 0.00000005 | 0.000000029 | 0.00000005 | 0.000000029 |

## Measurement procedure

Please provide below:

- Description of the measurements performed for the validation of the submitted gravimetric values, obtained from the preparation
- Calibrants and analysers details.

The prepared reference gas mixture was measured against Inmetro's PSMs. The reference values for the amount-of-substance fractions are obtained by interpolation applying a calibration curve using 05 (five) primary standard gas mixtures produced by Inmetro at the same period of the samples gravimetry production. The measurement results were performed using a non dispersive infrared (NDIR) from Servomex, with 05 (five) repetitions during 03 (three) different days as independent analysis. The analysis results from the non-dispersed infrared have been fitted using a quadratic model, in accordance with ISO 6143, applying the software XLgenline (NPL). The primary standards used in the calibration curve of the days of analysis are presented in Table 6, and the maximum absolute weighted residual of the regression, or the goodness of fitness (GOF) obtained are presented in Table 7.

Table 6 – Calibration mixtures

| Mixture | Amount fraction ($x10^{-6}$ mol/mol) | Standard uncertainty ($x10^{-6}$ mol/mol) |
|---|---|---|
| PSM133788 | 50.84 | 0.21 |
| PSM112269 | 97.66 | 0.41 |
| PSM173654 | 108.90 | 0.46 |
| PSM123653 | 122.08 | 0.51 |
| PSM133650 | 201.13 | 0.84 |

Table 7 – Regression of the calibration model GOF

| Date | GOF |
|---|---|
| 22/12/23 | 0.76 |
| 04/01/24 | 0.74 |
| 11/01/24 | 0.77 |

In order to have independent measurements and to evaluate the stability of the mixtures after the preparation, it was planned a set of 03 (three) days of analysis of the sample mixtures and all the standards produced for the calibration curve. The verification analysis result of the amount fraction of each PSM sample was obtained from the average of all days of measurement. Each measurement result and its respective relative standard uncertainty estimated are presented in Table 8.

A new analytical calibration curve was done after the return of the 2 mixtures, in May 21st 2025, and the results are presented in Table 8.

Table 8 – Measurement results of amount fraction and its uncertainty

| | Measurement results | |
|---|---|---|
| | PSM 1: M692271 | PSM 2: M692275 |
| | Measurement #1 (22/12/23) | |
| Amount fraction (x10$^{-6}$ mol/mol) | 113.08 | 129.14 |
| Standard uncertainty (%rel) | 0.24 | 0.23 |
| Number of replicates | 5 | 5 |
| | Measurement #2 (04/01/24) | |
| Amount fraction (x10$^{-6}$ mol/mol) | 113.09 | 129.14 |
| Standard uncertainty (%rel) | 0.25 | 0.23 |
| Number of replicates | 5 | 5 |
| | Measurement #3 (11/01/24) | |
| Amount fraction (x10$^{-6}$ mol/mol) | 113.17 | 129.15 |
| Standard uncertainty (%rel) | 0.25 | 0.24 |
| Number of replicates | 5 | 5 |
| Measurement #4 (21/05/25) – analysis after return of the mixtures | | |
| Amount fraction (x10$^{-6}$ mol/mol) | 113.17 | 129.15 |
| Standard uncertainty (%rel) | 0.25 | 0.24 |
| Number of replicates | 5 | 5 |

Table 9 – Final results of Amount fraction and its Uncertainty of Ethanol mixtures

| Mixture | Amount fraction ($y_{prep}$, micromol/mol) | Expanded uncertainty, $k$=2 (U ($y_{prep}$), micromol/mol) | Verification Amount fraction ($y_{ver}$, micromol/mol) | Preparation and Measurement Difference ($y_{prep}$-$y_{ver}$, %rel) | U (%rel) |
|---|---|---|---|---|---|
| PSM 1: M692271 | 113.63 | 0.76 | 113.11 | 0.45 | 0.67 |
| PSM 2: M692275 | 128.89 | 0.67 | 129.14 | -0.20 | 0.52 |

## Additional information

**Please include in this section a brief outline of any stability testing (including sorption effects investigation, if performed) and correction procedures for the two travelling standards between the time they were prepared and the time they were measured at NPL (NPL will provide the date of measurement to each participant for each travelling standard on measurement completion).**

The largest contributor for both mixtures in the gravimetry uncertainty budget is the effect of cylinder wall adsorption together with the dark uncertainty of the main component transference by syringe into the cylinder. It was made a study based on Kriss publication (Sangil Lee, Mi Eon Kim, Sang Hyub Oh and Jin Seog Kim. Metrologia, 54, L26-L33, 2017) for a similar mixture of ethanol and analysis by NDIR. The value assigned of this uncertainty component predicted from the mentioned study done of the cylinder adsorption effect is 0.42% relative to the assigned amount fraction of ethanol.

The stability uncertainty was derived by the analytical results of the amount fraction obtained of ethanol by NDIR (nondispersive infrared) at 03 (three) different days after the gravimetric production. This uncertainty was obtained from the standard deviation from the 03 amount fractions obtained by the calibration curves divided by the square root of 3 (days of analysis where the stability of the mixtures were being evaluated). A new analysis of the mixtures was done after the return of the cylinders, and the results showed consistency of the analysis value with the gravimetric value. It can also be noticed that the stability contribution of both mixtures are insignificant to the final preparation uncertainty, as the adsorption effect uncertainty has a high contribution to the preparation uncertainty composition.

# Participants report form, Part B

## Measurement results

**Please indicate below the final value and associated expanded uncertainty of the $C_2H_5OH$ amount fraction in each of the two travelling standards.**

| Measurements results for $C_2H_5OH$ in $N_2$ | | |
|---|---|---|
| | **Travelling standard 1** | **Travelling standard 2** |
| **Nominal amount fraction [µmol mol$^{-1}$]** | 105-110 µmol mol$^{-1}$ | 120-125 µmol mol$^{-1}$ |
| **Final amount fraction $\chi_{C_2H_5OH}$ [µmol mol$^{-1}$]** | 115,5 | 123,6 |
| **Expanded uncertainty $U_{\chi_{C_2H_5OH}}$ [µmol mol$^{-1}$]** | 1,4 | 2,2 |
| **Coverage factor** | 2,0 | 2,0 |

## Gravimetric preparation and purity

Please provide below the following information:

- Statement whether the reported values are true gravimetric values, based on the masses and purities of the components added, or they have been determined and/or corrected by analysis.
- Details on the correction procedure, if applicable.
- Purity table with uncertainties for all the parent gases, including < LOQ flags with the respective LOQ values for the impurities. Specify uncertainty distribution (Gaussian, rectangular etc.)
- Brief outline of the dilution series undertaken to produce the final travelling standard
- Purity table for each of the final travelling standard, including uncertainties, as above

The ethanol primary gas standards are realised by the primary gravimetric method according to ISO 6142-1. A syringe is used to weigh the liquid ethanol on the comparator balance and then to transfer the ethanol to the cylinder as can be seen in the figure. Small accurate amounts of ethanol are introduced into pressurized gas cylinders, together with the matrix gas of nitrogen. During this process a careful control of the weighing procedure, air density, gas impurities, as well as the environmental conditions (temperature, air pressure and humidity), allows to directly link the gas standards to national standards of mass, temperature and pressure, and, through the IUPAC molar mass definition to the base quantity amount of substance.



The reported values have been determined and corrected by analysis.

Purity table (Ethanol)

| | |
|---|---|
| Ethanol | 99,97 % |
| $H_2O$ | 0,03 % |

Purity table (Nitrogen)

| | |
|---|---|
| $N_2$ | 0,999999 |
| CO | 1,0E-07 |
| $CO_2$ | 1,0E-07 |
| $H_2O$ | 5,0E-07 |
| $H_2$ | 1,0E-07 |
| $O_2$ | 1,0E-07 |
| $C_nH_m$ | 1,0E-07 |

## Measurement procedure

**Please provide below:**

- **Description of the measurements performed for the validation of the submitted gravimetric values, obtained from the preparation**
- **Calibrants and analysers details.**

**The certification process takes place using an automated multichannel sampling system, to which all the cylinders to be analysed are connected.**

**During the analysis, cylinders are automatically selected, enabling individual circulation of gas through the analyser. This system employs the purpose-built IPQAnaliseQui software, which manages the sampling process and records all measurements taken by the analyser. Ultimately, all the gathered data, including records of standard and sample analyses, are entered into a spreadsheet. The results are corrected with zero and pressure data.**

**The calibration function determination is carried out using the XGENLINE program developed by the NPL - National Physical Laboratory. This software calculates the most suitable low-degree polynomial calibration function (1, 2, 3 or 4) for a set of measurement data (X, Y), considering the uncertainties associated with the data. In our case XGENLINE program calculated the most suitable low-degree polynomial calibration function of first order for each calibration.**

**Hence, the determined calibration function is employed to derive estimates of the amount fraction values for the samples under analysis and their corresponding associated uncertainties.**

**The XGENLINE program, which meets the requirements of the ISO 6143 standard, handles uncertainty, and a standard uncertainty is obtained for each analytical test.**

**Calibrants:**
**It was used two primary standard mixtures from VSL, two primary standard mixtures from NPL and one from LNE.**

| Cylinder | Molar fraction mol/mol | Expanded Uncertainty mol/mol |
|---|---|---|
| VSL3862 | 4,900E-05 | 8,6E-07 |
| VSL7680 | 5,020E-05 | 8,7E-07 |
| NPL0296 | 1,175E-04 | 1,2E-06 |
| LNE5418 | 2,094E-04 | 1,5E-06 |
| NPL1718 | 3,156E-04 | 2,0E-06 |

## Measurement procedure (continues)

**Please provide below:**

- **Description of the measurements performed for the validation of the submitted gravimetric values, obtained from the preparation**
- **Calibrants and analysers details**

**Analysers details:**

- Non Dispersive Infrared Spectroscopy (NDIR): Analyzer: URAS26, ABB, serie AO2000.

Data Collection: Auto-sampler - IPQAnaliseQui software

- GC-FID Agilent 6890N with software Clarity 9.1 Advanced Chromatography Software DataApex Ltd. (version 9.1.1.13).

| Test conditions | | |
|---|---|---|
| PCM | 30 °C | 2,6 psi |
| Column | 30 °C | 5 mL/min |
| FID detector | 30 °C | |

**The calibration instrument was done according to ISO 6143. We have used the XGENLINE program to determine the best model for data handling. All components of mixture have a goodness of fit less than 2 using a linear function.**

**For all components were used a set of five PRM (from VSL, NPL and LNE). At least three repeated analyses were performed in three independent days.**

**Manual calibration (zero and span are calibrated separately by pressing the analyser system display and control unit softkeys).**

## Uncertainty budget

**Please provide below the uncertainty budget used to calculate the uncertainty associated with the measurement of the ethanol amount fraction.**

**The calculated uncertainties were obtained using the XGENLINE program, which meets the requirements of the ISO 6143 standard uncertainties estimation.**

**The expanded uncertainty presented is expressed by the standard uncertainty multiplied by the coverage factor k, which for a t-distribution with $\nu_{eff}$ = γ effective degrees of freedom correspond to an expanded probability of approximately 95 %.**

The uncertainty measurement was done according to ISO GUM: 1995 "Guide to the Expression of Uncertainty in Measurement".
The uncertainty of measurement associated with the final result has been evaluated and includes three main uncertainty sources:

- Uncertainty in calibration;
- Uncertainty of repeatability;
- Uncertainty of reproducibility

These uncertainties were combined, and the result was multiplied by a coverage factor with a confidence interval of 95 %.

1) Uncertainty table:

| Uncertainty source $X_i$ | Estimate $x_i$ | Assumed distribution | Standard uncertainty $u(x_i)$ | Sensitivity coefficient $c_i$ | Contribution to standard uncertainty $u_i(y)$ |
|---|---|---|---|---|---|
| PRM208984 | | | | | |
| Repeatability | | normal | $4{,}791 \times 10^{-8}$ | 1 | $4{,}791 \times 10^{-8}$ |
| Reproducibility | | normal | $1{,}375 \times 10^{-7}$ | 1 | $1{,}375 \times 10^{-7}$ |
| Calibration | | normal | $6{,}730 \times 10^{-7}$ | 1 | $6{,}730 \times 10^{-7}$ |
| PRM203396 | | | | | |
| Repeatability | | normal | $3{,}617 \times 10^{-7}$ | 1 | $3{,}617 \times 10^{-7}$ |
| Reproducibility | | normal | $7{,}534 \times 10^{-7}$ | 1 | $7{,}534 \times 10^{-7}$ |
| Calibration | | normal | $7{,}139 \times 10^{-7}$ | 1 | $7{,}139 \times 10^{-7}$ |

Expanded uncertainty PRM208984: 1,4 $\times 10^{-6}$ mol/mol
Expanded uncertainty PRM203396: 2,2 $\times 10^{-6}$ mol/mol

## Additional information

**Please include in this section a brief outline of any stability testing (including sorption effects investigation, if performed) and correction procedures for the two travelling standards between the time they were prepared and the time they were measured at NPL (NPL will provide the date of measurement to each participant for each travelling standard on measurement completion).**

During this period there were no stability testing. We have made a stability study in 2017 for ethanol mixtures in nitrogen, where the expiration date is two years, for mixtures within these molar fractions and in aluminium cylinders with a special coating (ACULIFE IV treatment).

# Participants report form, Part B

## Measurement results

**Please indicate below the final value and associated expanded uncertainty of the $C_2H_5OH$ amount fraction in each of the two travelling standards.**

| Measurements results for $C_2H_5OH$ in $N_2$ | | |
|---|---|---|
| | **Travelling standard 1 D170152** | **Travelling standard 2 D170283** |
| **Nominal amount fraction [µmol mol$^{-1}$]** | **Range C 115 - 120** | **Range F 130 - 135** |
| **Final amount fraction $\chi_{C_2H_5OH}$ [µmol mol$^{-1}$]** | **117.77** | **132.81** |
| **Expanded uncertainty $U_{\chi_{C_2H_5OH}}$ [µmol mol$^{-1}$]** | **0.35** | **0.39** |
| **Coverage factor** | **2** | **2** |

## Gravimetric preparation and purity

Please provide below the following information:

- Statement whether the reported values are true gravimetric values, based on the masses and purities of the components added, or they have been determined and/or corrected by analysis.
- Details on the correction procedure, if applicable.
- Purity table with uncertainties for all the parent gases, including < LOQ flags with the respective LOQ values for the impurities. Specify uncertainty distribution (Gaussian, rectangular etc.)
- Brief outline of the dilution series undertaken to produce the final travelling standard
- Purity table for each of the final travelling standard, including uncertainties, as above

- Four gas mixture were prepared gravimetrically in each target nominal range, C (115 µmol/mol - 120 µmol/mol) and F (130 µmol/mol - 135 µmol/mol).
- All gas mixtures were independently prepared by directly injecting ethanol using a syringe and then diluted using nitrogen.
- In order to determine the purity of ethanol and nitrogen GC-FID, GC-TCD, moisture analyser (chilled mirror) and Karl-Fischer Coulometer were used. Table 1 and 2 show the purity of ethanol and nitrogen respectively.
- Buoyancy effect during weghing syringes and adsorption of ethanol to inside wall of cylinder were considered to determine the final amount fraction of ethanol.
- Adsorption loss of ethanol onto cylinder inner surface was estimated by subdivision experiments suggested by Lee et al. (Metrologia 54 (2017) L26 – L33) and then gravimetric values were corrected.

Table 1. Purity of ethanol

| | Distribution | Value µmol/mol | Standard uncertainty µmol/mol | Method |
|---|---|---|---|---|
| Benzene | Normal | 136.8 | 10.3 | GC-FID |
| $H_2O$ | Normal | 1 928.1 | 55.6 | Karl-Fischer Coulometer |
| Ethanol | | 997 935.1 | 56.5 | - |

Table 2. Purity of nitrogen

| | Distribution | Value µmol/mol | Standard uncertainty µmol/mol | Method |
|---|---|---|---|---|
| Ar | Normal | 7.085 | 0.354 | GC-TCD |
| $O_2$ | Rectangular | 0.250 | 0.144 | GC-TCD |
| CO | Rectangular | 0.028 | 0.016 | GC-FID with methanizer |
| $CH_4$ | Rectangular | 0.065 | 0.038 | GC-FID with methanizer |
| $CO_2$ | Rectangular | 0.042 | 0.024 | GC-FID with methanizer |
| $H_2O$ | Normal | 2.073 | 0.104 | Moisture analyzer (chilled mirror) |
| Ethanol | Rectangular | 0.004 | 0.002 | GC-FID |
| $N_2$ | | 999 990.512 | 0.397 | - |

## Measurement procedure

Please provide below:

- Description of the measurements performed for the validation of the submitted gravimetric values, obtained from the preparation
- Calibrants and analysers details.

- Four mixtures in each range were prepared gravimetrically in at similar amount fractions. All four mixtures in each range were analysed against each other to demonstrate their consistency. Each mixture was analyzed by backeting with a reference gas mixture (R) to correct drift as follows. The verification anlysis was repeated three times.

$$"R \rightarrow S_1 \rightarrow R \rightarrow S_2 \rightarrow R \rightarrow S_3 \rightarrow R \rightarrow S_4 \rightarrow R" \times 3 \text{ times}$$

- All gas mixtures were analyzed using GC-FID with analytical conditions shown in Table 3.

Table 3. Analytical conditions of GC-FID for verification

| | |
|---|---|
| GC-FID | Agilent 7890 |
| Valve box | 100 °C |
| Inlet | 200 °C<br>split 10:1 |
| Column | CP-Sil 5 CB (60 m x 0.32 mm x 5 µm) with a carrier flow of He 3 ml/min |
| Oven temperature | 180 °C |
| Detector temperature and flows | 250 °C, Air 400 ml/min, $H_2$ 40 ml/min, He 20 ml/min (makeup) |

- The verification uncertainty, $u(x_{ver})$, is the combination of analytical repeatability, analytical reproducibility, and consistency as follows.

$$u(x_{ver}) = \sqrt{u^2(x_{repeat}) + u^2(x_{repro}) + u^2(x_{consistency})}$$

Where $u(x_{repeat})$ and $u(x_{repro})$ is a standard uncertainty of analytical repeatability and reproducibility, respectively. $u(x_{repeat})$ is a standard uncertainty of dispersion.

## Uncertainty budget

**Please provide below the uncertainty budget used to calculate the uncertainty associated with the measurement of the ethanol amount fraction.**

- The final amount fractions, $x_{final}$, were drawn from the preparation amount fractions, $x_{prep}$. And the combined standard uncertainties of the final amount fractions were calculated by

$$u_c(x_{final}) = \sqrt{u^2(x_{prep}) + u^2(x_{ver})}$$

- Table 4 and 5 shows the uncertainty budgets of two travelling standards, respectively.

Table 4. Uncertainty budget of travelling standard (D170152) in range C (115 µmol/mol - 120 µmol/mol)

| Source | Distribution | Standard uncertainty [µmol/mol] | Contribution [%] |
|---|---|---|---|
| Preparation | | 0.10 | 36.1 |
| Gravimetric preparation | Normal | 0.04 | 4.4 |
| Correction for adsorption loss | Normal | 0.10 | 31.7 |
| Verification | | 0.14 | 63.9 |
| Repeatability | Normal | 0.14 | 61.7 |
| Reproducibility | Normal | 0.02 | 2.1 |
| Consistency | Normal | 0.01 | 0.1 |
| Combined standard uncertainty | | 0.17 | 100 |

Table 5. Uncertainty budget of travelling standard (D170283) in range F (130 µmol/mol - 135 µmol/mol)

| Source | Distribution | Standard uncertainty [µmol/mol] | Contribution [%] |
|---|---|---|---|
| Preparation | | 0.12 | 36.0 |
| Gravimetric preparation | Normal | 0.04 | 4.3 |
| Correction for adsorption loss | Normal | 0.11 | 31.7 |
| Verification | | 0.16 | 64.0 |
| Repeatability | Normal | 0.15 | 60.3 |
| Reproducibility | Normal | 0.03 | 2.0 |
| Consistency | Normal | 0.03 | 1.7 |
| Combined standard uncertainty | | 0.20 | 100 |

## Additional information

**Please include in this section a brief outline of any stability testing (including sorption effects investigation, if performed) and correction procedures for the two travelling standards between the time they were prepared and the time they were measured at NPL (NPL will provide the date of measurement to each participant for each travelling standard on measurement completion).**

LNE



# Participants report form, Part B

## Measurement results

Please indicate below the final value and associated expanded uncertainty of the $C_2H_5OH$ amount fraction in each of the two travelling standards.

| Measurements results for $C_2H_5OH$ in $N_2$ | | |
|---|---|---|
| | **Etha/N2 0041** | **Etha/N2 0042** |
| Nominal amount fraction [µmol mol$^{-1}$] | 110-115 | 125-130 |
| Final amount fraction $x_{C_2H_5OH}$ [µmol mol$^{-1}$] | 112.70 | 127.49 |
| Expanded uncertainty $U_{x_{C_2H_5OH}}$ [µmol mol$^{-1}$] | 0.40 | 0.35 |
| Coverage factor | 2 | 2 |

## Gravimetric preparation and purity

Please provide below the following information:

- Statement whether the reported values are true gravimetric values, based on the masses and purities of the components added, or they have been determined and/or corrected by analysis.
- Details on the correction procedure, if applicable.
- Purity table with uncertainties for all the parent gases, including < LOQ flags with the respective LOQ values for the impurities. Specify uncertainty distribution (Gaussian, rectangular etc.)
- Brief outline of the dilution series undertaken to produce the final travelling standard
- Purity table for each of the final travelling standard, including uncertainties, as above

The reference gas mixtures are produced directly from pure ethanol and nitrogen without dilution step, according to ISO 6142-1 standard.

- Purity Table of APE1279837

| Component | µmol/mol | uncertainty | % u/c |
|---|---|---|---|
| N2 | 999887.2129 | 0.28917115 | 0.000 |
| ethanol | 112.7030188 | 0.28714370 | 0.255 |
| methane | 0.04999436 | 0.02886426 | 57.735 |
| H2O | 0.03387105 | 0.01690879 | 49.921 |
| CO2 | 0.00004999 | 0.00002886 | 57.736 |
| H2 | 0.00004999 | 0.00002886 | 57.736 |
| O2 | 0.00004999 | 0.00002886 | 57.736 |
| CO | 0.00004999 | 0.00002886 | 57.736 |
| SO2 | 0.00000050 | 0.00000029 | 57.800 |
| NO2 | 0.00000025 | 0.00000014 | 57.600 |
| NO | 0.00000025 | 0.00000014 | 57.600 |

INPUTS

| File | Mass (g) | u/c (g) |
|---|---|---|
| G_d_f\N2Alpha2_F | 1744.925 | 0.01800 |
| Pur\ETHA_pur_006 | 0.32348 | 0.00082 |

INPUT DATA FILES

********* G_d_f\N2Alpha2_F902(déf).txt *********

| Component | mol/mol | uncertainty |
|---|---|---|
| N2 | 0.9999999497 | 0.0000000289 |
| H2O | 0.0000000001 | 0.0000000000 |
| O2 | 0.0000000001 | 0.0000000000 |
| CO | 0.0000000001 | 0.0000000000 |
| CO2 | 0.0000000001 | 0.0000000000 |
| H2 | 0.0000000001 | 0.0000000000 |
| methane | 0.0000000500 | 0.0000000289 |
| SO2 | 0.0000000000 | 0.0000000000 |
| NO | 0.0000000000 | 0.0000000000 |
| NO2 | 0.0000000000 | 0.0000000000 |

********** Pur\ETHA_pur_0063.txt **********

| Component | mol/mol | uncertainty |
|---|---|---|
| ethanol | 0.9997000000 | 0.0001500000 |
| H2O | 0.0003000000 | 0.0001500000 |

- **Purity Table of APE1516246**

| Component | µmol/mol | uncertainty | % u/c |
|---|---|---|---|
| N2 | 999872.4444 | 0.29223530 | 0.000 |
| ethanol | 127.4921257 | 0.29116383 | 0.228 |
| H2O | 0.03830911 | 0.01912754 | 49.929 |
| methane | 0.02499681 | 0.01443192 | 57.735 |
| CO2 | 0.00004999 | 0.00002886 | 57.736 |
| H2 | 0.00004999 | 0.00002886 | 57.736 |
| O2 | 0.00004999 | 0.00002886 | 57.736 |
| CO | 0.00004999 | 0.00002886 | 57.736 |
| SO2 | 0.00000050 | 0.00000029 | 57.800 |
| NO2 | 0.00000025 | 0.00000014 | 57.600 |
| NO | 0.00000025 | 0.00000014 | 57.600 |

INPUTS

| File | Mass (g) | u/c (g) |
|---|---|---|
| G_d_f\N2Bip_F902 | 1722.999 | 0.01700 |
| Pur\ETHA_pur_006 | 0.36134 | 0.00083 |

INPUT DATA FILES

********** G_d_f\N2Bip_F902(def).txt **********

| Component | mol/mol | uncertainty |
|---|---|---|
| N2 | 0.9999999747 | 0.0000000144 |
| H2O | 0.0000000001 | 0.0000000000 |
| O2 | 0.0000000001 | 0.0000000000 |
| CO | 0.0000000001 | 0.0000000000 |
| CO2 | 0.0000000001 | 0.0000000000 |
| H2 | 0.0000000001 | 0.0000000000 |
| methane | 0.0000000250 | 0.0000000144 |
| SO2 | 0.0000000000 | 0.0000000000 |
| NO | 0.0000000000 | 0.0000000000 |
| NO2 | 0.0000000000 | 0.0000000000 |

********** Pur\ETHA_pur_0063.txt **********

| Component | mol/mol | uncertainty |
|---|---|---|
| ethanol | 0.9997000000 | 0.0001500000 |
| H2O | 0.0003000000 | 0.0001500000 |

## Measurement procedure

Please provide below:

- Description of the measurements performed for the validation of the submitted gravimetric values, obtained from the preparation
- Calibrants and analysers details.

- Analyser

  The analyser used for ethanol measurements is a FTIR MG 05 from Bruker with a gas cell regulated at 50°C and an optical path length of 5 m. Ethanol is quantified between 2500 and 3100 $cm^{-1}$ with 1 $cm^{-1}$ spectral resolution and PNNL database is used to fit the experimental spectra.

- Procedure

  A third ethanol reference gas mixture (RGM) is produced and analysed at the same time than the 2 RGMs prepared for this comparison.
  A pure nitrogen is flowing through the gas cell at 1l/min for background acquisition (150 scans) during 30 min.
  The three reference gas mixtures are analysed during 30 minutes and the last 5 min measurements are used to calculate the average and standard deviation.
  The analytical values of the three RGMs are obtained by performed a WLS fit prediction of the measurements.
  The RGMs are validated if the normalized deviation $E_n$ is lower than 1.

The uncertainty of the analytical validation is taken into account in the uncertainty budget on submitted gravimetric amount fractions **(see the paragraph "Uncertainty budget").**

## Uncertainty budget

Please provide below the uncertainty budget used to calculate the uncertainty associated with the measurement of the ethanol amount fraction.

The reported values (see below) are the gravimetric amount fractions, based on the masses and purities of the components added in the cylinder.

The final uncertainty budget of Etha/N2 0041 is calculated according to the ISO 6142-1 standard with the following formula:

$$u_{gravi} = 0.5 \times \sqrt{(u_{prep})^2 + (u_{ver})^2 + (prep - ver)^2}$$

| Variable | Unit | Value | u(Xi) | Weight |
|---|---|---|---|---|
| ETOH purity | mol/mol | $9.997\ 10^{-1}$ | $1.50\ 10^{-4}$ | 0.2% |
| mass of ETOH | g | $3.23\ 10^{-1}$ | $8.20\ 10^{-4}$ | 52.6% |
| Molar mass of ETOH | g/mol | $4.61\ 10^{1}$ | $9.80\ 10^{-4}$ | 0.0% |
| $N_2$ Purity | mol/mol | 1.00 | $2.89\ 10^{-8}$ | 0.0% |
| mass of $N_2$ | g | $1.74\ 10^{3}$ | $1.80\ 10^{-2}$ | 0.0% |
| Molar mass of $N_2$ | g/mol | $2.80\ 10^{1}$ | $9.90\ 10^{-5}$ | 0.0% |
| Analytical verification | µmol/mol | 112.69 | $2.70\ 10^{-1}$ | 47.1% |
| Preparation - Verification | µmol/mol | 0.01 | $1.00\ 10^{-2}$ | 0.1% |

| | | | |
|---|---|---|---|
| Etha/N2 0041 | µmol/mol | 112.70 | ± 0.40 (k=2) |

The final uncertainty budget of Etha/N2 0042 is calculated according to the ISO 6142-1 standard with the following formula:

$$u_{gravi} = 0.5 \times \sqrt{(u_{prep})^2 + (u_{ver})^2 + (prep - ver)^2}$$

| Variable | Unit | Value | u(Xi) | Weight |
|---|---|---|---|---|
| ETOH purity | mol/mol | $9.997\ 10^{-1}$ | $1.50\ 10^{-4}$ | 0.3% |
| mass of ETOH | g | $3.61\ 10^{-1}$ | $8.30\ 10^{-4}$ | 72.1% |
| Molar mass of ETOH | g/mol | $4.61\ 10^{1}$ | $9.80\ 10^{-4}$ | 0.0% |
| $N_2$ Purity | mol/mol | 1.00 | $2.89\ 10^{-8}$ | 0.0% |
| mass of $N_2$ | g | $1.72\ 10^{3}$ | $1.70\ 10^{-2}$ | 0.0% |
| Molar mass of $N_2$ | g/mol | $2.80\ 10^{1}$ | $9.90\ 10^{-5}$ | 0.0% |
| Analytical verification | µmol/mol | 127.51 | $1.78\ 10^{-1}$ | 27.3% |
| Preparation - Verification | µmol/mol | 0.02 | $2.00\ 10^{-2}$ | 0.3% |

| | | | |
|---|---|---|---|
| Etha/N2 0042 | µmol/mol | 127.49 | ± 0.35 (k=2) |

## Additional information

**Please include in this section a brief outline of any stability testing (including sorption effects investigation, if performed) and correction procedures for the two travelling standards between the time they were prepared and the time they were measured at NPL (NPL will provide the date of measurement to each participant for each travelling standard on measurement completion).**

The two RGMs of ethanol in nitrogen were analysed three times (September to December 2023) before sending them to NPL and three other times after their return from NPL in april 2025. The measurements show no instability of the ethanol amount fractions during the period of the comparison as shown in the table below. For this reason, the gravimetric amount fractions are not corrected by stability analysis.

| | Etha/N2 0041 | | | | Etha/N2 0042 | | | |
|---|---|---|---|---|---|---|---|---|
| **Date** | Analytical value | u(prep) k=1 | u(FTIR) std | U (k=2) | Analytical value | u(prep) k=1 | u(FTIR) std | U (k=2) |
| **19/09/2023** | 112.69 | 0.27 | 0.056 | 0.55 | 127.51 | 0.18 | 0.04 | 0.37 |
| **08/11/2023** | 112.68 | 0.26 | 0.030 | 0.53 | 127.52 | 0.18 | 0.05 | 0.38 |
| **08/12/2023** | 112.68 | 0.26 | 0.041 | 0.53 | 127.53 | 0.18 | 0.05 | 0.38 |
| **02/04/2025** | 112.66 | 0.26 | 0.040 | 0.53 | 127.57 | 0.18 | 0.04 | 0.37 |
| **03/04/2025** | 112.69 | 0.26 | 0.039 | 0.53 | 127.52 | 0.18 | 0.05 | 0.37 |
| **04/04/2025** | 112.66 | 0.26 | 0.026 | 0.52 | 127.58 | 0.18 | 0.05 | 0.37 |

# NIM



## Participants report form, Part B

### Measurement results

**Please indicate below the final value and associated expanded uncertainty of the $C_2H_5OH$ amount fraction in each of the two travelling standards.**

| Measurements results for $C_2H_5OH$ in $N_2$ | | |
|---|---|---|
| | **Travelling standard 1 (200226018007)** | **Travelling standard 2 (200226018058)** |
| **Nominal amount fraction [µmol mol$^{-1}$]** | 119.006 | 133.404 |
| **Final amount fraction $\chi_{C_2H_5OH}$ [µmol mol$^{-1}$]** | **118.915** | **133.304** |
| **Expanded uncertainty $U_{\chi_{C_2H_5OH}}$ [µmol mol$^{-1}$]** | **0.262** | **0.293** |
| **Coverage factor** | **2** | **2** |

## Gravimetric preparation and purity

Please provide below the following information:

- Statement whether the reported values are true gravimetric values, based on the masses and purities of the components added, or they have been determined and/or corrected by analysis.
- Details on the correction procedure, if applicable.
- Purity table with uncertainties for all the parent gases, including < LOQ flags with the respective LOQ values for the impurities. Specify uncertainty distribution (Gaussian, rectangular etc.)
- Brief outline of the dilution series undertaken to produce the final travelling standard
- Purity table for each of the final travelling standard, including uncertainties, as above

**1. Purity Analysis**

The purity analysis of nitrogen is determined by GC-FID, GC-PED and other methods. The purity analysis results of nitrogen are shown in Table 1:

Table 1. Purity of nitrogen

| Nitrogen (113259032) | | | Uncertainty assessment | |
|---|---|---|---|---|
| Component | Content | Detection method | Distribution type | Standard uncertainty |
| | mol/mol | | | mol/mol |
| Oxygen | $2.60\times10^{-7}$ | Trace Oxygen Analyzer | Normal | $2.6\times10^{-8}$ |
| Hydrogen | $1.00\times10^{-8}$ | Hydrogen Sensor Analyzer | Normal | $1.0\times10^{-9}$ |
| Methane | $4.50\times10^{-10}$ | GC-FID (Conversion Method) | Rectangular | $2.6\times10^{-10}$ |
| Carbon monoxide | $5.00\times10^{-9}$ | GC-FID (Conversion Method) | Rectangular | $2.9\times10^{-9}$ |
| Carbon Dioxide | $9.00\times10^{-8}$ | GC-FID (Conversion Method) | Rectangular | $5.2\times10^{-9}$ |
| Argon | $6.00\times10^{-6}$ | GC-PED | Normal | $6.0\times10^{-7}$ |
| Ethanol | $1.44\times10^{-9}$ | GC-MS | Rectangular | $8.3\times10^{-10}$ |
| Water | $1.00\times10^{-7}$ | Trace Water Analyzer | Normal | $1.0\times10^{-8}$ |
| Nitrogen | 0.9999935 | - | - | $6.0\times10^{-7}$ |

In order to quantify the concentration of ethanol in nitrogen, GC-MS was used with a DB-624 column. The detection limit of the analysis method was $2.88\times10^{-9}$ mol/mol. No ethanol was detected in nitrogen. Half of the detection limit, $1.44\times10^{-9}$ mol/mol, was taken as the ethanol concentration in nitrogen. According to a rectangular distribution, the corresponding uncertainty was calculated to be $5.78\times10^{-10}$ mol/mol.

The moisture content and other impurities in ethanol were determined by Karl Fischer titration, GC-FID, and GC-MS methods. The water content in ethanol was determined to be $2.07\times10^{-4}$ mol/mol. The measurement results of GC-FID indicated that there were 0.018% unknown impurities in ethanol, and no impurities were detected by GC-MS method. The ethanol purity and associated uncertainty were calculated by normalization method, with detailed results presented in Table 2.

Table 2. Purity of Ethanol

| Ethanol | | | Uncertainty assessment | |
|---|---|---|---|---|
| Component | Content | Detection method | Distribution type | Standard uncertainty |
| | mol/mol | | | mol/mol |
| Water | $2.07\times10^{-4}$ | Karl Fischer | Rectangular | $1.09\times10^{-5}$ |
| Unknown impurity | $1.80\times10^{-4}$ | GC-FID | Rectangular | $5.03\times10^{-5}$ |
| Ethanol | 0.999613 | - | - | $5.15\times10^{-5}$ |

2. Gravimetric preparation of gas mixture

Liquid ethanol was injected into the evacuated gas cylinder by the method of syringe injection. The mass and uncertainty of nitrogen and liquid ethanol addition are shown in Table 3:

Table 3. The quality and uncertainty of nitrogen and ethanol added in the travelling standards

| Cylinder number | Ethanol added mass (g) | Uncertainty of ethanol mass (g) | Nitrogen added mass (g) | Uncertainty of nitrogen mass (g) |
|---|---|---|---|---|
| 200226018007 | 0.282165 | 0.00006 | 1441.263 | 0.0191 |
| 200226018058 | 0.323058 | 0.00006 | 1472.017 | 0.0194 |

Table 4 shows the value and uncertainty of the ethanol amount fraction for each of the travelling standard.

Table 4. The ethanol amount fraction value and uncertainty

| Cylinder Number | 200226018007 | | 200226018058 | |
|---|---|---|---|---|
| Component | Concentration (mol/mol) | Uncertainty (mol/mol) | Concentration (mol/mol) | Uncertainty (mol/mol) |
| $C_2H_5OH$ | $1.19006\times10^{-4}$ | $2.79\times10^{-8}$ | $1.33404\times10^{-4}$ | $2.81\times10^{-8}$ |
| $H_2O$ | $1.24664\times10^{-7}$ | $1.01\times10^{-8}$ | $1.27648\times10^{-7}$ | $1.01\times10^{-8}$ |
| Unknown | $2.14291\times10^{-8}$ | $5.99\times10^{-9}$ | $2.40218\times10^{-8}$ | $6.72\times10^{-9}$ |
| $O_2$ | $2.59969\times10^{-7}$ | $2.60\times10^{-8}$ | $2.59965\times10^{-7}$ | $2.60\times10^{-8}$ |
| $H_2$ | $9.99881\times10^{-9}$ | $1.00\times10^{-9}$ | $9.99867\times10^{-9}$ | $1.00\times10^{-9}$ |
| $CH_4$ | $4.49946\times10^{-10}$ | $2.60\times10^{-10}$ | 4.49940E-10 | $2.60\times10^{-10}$ |
| CO | $4.99940\times10^{-9}$ | $2.89\times10^{-9}$ | $4.99933\times10^{-9}$ | $2.89\times10^{-9}$ |
| $CO_2$ | $8.99893\times10^{-8}$ | $5.20\times10^{-8}$ | $8.99880\times10^{-8}$ | $5.20\times10^{-8}$ |
| Ar | $5.99929\times10^{-6}$ | $6.00\times10^{-7}$ | $5.99920\times10^{-6}$ | $6.00\times10^{-7}$ |
| $N_2$ | $9.99874\times10^{-1}$ | $6.03\times10^{-7}$ | $9.99860\times10^{-1}$ | $6.03\times10^{-7}$ |

**3. Calculation of adsorption correction inside gas cylinders**

To investigate the adsorption effect of the selected P-type gas cylinders of ethanol, we selected two gas cylinders of the same type as the travelling standards, and separately transferred 1MPa and 5MPa about 120 $\times 10^{-6}$ mol/mol ethanol in nitrogen gas mixture into cylinder A and cylinder B. After 48 hours of stabilization, the amount fraction of ethanol in cylinder A and cylinder Bdecreased by 1.6% and 0.19%, respectively. The result indicated lower decreased percentage of the amount fraction of ethanol with higher dispensed pressure in the cylinders. The pressure in the two travelling standards were 12.3MPa and 12.6MPa, respectively. After calculation, Table 5 shows the correction caused by adsorption and the final ethanol concentration values after correction.

Table 5. The final ethanol amount after adsorption correction

| Cylinder number | Gravimetric value (μmol/mol) | Adsorption correction value (μmol/mol) | Corrected fraction（Final amount fraction (μmol/mol) | Correction percentage |
|---|---|---|---|---|
| 200226018007 | 119.006 | -0.091 | **118.915** | 0.077% |
| 200226018058 | 133.404 | -0.100 | **133.304** | 0.075% |

## Measurement procedure

Please provide below:

- Description of the measurements performed for the validation of the submitted gravimetric values, obtained from the preparation
- Calibrants and analysers details.

An Agilent 7890 gas chromatograph was used to develop the analysis method, with a flame ionisation detector (FID), VBWAX column (30 m long×0.25 mm diameter×0.25 μm film thickness) and a sample loop of 1mL. The temperature in column oven was 100 ℃. The column flow rate was 1.5 mL/min and split ratio was 20:1. Each sample was injected 6 times with a 1-minute interval, and the average peak area of the 6 injections was taken as the result of this sample.

Each comparison consisted of a series of 6 injections of sample (the travelling standard) alternating with 6 injections of a reference standard. The reference standard was NIM's work reference standard (WRS) with an ethanol amount close to that of the sample.The average of six measurement values was the analytical result, and the quality control limit for the analytical result was set as RSD ≤ 0.07%.

The measurement results (in table 6) show that the relative deviation between the comparison sample and WRS is ≤ 0.05%, and there is no need to correct the ethanol concentration values of the travelling standards.

Table 6. The measurement results of two travelling standards by GC-FID

| Sample 1 | 200226018007 | | | Standard 1 | | | 200226018063 | |
|---|---|---|---|---|---|---|---|---|
| Sample gravimetric value μmol/mol | 118.915 | | | Standard gravimetric value μmol/mol | | | 117.875 | |
| No. of analysis | 1 | 2 | 3 | 4 | 5 | 6 | Average | Standard deviation |
| Analytical concentration μmol/mol | 118.921 | 118.967 | 118.946 | 118.912 | 118.997 | 119.067 | 118.968 | 0.04% |
| Sample 2 | 200226018058 | | | Standard 2 | | | 200226018012 | |
| Sample gravimetric value μmol/mol | 133.304 | | | Standard gravimetric value μmol/mol | | | 132.379 | |
| No. of analysis | 1 | 2 | 3 | 4 | 5 | 6 | Average | Standard deviation |
| Analytical concentration μmol/mol | 133.474 | 133.424 | 133.343 | 133.296 | 133.328 | 133.378 | 133.374 | 0.05% |

## Uncertainty budget

**Please provide below the uncertainty budget used to calculate the uncertainty associated with the measurement of the ethanol amount fraction.**

The sources of uncertainty of the final ethanol amount fraction include the following four parts:

(1) The uncertainty of gravimetric preparation($u_{grav,r}$): The uncertainty in weight method preparation is composed of the purity uncertainty of ethanol and nitrogen, the uncertainty of weighed mass, and the uncertainty of atomic weight. It was calculated as $u_{grav,r}$=0.02%, using a software developed by NIM.

(2) The uncertainty caused by the analysis method (represented as $u_{ana,r}$): the uncertainty of alternating high-frequency single point calibration is 0.06%.

(3) The uncertainty of long-term stability (expressed as $u_{lts,r}$): The uncertainty introduced by software calculation of long-term stability is 0.05%.

(4) The uncertainty of adsorption correction (expressed as $u_{ads,r}$): Conservatively estimated, using 100% of the adsorption correction amount as the standard uncertainty introduced by adsorption correction, $u_{ads,r}$ =0.08%.

Therefore, the final combined uncertainty was :

$$u_{c,rel} = \sqrt{u_{grav,r}^2 + u_{ana,r}^2 + u_{lts,r}^2 + u_{ads,r}^2}$$

Table 7. Uncertainty budget

| $u_{grav,r}$ | $u_{ana,r}$ | $u_{lts,r}$ | $u_{ads,r}$ | $u_{c,rel}$ | $U_{rel}(k=2)$ |
|---|---|---|---|---|---|
| 0.02% | 0.06% | 0.05% | 0.08% | 0.11% | 0.22% |

## Additional information

**Please include in this section a brief outline of any stability testing (including sorption effects investigation, if performed) and correction procedures for the two travelling standards between the time they were prepared and the time they were measured at NPL (NPL will provide the date of measurement to each participant for each travelling standard on measurement completion).**

Two newly prepared gas mixtures were used as standard to confirm the stability of the two travelling standards (200226108007 and 200226108058) by using GC-FID. The testing results are shown in the following table 8.

Table 8. The variation of the two travelling standards in the past two years.

| Cylinder No. | Final amount fraction in2023 [μmol/mol] | Calibrated value in 2025 [μmol/mol] | Relative deviation of the sample concentration | Relative standard deviation of analytical method |
|---|---|---|---|---|
| 200226108007 | 118.915 | 118.798 | -0.0987% | 0.12% |
| 200226108058 | 133.304 | 133.302 | 0.0013% | 0.06% |

The relative deviation of the two-sample concentration was less than 0.1% in two years, which is below the method's relative standard deviation. That means there was no instability found in the two cylinders. The stability-induced correction term for ethanol concentration was calculated to be zero ($\Delta c_{lts,r} \approx 0$). Uncertainty due to long time stability ($u_{lts,r}$) was taken as $u_{lts,r} = \frac{0.12\%}{\sqrt{6}} = 0.05\%$.

## Participants report form, Part B

### Measurement results

Please indicate below the final value and associated expanded uncertainty of the $C_2H_5OH$ amount fraction in each of the two travelling standards.

| Measurements results for $C_2H_5OH$ in $N_2$ | | |
|---|---|---|
| | **Travelling standard 1** | **Travelling standard 2** |
| Nominal amount fraction [µmol mol$^{-1}$] | 112.5 | 127.5 |
| Final amount fraction $x_{C_2H_5OH}$ [µmol mol$^{-1}$] | 112.43 | 127.42 |
| Expanded uncertainty $U_{x_{C_2H_5OH}}$ [µmol mol$^{-1}$] | 0.27 | 0.28 |
| Coverage factor | 2 | 2 |

## Gravimetric preparation and purity

The reported values are the actual measurements obtained from gravimetric weighing in accordance with the ISO 6142-1 standard. The measured weights have been verified in compliance with the ISO 12963 standard. For any necessary corrections, the associated uncertainty values have been included.

Purity of ethanol:

| Component | Amount fraction mol/mol | Uncertainty ($K = 2$) mol/mol | Uncertainty distribution |
|---|---|---|---|
| Water | 0.001447 | 0.000029 | rectangular |
| Ethanol | 0.99855 | 0.000029 | Normal |

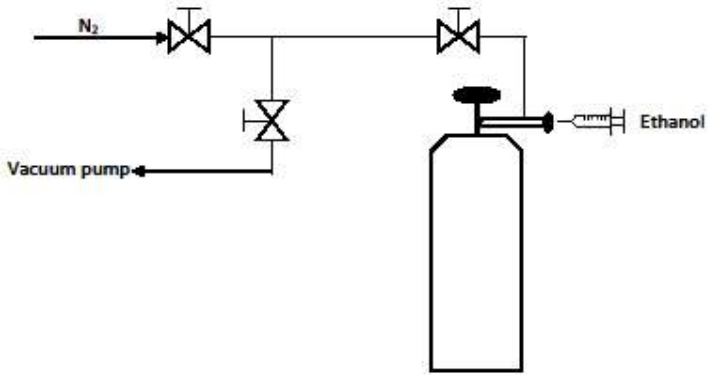
Note: Water concentration for impurity in the ethanol was 0.566 mg/g

Impurities of nitrogen:

| Component | Concentration (µmol/mol) | Detector | Distribution | Applied concentration (µmol/mol) | Standard uncertainty (µmol/mol) | |
|---|---|---|---|---|---|---|
| $O_2$ | 0.028 | CRDS | Rectangular | 0.028 | 0.010 | |
| Ar | 37.23 | GC/PDHID | Normal | 37.23 | 0.39 | |
| CO | <0.050 | GC/FID* | Rectangular | 0.025 | 0.014 | |
| $CO_2$ | <0.050 | GC/FID* | Rectangular | 0.025 | 0.014 | |
| $CH_4$ | <0.070 | GC/FID* | Rectangular | 0.035 | 0.020 | |
| $H_2O$ | 0.070 | CRDS | Rectangular | 0.070 | 0.041 | |
| | | | impurities | 37.42 | 0.39 | |
| | | | $N_2$ purity | 999962.58 | 0.78 | $k$=2 |

*GC/FID with methanizer

The gas standard for CCQM-K93.2023 was prepared gravimetrically using a one-step dilution process in accordance with ISO 6142-1. Two balances were employed: one for weighing the aluminium cylinders and the other for weighing the syringe. The mass of ethanol introduced into the cylinder was calculated by measuring the syringe's mass before and after the gas standard preparation.




Purity table for 112.5 µmol/mol
Cylinder ID: D094484

| Component | Gravimetric value | Gravimetric uncertainty $U(x_i)$, $k$=2 |
|---|---|---|
| Ethanol | 112.46 µmol/mol | 0.026 µmol/mol |
| $N_2$ | 99.987 cmol/mol | 0.007 cmol/mol |

Purity table for 127.5 µmol/mol
Cylinder ID: D094486

| Component | Gravimetric value | Gravimetric uncertainty $U(x_i)$, $k$=2 |
|---|---|---|
| Ethanol | 127.45 µmol/mol | 0.026 µmol/mol |
| N2 | 99.985 cmol/mol | 0.007 cmol/mol |

Uncertainty budget for the mole fraction of ethanol in the final mixture

Cylinder ID: D094484

| Quantity | Value | | Standard Uncertainty | | Distribution | Sensitivity Coefficient | Uncertainty Contribution | | Index |
|---|---|---|---|---|---|---|---|---|---|
| $n_{component1}$ | 4.86E-05 | mol | 3.54E-08 | mol | Normal | 1 | 3.04E-03 | %rel | 25.90% |
| $n_{component2}$ | 4.31E+01 | mol | 2.12E-05 | mol | Normal | 1 | 2.12E-05 | %rel | 0.18% |
| $n_{component3}$ | 4.31E+01 | mol | 2.12E-05 | mol | Normal | 1 | 2.12E-05 | %rel | 0.18% |
| | | | | | | | | | |
| $m_{cyl1}$ | 0.22 | g | 9.83E-03 | %rel | Normal | 1 | 9.83E-03 | %rel | 64.63% |
| $(Samp-Tare)_{empty}$ | 0.50 | g | 0.011 | mg | | | | | |
| $(Samp-Tare)_{cyl1}$ | 0.22 | g | 0.007 | mg | | | | | |
| $u_{bal}$ | 0.00 | g | 0.016 | mg | | | | | |
| $u_{res}$ | 0.50 | g | 0.000 | mg | | | | | |
| mol | 0.00 | mol | 0.000 | mol | | | | | |
| | | | | | | | | | |
| $m_{cyl2}$ | 98.56 | g | 2.16E-03 | %rel | Normal | 1 | 1.38E-03 | %rel | 11.76% |
| $(Samp-Tare)_{empty}$ | -19.16 | g | 0.000 | mg | | | | | |
| $(Samp-Tare)_{cyl1}$ | 79.50 | g | 0.000 | mg | | | | | |
| $u_{bal}$ | 0.00 | g | 1.789 | mg | | | | | |
| $u_{res}$ | 0.00 | g | 0.000 | mg | | | | | |
| mol | 43.10 | mol | 0.001 | mol | | | | | |
| | | | | | | | | | |
| $m_{cyl3}$ | 1111.65 | g | 1.49E-03 | %rel | Normal | 1 | 1.38E-03 | %rel | 11.76% |
| $(Samp-Tare)_{empty}$ | 79.50 | g | 0.000 | mg | | | | | |
| $(Samp-Tare)_{cyl1}$ | 1191.15 | g | 0.000 | mg | | | | | |
| $u_{bal}$ | 0.00 | g | 1.789 | mg | | | | | |
| $u_{res}$ | 0.00 | g | 16.414 | mg | | | | | |
| mol | 43.10 | mol | 0.001 | mol | | | | | |
| | | | | | | | | | |
| | | | | | | | | | |
| C2H5OH | 112.46 | µmol/mol | 0.0132 | µmol/mol | | | 0.01 | %rel | |
| N2 | 99.9887 | cmol/mol | 0.0038 | cmol/mol | | | 0.00 | %rel | |

Results:

| Quantity | Value | | Expanded Uncertainty | | Coverage factor | Coverage |
|---|---|---|---|---|---|---|
| C2H5OH | 112.46 | µmol/mol | 0.02 | %rel | 2.00 | 95% |
| N2 | 99.99 | cmol/mol | 0.01 | %rel | 2.00 | 95% |

## Measurement procedure

The assigned value of the gas content in the final gas mixture was determined using the gravimetric method in accordance with ISO 6142-1 and verified through composition analysis by the comparison method in compliance with ISO 12963.

The assigned value (mole fraction) of ethanol in nitrogen was determined in accordance with ISO 6142-1:2015 using the gravimetric method. The mole fraction of ethanol was verified by Gas Chromatography with Flame Ionization Detection (GC-FID) using a one-point calibration against a PRM traceable to the NIMT standard. The analytical conditions for the ethanol gas analysis are presented below.

| Ethanol | GC-FID |
|---|---|
| Column | PoraBOND Q |
| Carrier flow | 3 mL/min |
| Oven temperature | 120 °C |
| Detector temperature | 150 °C |
| $H_2$ flow | 30 mL/min |
| Air flow | 400 mL/min |
| Sample flow | 45 mL/min |
| Sample loop | 1 mL |

## Uncertainty budget

Cylinder No. PRM1094484

| Uncertainty source | Estimate (absolute unit) | Standard uncertainty (%relative) | Contribution to standard uncertainty (%relative) |
|---|---|---|---|
| - The Gravimetric gas mixture, ($X_i$) | 112.46 | 0.01 | 0.01 |
| - The standard gas mixture, ($X_{ref}$) | 112.43 | 0.01 | 0.01 |
| - Response of CRM, u($Y_{ref}$) | 369.10 | 0.04 | 0.04 |
| - Response of sample, u($Y_s$) | 369.31 | 0.02 | 0.02 |
| - Analytical content between cycle, u($x_{sb}$) | - | 0.01 | 0.01 |
| - Measurement Bias, u($X_B$) | 0.03 | 0.02 | 0.02 |
| Stability, u(Xstab) 0.1% | 0.11 | 0.10 | 0.10 |
| Analytical content of sample, ($X_s$) | 112.50 | Combined uncertainty | 0.12 |
| Expanded uncertainty ($k$ = 2), %relative | | | 0.24 |

Cylinder No. PRM1094486

| Uncertainty source | Estimate (absolute unit) | Standard uncertainty (%relative) | Contribution to standard uncertainty (%relative) |
|---|---|---|---|
| - The Gravimetric gas mixture, ($X_G$) | 127.45 | 0.01 | 0.01 |
| - The standard gas mixture, ($X_{ref}$) | 127.41 | 0.01 | 0.01 |
| - Response of CRM, u($Y_{ref}$) | 415.66 | 0.03 | 0.03 |
| - Response of sample, u($Y_s$) | 415.75 | 0.03 | 0.03 |
| - Analytical content between cycle, u($x_{sb}$) | - | 0.00 | 0.00 |
| - Measurement Bias, u($X_B$) | 0.01 | 0.00 | 0.00 |
| Stability, u(Xstab) 0.1% | 0.13 | 0.10 | 0.10 |
| Analytical content of sample, ($X_s$) | 127.44 | Combined uncertainty | 0.11 |
| Expanded uncertainty ($k$ = 2), %relative | | | 0.22 |

## Additional information about stability testing

NIMT prepared the first ethanol-in-nitrogen standard using a gravimetric method on 1 December 2023, and the second on 14 March 2025. In the long-term stability test, the difference between the gravimetric and verified mole fractions of ethanol after transportation was found to be less than 0.1%.

**Cylinders D094484 and D094486 showed drift correction rates of −0.00015 and −0.00019 µmol/mol per day, respectively.** Considering the elapsed time prior to analysis at NPL, the corrected mole fractions of ethanol in the two gas standards were calculated to be 112.43 **µmol/mol and 127.42 µmol/mol, respectively.**

NIST

# Participants report form, Part **B**

## Measurement results

| **Measurements results for $C_2H_5OH$ in $N_2$** | | |
|---|---|---|
| | **Mixture 1**<br>CC750302 | **Mixture 2**<br>CC750296 |
| Nominal amount fraction [µmol mol$^{-1}$] | 108.5 | 121.1 |
| Final amount fraction $\chi_{C_2H_5OH}$ [µmol mol$^{-1}$] | 107.92 | 121.80 |
| Expanded uncertainty $U_{\chi_{C_2H_5OH}}$ [µmol mol$^{-1}$] | 0.65 | 1.37 |
| Coverage factor | k=2 | k=2 |

## Gravimetric preparation and purity

**Cylinder Preparation**

New aluminium compressed gas cylinders with an approximate internal volume of 30L and treated with Airgas's proprietary Aculife IV technique and equipped with brass CGA 350 valves, were used to prepare two ethanol in nitrogen (EtOH / $N_2$) mixtures. The cylinders were connected to a fill manifold and evacuated to a pressure of approximately <3 millitorr (mTorr) for three days.

The cylinders were removed from the fill manifold and the evacuated mass was measured using a Mettler SR64001 floor balance with a resolution of 0.1 g. Each cylinder was manually placed onto the balance pan and weighed. The cylinder was removed and zero was verified before being replaced for replicate measurements. This process was repeated a minimum of ten times for each cylinder.

**Ethanol (Minor Component) Addition**

One 100 mL bottle of anhydrous ethanol (Sigma, stock number 459836, lot number SHBJ7925) equipped with a sure seal cap and septa and a certified purity of ≥ 99.5% was used without further purification for the preparation of both mixtures. Water impurity was determined before the ethanol addition using a Coulometric Karl Fisher titration technique prior to the minor component addition to both standards.

One gas tight, micro syringe from Hamilton (capacity 2.0 mL) was used for the ethanol addition. A 1.0 ml micro from Hamilton syringe was used as a control, and the 2.0 mL was used for the actual injection. Both syringes were weighed on a Mettler Toledo balance AT261 with a 62 g capacity and a resolution of 0.01 mg. The weighing sequence was control; ten weighings of the injection syringe; control.

Calculations were performed to determine the mass of ethanol required to produce the nominal value gas mixture for a final fill pressure of 1800 psig, and the addition syringe was loaded. After a small amount of air was eliminated from the syringe, the gas tight plunger was closed. The loaded syringe mass was obtained using the same weighing scheme as above.

The sample cylinder was attached to the fill manifold via a stainless steel CGA 350 fitting with a 0.25-inch stainless steel tee fitting. The end of the tee was fitted with syringe injection cap fitted with a graphite ferrule and neoprene septa. A cylinder or Airgas ISP nitrogen ($N_2$) was also attached to the manifold. The manifold lines were opened to the pump and evacuated. The pump was isolated, and the system was filled with approximately 100 psi of N2 and evacuated three times. The sample line was again isolated from the pump and the vacuum gauge was observed to verify that the septum was holding a gas tight seal. The sample line was isolated from the manifold,

and the ethanol loaded syringe needle was introduced through the septum and a heat gun was used to heat the tee and CGA connection. The evacuated cylinder valve was opened, the gas tight seal was opened on the syringe and the plunger on the loaded syringe was depressed. After all of the EtOH was removed from the syringe, the gas tight plunger was closed, and the needle was removed from the system. The remaining ethanol in the sample line was purged into the cylinder by pressurizing the line to approximately 100 psig of $N_2$, isolating the $N_2$ source, and opening the cylinder valve to allow the $N_2$ to bleed into the cylinder. This sequence was repeated ten times.

After injection the syringe was weighed following the previous weighing sequence and the mass of ethanol transferred into the cylinder was measured. These values are listed in Table 1.

**Table 1.** Ethanol addition amounts. Value includes purity adjustments.

| Cylinder Number | Ethanol Addition Mass (g) | Standard Uncertainty (g) |
|---|---|---|
| CC750302 | 0.7576193 | 0.00012 |
| CC750296 | 0.8570585 | 0.0001386 |

**Nitrogen (Major Component) Addition**

The tee device containing the injection port was removed from the sample line and the CGA fitting was connected to the 0.25-inch stainless steel sample line. The fill manifold was evacuated to a pressure of < 5 mTorr and then purged and vented ten times with 200 psia of $N_2$. Nitrogen was then transferred to the sample cylinder until a fill pressure of 1420 psia (warm). The sample was isolated, and the fill manifold was evacuated. A new cylinder of $N_2$ was added to the manifold and the flushing procedure described previously was conducted again. The fill process continued until the sample cylinder was filled to 1810 psia (warm). The sample cylinder was allowed to cool for three hours before being topped off to a final fill pressure of 1811 psia. The sample cylinder was removed from the fill manifold and allowed to equilibrate to room temperature for an hour before being weighed. Each cylinder was manually placed onto the balance pan and weighed. The cylinder was removed and zero was verified before being replaced for replicate measurements. This process was repeated a minimum of ten times for each cylinder.

The ethanol concentration was then calculated from the weight of the ethanol and nitrogen mixture, Table 2.

**Table 2.** Gravimetric amount fraction of ethanol standards. Value includes purity adjustments.

| Cylinder Number | Ethanol amount fraction (µmol/mol) | Standard uncertainty (µmol/mol) k=2 |
|---|---|---|
| CC750302 | 107.92 | 0.65 |
| CC750296 | 122.38 | 0.74 |

**Purity Analysis of Pure Ethanol**

**Water Analysis**

Water analysis of the ethanol component was performed by Dr. B. Lang of the NIST Chemical Sciences Division using the Karl Fisher Titration method. The results are listed in Table 3.

**Table 3.** Karl Fisher water analysis of Ethanol parent.

| Component | Water to Ethanol Value (g/g) | Water to Ethanol uncertainty (g/g) |
|---|---|---|
| Ethanol | 0.0004099 | 0.0000045 |

**Water Analysis of Balance Gas Component**

Water analysis of the balance gas component was achieved with a Tiger Optics Laser Trace 3 cavity ring down instrument equipped with a water measurement module. All balance gas cylinders were analyzed and found to be below 100 nmol/mol which was considered negligible and not included in the final value assignment of the mixtures.

## Measurement procedure

**Analytical Method**

The EtOH component of the mixtures were analyzed with a Fourier Transform Infrared (FTIR) spectrometer (Nicolet Model Nexus 670) equipped with a 10 m folding path, quartz gas cell (Specac, Model Cyclone 10C, NIST # 623477) with potassium bromide windows and a liquid nitrogen cooled mercury-cadmium-telluride (MCT-A) detector. The FTIR collection parameters are shown in Table 4.

The gas cell temperature was regulated with an external heating jacket and was maintained at 48 °C. Sample selection was achieved manually by changing sample lines after each analysis collection.

**Table 4:** FTIR Collection Parameters.

| Parameter | Value |
|---|---|
| Number of Scans | 256 |
| Apodization | Boxcar |
| Resolution | 0.5 $cm^{-1}$ |
| Beamsplitter | KBr |
| Detector | MCT-A |

The gas cell was purged with dry N2 and vacuum evacuated between each sample to ensure that the previous gas matrix was removed from the sample cell. Prior to sample analysis, the bypass loop of the sampling system was opened, and the gas cell was filled to a nominal pressure of 0.107 MPa (800 mmHg) of sample and vacuum evacuated twice. Upon the third fill, the cell was filled to a nominal pressure of 0.104 MPa (780 mmHg), the bypass loop was closed, sample flow (100 mL $min^{-1}$) to the gas cell was regulated by utilizing an MKS mass flow controller, and the internal cell pressure was regulated by an MKS back pressure controller by adjusting the flow through a rotameter downstream of the gas cell. The sample volumetric gas flow rate, measured via the downstream rotameter, was approximately 50 mL $min^{-1}$, ensuring positive flow through the gas cell during spectra acquisition. For measurement system set up see Figure 1.

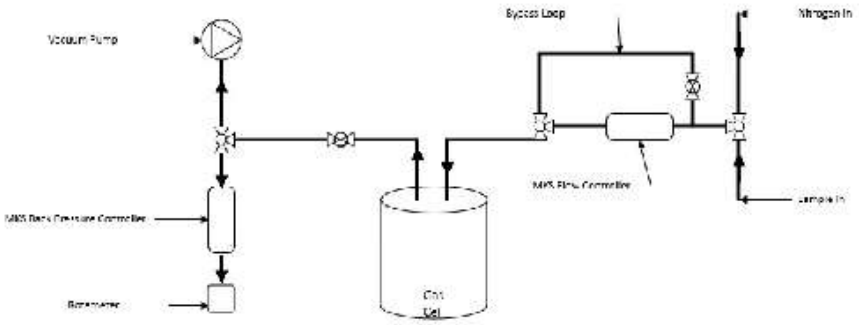



**Figure 1:** FTIR gas sampling setup.

The resulting spectra were evaluated with the area under curve being taken between 952.44 $cm^{-1}$ to 1163.91 $cm^{-1}$. At least six spectrums were collected per sample, with each being comprised of 256 scans, taken at 1 s intervals, at 0.5 $cm^{-1}$ resolution that were co-added.

**Verification:**

The amount fraction of the mixtures were verified by comparison to four NIST gravimetrically prepared primary standard mixtures (PSM) ranging from (70.54 to 149.0) µmol $mol^{-1}$ EtOH in N2 (see Table 5). A new background scan was completed at the start of each analysis day, and a nitrogen blank was collected to verify a zero baseline was achieved.

Each PSM and mixture was compared to a control cylinder a minimum of three times over three days, with two cylinders sampled between subsequent samples of the control (e.g., "control, sample 1, sample 2, control"). The sampling order of the standards was randomized in each set collected.

**Table 5:** Ethanol in nitrogen NIST Primary Standard Mixtures. The stated uncertainties are expanded ($k = 2$).

| Cylinder Number | EtOH (µmol $mol^{-1}$) | Reference |
|---|---|---|
| ALM040277 | 70.54 ± 0.14 | 1/94-GCR-ETHANOL SCOTT CRADA, P. 6 |
| ALM040295 | 100.7 ± 0.2 | 2/93-GCR-ETHANOL SCOTT CRADA, p. 5 |
| ALM009006 | 121.8 ± 0.2 | 8/97-GCR-ETHANOL p.19 |
| ALM040288 | 149.0 ± 0.3 | 12/93-GCR-ETHANOL SCOTT CRADA, p. 4 |

Each instrument response ($r$) collected, including both control responses and sample responses, was pressure corrected to account for the fluctuations of pressure inside of the sample cell during the measurement:

$$r = \left(\frac{780\ mmHg}{P}\right) * r_a \qquad \text{(Eq. 1)}$$

where $P$ is the actual recorded pressure in mmHg within the cell and $r_a$ is the calculated area under the curve for the peak located between 952.44 $cm^{-1}$ to 1163.91 $cm^{-1}$.

Instrument response ratios ($R$) were calculated as:

$$R = \frac{r_S}{r_C} \quad \text{(Eq. 2)}$$

where $r_S$ is the instrument response of each sample, and $r_C$ is the drift-corrected response of the control, calculated as:

$$r_C = r_1 + \frac{r_2 - r_1}{N-1} \cdot (n-1) \quad \text{(Eq. 3)}$$

In Equation 3, $r_1$ and $r_2$ are the instrument responses of the control taken before and after the sample measurements; $N$ is the total number of measurements in the sampling sequence; and $n$ is the order number of the sample measurement within the sequence.

An ISO 6143 compliant generalized least-squares regression program (GenLine) [1,2] was used to assign a first-order regression to the gravimetric values and average response ratios of the PSMs. This regression equation was then used to predict the EtOH amount fraction of the mixtures based on a response ratio for each cylinder.

## Uncertainty budget

**Uncertainty Budget and Final Value Assignment**

The final amount fraction values and associated uncertainties were assigned to the mixtures in accordance with ISO 6142-1:2015 [3], including contributions from gravimetry ($y_{grav}$) and verification and stability ($y_{pool}$). The uncertainty values for the gravimetric calculations are included in Table 2, and the uncertainty contributions from the verification and stability analyses are included in Figures 2 thru 6, respectively. The summarized uncertainty budget for each cylinder is listed in Table 6.

For CC750302, the analysed and gravimetric values agreed within their corresponding uncertainties. Therefore, the gravimetric amount fraction was used for the final value assignment:

$$y_{CC750302} = y_{grav} \quad \text{(Eq. 4)}$$

and the combined standard uncertainty was calculated as:

$$u_c(y) = \frac{1}{2}\sqrt{u^2(y_{grav}) + u^2(y_{pool}) + (y_{grav} - y_{pool})^2} \quad \text{(Eq. 5)}$$

For CC750296, the verification revealed a bias between the analysed and gravimetric values. Since no error could be found within any of the gravimetric calculations, this bias was believed to be attributable to error during sample preparation. As a result, the average of the gravimetric value and the pooled analysis amount fraction was used for the final value assignment:

$$y_{CC750296} = \frac{(y_{grav} + y_{pool})}{2} \quad \text{(Eq. 6)}$$

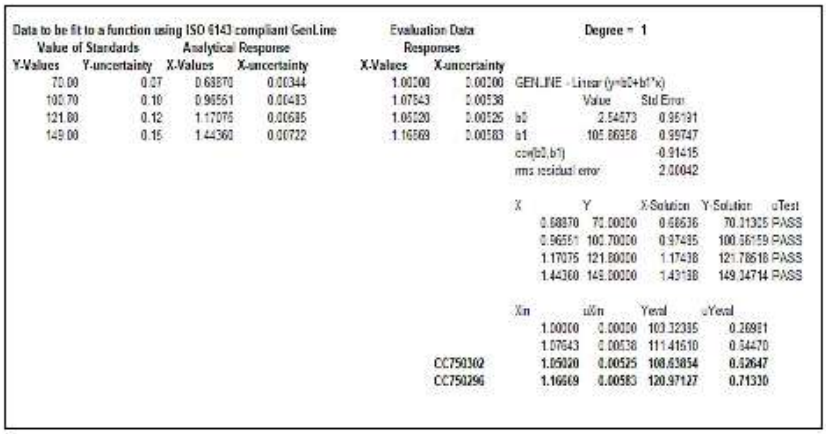
and the combined standard uncertainty was calculated using equation 5.

Both mixtures were reanalysed upon their return to NIST in February 2025 using the same measurement technique as described previously. The stability results agreed with the original assigned values within the associated expanded uncertainties, and as a result no corrections to the amount fractions were made.

The final expanded uncertainty for both mixtures is expressed as:

$$U(y) = k u_{final}(y) \quad \text{(Eq. 7)}$$

where the coverage factor $k$ is equal to 2. The true value is therefore asserted to lie in the interval defined by the assigned amount fraction ± U, with a confidence of approximately 95 % [4].



Data to be fit to a function using ISO 6143 compliant GenLine — Degree = 1

| Value of Standards Y-Values | Y-uncertainty | Analytical Response X-Values | X-uncertainty | Evaluation Data Responses X-Values | X-uncertainty |
|---|---|---|---|---|---|
| 70.00 | 0.07 | 0.68870 | 0.00344 | 1.00200 | 0.00200 |
| 100.70 | 0.10 | 0.96551 | 0.00483 | 1.07643 | 0.00538 |
| 121.80 | 0.12 | 1.17075 | 0.00585 | 1.05020 | 0.00525 |
| 149.00 | 0.15 | 1.44360 | 0.00722 | 1.16569 | 0.00583 |

GENLINE - Linear (y=b0+b1*x)

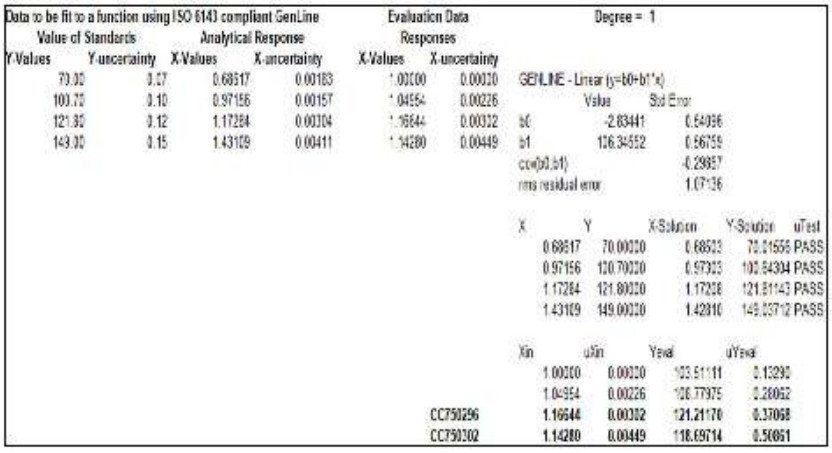
| | Value | Std Error |
|---|---|---|
| b0 | 2.54573 | 0.95191 |
| b1 | 105.86358 | 0.99747 |
| cov(b0,b1) | | -0.91415 |
| rms residual error | | 2.00042 |

| X | Y | X-Solution | Y-Solution | uTest |
|---|---|---|---|---|
| 0.68870 | 70.00020 | 0.68636 | 70.01325 | PASS |
| 0.96551 | 100.70020 | 0.97495 | 100.56159 | PASS |
| 1.17075 | 121.80020 | 1.17438 | 121.78618 | PASS |
| 1.44360 | 149.00020 | 1.43138 | 149.04714 | PASS |

| Xin | uXin | Yeval | uYeval |
|---|---|---|---|
| 1.00200 | 0.00020 | 103.32335 | 0.26981 |
| 1.07643 | 0.00538 | 111.41610 | 0.54470 |
| **1.05020** | **0.00525** | **108.63854** | **0.52647** |
| **1.16569** | **0.00583** | **120.97127** | **0.71330** |

CC750302
CC750296

**Figure 2:** Initial verification 1: amount fractions and standard uncertainties for CC750302 and CC750296 (shown in bold), as determined by first-order GenLine regression [1,2] using 4 PSMs.



Data to be fit to a function using ISO 6143 compliant GenLine — Degree = 1

| Value of Standards Y-Values | Y-uncertainty | Analytical Response X-Values | X-uncertainty | Evaluation Data Responses X-Values | X-uncertainty |
|---|---|---|---|---|---|
| 70.00 | 0.07 | 0.68817 | 0.00183 | 1.00200 | 0.00020 |
| 100.70 | 0.10 | 0.97156 | 0.00157 | 1.04554 | 0.00226 |
| 121.80 | 0.12 | 1.17284 | 0.00304 | 1.16644 | 0.00302 |
| 149.00 | 0.15 | 1.43109 | 0.00411 | 1.14280 | 0.00449 |

GENLINE - Linear (y=b0+b1*x)

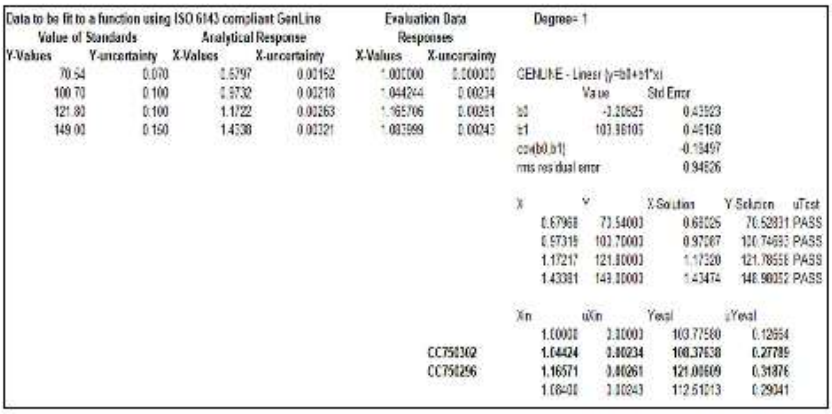
| | Value | Std Error |
|---|---|---|
| b0 | -2.83441 | 0.64096 |
| b1 | 126.34552 | 0.56759 |
| cov(b0,b1) | | -0.29857 |
| rms residual error | | 1.07126 |

| X | Y | X-Solution | Y-Solution | uTest |
|---|---|---|---|---|
| 0.68817 | 70.00020 | 0.68523 | 70.01556 | PASS |
| 0.97156 | 100.70020 | 0.97323 | 100.84304 | PASS |
| 1.17284 | 121.80020 | 1.17238 | 121.81143 | PASS |
| 1.43109 | 149.00020 | 1.42810 | 149.03712 | PASS |

| Xin | uXin | Yeval | uYeval |
|---|---|---|---|
| 1.00200 | 0.00020 | 123.51111 | 0.13290 |
| 1.04554 | 0.00226 | 128.77975 | 0.28052 |
| **1.16644** | **0.00302** | **121.21170** | **0.37068** |
| **1.14280** | **0.00449** | **118.69714** | **0.56051** |

CC750296
CC750302

**Figure 3:** Initial verification 2: amount fractions and standard uncertainties for CC750302 and CC750296 (shown in bold), as determined by first-order GenLine regression [1,2] using 4 PSMs.



Data to be fit to a function using ISO 6143 compliant GenLine

| Value of Standards | | Analytical Response | | Evaluation Data Responses | | |
|---|---|---|---|---|---|---|
| Y-Values | Y-uncertainty | X-Values | X-uncertainty | X-Values | X-uncertainty | |
| 70.54 | 0.070 | 0.6797 | 0.00152 | 1.000000 | 0.000000 | |
| 100.70 | 0.100 | 0.9732 | 0.00218 | 1.044244 | 0.00234 | |
| 121.80 | 0.100 | 1.1722 | 0.00263 | 1.165706 | 0.00261 | |
| 149.00 | 0.150 | 1.4338 | 0.00321 | 1.083999 | 0.00243 | |

Degree= 1

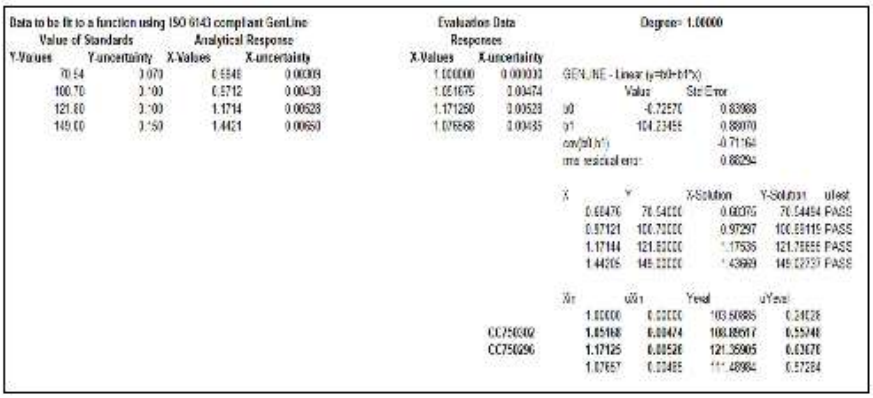
GENLINE - Linear (y=b0+b1*x)

| | Value | Std Error |
|---|---|---|
| b0 | -3.20625 | 0.43923 |
| b1 | 103.98105 | 0.46158 |
| cov(b0,b1) | | -0.18497 |
| rms residual error | | 0.94826 |

| X | Y | X-Solution | Y-Solution | uTest |
|---|---|---|---|---|
| 0.67968 | 73.54000 | 0.68025 | 70.52831 | PASS |
| 0.97319 | 102.70000 | 0.97267 | 100.74693 | PASS |
| 1.17217 | 121.80000 | 1.17320 | 121.78558 | PASS |
| 1.43381 | 149.00000 | 1.43474 | 148.98052 | PASS |

| | Xn | uXn | Yeval | uYeval |
|---|---|---|---|---|
| | 1.00000 | 0.00000 | 103.77580 | 0.12554 |
| CC750302 | **1.04424** | **0.00234** | **108.37638** | **0.27789** |
| CC750296 | **1.16571** | **0.00261** | **121.00609** | **0.31876** |
| | 1.08400 | 0.00243 | 112.61213 | 0.29041 |

**Figure 4:** Stability reanalysis 1: amount fractions and standard uncertainties for CC750302 and CC750296 (shown in bold), as determined by first-order GenLine regression [1,2] using 4 PSMs.



Data to be fit to a function using ISO 6143 compliant GenLine

| Value of Standards | | Analytical Response | | Evaluation Data Responses | | |
|---|---|---|---|---|---|---|
| Y-Values | Y-uncertainty | X-Values | X-uncertainty | X-Values | X-uncertainty | |
| 70.54 | 0.070 | 0.6848 | 0.00309 | 1.000000 | 0.000000 | |
| 100.70 | 0.100 | 0.9712 | 0.00438 | 1.051675 | 0.00474 | |
| 121.80 | 0.100 | 1.1714 | 0.00528 | 1.171250 | 0.00528 | |
| 149.00 | 0.150 | 1.4421 | 0.00650 | 1.076668 | 0.00485 | |

Degree= 1.00000

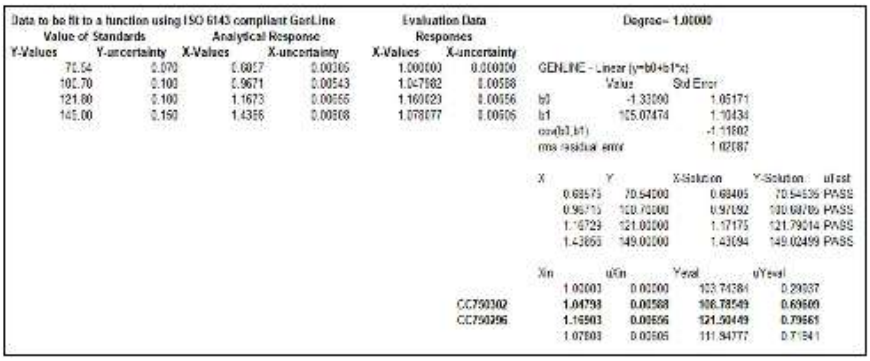
GENLINE - Linear (y=b0+b1*x)

| | Value | Std Error |
|---|---|---|
| b0 | -0.72570 | 0.83988 |
| b1 | 104.23455 | 0.88070 |
| cov(b0,b1) | | -0.71164 |
| rms residual error | | 0.88294 |

| X | Y | X-Solution | Y-Solution | uTest |
|---|---|---|---|---|
| 0.68476 | 70.54000 | 0.68375 | 70.54484 | PASS |
| 0.97121 | 100.70000 | 0.97297 | 100.88115 | PASS |
| 1.17144 | 121.80000 | 1.17535 | 121.75855 | PASS |
| 1.44305 | 149.00000 | 1.43669 | 149.02737 | PASS |

| | Xn | uXn | Yeval | uYeval |
|---|---|---|---|---|
| | 1.00000 | 0.00000 | 103.50885 | 0.24028 |
| CC750302 | **1.05168** | **0.00474** | **109.69617** | **0.55748** |
| CC750296 | **1.17125** | **0.00528** | **121.35905** | **0.63670** |
| | 1.07657 | 0.00485 | 111.48984 | 0.57284 |

**Figure 5:** Stability reanalysis 2: amount fractions and standard uncertainties for CC750302 and CC750296 (shown in bold), as determined by first-order GenLine regression [1,2] using 4 PSMs.



Data to be fit to a function using ISO 6143 compliant GenLine

| Value of Standards | | Analytical Response | | Evaluation Data Responses | |
|---|---|---|---|---|---|
| Y-Values | Y-uncertainty | X-Values | X-uncertainty | X-Values | X-uncertainty |
| 70.54 | 0.070 | 0.6857 | 0.00305 | 1.000000 | 0.000000 |
| 100.70 | 0.100 | 0.9671 | 0.00543 | 1.047682 | 0.00568 |
| 121.80 | 0.100 | 1.1673 | 0.00555 | 1.160023 | 0.00556 |
| 149.00 | 0.150 | 1.4366 | 0.00808 | 1.078877 | 0.00505 |

Degree= 1.00000

GENLINE - Linear (y=b0+b1*x)

| | Value | Std Error |
|---|---|---|
| b0 | -1.33090 | 1.05171 |
| b1 | 105.07474 | 1.10434 |
| cov(b1,b1) | | -1.11802 |
| rms residual error | | 1.02087 |

| X | Y | X-Solution | Y-Solution | uTest |
|---|---|---|---|---|
| 0.68575 | 70.54000 | 0.68405 | 70.54636 | PASS |
| 0.96715 | 100.70000 | 0.97092 | 100.68705 | PASS |
| 1.16729 | 121.80000 | 1.17175 | 121.79014 | PASS |
| 1.43665 | 149.00000 | 1.43694 | 149.02499 | PASS |

| | Xin | uXin | Yeval | uYeval |
|---|---|---|---|---|
| | 1.00000 | 0.00000 | 103.74384 | 0.29037 |
| CC750302 | **1.04798** | **0.00568** | **108.78549** | **0.69609** |
| CC750296 | **1.16503** | **0.00556** | **121.50449** | **0.79661** |
| | 1.07800 | 0.00505 | 111.94777 | 0.71541 |

**Figure 6:** Stability reanalysis 3: amount fractions and standard uncertainties for CC750302 and CC750296 (shown in bold), as determined by first-order GenLine regression [1,2] using 4 PSMs.

**Table 6.** Final value assignment and uncertainty budget for CC750302 and CC750296, including contributions from gravimetry ($y_{grav}$), and verification and stability ($y_{pool}$). All values are expressed as nmol/mol with associated standard uncertainties. The final expanded uncertainty, $U(y)$, is expressed at approximately 95 % confidence, $k = 2$.

| | **CC750302** | **CC750296** |
|---|---|---|
| $y_{grav}$ | 107.92 | 122.38 |
| $u(y_{grav})$ | 0.32 | 0.37 |
| $y_{pool}$ | 108.70 | 121.21 |
| $u(y_{pool})$ | 0.52 | 0.60 |
| $y_{grav} - y_{pool}$ | 0.77 | −1.17 |
| $\boldsymbol{y}$ | **107.92** | **121.80** |
| $u_{final}(y)$ | 0.32 | 0.68 |
| $\boldsymbol{U(y)}$ | **0.65** | **1.37** |

## Additional information

The mixtures were prepared a few weeks prior to shipment to the NPL, which did not allow sufficient time for stability testing. Therefore, the cylinders were reanalysed upon their return to NIST, approximately 13 months after initial preparation and verification, to evaluate stability over the duration of the comparison.

The mixtures and 4 PSMs were reanalysed over approximately 2 weeks (for a total of 3 ratios per cylinder), following the same measurement procedure as described for the initial verification. The resulting amount fraction values are shown in Figures 4, 5, and 6.

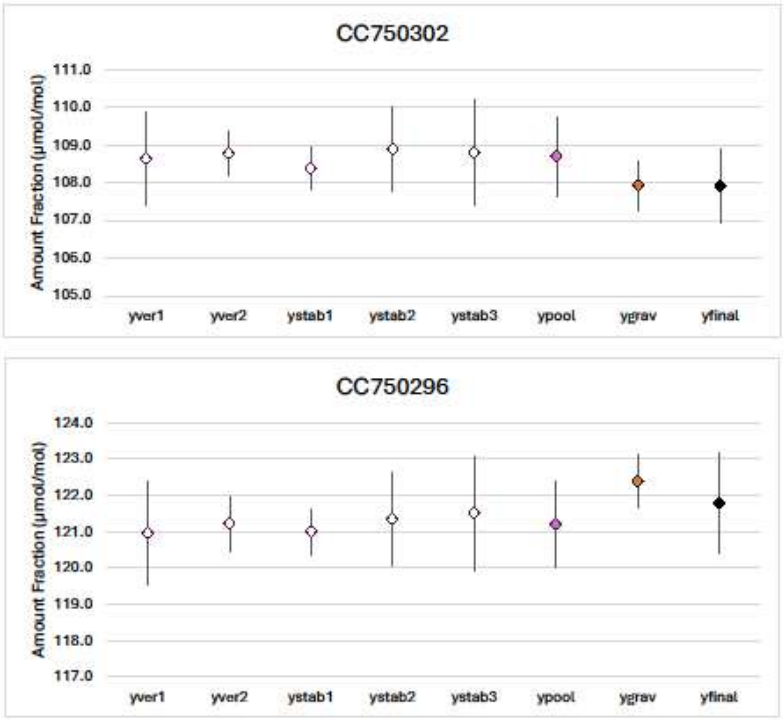



**Figure 9.** Final amount fraction value ($y_{final}$) assigned to CC750302 (top) and CC750293 (bottom), as compared to the values determined by gravimetry ($y_{grav}$), verification ($y_{ver}$), and stability testing ($y_{stab}$). Error bars represent associated expanded ($k = 2$) uncertainties.

**References**


[1] M.J.T. Milton, P.M. Harris, I.M. Smith, A.S. Brown, and B.A. Goody, Implementation of a generalized least-squares method for determining calibration curves from data with general uncertainty structures, *Metrologia*, 4(4), S291–S298 (2006).

[2] International Organization for Standardization, ISO 6143:2001 Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures, 2nd edition.

[3] International Organization for Standardization, ISO 6142-1:2015 Gas analysis – Preparation of calibration gas mixtures – Part 1: Gravimetric method for Class I mixtures.

[4] JCGM 100:2008, Evaluation of measurement data – Guide to the expression of uncertainty in measurement (Gum 1995 with minor corrections), Joint Committee for Guides in Metrology, BIPM, Sèvres, France (2008).

# Participants report form, Part B

## Measurement results

Please indicate below the final value and associated expanded uncertainty of the $C_2H_5OH$ amount fraction in each of the two travelling standards.

| Measurements result for $C_2H_5OH$ in $N_2$ | | |
|---|---|---|
| | **Travelling standard 1 D62 6508** | **Travelling standard 2 M39 5423** |
| Nominal amount fraction [µmol mol$^{-1}$] | 120 - 125 | 105 - 110 |
| Gravimetric amount fraction $c_{C_2H_5OH}$ [µmol mol$^{-1}$] | 122,898 | 108,05 |
| Expanded uncertainty $U_{c_{C_2H_5OH}}$ [µmol mol$^{-1}$] | 0,073 | 0,16 |
| Coverage factor | 2 | 2 |

## Gravimetric preparation and purity

Please provide below the following information:

- Statement whether the reported values are true gravimetric values, based on the masses and purities of the components added, or they have been determined and/or corrected by analysis.
- Details on the correction procedure, if applicable.
- Purity table with uncertainties for all the parent gases, including < LOQ flags with the respective LOQ values for the impurities. Specify uncertainty distribution (Gaussian, rectangular etc.)
- Brief outline of the dilution series undertaken to produce the final travelling standard
- Purity table for each of the final travelling standard, including uncertainties, as above

## Purity assessment of the starting materials

The purity assessment of the high purity ethanol was performed using Karl Fischer titration technique for the quantification of the $H_2O$ (moisture content). Agilent gas chromatography coupled with various detectors was utilised for purity analysis of high purity BIP™ nitrogen using NMISA primary standard gas mixture with impurities similar to those found in the high purity BIP™ nitrogen. **Table 1 and Table 2** show purity tables for high purity ethanol and BIP™ nitrogen used to prepare the comparison samples respectively.

Table 1. Purity table for high purity ethanol

| Component | Amount fraction ($\mu mol.mol^{-1}$) | Expanded uncertainty ($\mu mol.mol^{-1}$), U(k=2) | Distribution |
|---|---|---|---|
| $H_2O$ | $7{,}0 \times 10^{2}$ | $1{,}6 \times 10^{2}$ | Normal |
| $C_2H_5OH$ | $9{,}9 \times 10^{5}$ | $1{,}6 \times 10^{2}$ | Normal |

Table 2. Purity table for high purity nitrogen

| Component | Amount fraction ($\mu mol.mol^{-1}$) | Expanded uncertainty ($\mu mol.mol^{-1}$), U(k=2) | Distribution |
|---|---|---|---|
| CO | $6{,}6 \times 10^{-3}$ | $7{,}6 \times 10^{-3}$ | Rectangular |
| $CO_2$ | $4{,}1 \times 10^{-2}$ | $4{,}8 \times 10^{-2}$ | Rectangular |
| $CH_4$ | $9{,}0 \times 10^{-3}$ | $1{,}1 \times 10^{-2}$ | Rectangular |
| Ar | $6{,}9 \times 10^{0}$ | $4{,}1 \times 10^{-2}$ | Normal |
| $O_2$ | $2{,}1 \times 10^{0}$ | $9{,}8 \times 10^{-2}$ | Normal |
| $H_2O$ | $1{,}0 \times 10^{-2}$ | $1{,}2 \times 10^{-2}$ | Rectangular |
| $H_2$ | $3{,}2 \times 10^{1}$ | $2{,}2 \times 10^{0}$ | Normal |
| $N_2$ | $9{,}9 \times 10^{5}$ | $2{,}1 \times 10^{0}$ | Normal |

## Purity tables of the final travelling standards

**Table 3** and **Table 4** indicate purity tables for the two travelling standards, that is D62 6508 and M39 5423 respectively.

**Table 3.** Purity table for the travelling standard D62 6508

| Component | Gravimetric amount fraction (µmol.mol$^{-1}$) | Standard uncertainty (µmol.mol$^{-1}$), k=1 |
|---|---|---|
| $C_2H_5OH$ | $1,2 \times 10^{2}$ | $3,7 \times 10^{-2}$ |
| CO | $6,6 \times 10^{-3}$ | $3,8 \times 10^{-3}$ |
| $CO_2$ | $4,1 \times 10^{-2}$ | $2,4 \times 10^{-2}$ |
| $CH_4$ | $8,8 \times 10^{-3}$ | $5,1 \times 10^{-3}$ |
| Ar | $6,9 \times 10^{0}$ | $2,0 \times 10^{-2}$ |
| $O_2$ | $2,0 \times 10^{0}$ | $4,9 \times 10^{-2}$ |
| $H_2O$ | $9,6 \times 10^{-2}$ | $1,1 \times 10^{-2}$ |
| $H_2$ | $3,2 \times 10^{1}$ | $1,1 \times 10^{0}$ |
| $N_2$ | $9,9 \times 10^{5}$ | $1,1 \times 10^{0}$ |

**Table 4.** Purity table for the travelling standard M39 5423

| Component | Gravimetric amount fraction (µmol.mol$^{-1}$) | Standard uncertainty (µmol.mol$^{-1}$), k=1 |
|---|---|---|
| $C_2H_5OH$ | **$1,1 \times 10^{2}$** | **$7,8 \times 10^{-2}$** |
| CO | $6,6 \times 10^{-3}$ | $3,8 \times 10^{-3}$ |
| $CO_2$ | $4,1 \times 10^{-2}$ | $2,4 \times 10^{-2}$ |
| $CH_4$ | $8,8 \times 10^{-3}$ | $5,1 \times 10^{-3}$ |
| Ar | $6,9 \times 10^{0}$ | $2,0 \times 10^{-2}$ |
| $O_2$ | $2,0 \times 10^{0}$ | $4,9 \times 10^{-2}$ |
| $H_2O$ | $8,6 \times 10^{-2}$ | $1,1 \times 10^{-2}$ |
| $H_2$ | $3,2 \times 10^{1}$ | $1,1 \times 10^{0}$ |
| $N_2$ | $9,9 \times 10^{5}$ | **$1,1 \times 10^{0}$** |

## Method of preparation

The travelling standards containing ethanol in nitrogen were prepared in accordance with ISO 6142:2015 (Gas analysis – Preparation of calibration gas mixtures – Gravimetric method). These standards were prepared using a single-step dilution method from high purity ethanol purchased from Sigma Aldrich and the BIP™ nitrogen purchased from Air Products South Africa as indicated Figure 1.

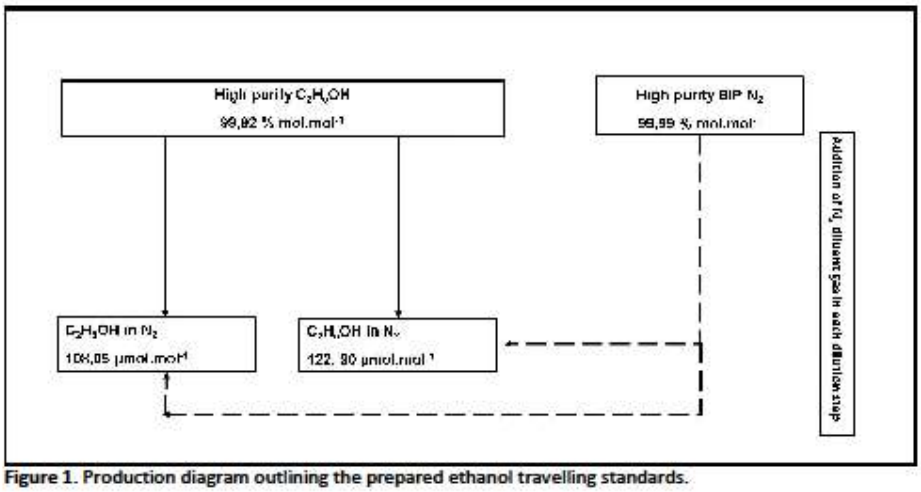



**Figure 1.** Production diagram outlining the prepared ethanol travelling standards.

## Method of Analysis

The gravimetric amount fractions of the travelling standards are the true gravimetric values based on the masses and the purities of the components added. These were analysed in accordance with ISO 6143:2001 (Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures). The gravimetric and analysis amount fractions of the prepared travelling standards are detailed in **Table 5**.

**Table 5.** Gravimetric and analysis amount fractions with expanded uncertainties of the comparison samples.

| Cylinder Number | Component | Gravimetric amount fraction and expanded uncertainty (µmol.mol$^{-1}$), U(k=2) | Analysis amount Fraction and expanded uncertainty (µmol.mol$^{-1}$), U(k=2) |
|---|---|---|---|
| M39 5423 | $C_2H_5OH$ | $1,1 \times 10^2 \pm 1,6 \times 10^{-1}$ | $1,1 \times 10^2 \pm 5,4 \times 10^{-1}$ |
| D62 6508 | $C_2H_5OH$ | $1,2 \times 10^2 \pm 7,3 \times 10^{-2}$ | $1,2 \times 10^2 \pm 4,1 \times 10^{-1}$ |

## Measurement procedure

Please provide below:

- Description of the measurements performed for the validation of the submitted gravimetric values, obtained from the preparation
- Calibrants and analysers details.

### Analysis of the gravimetric amount fraction

Two techniques were used for the analysis of the 120 to 125 µmol.mol$^{-1}$ gravimetric amount fractions. The techniques were gas chromatography coupled with flame ionisation detector (GC-FID) and a non-dispersive infrared (NDIR) Spectroscopy. The single-point and multi-point calibration methods were utilised for the analysis of the 120 to 125 µmol.mol$^{-1}$ comparison sample. For the lower range (105 to 110 µmol.mol$^{-1}$), only one technique (GC-FID) which adopted single-point calibration method. Both the GC-FID and NDIR were calibrated with NMISA developed primary standard gas mixtures (PSGMs).

### Single-point calibration method

The single-point calibration formula was adopted as shown in **Equation 1** to analyse the gravimetric amount fraction of the comparison samples:

$$x_{Sample} = \frac{y_{Sample}}{y_{Reference}} \times x_{Reference} \quad (1)$$

Where $x_{Sample}$ is the amount fraction of the comparison sample, $x_{Reference}$ is the amount fraction of the NMISA calibration standard, $y_{Sample}$ is the analytical response of the comparison sample and $y_{Reference}$ is the analytical response of the NMISA calibration standard.

### Multi-point calibration method

The analysis of gravimetrically prepared 120 to 125 µmol.mol$^{-1}$ amount fraction comparison sample was also performed using the multi-point calibration method. The calibration standards used are listed in **Table 6**. Data generated was analysed using a generalised least square method on the XLgenlinev1.1 software. The multi-point calibration formula was adopted as shown in **Equation 2** to analyse the gravimetric amount fraction of the comparison sample:

The second-order polynomial mathematical function used for multi-point calibration:

$$x = b_0 + b_1 y + b_2 y^2 \quad (2)$$

Table 6: Multi-point calibration standards

| Cylinder Number | Gravimetric amount fraction (µmol.mol$^{-1}$) | Expanded uncertainty (µmol.mol$^{-1}$), U(k=2) |
|---|---|---|
| D62 6418 | 1,1 x10$^{2}$ | 7,9 x 10$^{-2}$ |
| D62 6662 | 2,1 x10$^{2}$ | 7,7 x 10$^{-2}$ |
| D67 9474 | 8,2 x10$^{1}$ | 8,4 x 10$^{-2}$ |
| D62 6597 | 3,5 x10$^{1}$ | 8,2 x 10$^{-2}$ |
| M39 5407 | 1,2 x10$^{2}$ | 1,6 x 10$^{-1}$ |
| M39 5400 | 5,4 x10$^{1}$ | 1,5 x 10$^{-1}$ |
| D67 9609 | 1,9 x10$^{2}$ | 8,0 x 10$^{-2}$ |

## Instrumentation

**Two techniques were adopted for the analysis of the gravimetrically prepared comparison samples.**

#### For non-dispersive infrared (NDIR) spectroscopy

The Xstream ethanol analyser was purged with BIP nitrogen before and after every sample analysis using sulfinert treated tubing connected to a multi-position valve sampler box. The calibration standards and comparison sample were connected randomly on the 16-port sampler box that is connected to the Xstream NDIR analyser. Data acquisition was performed using in-house LabView software program. **Table 7** below shows the analytical conditions adopted on NDIR analyser.

Table 7: NDIR analytical conditions

| | |
|---|---|
| Purging time | 300s |
| Number of measurements taken | 30 |
| Number of cycle repeats | 4 |
| Sample flow | 100 mℓ.min$^{-1}$ |

**For Gas Chromatography (GC) technique:**

Agilent 7890B gas chromatography coupled with dual flame ionisation detection system was utilised for the analysis of the gravimetrically prepared comparison samples. The sample and calibration standard were connected to the regulators and purged before use. The gas mixtures were then connected to a sampler box with sulfinert treated tubing and set to a sample flow of 35 **$m\ell.min^{-1}$**. The analysis sequence followed the standard-sample-standard pattern with a minimum of ten repeats. The instrument conditions are presented in **Table 8**. Data acquisition was done using ChemStation OpenLab software program.

Table 8. GC-FID analytical conditions for the validation of Ethanol in nitrogen

| Instrument Parameters | Agilent Technologies (7890B) |
|---|---|
| Column | 60 m x 320 µm x 1 µm capillary Restek, Rtx®-WAX |
| Oven Temperature | 100 °C for 3 minutes |
| Detector | Flame Ionisation Detector (FID) |
| Detector Temperature | 250 °C |
| Carrier Gas | Hydrogen |
| Sample Flow | 35 **$m\ell.min^{-1}$** |

## Uncertainty budget

**The Uncertainty budget refers to the various factors that** contributes to the final uncertainty in measurement results. It indicates essential information that identifies, measures and characterises each source of uncertainty. **Table 9 and Table 10 summarise the factors contributing to the uncertainty of the 108 µmol.mol$^{-1}$ and 123 µmol.mol$^{-1}$ ethanol travelling standards, respectively. It is an essential tool to calculate measurement uncertainty following the GUM approach.**

A list of potential uncertainty sources considered is given and compiled from ISO-Standards, ISO-6142-1:2015 and ISO-6143:2001. The uncertainty contributors associated with the travelling standards were as follows:

a. Gravimetric uncertainty

b. Verification uncertainty (Repeatability)

c. Short-term stability (Estimated standard deviation of the mean)

Table 9: Factors contributing to the uncertainty of ethanol amount fraction at 108 µmol.mol$^{-1}$

| Uncertainty Source | Evaluation Type | Distribution | Standard Uncertainty (µmol.mol$^{-1}$), k=1 | Expanded Uncertainty (µmol.mol$^{-1}$),k=2 |
|---|---|---|---|---|
| Gravimetric | Type A | Normal | $7{,}8 \times 10^{-2}$ | $1{,}6 \times 10^{-1}$ |
| Verification | Type A | Normal | $2{,}7 \times 10^{-1}$ | $5{,}4 \times 10^{-1}$ |
| Stability | Type A | Normal | $2{,}6 \times 10^{-2}$ | $5{,}2 \times 10^{-2}$ |

**Table 10:** Factors contributing to the uncertainty of ethanol amount fraction at 123 µmol.mol$^{-1}$

| Uncertainty Source | Evaluation Type | Distribution | Standard Uncertainty (µmol.mol$^{-1}$), k=1 | Expanded Uncertainty (µmol.mol$^{-1}$),k=2 |
|---|---|---|---|---|
| Gravimetric | Type A | Normal | 3,7x $10^{-2}$ | 7,3 x $10^{-2}$ |
| Verification | Type A | Normal | 2,1 x $10^{-1}$ | 4,1 x $10^{-1}$ |
| Stability | Type A | Normal | 3,5 x $10^{-2}$ | 6,9 x$10^{-2}$ |

## Additional information

**Please include in this section a brief outline of any stability testing (including sorption effects investigation, if performed) and correction procedures for the two travelling standards between the time they were prepared and the time they were measured at NPL (NPL will provide the date of measurement to each participant for each travelling standard on measurement completion).**

NPL



# Participants report form, Part B

## Measurement results

Please indicate below the final value and associated expanded uncertainty of the $C_2H_5OH$ amount fraction in each of the two travelling standards.

| **Measurements results for $C_2H_5OH$ in $N_2$** | | |
|---|---|---|
| | **Travelling standard 1 3018-R1** | **Travelling standard 2 A668-R1** |
| Nominal amount fraction [µmol mol$^{-1}$] | 115 - 120 | 130 - 135 |
| Final amount fraction $x_{C_2H_5OH}$ [µmol mol$^{-1}$] | 115.91 | 132.63 |
| Expanded uncertainty $U_{x_{C_2H_5OH}}$ [µmol mol$^{-1}$] | 0.37 | 0.51 |
| Coverage factor | 2 | 2 |

# Gravimetric preparation and purity

Two NPL participant mixtures (NPL PRMs; 3018-R1 & A668-R1) of nominally 115 – 135 µmol $mol^{-1}$ of ethanol (Fisher Chemicals, Fisher Scientific, UK) in nitrogen (BIP+, Air Products, UK) were gravimetrically prepared in accordance with ISO 6142-1. Both mixtures were prepared in 10 litre aluminium cylinders (Luxfer, UK), with a proprietary passivation treatment of the internal surfaces (Spectraseal, BOC Limited, UK). The purity of the source compounds (ethanol and nitrogen) is shown below in Table 3 and Table 4, respectively. The NPL participant mixtures were prepared from pure ethanol by indirect filling using a transfer vessel, followed by the addition of the nitrogen matrix gas via direct filling. Following the preparation, these mixtures were validated against existing in-house NPL PRMs to verify the integrity of the preparation. The reported values are true gravimetric values, based on the masses and purities of the added components. No analytical corrections have been performed. Table 1 and Table 2 show the gravimetric amount fractions and uncertainties for each of the travelling standards.

**Table 1. Gravimetric amount fractions and associated gravimetric uncertainties of travelling standard 3018-R1.**

| Component | Amount fraction (µmol $mol^{-1}$) | Standard uncertainty (µmol $mol^{-1}$) |
|---|---|---|
| $N_2$ | 999884 | 6 |
| Ethanol | 115.91 | 0.06 |
| $H_2O$ | 0.00125 | 0.00018 |
| acetic acid* | < LOQ | 0.0000009** |
| acetaldehyde* | < LOQ | 0.0000009** |
| methanol* | < LOQ | 0.0000017** |
| acetone* | < LOQ | 0.0000009** |
| isopropanol* | < LOQ | 0.00000029** |
| benzene* | < LOQ | 0.00000015** |
| furfuraldehyde* | < LOQ | 0.00000017** |

* amount fraction below LOQ, ** half LOQ value

**Table 2. Gravimetric amount fractions and associated gravimetric uncertainties of travelling standard A668-R1**

| Component | Amount fraction (µmol $mol^{-1}$) | Standard uncertainty (µmol $mol^{-1}$) |
|---|---|---|
| $N_2$ | 999867 | 6 |
| ethanol | 132.6 | 0.06 |
| $H_2O$ | 0.00143 | 0.00020 |
| acetic acid* | < LOQ | 0.00000010** |
| acetaldehyde* | < LOQ | 0.00000010** |
| methanol* | < LOQ | 0.0000020** |
| acetone* | < LOQ | 0.00000010** |
| isopropanol* | < LOQ | 0.00000033** |

| | | |
|---|---|---|
| **benzene*** | < LOQ | 0.00000017** |
| **furfuraldehyde*** | < LOQ | 0.0000010** |

* amount fraction below LOQ, ** half LOQ value

The estimated purity of ethanol (Fisher Chemical) was exceeding 99.99 cmol mol$^{-1}$. The main impurity identified in pure ethanol was water. The gravimetric amount fraction of water was measured via Karl-Fischer titration by sampling in triplicate two random 20 mL ethanol vials, which represent 10 % of all aliquoted vials from the stock standard. As a single vial of ethanol was used for K93 travel standard preparation, the two titrated vials were treated as independent samples to better estimate between vial variability, thereby standard uncertainty was used instead of standard uncertainty of the mean. To evaluate the uncertainty contribution of the water impurity to the overall purity, both the uncertainty contributions to ethanol and water amount fractions were calculated. These uncertainties were then combined using the law for the propagation of uncertainties to provide the water impurity amount fraction uncertainty (Equation 1).

**Equation 1. Uncertainty of the amount fraction of water impurity in pure ethanol.**

$$u_{H2O} = \sqrt{u_{H2O\ contribution}^2 + u_{C2H5OH\ contribution}^2}$$

**Where:**
**$u_{H2O}$ is the standard uncertainty of the water amount fraction**
**$u_{H2O\ contribution}$ is the water uncertainty contribution of the water amount fraction**
**$u_{C2H5OH\ contribution}$ is the water uncertainty contribution of the ethanol amount fraction**

No further re-calculations of the purity value, based on the measured impurities amount fractions were performed, since the purity value and its uncertainty had negligible effect on the ethanol amount fraction and its uncertainty in the traveling standards, respectively. Details are presented in the 'Uncertainty budget' section, below. To estimate the organic impurities amount fractions, an aliquot of the pure component was analysed using GC-FID/MS. The Mass spectrometer (MS) was used for compound identification, and the flame ionisation detector (FID) was used for impurity quantification. Further organic impurity analysis was performed on a gas mixture of nominally 20 µmol mol$^{-1}$ ethanol in nitrogen using a GC-FID with installed sample pre-concentration trap (SPT). This methodology enables the determination of lower levels of organic impurities. No organic impurities were observed above the limit of quantification, and therefore the components listed as potential impurities in the supplier Certificate of Analysis were given an amount fraction of zero (0) with an associated uncertainty of half the limit of quantification with respect to effective carbon number of the impurity. **The standard uncertainty in the amount fraction of the 'pure ethanol' component was** calculated based individual impurities uncertainty ($u_{xi}$) using the law for the propagation of uncertainty shown in Equation 2.

**Equation 2. Uncertainty of ethanol purity calculation.**

$$u^2(x_{mon}) = \sum_{i=1}^{n} u^2(x_i)$$

The matrix gas BIP+ nitrogen (Air Products) was also analysed for ethanol, as a critical impurity, using a GC-FID with installed sample pre-concentration trap (SPT). No ethanol or other organic impurities were detected in the $N_2$ parent, and therefore 100.00 % purity (100 cmol mol$^{-1}$) was assigned for the purpose of this comparison. Other non-critical and non-

significant impurities were omitted in this study. The uncertainty associated with nitrogen purity was evaluated by calculating the limit of quantification for ethanol (Table 3), based on equivalent amount fraction of 3 x baseline noise band. The uncertainty of the $N_2$ purity was then set to half of this value. Table 3 and Table 4 summarise the amount fractions and associated standard uncertainties of the relevant impurities in the pure components.

**Table 3. Ethanol purity and list of most relevant impurities.**

| Component | Amount fraction (µmol mol$^{-1}$) | Standard uncertainty (µmol mol$^{-1}$) |
|---|---|---|
| **ethanol** | 999989.2 | 1.6 |
| **$H_2O$** | 10.8 | 1.6 |
| **acetic acid*** | < LOQ | 0.008** |
| **acetaldehyde*** | < LOQ | 0.008** |
| **methanol*** | < LOQ | 0.015** |
| **acetone*** | < LOQ | 0.008** |
| **isopropanol*** | < LOQ | 0.0025** |
| **benzene*** | < LOQ | 0.0012** |
| **furfuraldehyde*** | < LOQ | 0.0014** |

* amount fraction below LOQ, ** half LOQ value

**Table 4. Nitrogen gas purity.**

| Component | Amount fraction (µmol mol$^{-1}$) | Standard uncertainty (µmol mol$^{-1}$) |
|---|---|---|
| Nitrogen | 100000 | 6* |

*Half of ethanol LOQ

# Measurement procedure

To confirm the gravimetric amount fractions of travelling gas standards, they were measured against existing traceable in-house standard mixtures of similar nominal amount of substance fractions. These mixtures were analysed on an Agilent 6890 Gas Chromatography system (GC) equipped with a J&W capillary column DB624 (60 m x 0.53 mm x 3 µm), a 0.5 mL sample loop, and a flame ionisation detector (FID). The GC analytical method consisted of a series of six loop injections of the traceable in-house standard alternating every 3 minutes with six loop injections of the travelling standard resulting in a total of 12 injections per sequence. This method was run isothermally at 40 °C and used BIP grade helium (Air Products) as a carrier gas. The total length of this method was 42 minutes.

The first and last injection from each of the sequence lines of 12 injections were omitted, the ratio of the mean of the remaining five measurements of the travelling standards to the mean of the remaining five measurements of the in-house standard were evaluated. These injections were repeated until the system was conditioned, *i.e.* the mean of six consecutive signal ratios, expressed as peak area ratios of sample to calibrant, were repeatable within 0.1 %. The average ratio across all selected injections was used to calculate the closeness of the

gravimetrically prepared and analytically determined amount fractions, relative to the calibrant. An example chromatogram for this measurement procedure is shown below in Figure 1.

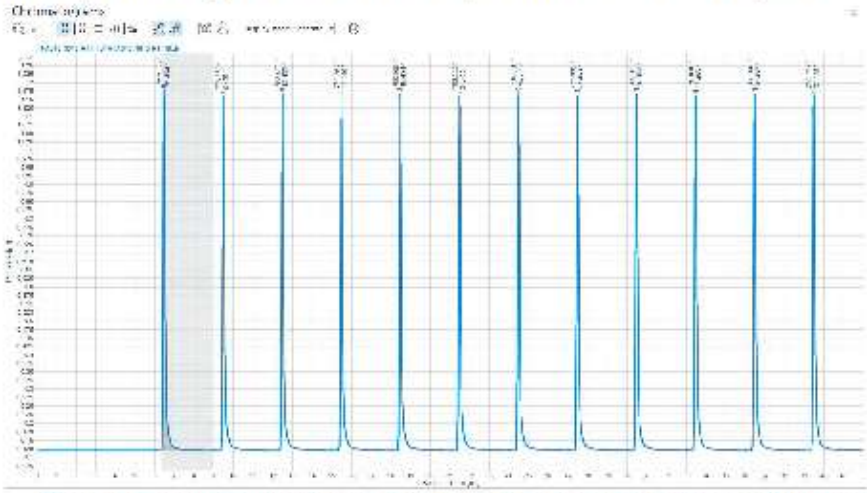


Figure 1. Example Chromatogram from an analytical validation of a traveling standard

# Uncertainty budget

The estimated uncertainty for the amount fraction for each of the travelling standards includes the following sources of uncertainty:

- Stability
- Analytical validation
- Difference between analytical and gravimetric results
- Gravimetric preparation
- Purity value

Table 5 below summarises the uncertainty contribution of each of the above components. The uncertainty budget for each traveling standard is presented in Figure 2.

**Table 5. Uncertainty sources and values for travelling standards 3018-R1 and A668-R1.**

| Uncertainty Source | Travelling Standard ID | | Unit |
|---|---|---|---|
| | 3018-R1 | A668-R1 | |
| Stability ($\mu_{stab}$) | 1.40E-07 | 1.60E-07 | mol mol$^{-1}$ |
| Analytical Validation ($\mu_{val}$) | 8.20E-08 | 8.20E-08 | mol mol$^{-1}$ |
| **u(Δ(Analytical**-Gravimetric)) ($\mu_{\Delta}$) | 7.50E-08 | 1.00E-07 | mol mol$^{-1}$ |
| Gravimetric Preparation ($\mu_{grav}$) | 5.50E-08 | 5.50E-08 | mol mol$^{-1}$ |
| Purity Value ($\mu_{pur}$) | 1.70E-10 | 2.00E-10 | mol mol$^{-1}$ |
| **Combined Uncertainty ($\mu_{EtOH}$)** | **1.85E-07** | **2.53E-07** | **mol mol$^{-1}$** |

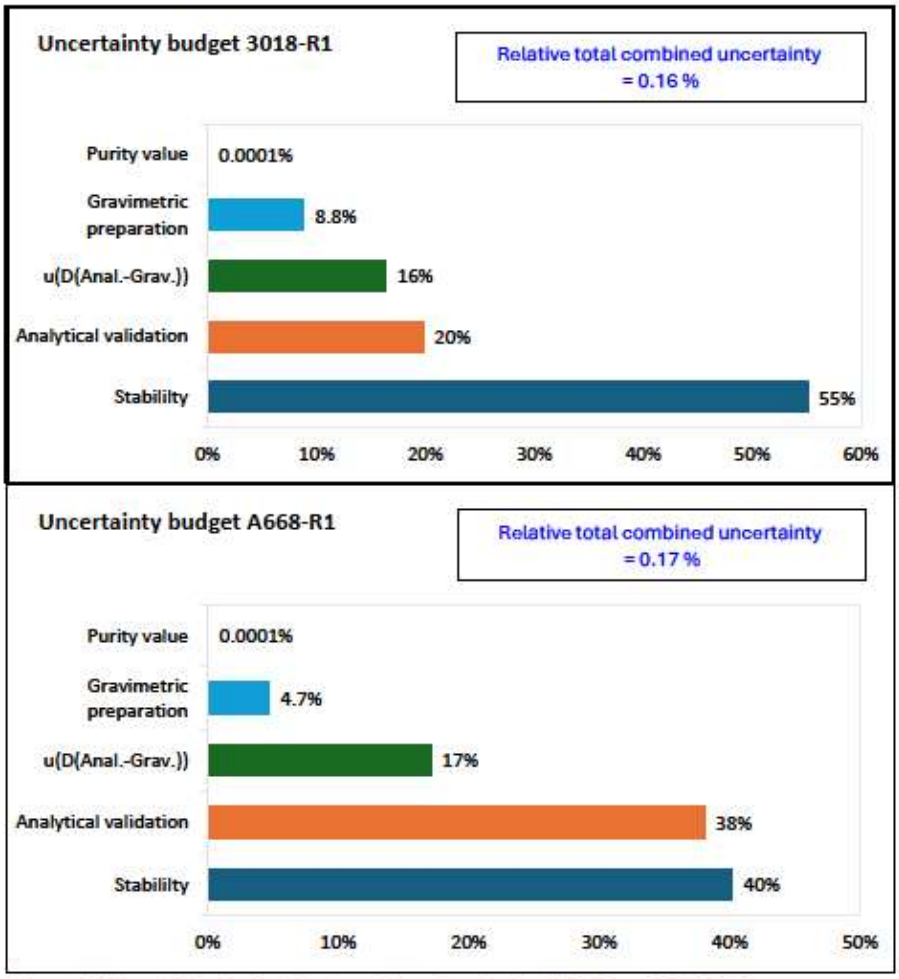



Figure 2. Uncertainty budget for travelling standards 3018-R1 and A668-R1.

The final uncertainty in the ethanol amount fraction (referred as total combined uncertainty) was calculated by propagating the individual combined standard uncertainties (Equation 3).

**Equation 3 Ethanol amount fraction uncertainty.**

$$u_{EtOH} = \sqrt{u_{pur}^2 + u_{Grav}^2 + u_{Val}^2 + u_{stab}^2 + u_A^2}$$

**Where:**

$u_{pur}$ is the standard uncertainty from purity estimation
$u_{grav}$ is the uncertainty from the gravimetric preparation
$u_{val}$ is the uncertainty from the analytical validation
$u_{stab}$ is the uncertainty in the stability of ethanol amount fraction
$u_A$ is the uncertainty from the difference between analytical and gravimetric results

The reported expanded uncertainty is based on the combined uncertainty multiplied by a coverage factor of 2 ($k$=2), providing a level of confidence of approximately 95 %.

## Additional information

The ethanol amount fraction stability was investigated to ensure that the nominal amount fraction of EtOH in the traveling was representative throughout the final study. A stability check gas mixture was freshly prepared and regularly validated over a 15-month period. The results of these validations were plotted against the age of the cylinder to evaluate the drift rate of ethanol over time. This drift rate was fitted as a 1st order polynomial function using XLGENLINE2 software. To evaluate the uncertainty contribution of drift rate to the travelling standards, the time elapsed between the preparation and analysis date was use. Based on this, the uncertainty contribution was found to be 1.4E-07 and 1.6E-07 mol mol$^{-1}$ for 3018-R1 and A668-R1 respectively.

# Participants report form, Part B

## Measurement results

**Please indicate below the final value and associated expanded uncertainty of the $C_2H_5OH$ amount fraction in each of the two travelling standards.**

| Measurements results for $C_2H_5OH$ in $N_2$ | | |
|---|---|---|
| | **Travelling standard 1** | **Travelling standard 2** |
| **Nominal amount fraction [µmol mol$^{-1}$]** | 116.77 | 131.68 |
| **Final amount fraction $\chi_{C_2H_5OH}$ [µmol mol$^{-1}$]** | 116.77 | 131.68 |
| **Expanded uncertainty $U_{\chi_{C_2H_5OH}}$ [µmol mol$^{-1}$]** | 0.82 | 0.97 |
| **Coverage factor** | 2 | 2 |

## Gravimetric preparation and purity

Reported values are true gravimetric values based on the masses and purities of ethanol and nitrogen.

Mixtures were prepared in aluminium cylinders. V= 5 $dm^3$. Inner surface of the cylinder was Aculife IV type. Before preparation. the cylinder was evacuated at least 15 hours using dry evacuation system.

Liquid ethanol was inserted to the evacuated gas cylinder by the method of syringe injection. The heated sample loop was used for the gasification of ethanol. Weighted syringe with ethanol component was inserted through septum. Filled cylinder valve and the syringe valve were opened simultaneously. Then the liquid was injected to the sample loop. Following filling with nitrogen were carried out at very low flow. Added amount of liquid component was determined from mass difference of the syringe on analytical balance Sartorius ME215P with resolution 0.01 mg. Difference weighing for gas syringe before and after adding of liquid component was used with no buoyancy correction.

Added mass of nitrogen was determined from mass difference of filled cylinder before and after filling on automatic SMU weighing system with Sartorius CC 10000 balance of 1 mg resolution for 5 L cylinders with comparator.

Purity analysis of Ethanol focused on water content was executed on SMU Primary Densitometer device. Each component has its purity table with composition from purity measurements and manufacturer specifications.

Table 1 *Ethanol purity table*

| Component | mole fraction (mol/mol) | uncertainty k=1 (mol/mol) | assumed distribution |
|---|---|---|---|
| 2-propanol[2] | 0.000050 | 0.000029 | rectangular |
| Methanol[2] | 0.00025 | 0.00014 | rectangular |
| Acetone[2] | 0.000050 | 0.000029 | rectangular |
| $H_2O$[1] | 0.00097 | 0.00000019 | normal |
| Ethanol | 0.99868 | 0.000015 | normal |

1): components measured by SMU
2): components from specifications of the manufacturer

Table 2 *Nitrogen purity table*

| Component | mole fraction (mol/mol) | uncertainty k=1 (mol/mol) | assumed distribution |
|---|---|---|---|
| CO[1] | 0.0000000044 | 0.000000000025 | normal |
| $CO_2$[1] | 0.00000064 | 0.00000010 | rectangular |
| $H_2O$[2] | 0.000000010 | 0.0000000058 | rectangular |
| $O_2$[1] | 0.0000000081 | 0.0000000011 | normal |
| $H_2$[2] | 0.000000025 | 0.00000014 | rectangular |
| $CH_4$[1] | 0.000000090 | 0.000000052 | rectangular |
| Nitrogen | 0.99999922 | 0.00000012 | normal |

1): components measured by SMU
2): components from specifications of the manufacturer

Uncertainty budgets for added mass of Ethanol in travelling standards are given in following tables:

Table 3 *Uncertainty budget ($m_{et}$) 0695E_13 Preparation date 19.10.2023*

| Quantity | Estimate | Standard uncertainty | Assumed distribution | Sensitivity coefficient | Uncertainty contribution |
|---|---|---|---|---|---|
| $\overline{\Delta m_1}$ | 189.93 mg | 0.02 mg | normal | 1 | 0.02mg |
| $\overline{\Delta m_2}$ | 59.13 mg | 0.03 mg | normal | -1 | -0.03 mg |
| *Resolution (1st weighting)* | 0.01 mg | 0.003 mg | rectangular | 1 | 0.003 mg |
| $m_{cal}$ | 50 g | 0,045 mg | normal | 1 | 0,045 mg |
| *Resolution (2nd weighting)* | 0.01 mg | 0.003 mg | rectangular | -1 | -0.003 mg |
| $m_{cal}$ | 50 g | 0,045 mg | normal | -1 | 0,045 mg |
| $m_{et}$ | 130.803 mg | | | | 0.073mg |

Laboratory of gases gives for added mass $m_{et}$ 130.80 mg standard combine uncertainty 0.10 mg.

Table 4 *Uncertainty budget ($m_{et}$) 0072F_11 Preparation date 06.10.2023*

| Quantity | Estimate | Standard uncertainty | Assumed distribution | Sensitivity coefficient | Uncertainty contribution |
|---|---|---|---|---|---|
| $\overline{\Delta m_1}$ | 210.84 mg | 0.04 mg | normal | 1 | 0.04mg |
| $\overline{\Delta m_2}$ | 56.86mg | 0.03 mg | normal | -1 | -0.03 mg |
| *Resolution (1st weighting)* | 0.01 mg | 0.003 mg | rectangular | 1 | 0.003 mg |
| $m_{cal}$ | 50 g | 0,045 mg | normal | 1 | 0,045 mg |
| *Resolution (2nd weighting)* | 0.01 mg | 0.003 mg | rectangular | -1 | -0.003 mg |
| $m_{cal}$ | 50 g | 0,045 mg | normal | -1 | 0,045 mg |
| $m_{et}$ | 153.980 mg | | | | 0.081 mg |

Laboratory of gases gives for added mass $m_{et}$ 153.98 mg standard combine uncertainty 0.10 mg.

Table 5 *Uncertainty budget ($x_{et}$) 0695E_13*

| Quantity | Estimate | Standard uncertainty | Assumed distribution | Sensitivity coefficient | Uncertainty contribution |
|---|---|---|---|---|---|
| $m_{et}$ | 0.1308 g | 0.0001 g | normal | 0.00407 mol/g.mol | 0.00000041 mol/mol |
| $M_{et}$ | 46.06845 g/mol | 0.00126 g/mol | rectangular | 0.0000030 $mol^2/g$ | 0.0000000038 mol/mol |
| $x_{etpur}$ | 0.99868 mol/mol | 0.000015 mol/mol | normal | 0.00088 | 0.000000013 mol/mol |
| $x_{et}$ | 0.00011677 mol/mol | | | | 0.00000041 mol/mol |

The result for amount fraction of Ethanol in mixture 0695E_13 is: (116.77 ± 0.82) µmol/mol U(k=2).

Table 6 *Uncertainty budget ($x_{et}$) 0072F_11*

| Quantity | Estimate | Standard uncertainty | Assumed distribution | Sensitivity coefficient | Uncertainty contribution |
|---|---|---|---|---|---|
| $m_{et}$ | 0.15398 g | 0.0001 g | normal | 0.00480 mol/g.mol | 0.00000048 mol/mol |
| $M_{et}$ | 46.06845 g/mol | 0.00126 g/mol | rectangular | 0.0000033 $mol^2/g$ | 0.0000000043 mol/mol |
| $x_{etpur}$ | 0.99868 mol/mol | 0.000015 mol/mol | normal | 0.00099 | 0.000000015 mol/mol |
| **$x_{et}$** | **0.00013168 mol/mol** | | | | **0.000000483 mol/mol** |

**The result for amount fraction of Ethanol in mixture 0072F_11 is: (131.68 ± 0.97) µmol/mol U(k=2).**

**For the calculations of the gravimetric composition with associated uncertainties, validated spreadsheet xlISO6142 v1.11 was used based on the models described in ISO 6142-1:2015 and ISO 19229.**

Table 7 *Purity table 0695E_13*

| Component | Mole fraction mol/mol | Uncertainty (k=1) (mol/mol) |
|---|---|---|
| 2-propanol | 0.0000000059 | 0.0000000034 |
| Methanol | 0.000000029 | 0.000000017 |
| Acetone | 0.0000000059 | 0.0000000034 |
| $H_2O$ | 0.00000011 | 0.0000000004 |
| CO | 0.0000000044 | 0.000000000025 |
| $CO_2$ | 0.00000064 | 0.00000011 |
| $O_2$ | 0.0000000081 | 0.0000000011 |
| $H_2$ | 0.000000025 | 0.0000000072 |
| $CH_4$ | 0.00000009 | 0.000000026 |
| $N_2$ | 0.999882 | 0.000000425 |
| ***Ethanol*** | ***0.00011677*** | ***0.000000407*** |

Table 8 *Purity table 0072F_11*

| Component | Mole fraction (mol/mol) | Uncertainty (k=1) (mol/mol) |
|---|---|---|
| 2-propanol | 0.0000000066 | 0.0000000038 |
| Methanol | 0.000000033 | 0.000000019 |
| Acetone | 0.0000000066 | 0.0000000038 |
| $H_2O$ | 0.00000013 | 0.0000000005 |
| CO | 0.0000000044 | 0.000000000025 |
| $CO_2$ | 0.00000064 | 0.00000011 |
| $O_2$ | 0.0000000081 | 0.0000000011 |
| $H_2$ | 0.000000025 | 0.0000000072 |
| $CH_4$ | 0.00000009 | 0.000000026 |
| $N_2$ | 0.999867 | 0.000000498 |
| ***Ethanol*** | ***0.00013168*** | ***0.000000483*** |

## Measurement procedure

Two travelling standard mixtures were validated on NDIR URAS 14 analyser. All measurements were done in automatic way using selector gas valve. Before entering sample loops all gas mixtures went through a mass flow controller for regulation. 4 PSMs calibration standards used for the validation were made gravimetrically in SMU according ISO 6142-1:2015 and verified against primary standard gas mixtures in accordance to ISO 6143:2001. Measurement method with 6 automated runs was used. From each run was made one calibration curve with sample signals. Data were subjected to the B_least program (weighted least square regression). The result of the measurement sequence $x_{an}$ was the average of molar fractions from six results. Goodness of fit of the 6 linear calibration curves was under 2. The model of linear calibration curve was taken : $y = b_1 . x + b_0$. Validation criterion of travelling standards was tested.

Table 9 *Calibration standards*

| Cylinder number | Component | $x_{cert}$ (mol/mol) | $U_{xcert}$ (k=2) (mol/mol) | $U_{xcert,rel}$ (k=2) (%) | Preparation date |
|---|---|---|---|---|---|
| 0031F_12 | Ethanol | 0.00007013 | 0.00000064 | 0.93 | 21.08.2023 |
| 0021F_11 | Ethanol | 0.00011789 | 0.00000076 | 0.64 | 02.10.2023 |
| 0036F_6 | Ethanol | 0.00014895 | 0.0000011 | 0.74 | 23.08.2023 |
| 0022F_10 | Ethanol | 0.00026025 | 0.0000020 | 0.77 | 24.08.2023 |

Table 10 *Linear calibration results measurement date 9.-10.11.2023*

| Cylinder number | x(an) (mol/mol) | $u(x_{an})(k=1)$ (mol/mol) | $u(x_{an})$ (%) | x(grav) (mol/mol) | $u(x_{gr})k=1$ (mol/mol) | \|x(an)-x(grav)\| | criterion 2*odm(u(an)^2 +u(gr)^2) |
|---|---|---|---|---|---|---|---|
| 0031F_12 | 0.00007015 | 0.00000032 | 0.46% | | | | |
| 0695E_13 | 0.00011685 | 0.00000048 | 0.41% | 0.00011677 | 0.00000041 | 8E-08 | 1.26E-06 OK |
| 0021F_11 | 0.00011741 | 0.00000037 | 0.32% | | | | |
| 0072F_11 | 0.00013188 | 0.00000039 | 0.30% | 0.00013168 | 0.00000048 | 2E-07 | 1.24E-06 OK |
| 0036F_6 | 0.00014980 | 0.00000058 | 0.39% | | | | |
| 0022F_10 | 0.0002598 | 0.0000011 | 0.42% | | | | |

Table 11 *Linear calibration curve parameters of sixth run*

| $b_0$ | $u(b_0)$ | $b_1$ | $u(b_1)$ |
|---|---|---|---|
| -1,5323E-06 | 6,0828E-07 | 2,8307E-07 | 1,4486E-09 |

## Uncertainty budget

Uncertainty $u(x_i)$ was calculated using B_least program. The inputs were: mole fractions and uncertainties of calibration standards, signals from the analyser with associated uncertainties.

From six runs results = average of amount fractions standard deviations were found $u_1(\overline{x}_i)$ and from runs results uncertainties the mean (through squares) was found $u_2(\overline{x}_i)$. These 2 figures were combined to give standard uncertainty $u_{an}(\overline{x}_i)$. Following formulas were used for the result and uncertainty calculations:

$$u_1(\overline{x}_i) = 1.3 * \sqrt{\frac{\sum_{j=1}^{n}(x_j - \overline{x}_i)^2}{n*(n-1)}}$$

$$u_2(\overline{x}_i) = \sqrt{\frac{\sum_{j=1}^{n}u(x_j)^2}{n^2}}$$

$$u_{an}(\overline{x}_i) = \sqrt{u_1(\overline{x}_i)^2 + u_2(\overline{x}_i)^2}$$

$$\overline{x}_i = \frac{\sum_{j=1}^{n}x_j}{n}$$

Results for measurement uncertainty calculations are given in following tables.

**Table 12** *Uncertainty budget $x_{an}$ 0695E_13*

| Quantity | Estimate (mol/mol) | Standard uncertainty (mol/mol) | Probability distribution | Sensitivity coefficient | Uncertainty contribution (mol/mol) |
|---|---|---|---|---|---|
| $\overline{x}_i$ | 0.00011685 | 0.000000047 | Normal | 1 | 0.000000047 |
| $x_{jfb\text{-}least}$ | 0.00011685 | 0.00000048 | Normal | 1 | 0.00000048 |
| $x_{an}$ | **0.00011685** | | | | **0.00000048** |

**Table 13** *Uncertainty budget $x_{an}$ 0072F_11*

| Quantity | Estimate (mol/mol) | Standard uncertainty (mol/mol) | Probability distribution | Sensitivity coefficient | Uncertainty contribution (mol/mol) |
|---|---|---|---|---|---|
| $\overline{x}_i$ | 0.00013188 | 0.000000095 | Normal | 1 | 0.000000095 |
| $x_{jfb\text{-}least}$ | 0.00013188 | 0.00000038 | Normal | 1 | 0.00000038 |
| $x_{an}$ | **0.00013188** | | | | **0.00000039** |

## Additional information

**Please include in this section a brief outline of any stability testing (including sorption effects investigation, if performed) and correction procedures for the two travelling standards between the time they were prepared and the time they were measured at NPL (NPL will provide the date of measurement to each participant for each travelling standard on measurement completion).**

Results of stability testing of the two travelling standards performed after arriving of the cylinders back to SMU are in following tables.

Table 12 *Calibration results measurement of the 0072F_11, date 04.02.2025*

| Cylinder number | x(an) (mol/mol) | $u(x_{an})(k=1)$ (mol/mol) | $u(x_{an})$ (%) | x(grav) (mol/mol) | $u(x_{gr})k=1$ (mol/mol) | \|x(an)-x(grav)\| | criterion 2*odm(u(an)^2 +u(gr)^2) |
|---|---|---|---|---|---|---|---|
| 0072F_11 | 0.00013164 | 0.00000046 | 0.35% | 0.00013168 | 0.00000048 | 4E-08 | 1.33E-06 OK |

Table 13 *Calibration results measurement of the 0695E_13, date 10.02.2025*

| Cylinder number | x(an) (mol/mol) | $u(x_{an})(k=1)$ (mol/mol) | $u(x_{an})$ (%) | x(grav) (mol/mol) | $u(x_{gr})k=1$ (mol/mol) | \|x(an)-x(grav)\| | criterion 2*odm(u(an)^2 +u(gr)^2) |
|---|---|---|---|---|---|---|---|
| 0695E_13 | 0.00011706 | 0.00000041 | 0.35% | 0.00011677 | 0.00000041 | 2.9E-07 | 1.16E-06 OK |

There were no sorption effects investigation and no correction procedures for the two SMU travelling standards.

# Ukrmetrteststandard



## Participants report form, Part B

### Measurement results

**Please indicate below the final value and associated expanded uncertainty of the $C_2H_5OH$amount fraction in each of the two travelling standards.**

| **Measurement results for $C_2H_5OH$ in $N_2$** | | |
|---|---|---|
| | **Travelling standard 1** | **Travelling standard 2** |
| **Nominal amount fraction [µmol mol$^{-1}$]** | **117,5** | **132,5** |
| **Final amount fraction $\chi_{C_2H_5OH}$ [µmol mol$^{-1}$]** | **117,5** | **133,0** |
| **Expanded uncertainty $U_{\chi_{C_2H_5OH}}$ [µmol mol$^{-1}$]** | **1,2** | **1,4** |
| **Coverage factor** | **2** | **2** |

**The reported values are true gravimetric values based on the masses and purities of the components added.**

**No intermediate dilution steps were used.**

**Purity tables are given below.**

Table 1. Purity data for ethanol used to prepare travelling standards and verification mixtures

| Component | Amount fraction, µmol/mol | Std. uncertainty, µmol/mol |
|---|---|---|
| $C_2H_5OH$ | 988497 | $5{,}7\times10^{2}$ |
| $H_2O$ | 11490 | $5{,}7\times10^{2}$ |
| $CH_3OH$ | 12 | 1 |
| $C_2H_4O$ | 0,7 | 0,2 |
| Note. Commercially available rectified ethanol was dehydrated by our laboratory | | |

Table 2. Purity data for nitrogen used to prepare travelling standards and verification mixtures

| Component | Amount fraction, µmol/mol | Std. uncertainty, µmol/mol | LOD, mol/mol |
|---|---|---|---|
| $N_2$ | 999990,95 | 0,32 | - |
| $O_2$ | 0,060 | 0,005 | - |
| $H_2O$ | 3,9 | 0,2 | - |
| $CO_2$ | 0,040 | 0,005 | - |
| Ar | 5,0 | 0,3 | - |
| $CH_4$ | 0,040 | 0,005 | - |
| CO | 0,005* | 0,003* | 0,01 |
| $H_2$ | 0,005* | 0,003* | 0,01 |
| *Estimated via LOQ. Uncertainty distribution – rectangular. | | | |

Table 3. Purity data for travelling standard 1

| Component | Amount fraction, µmol/mol | Std. uncertainty, µmol/mol |
|---|---|---|
| $C_2H_5OH$ | 117,53 | 0,07 |
| $N_2$ | 999872,0 | 0,3 |
| $O_2$ | 0,060 | 0,005 |
| $H_2O$ | 5,27 | 0,21 |
| $CO_2$ | 0,040 | 0,005 |
| Ar | 5,00 | 0,25 |
| $CH_4$ | 0,040 | 0,005 |
| CO | 0,005 | 0,003 |
| $H_2$ | 0,005 | 0,003 |
| $CH_3OH$ and $C_2H_4O$ not shown as negligible | | |

Table 4. Purity data for travelling standard 2

| Component | Amount fraction, µmol/mol | Std. uncertainty, µmol/mol |
|---|---|---|
| $C_2H_5OH$ | 132,98 | 0,07 |
| $N_2$ | 999856,4 | 0,3 |
| $O_2$ | 0,060 | 0,005 |
| $H_2O$ | 5,44 | 0,21 |
| $CO_2$ | 0,040 | 0,005 |
| Ar | 5,00 | 0,25 |
| $CH_4$ | 0,040 | 0,005 |
| CO | 0,005 | 0,003 |
| $H_2$ | 0,005 | 0,003 |
| $CH_3OH$ and $C_2H_4O$ not shown as negligible | | |

Travelling standards were prepared gravimetrically according to ISO 6142-1 [1] using the automatic weighing devices. Their composition was calculated by formula (3) from ISO 6142-1 [1].

Portion of ethanol to be introduced into the cylinder was first prepared in a glass vial. Ethanol mass was determined as a difference between masses of the vial with ethanol and the empty vial, using low-load balance. After weighing, the vial with ethanol was placed into the cylinder, then a valve was installed on the cylinder, and the cylinder was evacuated. Then the vial was broken by mechanical contact with the cylinder wall, and ethanol evaporated immediately. Then balance gas, nitrogen, was introduced into the cylinder, and its mass determined using high-load balance.

Amount fraction of impurities was measured/calculated according to ISO 19229 [2].

Weighing data for the travelling standards are given in Tables 5 and 6.

Table 5. Weighing data for travelling standard 1

| Parent gas | Transferred mass, g | Std. uncertainty, g |
|---|---|---|
| $C_2H_5OH$ | 0,16162 | 0,00009 |
| $N_2$ | 832,32 | 0,01 |

Table 6. Weighing data for travelling standard 2

| Parent gas | Transferred mass, g | Std. uncertainty, g |
|---|---|---|
| $C_2H_5OH$ | 0,19196 | 0,00009 |
| $N_2$ | 873,69 | 0,01 |

Travelling standards were verified by comparison with two primary standard gas mixtures (PSGM) and a new verification mixture prepared gravimetrically in the same way as the travelling standards. The comparison was fulfilled according to ISO 6143 [3].

Verification mixture composition is given in Tables 7 – 9.

Table 7. Composition of the verification mixture 1 (PSGM №1)

| Component | Amount fraction, µmol/mol | Std. uncertainty, µmol/mol |
|---|---|---|
| $C_2H_5OH$ | 109,55 | 0,5 |
| $N_2$ | 999 890,5* | 0,4 |
| * Including impurities | | |

Table 8. Composition of the verification mixture 2 (PSGM №2)

| Component | Amount fraction, µmol/mol | Std. uncertainty, µmol/mol |
|---|---|---|
| $C_2H_5OH$ | 119,74 | 0,5 |
| $N_2$ | 999 880,26* | 0,4 |
| * Including impurities | | |

Table 9. Composition of the verification mixture 3 (newly prepared)

| Component | Amount fraction, µmol/mol | Std. uncertainty, µmol/mol |
|---|---|---|
| $C_2H_5OH$ | 132,43 | 0,08 |
| $N_2$ | 999 867,57* | 0,4 |
| * Including impurities | | |

Balances used for gas mixture preparation by gravimetric method:

- Sartorius CCE66 electronic balance (max. load 61g; standard deviation 0,003 mg) for ethanol;

- LLC "SARTOKARAT" BK-CXT40 electronic balance (max. load 41 kg; standard deviation 0,005 g) for nitrogen.

Purity analysis of parent gases was performed using Agilent 6890N gas chromatographs with helium ionisation detector, flame ionization detector, and thermal conductivity detector. Oxygen content in nitrogen was measured using ABB AO 2020 gas analyser. Water content in nitrogen was measured using Michell MDM 300 I.S. dew-point hygrometer. Water content in ethanol was measured by Karl Fischer method using Mettler-Toledo DL32D titrator.

For verification, the mixtures were analysed using gas chromatograph Agilent 6890N. Detector – FID, temperature 250 °C. Carrier gas – helium, flow rate 5,0 $cm^3$/min. Quartz capillary column DB-ALC2, 30 m, i.d. 0,53 mm. Temperature mode – isothermal at 80 °C. Injector split/splitless in split (2:1) mode, temperature 250 °C.

Verification was performed according to ISO 6143 [3] using linear model. Nine measurements were made, each for one day, from 18.10.2023 to 15.11.2023. Four runs, each including three verification mixtures and two travelling standards, were performed for each measurement. For each measurement, peak areas obtained during the runs were averaged, and the averaged values were used to obtain linear function coefficients and, consequently, measured values of the ethanol amount fraction. Calculations were performed using B_LEAST software. The values from nine measurements were pooled to give the final verification values.

## Uncertainty budget

**A combined standard uncertainty of the amount fraction of ethanol, $u_c(y_k)$, in the final mixtures was calculated using formula (9) from ISO 6142-1:2015:**

$$u_c(y_k) = \frac{1}{2}\sqrt{u^2(y_{k,prep}) - u^2(y_{k,ver}) + (y_{k,prep} - y_{k,ver})^2}$$

**where $u(y_{k,prep})$ is preparation standard uncertainty, $u(y_{k,ver})$ is verification standard uncertainty, $y_{k,prep}$ and $y_{k,ver}$ are amount fraction values obtained by gravimetric procedure and by verification, respectively.**

**$u(y_{k,prep})$ was calculated using formula (7) from ISO 6142-1:2015:**

$$u(y_{k,prep}) = \sqrt{u^2(y_{k,grav}) - u^2(y_{k,stab})}$$

**where $u(y_{k,grav})$ is gravimetric standard uncertainty, $u(y_{k,stab})$ is standard uncertainty due to instability.**

**$y_{k,prep}$ and $u(y_{k,prep})$ were calculated according to the ISO 6142-1:2015 based on the transferred parent-gas masses with their uncertainties, as well as purity tables for parent gases using GravCalc software.**

**$y_{k,ver}$ and $u(y_{k,ver})$ were calculated according to ISO 6143:2001 using B_LEAST software. Between-day variance was taken into account, being the prevailing term in verification uncertainty.**

**$u(y_{k,stab})$ was evaluated as a conservative estimate based upon the historical data for the ethanol gas mixtures.**

**An expanded uncertainty, $U_c(y_k)$, was calculated as $U_c(y_k) = k \cdot u_c(y_k)$, where $k = 2$.**

**Uncertainty budget is given in table 10.**

**Table 10. Uncertainty budget**

| Travelling standard | $u(y_{k,grav})$, µmol/mol | $u(y_{k,stab})$, µmol/mol | $u(y_{k,prep})$, µmol/mol | $u(y_{k,ver})$, µmol/mol | $\lvert y_{k,prep} - y_{k,ver} \rvert$, µmol/mol | $u_c(y_k)$, µmol/mol | $U_c(y_k)$, µmol/mol |
|---|---|---|---|---|---|---|---|
| № 1 (117,5 µmol/mol) | 0,07 | 0,47 | 0,47 | 1,06 | 0,11 | 0,58 | 1,17 |
| № 2 (133,0 µmol/mol) | 0,08 | 0,53 | 0,54 | 1,15 | 0,50 | 0,68 | 1,36 |

## Additional information

Due to delay in cylinders delivery back to us, it was not possible to re-analyse the mixtures before the deadline for submitting the report. Consequently, the reported amount fractions were not corrected for instability, but the instability term was introduced to the uncertainty budget. The term was evaluated as a conservative estimate based upon the historical data for the ethanol gas mixtures.

### References

1. ISO 6142-1:2015 Gas analysis – Preparation of calibration gas mixtures – Part 1: Gravimetric method for Class I mixtures

2. ISO 19229:2019 Gas analysis – Purity analysis and the treatment of purity data

3. ISO 6143:2001 Gas analysis – Comparison methods for determining and checking the composition of calibration gas mixtures

# Participants report form, Part B

## Measurement results

**Please indicate below the final value and associated expanded uncertainty of the $C_2H_5OH$ amount fraction in each of the two travelling standards.**

| **Measurements results for $C_2H_5OH$ in $N_2$** | | |
|---|---|---|
| | **Travelling standard 1** | **Travelling standard 2** |
| **Nominal amount fraction [µmol mol$^{-1}$]** | 107.5 (µmol/mol) | 122.5 (µmol/mol) |
| **Final amount fraction $\chi_{C_2H_5OH}$ [µmol mol$^{-1}$]** | 107.5 (µmol/mol) | 122.5 (µmol/mol) |
| **Expanded uncertainty $U_{\chi_{C_2H_5OH}}$ [µmol mol$^{-1}$]** | 2.0 | 2.3 |
| **Coverage factor** | 2 | 2 |

## Gravimetric preparation and purity

The ethanol in nitrogen mixtures were prepared gravimetrically in two steps according to ISO 6142-1:2015. In the initial step, pure $C_2H_5OH$ was diluted using pure $N_2$ to 1 mmol $mol^{-1}$. Liquid injection method was performed to transfer the ethanol to the gas cylinder. In order to determine the weight of the $C_2H_5OH$, the substitution method based on the weighing sample syringe and a reference syringe was used. The syringes were weighed before and after filling. During the injection, the stainless steel gas flow lines were heated.

In the second step, this pre-mixture was diluted to final mixtures, i.e., 107.5 µmol $mol^{-1}$ and 122.5 µmol $mol^{-1}$ using pure $N_2$.

Pure $C_2H_5OH$ and $N_2$ (6.0 grade) used for fillings were from TÜBİTAK UME and Linde Gas Company, respectively. The purity of the $C_2H_5OH$ was determined by both mass balance (MB) approach and quantitative nuclear magnetic resonance (qNMR). Purity table with uncertainties for the pure $C_2H_5OH$ was given in Table 1.

**Table 1.** Purity table with uncertainties for the pure $C_2H_5OH$

| Cylinder | Pure EtOH | |
|---|---|---|
| Component | Mole fraction (µmol/mol) | Standard uncertainty (µmol/mol) |
| $H_2O$ | 2808.1 | 3.0 |
| $C_2H_5OH$ | 997191.9 | 1057.0 |

The purity of the $N_2$ gas was given in Table 2 based on the gas producers' specifications.

**Table 2.** Purity table with uncertainties for the pure $N_2$ parent gas

| Cylinder | Pure $N_2$ (cylinder code: LG2066) | |
|---|---|---|
| Component | Mole fraction (µmol/mol) | Standard uncertainty (µmol/mol) |
| CO | 0.050 | 0.029 |
| $O_2$ | 0.250 | 0.144 |
| $CO_2$ | 0.050 | 0.029 |
| $H_2O$ | 0.250 | 0.144 |
| $C_xH_y$ | 0.050 | 0.029 |
| $N_2$ | 999999.350 | 0.210 |

Purity tables for each of the final travelling standard including uncertainties are presented in Table 3.

**Table 3.** Purity table of final travelling standards

| Cylinder | PSM206680 | | PSM206683 | |
|---|---|---|---|---|
| Component | Mole fraction (µmol/mol) | Standard uncertainty (µmol/mol) | Mole fraction (µmol/mol) | Standard uncertainty (µmol/mol) |
| CO | 0.050 | 0.026 | 0.050 | 0.025 |
| $CO_2$ | 0.050 | 0.026 | 0.050 | 0.025 |
| $C_xH_y$ | 0.050 | 0.026 | 0.050 | 0.025 |
| $H_2O$ | 0.562 | 0.129 | 0.610 | 0.127 |
| $N_2$ | 999891.567 | 0.671 | 999876.457 | 0.766 |
| $O_2$ | 0.250 | 0.129 | 0.250 | 0.127 |
| $C_2H_5OH$ | 107.471 | 0.643 | 122.533 | 0.741 |

## Measurement procedure

The ethanol in nitrogen mixtures were analyzed using an Agilent 6890N gas chromatography (GC) system with FID, split/splitless injector, gas injection valve, including Chemstation software to collect and process data.

Verification of mixtures was performed using own standard PSM206722 (105.6 µmol/mol $C_2H_5OH$ in $N_2$) using single point calibration approach according to ISO 12963:2017 [2].

Reference gas mixture and travelling standards were stored in the same laboratory during all measurements. They were equipped with pressure reducers and connected to computer programmed multiposition valve gas sampling box. They were flushed at least 3 times before the first measurement. During the sampling of gas mixtures, the gas flow was controlled by an electronic pressure controller at 30 mbar.

Each sample in the sequence was injected 20 times, and the first ten injections in each case were discarded as they were considered as flushing of sample loop. The data was collected using ChemStation software. The measurement data were evaluated using MS Excel.

## Uncertainty budget

The uncertainty budget is based on the uncertainty evaluation from the gravimetric preparation and analytical measurements. Gravimetric preparation contains uncertainty sources from weighing and those from purity of the parent gases. Gravimetric preparation and uncertainty evaluation were performed according to ISO 6142-1:2015 [1]. The measurement uncertainty of each mixture was determined in accordance with ISO 12963:2017 [2].

The combined standard uncertainty of each mixture was determined by the following equation:

$$u_c = \sqrt{u_m^2 + u_g^2}$$

where

$u_m$, standard uncertainty from measurements

$u_g$, standard uncertainty from gravimetric preparation

The expanded uncertainty was determined by multiplying the combined standard uncertainty by a coverage factor of 2 with a confidence interval of 95%.

## Additional information

Stability testing was performed after receiving the travelling standards from NPL in February 2025. Two new standards were prepared using the same method specified in the "gravimetric preparation and purity" section. Amount of fractions of ethanol in the cylinders were 122.5 µmol/mol $C_2H_5OH/N_2$ and 107.5 µmol/mol $C_2H_5OH/N_2$ for PSM706019 and PSM706015, respectively.

Travelling standards were analysed against these new reference materials to check if there was any stability issue. Results showed that there were no stability issue for the travelling standards.

CCQM-K93.2023 19/12/2022

**References**

[1] International Organization for Standardization, ISO 6142-1:2015 "Gas analysis - Preparation of calibration gas mixtures - Part 1: Gravimetric method for Class I mixtures"

[2] International Organization for Standardization, ISO 12963:2017+A1:2020 "Gas analysis — Comparison methods for the determination of the composition of gas mixtures based on one- and two-point calibration".

**Authorship**

**Participant's List** : Dr. Aylin BOZTEPE, Dr. Tanıl TARHAN, Dilara KURT

VSL

# Participants report form, Part B

## Measurement results

**Please indicate below the final value and associated expanded uncertainty of the $C_2H_5OH$ amount fraction in each of the two reference materials.**

| **Measurements results for $C_2H_5OH$ in $N_2$** | | |
|---|---|---|
| | **Reference material 1 (VSL173312/D153312)** | **Reference material 2 (VSL173425/D153425)** |
| **Nominal amount fraction [µmol mol$^{-1}$]** | (110 to 115)<br>112.095 | (125 to 130)<br>128.506 |
| **Final amount fraction $\chi_{C_2H_5OH}$ [µmol mol$^{-1}$]** | 111.565 | 127.976 |
| **Expanded uncertainty $U_{\chi_{C_2H_5OH}}$ [µmol mol$^{-1}$]** | 0.462 | 0.513 |
| **Coverage factor** | 2 | 2 |

## Uncertainty budget

**Please provide below the uncertainty budget used to calculate the uncertainty associated with the measurement of the ethanol amount fraction.**

**The overall uncertainty consists of the associated standard uncertainty of the gravimetry preparation (which including the sources from the accuracy of weighing, from the purity of pure components, from the Molar Masses, and from the effects of buoyancy and pressure on the gas cylinder, etc.), the uncertainty budget from the measurements (including within-run repeatability and between-run reproducibility), the correction of the adsorption effect, the between-cylinder homogeneity effect, and the stability.**

| Uncertainty sources (k=1) | VSL173312 (D153312) [µmol mol$^{-1}$] | VSL173425 (D153425) [µmol mol$^{-1}$] |
|---|---|---|
| Gravimetric preparation | 0.013 | 0.017 |
| Within-run repeatability | 0.080 | 0.100 |
| Between-run reproducibility | 0.039 | 0.037 |
| Between-cylinder homogeneity effect | 0.168 | 0.193 |
| Correction of the adsorption effect | 0.130 | 0.130 |
| Stability | negligible | ngeligible |
| | | |
| Combined uncertainty | 0.231 | 0.256 |
| Expanded uncertainty (k=2) | 0.462 | 0.513 |

## Measurement procedure

**Please provide below a description of the measurements performed for the validation of the submitted gravimetric values obtained from the preparation, and calibrants and analysers details.**

The gravimetrically prepared gas mixtures were verified in accordance with ISO 6143:2001 using Non Dispersive InfraRed spectroscopy (NDIR).

The measurement procedure starts with connecting dedicated reducers to the newly prepared mixtures and to the selected Primary Standard Mixtures (PSMs). The reducers were flushed a number of times and being conditioned before the gas mixtures were being analyzed.

The measurements were carried out on a NDIR monitor with a gas-filled detector. The instrument is automated using two multi-position valves, allowing a maximum of 30 cylinders to be connected and analysed sequentially. Before each gas mixture, a zero measurement is carried out with pure nitrogen in order to eliminate the effects of the zero point drift. The entire cycle of measurements is repeated 3 times so that the repeatability within these measurements can be determined. The measurement data are processed and used by the ISO 6143 program for the verification of the prepared gas mixtures. The linear model of the first order was applied for the verification of the mixtures.

All the prepared gas mixtures used for this comparison were analyzed four times in four sequences (with measurement date 2023-11-28, 2023-11-29, 2023-12-04, 2023-12-07) before they were shipped to NPL. Within each sequence, a control mixture and two shadow mixtures were included as well for extra-check. After the comparison mixtures were returned to VSL, these mixtures together with the shadow mixtures were analyzed three times again (with measurement date 2025-03-19, 2025-03-26 and 2025-03-27) for stability assessment. Therefore, in total there were 7 measurements performed for this comparison. For the measurement performed on 2023-11-28 and 2023-11-29, a set of 6 PSMs were used in fit covering the range of 50-225 µmol $mol^{-1}$. For the measurement performed on 2023-12-04 and 2023-12-07, a set of 6 PSMs were used in fit covering the range of 100-400 µmol $mol^{-1}$. For the measurement performed on 2025-03-19, 2025-03-26 and 2025-03-27, a set of 7 PSMs were used in fit covering the range of 50-225 µmol $mol^{-1}$.

## Additional information

Please include in this section the following information:

- Purity table with uncertainties for all the parent gases, including < LOQ flags with the respective LOQ values for the impurities. Specify uncertainty distribution (Gaussian, rectangular etc.)
- Brief outline of the dilution series undertaken to produce the final mixtures
- Purity table for each of the final mixtures, including uncertainties, as above
- Brief outline of the validation procedure applied to the final mixtures
- Brief outline of any stability testing and correction procedures for the two reference materials between the time they were prepared and the time they were measured at NPL (NPL will provide the date of measurement to each participant for each reference material on measurement completion

The gas mixtures were prepared gravimetrically in according with ISO 6142-1:2015. The preparation started with introduction of ethanol in to a vacuumed gas cylinder by liquid injection using a syringe. Then nitrogen was added to the cylinder as balance gas. There is no further dilution step involved.

The compositions of the starting materials are given in table 1 (nitrogen) and table 2 (ethanol). The column labelled "x" is the amount of fraction of a component and the u(x) is the associated standard uncertainty of the fraction.

Table 1: Purity table nitrogen (APN26B)

| Component | | $x$ (mol mol$^{-1}$) | $u(x)$ (mol mol$^{-1}$) |
|---|---|---|---|
| Argon | Ar | 0.000005 | 0.000003 |
| Methane | $CH_4$ | 0.0000000010 | 0.0000000006 |
| Carbon monoxide | CO | 0.0000000010 | 0.0000000006 |
| Carbon dioxide | $CO_2$ | 0.000000010 | 0.000000006 |
| Hydrogen | $H_2$ | 0.000000025 | 0.000000015 |
| Water | $H_2O$ | 0.000000010 | 0.000000006 |
| Oxygen | $O_2$ | 0.000000005 | 0.000000003 |
| Nitrogen | $N_2$ | 0.999995 | 0.000006 |

Table 1: Purity table ethanol (MES390)

| Component | | $x$ (mol mol$^{-1}$) | $u(x)$ (mol mol$^{-1}$) |
|---|---|---|---|
| Water | $H_2O$ | 0.000062300 | 0.000012460 |
| Ethanol | $C_2H_5OH$ | 0.999937700 | 0.000012460 |

The purity table of the prepared final gas mixtures are given in table 3 (VSL173312) and table 4 (VSL173425). The column labelled "x" is the amount of fraction of a component and the u(x) is the associated standard uncertainty of the fraction.

Table 3: Purity table VSL173312 (cylinder D153312)

| Component | | $x$ (mol mol$^{-1}$) | $u(x)$ (mol mol$^{-1}$) |
|---|---|---|---|
| Argon | Ar | 0.000005 | 0.000003 |
| Methane | $CH_4$ | 0.0000000010 | 0.0000000006 |
| Carbon monoxide | CO | 0.0000000010 | 0.0000000006 |
| Carbon dioxide | $CO_2$ | 0.000000010 | 0.000000006 |
| Hydrogen | $H_2$ | 0.000000025 | 0.000000015 |
| Water | $H_2O$ | 0.000000028 | 0.000000006 |
| Oxygen | $O_2$ | 0.000000005 | 0.000000003 |
| Nitrogen | $N_2$ | 0.999883 | 0.000006 |
| Ethanol | $C_2H_5OH$ | 0.000112095 | 0.000000013 |

Table 4: Purity table VSL173425 (cylinder D153425)

| Component | | $x$ (mol mol$^{-1}$) | $u(x)$ (mol mol$^{-1}$) |
|---|---|---|---|
| Argon | Ar | 0.000005 | 0.000003 |
| Methane | $CH_4$ | 0.0000000010 | 0.0000000006 |
| Carbon monoxide | CO | 0.0000000010 | 0.0000000006 |
| Carbon dioxide | $CO_2$ | 0.000000010 | 0.000000006 |
| Hydrogen | $H_2$ | 0.000000025 | 0.000000015 |
| Water | $H_2O$ | 0.000000028 | 0.000000006 |
| Oxygen | $O_2$ | 0.000000005 | 0.000000003 |
| Nitrogen | $N_2$ | 0.999866 | 0.000006 |
| Ethanol | $C_2H_5OH$ | 0.000128506 | 0.000000017 |

**Validation procedure**

See information described in above section **'Measurement procedure'**.

**Stability evaluation**

All the prepared gas mixtures used for this comparison were analyzed four times in four sequences before they were shipped to NPL. Within each sequence, a control mixture and two shadow mixtures were included as well for extra-check. The two shadow mixtures were analyzed several times during the absence of the comparison mixtures. After the comparison mixtures were returned to VSL, these mixtures together with the shadow mixtures were analyzed three times again. To conclude, no in-stability issue found in these mixtures (negligible), which is consistent with the stability information that VSL contained for this type of mixtures (within the shelf life of the Primary Reference Materials of ehtanol in this range).

**Correction procedures**

Due to adsorption effect of ethanol component on the cylinder wall, a correction of the gravimetric value was applied using VSL internal procedure. The corrected values were submitted in this report.

[i] https://www.npl.co.uk/resources/software/xlgenline-and-xgenline - XLGenLine documentation. Last visited 09/10/2025

[ii] Reference: Scott, D.W. (1992) Multivariate Density Estimation. Theory, Practice and Visualization. New York: Wiley.