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EURAMET 1609: BILATERAL COMPARISON OF ETHANOL IN AIR

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ABSTRACT

This bilateral comparison between the National Physical Laboratory (NPL) and the National Institute of Standards and Technology (NIST) supports the Declaration of Equivalence (DoE) and the Memorandum of Cooperation (MoC) between these two National Metrology Institutes (NMIs). This bilateral comparison demonstrated comparability between NPL's and NIST's ethanol in air Primary Reference Materials (PRMs) at a nominal amount fraction of 120 µmol mol^{-1} in a balance of dry air. This composition is typical of the levels used to calibrate evidential breath analysers in many countries. The demonstrated agreed agreement was 0.38 % ± 0.67 % fulfilling the requirements stated in Annex 1 of the DoE for this component and thus demonstrating equivalence between NPL and NIST for ethanol in air (or nitrogen) in the range of 50 to 500 µmol mol^{-1}.

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Approved on behalf of NPL by
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CONTENTS

1 INTRODUCTION

This bilateral comparison between NPL and NIST supports the Declaration of Equivalence (DoE) and the Memorandum of Cooperation (MoC) and is aimed at evaluating the level of comparability between NPL's and NIST's ethanol in air Primary Reference Materials (PRMs) at a nominal amount fraction of 120 µmol mol^{-1} in a balance of dry air.

This composition is typical of the levels used to calibrate evidential breath analysers in many countries. Such standards fulfil the agreed requirements of the International Organization of Legal Metrology (OIML) for the calibration of evidential breath-alcohol analysers and provide a more accurate calibration at field level than ethanol/water solution-based simulators, which are highly sensitive to variations in the temperature of the solution.

2 MEASURAND

The measurand is the amount fraction of ethanol (C_2H_5OH) in synthetic air with measurement results being expressed in **µmol mol^{-1}**.

3 PARTICIPANTS

Participants: NPL, NIST.
NPL was the coordinating laboratory for this comparison.

4 COMPLETION DATE

The completion date of this comparison was: March 2025.

5 COMPARISON PROTOCOL

NPL prepared one new travelling primary reference material (PRM), according to ISO-6142-1 [1], of nominally 120 µmol mol^{-1} ethanol in synthetic air and this was sent to NIST for analysis. The cylinder number was D133063. The travelling standard was prepared in a 10 dm^3 aluminium cylinder with a BOC Spectraseal internal surface treatment with a nominal pressure of 10 MPa and a BS 341 No. 15 valve.

Table 1. Comparison schedule.

Due Date	Event
June 2023	Preparation and validation of travelling standard at NPL
July 2023	Shipment of travelling standard to NIST
Sept – Oct 2023	Measurements at NIST
Sept 2024	Shipment of travelling standard to NPL
Oct 2024	Verification measurement at NPL NIST measurement report to be sent to NPL
March 2025	Final report completed

6 ANALYTICAL METHOD USED BY THE COORDINATING LABORATORY

NPL developed a highly repeatable method to determine the amount fraction of ethanol in air as demonstrated in key comparison CCQM-K93 [2]. This method uses an Agilent 6890 gas chromatograph with a flame ionisation detector (FID), DB-624 column (75 m long x 0.535 mm diameter with a 3 µm film thickness) and a 0.5 mL sample loop. Ultra-pure helium (Air Products BIP grade) was used as the carrier gas. The variation in the response of the FID detector to the amount fraction of ethanol was shown to be linear in nature in the range of 105 to 135 µmol mol^{-1}. For the initial measurement on the 22/06/2023 a column of DB 624 30m x 0.53 mm i.d., 3.0 µm film thickness was used and for the second measurement on the 1/10/2024 a column of (75 m long x 0.535 mm diameter with a 3 µm film thickness) was used.

Immediately prior to an analysis, each cylinder valve was opened and the pressure reducer purged six times. Each measurement comparison consisted of a series of six injections of the sample (the travelling PRM) alternating with seven alternate injections of the calibrant (an NPL PRM – in house National Standard) that is repeated six times. The average ratio and the standard deviation were then determined. The analytical amount fraction of the sample was assigned by multiplying the ratio in response with the gravimetric amount fraction of the calibrant. The expanded uncertainty was assigned by combining in quadrature the gravimetric uncertainty and the standard deviation in the analytical response and multiply by a coverage factor of 2 to provide a confidence interval of approximately 95 %.

$$r_i = \frac{2 \times A_{S_i}}{\left(A_{C_{i-1}} + A_{C_i}\right)}$$

$$\bar{r} = \frac{\sum_{i=1}^{n} r_i}{n}$$

$$u(\bar{r}) = \frac{sd(r)}{\sqrt{n}}$$

$$x_{s(val)} = x_{c(grav)} \times \bar{r}$$

$$u\left(x_{s(val)}\right) = x_{s(val)} \sqrt{\left(\frac{u(x_{c(grav)})}{x_{c(grav)}}\right)^2 + \left(\frac{u(\bar{r})}{\bar{r}}\right)^2}$$

$$U(x_{cert}) = 2 \times \mathrm{u}\left(x_{s(val)}\right)$$

where r = moving average ratio, A = peak area, s = sample, c = calibrant, val = validation, grav = gravimetric, anal = analytical, x = amount fraction, cert = certified, r = moving average ratio, n = number of repeated measurements.

7 COMPARISON MIXTURE STABILITY

NPL verified the travelling PRM before and after shipment and no instability was observed. The results are summarised in Table 2.

Table 2. Summary of validation data for the comparison PRM (D133063) before and after the NIST measurements.

Date	Description	Amount fraction (µmol mol^{-1})	Expanded uncertainty (µmol mol^{-1})
22/6/2023	Gravimetric preparation data ($x_{g,NPL}$), uncertainty includes analytical verification	119.9	0.6
22/6/2023	Analytical validation versus A646 (NPL PRM in house National Standard) prior to shipment to NIST	119.8	0.6
1/10/2024	Re-analysis versus D180693* (NPL PRM in house National Standard) after return from NIST	119.4	0.6

*A646 and D180693 have been compared and agree within 0.1 %.

8 SUMMARY OF RESULTS

The NIST reported value data is summarised in Table 3. The difference between the NPL gravimetric data and the NIST reported value is shown in Table 4 and Figure 1.

Table 3. Summary of the NIST measurements.

Date	Description	Amount fraction (µmol mol^{-1})	Expanded uncertainty (µmol mol^{-1})
13/09/2023	NIST reported value (x_{NIST})	119.45	0.53

Table 4. Summary of the absolute difference (µmol mol^{-1}), relative difference (%), calculated as $((x_{g,NPL}-x_{NIST})/\ x_{g,NPL}) \times 100$ and associated expanded uncertainties (k = 2) determined by combining NPL's and NIST's uncertainties in quadrature.

Absolute difference (µmol mol^{-1})	Expanded uncertainty (µmol mol^{-1})	Relative difference (%)	Relative expanded uncertainty (%)
0.45	0.80	0.38	0.67

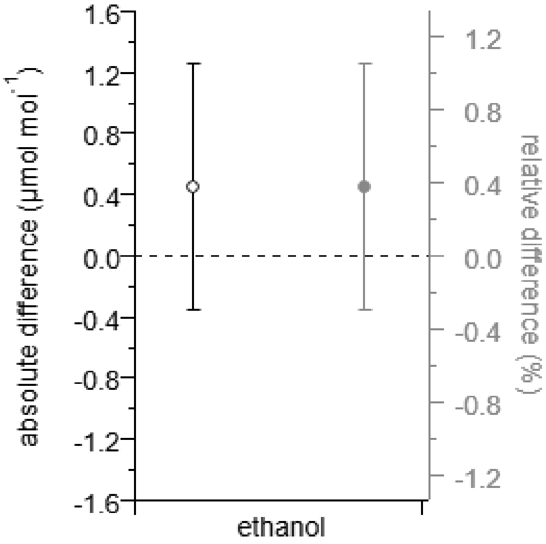

Figure 1. Plot showing the absolute difference (open symbols; left axis) and relative difference (filled symbols; right axis) between NPL and NIST as given in Table 4.

9 DISCUSSIONS AND CONCLUSIONS

The NPL-NIST declaration of equivalence states in Annex 1 that the maximum allowable difference between the NPL and NIST reference values, to ensure equivalence, for ethanol in nitrogen or air is 2.09 % relative. Here we demonstrate agreement between NPL and NIST of 0.38 % ± 0.67 % fulfilling the requirements of the DoE for this component and thus demonstrating equivalence between NPL and NIST for ethanol in air (or nitrogen) in the range of 50 to 500 µmol mol^{-1}.

10 REFERENCES

[1] ISO: 6142-1:2015 Gas analysis - Preparation of calibration gas mixtures - Gravimetric method for class I mixtures. International Organization for Standardisation (ISO), Geneva, Switzerland, 2015.

[2] Brown, A. S., Milton, M. J. T., Brookes, C., Vargha, G. M., Downey, M. L., Uehara, S., Augusto, C. R., Fioravante, A. d. L., Sobrinho, D. G., Dias, F., Woo, J. C., Kim, B. M., Kim, J. S., Mace, T., Fükö, J. T., Qiao, H., Guenther, F., Rhoderick, J., Gameson, L., Botha, A., Tshilongo, J., Ntsasa, N. G., Val'ková, M., Durisova, Z., Kustikov, Y., Konopelko, L., Fatina, O., and Wessel, R.: Final report on CCQM-K93: Preparative comparison of ethanol in nitrogen, Metrologia, 50, 08025-08025, 10.1088/0026-1394/50/1a/08025, 2013.

Annex A: Measurement Report NPL-NIST bilateral on ethanol in air

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NIST Measurement results

Cylinder number: D133063

Measurement #1

Component	Date	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Ethanol	**7-12 Sep 2023**	**119.57**	**0.16 %**	**1**

Measurement #2

Component	Date	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Ethanol	**12-13 Sep 2023**	**119.30**	**0.20 %**	**1**

Measurement #3

Component	Date	Result (µmol/mol)	Standard deviation (% relative)	number of replicates
Ethanol	**14-19 Sep 2023**	**119.51**	**0.14 %**	**1**

Results

Component	Date	Result (µmol/mol)	expanded uncertainty (µmol/mol)	coverage factor
Ethanol	**7-19 Sep 2023**	**119.45**	**0.53**	**2**

Instrumentation

The ethanol (EtOH) component of the submitted NPL sample, D133063, was analyzed with a Fourier Transform Infrared (FTIR) spectrometer (Nicolet Model Nexus 670, NIST # 593134)1 equipped with a 10 m folding path, quartz gas cell (Specac, Model Cyclone 10C, NIST # 623477)[1] with potassium bromide windows and a liquid nitrogen cooled mercury-cadmium-telluride (MCT-A) detector. The FTIR collection parameters are shown in Table 1. Sample flow (100 mL min^{-1}) to the instrument was achieved by utilizing an MKS[1] mass flow controller. Sample selection was achieved manually by changing sample lines after each analysis collection.

Table 1: 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 nitrogen and vacuum evacuated between each sample to ensure that the previous gas matrix was removed from the sample cell. Prior to sample analysis 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) and the internal cell pressure was regulated 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}.

The resulting spectra were evaluated with the area under curve being taken between 952.44 cm^{-1} to 116.91 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.

Calibration method

The amount fraction of the NPL sample was determined by comparison to four NIST gravimetrically prepared PSMs ranging from (70.54 to 149.0) µmol mol^{-1} EtOH in nitrogen (see Table 2). 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.

Table 2: Ethanol in nitrogen NIST Primary Gas Standards. 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

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[1] Identification of commercial items, products, or companies in this document does not imply endorsement by NIST or that the items, products, or companies are necessarily the best for the purpose stated.

The NPL sample was used as the analytical control for this analysis. Each PSM was compared to the control 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.

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 116.91 cm^{-1}.

Instrument response ratios (R) were calculated as:

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

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

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

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, as listed in Tables 3 and 4. This regression equation was then used to predict the EtOH amount fraction of the NPL sample based on a response ratio of 1.

Table 3: EtOH first order calibration, for area under curve 952.44 cm^{-1} to 116.91 cm^{-1}, average ratio and standard deviation as *x*-value and *x*-uncertainty, and the EtOH gravimetric amount fraction and standard uncertainty as *y*-value and *y*-uncertainty for each primary standard.

Value of Standards		**Analytical Response**	
***y*-Value**	***y*-uncertainty**	***x*-Value**	***x*-uncertainty**
70.54	0.07	0.5910	0.0023
100.70	0.10	0.8441	0.0033
121.80	0.10	1.0153	0.0039
149.00	0.15	1.2507	0.0048

Table 4: EtOH linear calibration curve solution, with associated standard uncertainties.

$y = b_0 + b_1 x$		cov (b_0,b_1)
b_0	b_1	
-0.0757 ± 0.7169	119.5303 ± 0.8683	-0.5986

Value assignment and uncertainty evaluation

The NIST value assignment of the amount fraction of EtOH in the NPL sample is given in Table 5. The uncertainty is expressed as $U = ku_c$, where u_c is estimated from the gravimetric uncertainties of the PSMs and the repeatability of the instrument response, and the coverage factor k is equal to 2. The true amount fraction is therefore asserted to lie within the interval defined by the assigned value $\pm U$ with a level of confidence of approximately 95 % [3].

Table 5: Value assignment for NPL EtOH sample. The stated uncertainty is expanded (*k* = 2).

Cylinder Number	Value Assigned Amount Fraction	Value Assigned Component
D133063	119.45 ± 0.53 µmol mol^{-1}	EtOH

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] 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 (2008); available at: http://www.bipm.org/utils/common/documents/jcgm/JCGM_100_2008_E.pdf.