SIM.QM-S17 Ethanol in Aqueous Matrix: Supplement Key Comparison
Model 1

Final Report
September 2022

Marco A. Ávila C., Hugo Gasca A., Víctor M. Serrano C. and Mariana Arce O.
Centro Nacional de Metrología.
El Marqués Qro. 76246 México.

Eliane C. P. do Rego, Bruno C. Garrido, and Valnei S. da Cunha.
Instituto Nacional de Metrologia, Qualidade e Tecnologia.
25250-020 Duque de Caxias, Rio de Janeiro, Brazil.

With contributions from:

Jelena Bebić and Katarina Banjanac
Directorate of Measures and Precious Metals (DMDM), Belgrade, Serbia.

Adrian Vicent Claramunt
Center for Physical Science and Technology (FTMC), Vilnius, Lithuania.

Paola Avendaño Rivera
Instituto Boliviano de Metrologia (IBMETRO), La Paz, Bolivia.

Aida Jotanović and Katarina Hafner-Vuk
Institute of Metrology of Bosnia and Herzegovina (IMBIH), Sarajevo, Bosnia and Herzegovina.

Steve Acco García
Instituto Nacional de Calidad (INACAL), Lima, Perú

Juliana Barrios, Ivonne Gonzalez
Instituto Nacional de Metrologia Colombia (INMC), Bogotá, Colombia.

Wagner Wollinger, Lucas J. Carvalho, Tânia M. Monteiro
Instituto Nacional de Metrologia, Qualidade e Tecnologia (INMETRO), Rio de Janeiro, Brazil.

Tomas Castañeda, Jimena Etcheverry
Instituto Nacional de Tecnología Industrial (INTI), Buenos Aires, Argentina.

Marcelo Soto Varas
Public Health Institute of Chile (ISPCH), Santiago, Chile

Florencia Almirón, Ana Silva
Laboratorio Tecnológico del Uruguay (LATU), Montevideo, Uruguay.

Kittiya Shearman and Thitiphan Chaiphet
National Institute of Metrology, Thailand (NIMT), Pathumthani, Thailand.

Dominique Marajh, Phaswe Makgatho, Ria Visser and Dr. Maria Fernandes-Whaley
National Metrology Institute of South Africa (NMISA), Pretoria, South Africa.

ABSTRACT

To establish international measurement capabilities for the determination of ethanol in aqueous matrices, the CCQM Organic Analysis Working Group (OAWG) has performed three ethanol Key comparisons (2002: CCQM-K27a for forensic aqueous ethanol and CCQM-K27b for ethanol in wine as a commodity; 2005: CCQM-K27 subsequent studies – four levels of ethanol in water; 2007: CCQM-K27.2 Subsequent 2 for forensic levels). To provide an opportunity for the NMIs and DIs within the RMOs, three Key comparisons has been conducted within SIM (SIM.QM-K1, SIM.QM-K27) and AFRIMETS (AFRIMETS.QM-K27). In addition, for the NMIs to support their ethanol in aqueous matrices measurements capabilities, a Track A Model 2 (formerly known as Track B) Key comparison CCQM-K79 (2010) has been completed to compare aqueous ethanol certified reference material (CRM) solutions certified by the participant NMIs and DIs. The current comparison is important to NMIs and DIs to maintain their ethanol in water measurement capabilities, to claim it as a new one as well as to complement their existing measurement capabilities, mainly within the range where the alcohol meter (breathalyzer) needs to be calibrated and verified.

In 2017, several NMIs and DIs in SIM expressed their interest in a complementary SIM.QM-K27 comparison, therefore CENAM and INMETRO agreed to collaborate for the realization of a SIM supplement comparison, which was identified as SIM.QM-K27.2019 by the OAWG, and the final assigned name by SIM was SIM.QM-S17. The main purpose of this comparison was to offer to SIM countries and other regions an additional opportunity for the NMI and DIs to evaluate their measurements capabilities in determining mass fraction of ethanol in an aqueous matrix within the mass fraction range from 0.1 mg/g to 5 mg/g. Fourteen laboratories were registered to take part in this comparison, and thirteen sent their results. The NMI from Kenya (KEBS) was registered, but they did not send theirs results because of equipment problems. This report presents the results of the SIM Key comparison SIM.QM-S17.

The measurements capabilities demonstrated by the participants in SIM.QM-S17, underpin their ability to assign reference values of ethanol content in aqueous samples for both forensic and commodities applications. Successful participation in SIM.QM-S17 demonstrates the laboratories measurement capabilities in determining mass fraction of ethanol in an aqueous matrix within the mass fraction range from 0.1 mg/g to 5 mg/g. The study material was two batches of solutions of ethanol in water prepared gravimetrically at concentrations between 0.1 mg/g - 5 mg/g by CENAM, dispensed in glass bottles of 50 mL sealed with tear off aluminum crimp seals, with rubber stoppers. In previous SIM.QM.K27 comparison, the purity-corrected gravimetric value of the aqueous ethanol solutions assigned by the coordinating NMI was used to link SIM.QM-K27 to the CCQM-K27 Key comparison reference value (KCRV), where 1 % uncertainty was assigned to the KCRV to have the same uncertainty from the CCQM-K27.2. For this comparison, SIM.QM-S17 two levels aqueous ethanol solutions, the purity assigned by CENAM was not used for KCRV as was informed initially in the protocol, instead in 5-June-2020 at the OAWG, CENAM gravimetric values were presented, as well as the participants results evaluated by four different statistical approaches to assess the candidate KCRV. For both levels of ethanol in aqueous matrix solutions, the DerSimonian-Laird Weighted mean and the Hierarchical Bayes mean methods seem to give a better estimation of the KCRV ± KCRU95 candidate and was agreed by OAWG to use the Hierarchical Bayesian mean, from where the KCRV for SIM.QM-S17 Level 1 (Low-level) and Level 2 (high-level) were (240.92 ± 1.28) mg/kg (k =2) and (389.87 ± 1.52) mg/kg (k =2), respectively. All the thirteen participants in the SIM.QM-S17, including both coordinators, demonstrated their capability to measure ethanol in aqueous matrix in the mass fraction range of 0.1 mg/g to 5 mg/g.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

ACRONYMS

CCQM	Consultative Committee for Amount of Substance: Metrology in Chemistry and Biology
CENAM	Centro Nacional de Metrología (NMI: México)
CMC	Calibration and Measurement Capability
CRM	certified reference material
CV	coefficient of variation, expressed in %: $CV = 100 \cdot s/\bar{x}$
DI	designated institute
DMDM	Dictatoriate of Measures and Precious Metals, Serbia (NMI: Serbia)
DoE	degrees of equivalence
FTMC	State Research Institute, Center for Physical Sciences and Technology (NMI: Lithuania)
GCxGC	two-dimensional gas chromatography
GC-HRMS	gas chromatography with high-resolution mass spectrometry detection
GC-IT-MS	gas chromatography with ion trap mass spectrometry detection
GC-MS	gas chromatography with mass spectrometry detection
GC-MS/MS	gas chromatography with tandem mass spectrometry detection
GC-TOFMS	gas chromatography with time-of-flight mass spectrometry detection
GPC	gel permeation chromatography
HPLC-DAD	high pressure liquid chromatography with diode array detection
IBMETRO	Instituto Boliviano de Metrología (NMI: Bolivia)
ID	Isotope dilution
INACAL	Instituto Nacional de Calidad (NMI: Perú)
INBIH	Institute of Metrology of Bosnia and Herzegovina (INM: Bosnia and Herzegovina)
INM	Instituto Nacional de Metrologia de Colombia (NMI: Colombia)
INMETRO	Instituto Nacional de Metrologia, Qualidade e Tecnología (NMI: Brazil)
INTI	Instituto Nacional de Tecnología Industrial (NMI: Argentina)
ISP	Instituto de Salud Pública de Chile (DI: Chile)
KC	Key Comparison
KCRV	Key Comparison Reference Value
KEBS	Kenya Bureau of Standards (NMI: Kenya)
LATU	Laboratorio Tecnológico de Uruguay (NMI: Uruguay)
LC	liquid chromatography
MADe	median absolute deviation from the median (MAD)-based estimate of s: MADe = 1.4826·MAD, where MAD = median(|xi-median(xi)|)
MRM	multiple reaction monitoring
NIMT	National Institute of Metrology (NMI: Thailand)
NMI	National Metrology Institute
NMISA	National Measurement Institute South Africa (NMI: South Africa)
OAWG	Organic Analysis Working Group
RMP	Reference Measurement Procedure
SIM	Interamerican Metrology System
SRM	Standard Reference Material, a NIST CRM

SYMBOLS

di	degree of equivalence: xi - KCRV
%di	percent relative degree of equivalence: 100·di/KCRV
k	coverage factor: $U(\mathrm{x}) = k \cdot u(\mathrm{x})$
n	number of quantity values in a series of quantity values
s	standard deviation of a series of quantity values: $s = \sqrt{\sum_{i=1}^{n}(x_i - \bar{x})^2/(n-1)}$
t_s	Student's *t*-distribution expansion factor
$u(x_i)$	standard uncertainty of quantity value x_i
$\bar{u}(x)$	pooled uncertainty: $\bar{u}(x) = \sqrt{\sum_{i=1}^{n} u^2(x_i)/n}$
τ	between participant uncertainty component, also called dark uncertainty
$U(x)$	expanded uncertainty
$U_{95}(x)$	expanded uncertainty defined such that $x \pm U_{95}(x)$ is asserted to include the true value of the quantity with an approximate 95 % level of confidence
$U_{k=2}(x)$	expanded uncertainty defined as $U_{k=2}(x) = 2 \cdot u(x)$
x	a quantity value
x_i	the i^{th} member of a series of quantity values
$\bar{x}$	mean of a series of quantity values: $\bar{x} = \sum_{i=1}^{n} x_i/n$
z_i	z-score, a standardized quantity value: $z_i = (x_i - \bar{x})/s$
E_n	normalized error

BACKGROUND

The determination of ethanol in water is important since blood and breath alcohol testing can be imposed on individuals operating private vehicles or operators of commercial vehicles. The various levels of blood alcohol that determine whether these operators are considered legally impaired vary depending on the circumstances, nation, state within the nation, and even month in which the testing is occurring. As a result, practitioners in the field of alcohol testing have a need for reliable and stable standards at many concentrations.

CCQM Organic Analysis Working Group has performed three key comparisons on the determination of ethanol in aqueous matrices (2002: CCQM-K27a for forensic aqueous ethanol and CCQM-K27b for ethanol in wine as a commodity; 2005: CCQM-K27.1 subsequent studies – four levels of ethanol in water; 2007: CCQM-K27.2 Subsequent 2 for forensic levels). The CCQM-K27 studies establish international measurement comparability between NMIs and DIs for the determination of this much traded and forensically important compound. In addition, the Track A Model 2 (formerly known as Track B) Key comparison CCQM-K79 (2010) compared aqueous ethanol certified reference material (CRM) solutions produced and assayed by various NMIs and DIs. The CCQM-K79 comparison also supports capabilities demonstrated in the CCQM-K27 comparison series. Within the RMOs, both SIM (2009: SIM.QM-K1, 2016: SIM.QM-K27) and AFRIMETS (2013: AFRIMETS.QM-K27) have conducted regional key comparisons for the determination of aqueous ethanol solutions [1-8].

Within the SIM RMO, there are NMIs/DIs who have informed of their need to demonstrate measurement capabilities for ethanol measurements in aqueous matrices, even after SIM.QM-K27 (2016), especially across the interval where the alcohol testing requires to be calibrated and verified. This comparison was intended to provide to SIM countries an additional opportunity to evaluate their measurement capabilities, and other regions were also welcomed to participate. SIM CMWG conducted this subsequent regional Key Comparison (SIM.QM-K27.1). Key comparisons performed by regional metrology organizations (RMOs) normally are linked to the CIPM equivalent comparisons through reference to the results from those institutes, which have also taken part in the CIPM key comparison. Due to the long time since the last CCQM aqueous ethanol comparison and the plan that there are unlikely to be future comparisons at the CCQM level it is envisaged that ethanol comparisons will occur at the RMO level and will be coordinated as supplementary comparisons. This model has been implemented for this comparison with the reference value set from the consensus of results.

In this report, candidate estimates of the reference value and its uncertainty are provided as reviewed and discussed by the OAWG during June 2020.

In this SIM.QM-S17 Supplement comparison, as a SIM study, it was expected that all SIM NMIs or DIs who have, or expect to have, services related to the capabilities related to the How Far the Light Shines statement for this Key comparison had participated if they had not recently demonstrated their capabilities in another comparison.

Conduct of Supplementary Comparison SIM.QM-S17

TIMELINE

Table 1 relates the actions with its date when had been completed in this comparison.

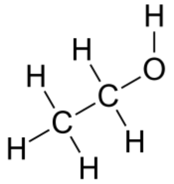
Table 1. Timeline for SIM.QM-S17.

Date	Action
September 2018	Proposed to OAWG
October 2018	Draft proposal presented to OAWG
Nov 2018	SIM approved SIM.S17
April 3, 2019	OAWG approved SIM.S17
September 18, 2019	Approval of protocol and call for participation to OAWG members
October 7, 2019	Deadline to confirm participation
October 15, 2019	Study samples shipped to participants. The range in shipping times reflects delays from shipping and customs.
December 31, 2019	Results due to coordinating laboratory
April 2020	Data analysis completed
June 2020	Initial results presented, discussion at OAWG
June 2022	Draft A report distributed to OAWG
September 2022	Draft B report distributed to OAWG

MEASURANDS

The measurand of this study is the mass fraction ethanol in each of the two aqueous matrices in mg/g, and ethanol chemical properties are presented in Table 2.

Table 2. Information of ethanol

Ethanol	
CAS	64-17-5
Molecular formula	C_2H_5OH
M_W	46.07
Structure	

STUDY MATERIALS

The study materials were two batches of solutions of ethanol in water prepared gravimetrically at concentrations between 0.1 mg/g - 5 mg/g by CENAM, dispensed in glass bottles of 50 mL sealed with tear off aluminum crimp seals, with rubber stoppers. The evaporation loss has been evaluated during a period of one year, there was not a significant loss of solution. The purity of the ethanol used to prepare the solution was assessed at CENAM prior to solution preparation, using the mass balance approach.

Homogeneity Assessment of Study Material

Homogeneity analyses for both lots of ethanol in water solutions were performed by gas chromatography with a flame ionization detector (GC-FID), with samples analyzed in duplicate, and three aliquots from each of ten bottles were taken (Figure 1). Three different techniques were used to estimate the probable inhomogeneity: 1) The results of the homogeneity assessment based on ANOVA indicated that standard relative uncertainty due to probable heterogeneity was 0% for the target ethanol; 2) a Monte Carlo simulation was conducted in order to estimate an unbiased upper bound for this heterogeneity component, the estimate for probable heterogeneity was 0.02 %; and 3) using ISO Guide 35 recommendation in section 7.9, we obtain an estimate of 0.12 % for this upper bound. In all these cases, the component due to probable inhomogeneity was not significant. One-way ANOVA with *F*-test in accordance with the requirements as is stipulated in ISO Guide 35 was used to test whether there was significant difference between-bottle of the measurand mass fraction (Table 3). The estimated between-bottle mean squares proved to be smaller than within group mean squares. The value of the relevant *F*-test ratios, *F*, is small and *p*-value is larger than the usual critical 0.05 risk level, which indicates that the heterogeneity of the study material was not significant.

Figure 1. Homogeneity of ethanol

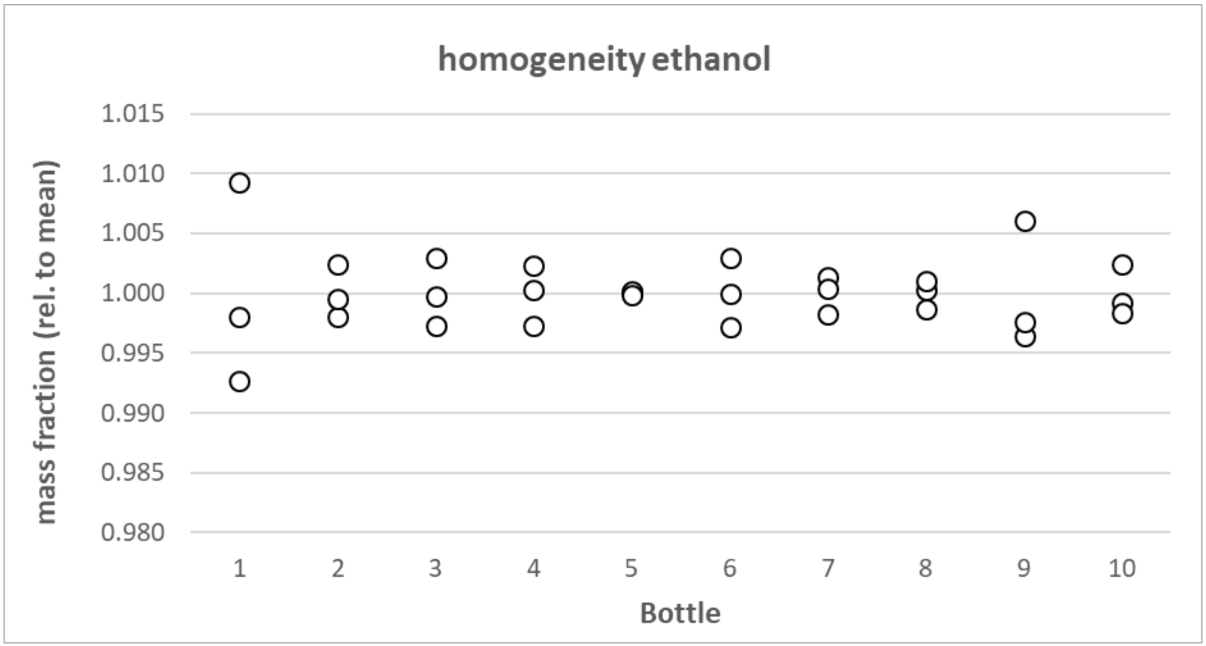


Table 3. Summary of ANOVA for homogeneity test of ethanol

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F $_{crit}$*
Between Groups	5.2228E-05	9	5.80311E-06	0.424	0.90662	2.393
Within Groups	2.7363E-04	20	1.36825E-05			
Total	3.2586E-04	29				

Stability Assessment of Study Material

CENAM has performed formal long-term and short-term stability studies for this solution for one year using the GC-FID method. CENAM had been preparing ethanol solution CRMs in the last 8 years, based on previous experience and from the results of stability studies on both lots of material used for this comparison, no stability problems were observed. Samples were stored at 40 °C for 0, 40, 60, 80, 90 and 100 days for the short-term stability with two bottles being analyzed at each selected date. Duplicate samples were analyzed, and the absolute values were transformed to be relative to the mean. For the long-term stability study, duplicate or triplicate samples were selected randomly at the storage condition of 20 °C for testing at the 0, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, and 14-month time points. Duplicate sub-samples were taken from each bottle to be measured, and the absolute values were transformed to be relative to the mean. The trend graphs of stability are shown in Figures 2 and 3.

The results of the stability assessment indicated that standard relative uncertainty due to possible instability was 0.65 % for the target ethanol under both circumstances, which is the main source of uncertainty for the CENAM gravimetric value. Therefore, we anticipate that the ethanol would be stable in the solution material during the period of the study. The trend-analysis technique proposed by ISO Guide 35 was applied to assess the stability. The effect of time on the stability was evaluated using linear approximation model by fitting linear regression lines to the data set. The statistical results indicated that no significant trend at 95 % confidence level was detected. Hence, the instability of the material was insignificant at the study temperature over the study period. CENAM has used this measurand in similar materials in the past as part of a PT study and the results showed good stability for more than two years.

The stability of the study material was also evaluated through ANOVA test on the regression with results summarized in Tables 4 and 5. The obtained respective *p*-value for the test is greater than 0.05, indicating that the instability was insignificant at 95 % confidence level.

Figure 2. Short-term stability of ethanol

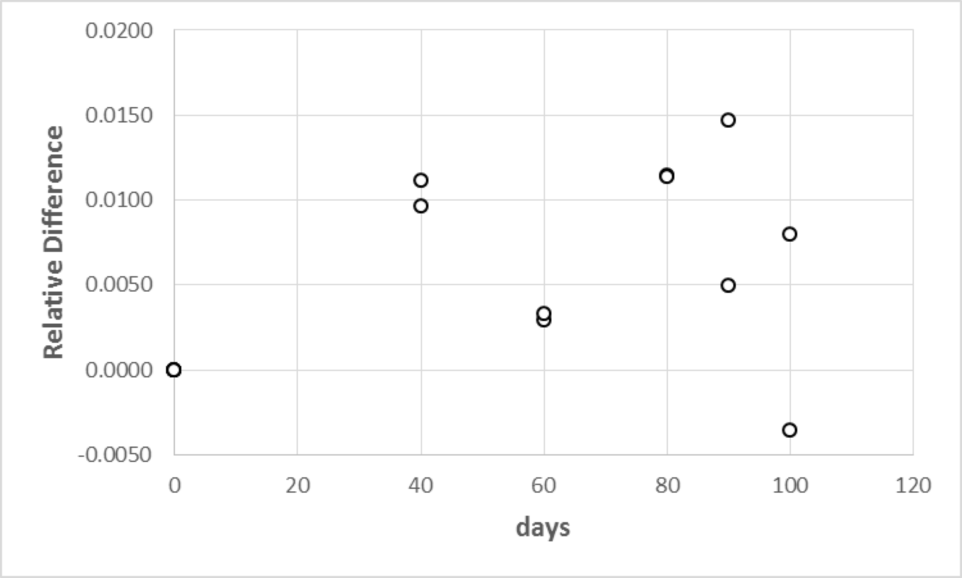


Table 4. Summary of ANOVA test for the short-term stability study of ethanol

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Regression	1.1035E-4	1	1.1035E-4	4.2329	0.0603	4.6672
Within Groups	3.3890E-4	13	2.6069E-5			
Total	4.4925E-4	14				

Figure 3. Long-term stability of ethanol

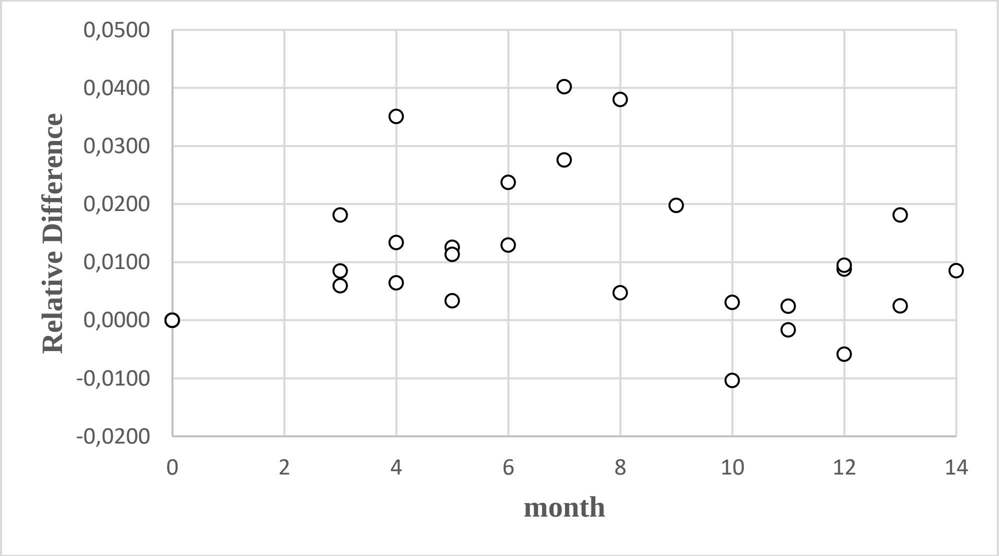


Table 5. Summary of ANOVA test for the long-term stability study of ethanol

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	F_{crit}
Regression	0.000052	1	0.00005236	0.33076	0.5695	4.1709
Within Groups	0.004749	30	0.0001583			
Total	0.004801	31				

PARTICIPANTS

The call for participation was distributed in September 2019 and distribute samples in October 2019, results were received in December 2019, and results discussion at the Spring OAWG meeting, June 2020. Appendix A reproduces the Call for Participation; Appendix B reproduces the study Protocol. Due to shipping practicalities, sample shipping was delayed to October 2019. Due to customs issues, the last set of materials was delivered on 25 October 2019. Because of these delays, the deadline for submission of results was several times postponed with a final deadline of 31 December 2019 to enable discussion of results at the June 2020 OAWG meeting.

Table 6. Institutions receiving SIM.QM-S17 Sample Materials

NMI or DI	**Code**	**Contact**
Centro Nacional de Metrología, México	CENAM	Mariana Arce Osuna/Marco Antonio Avila
Instituto Boliviano de Metrología	IBMETRO	Mabel Delgado/Paola Avendaño
National Metrology Institute of Lithuania	FTMC	Adrian Vicent Claramunt
Instituto Nacional de Calidad, Perú	INACAL	Steve Acco García
Institute of Metrology of Bosnia and Herzegovina	INBIH	Aida Jotanović
Instituto Nacional de Metrología, Colombia	INM	Juliana Barrios
Instituto Nacional de Metrologia, Qualidade e Tecnologia, Brazil	INMETRO	Wagner Wollinger
Instituto Nacional de Tecnología Industrial, Argentina	INTI	Lic. Jimena Etcheverry
Instituto de Salud Pública de Chile	ISP	Soraya Sandoval Riquelme
Dictatoriate of Measures and Precious Metals, Serbia	DMDM	Jelena Bebić/Cedomir Belić
Kenya Bureau of Standards	KEBS	Boniface Mbithi Muendo/Geoffrey Muriira Karau
Laboratorio Tecnológico de Uruguay	LATU	Ana Silva
National Institute of Metrology, Thailand	NIMT	Kittiya Shearman

National Metrology Institute of South Africa	NMISA	Dominique Marajh/Maria Fernandes-Whaley

RESULTS

Participants were requested to report a single estimate of the mass fraction (mg/kg) for the two solutions based on measurements for three (3) individual subsamples of minimum 1 mL from each of two (2) bottles of each solution.

In addition to the quantitative results, participants were requested to describe their analytical methods, and approach for uncertainty estimation.

Methods Used by Participants

Participants were instructed to base their measurement method on either gas chromatography with a flame ionization detector (GC-FID) or gas chromatography with mass spectrometry (GC-MS). Approaches involving internal or external standards were acceptable. The methods employed in this study were intended to represent the way the NMI delivers this measurement service.

Table 7. Methods used by participants

NMI/DI	Analytical method	Calibrant and source	Calibration	Method of quantification	Internal standard used
CENAM	GC-FID	Pure compound, CENAM: DMR-95	Calibration Curve, 5 points	Internal Standard	1-propanol
FTMC	GC-FID	Calibration solutions, BAM: BAM-K003, BAM-K006	Calibration Curve, 5 points	Internal Standard	n-propanol
IBMETRO	GC-FID	Calibration solutions, CENAM: DMR-381b	Calibration Curve, 5 points	Internal Standard	1-propanol
IMBIH	GC-FID	Calibration solutions, BAM: BAM-K001	Calibration Curve	Internal Standard	n-propanol
INACAL	GC-FID	Pure compound (in house purity assessment)	Bracketing	Internal Standard	3-pentanol
INM	GC-FID	Calibration solution, NIST: SRM 2899a	Bracketing	Internal Standard	1-propanol
INMETRO	GC-FID	Pure compound (in house purity assessment)	Calibration Curve, 8 points	Internal Standard	1-propanol
INTI	GC-FID	Pure compound (in house purity assessment)	Calibration Curve, 6 points	Internal Standard	Methyl ethyl ketone
ISP	HSGC–FID	Pure compound (in house purity assessment)	Calibration Curve, 8 points	Internal Standard	2-propanol

DMDM	HSGC–FID	Calibration solutions, NIST: SRM-2895	Calibration Curve, 5-8 points	Internal Standard	1-propanol
LATU	GC-FID	Pure compound (in house purity assessment)	Bracketing	Internal Standard	1-propanol
NIMT	GC-FID	Calibration solution, NIST: SRM 2900	Calibration Curve, 6 points	Internal Standard	1-propanol
NMISA	Titrimetric back titration	Potassium Dichromate NIST SRM 136f-4 and NMIJ CRM 3002-a	NA	NA	NA

SIM.QM-S17 results were received from thirteen of the fourteen institutions that received samples; KEBS withdrew from participation because of equipment difficulties. All the participants based their analyses on some form of GC-FID, GC-MS, and Titration quantification.

Table 8. Calibrants used by participants

NMI/DI	Source, purity and traceability of calibrant
CENAM	DMR-95c/CENAM
NIMT	SRM-2900 (ethanol-water solution)/ NIST, 95.6 % ± 1.9 %, the certified value is metrologically traceable to the SI unit of mass, expressed as a percent.
INMETRO	Pure material/Ethanol Lichrosolv Merck®, purity determined in-house by GC-FID with two columns of different polarities, and water content by Karl Fischer - purity: 99.813 % ± 0.077 g/100 g (*k*=2)
ISP	Calibration curve made gravimetrically from pure solvent ethanol/ J.T. Baker, purity 0.99939%, lot T49C56, traceable to the International System of units through gravimetry, the primary method used to prepare the calibration curve. In addition, traceability is given by the determination of the purity of ethanol, which was determined by coulombimetry by the Karl Fisher technique and Gas Chromatography - Head Space with flame ionization detector (HS-GC / FID) with 2 columns of different polarity.
INACAL	Calibration solution/Ethanol 99.9 %, Merck (in house purity assessment by GC-FID, two columns and KF). Calibration solution obtained from pure material (99.97 %) by gravimetric dilution / impurity determination
DMDM	Calibration solutions/Standard reference material 2895, Ethanol in water solution, (nominal mass fraction 0.2 %), NIST, ID160419
IBMETRO	Calibration solution/CENAM, Etanol acuoso al 5% en volumen DMR-381b
LATU	pure material/Commercial ethanol (LiChrosolv/Merck) with in-house purity determination consisting of GC-FID analysis using two columns of different polarity, coulombimetric Karl-Fischer determination of water content and inorganic impurity determination through evaporation of samples.

NMISA	For sample 10 and 17 Potassium Dichromate used was NIST SRM 136f-4 and for sample 9 and 18 it was NMIJ CRM 3002-a Sample 31/Potassium Dichromate Certified Reference Material from NIST and NMIJ
FTMC	Calibrant solution/CRMs obtained from Bundesanstalt fur Materialforschung und - prufung (BAM) Germany // Ethanol in Water BAM-K003 (Concentration 0.6099 ± 0.0006 g/l) // Ethanol in Water BAM-K006 (Concentration 1.8201 ± 0.0018 g/l)
IMBIH	Calibration solution: certified reference material, Ethanol in water solution/Certified reference material, Ethanol in water solution - 1.0293 g/l; BAM K-001 No. 19101816
INM	Calibration solution/ NIST. Ethanol-water solution SRM 2899a, certified mass fraction: 24.95 % ± 0.52 %
INTI	Ethanol Carlo Erba, purity assigned by INTI, MRC NIST 2896 (quality control)/Purity assigned by INTI (99.948 ± 0.011) g/100g. Mass balance 100- water (Karl Fisher)-organic impurities (GC-FID using 2 different columns)-inorganic impurities (XRF)

The calibrants used by each participant were assessed. All participants either used an appropriate CRM from another NMI or carried out appropriate in-house purity assessment of the ethanol as described in the table above. Thus, all participants met the criteria of using a traceable calibrant and were deemed eligible to be included in the reference value calculation.

Participant Results for Aqueous Ethanol

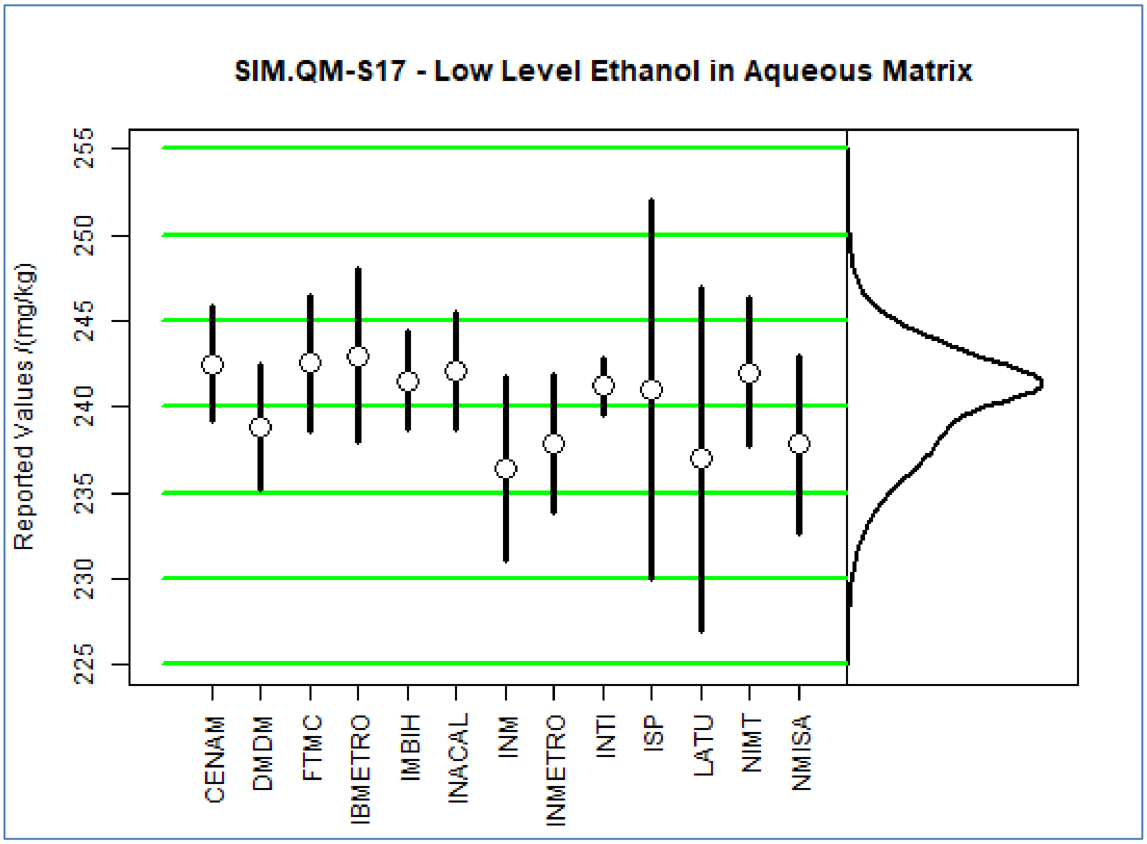
The results for SIM.QM-S17 for the determination of Ethanol in Aqueous matrix are detailed in Table 9 and presented graphically in Figure 4.

In January 2023 NMIT notified the co-ordinators that they had found an error in their reported value. Their reported measurement uncertainties were incorrectly calculated due to a ransomware attack on NMIT that caused a mis-link in their Excel files. The correct values for the low level should be, 242.0 mg/kg, u=2.96 mg/kg, k=2.03 and U=6.0 mg/kg and for the high level, 394.4 mg/kg, u=4.63 mg/kg, k=2.03, U=9.4 mg/kg. As the problem was only identified after the reference value had been agreed upon and the report finalized it was agreed that the correct values would be simply noted in the report and the reported values would remain the values used in the graphs and calculations.

Table 9. Reported results for low-level and high-level ethanol

		Low-level Ethanol, mg/kg				**High-level Ethanol, mg/kg**			
NMI		x	$u(x)$	k	$U(x)$	x	$u(x)$	k	$U(x)$
INM	K27.2019	236.4	2.7	1.96	5.3	390.2	2.3	1.96	4.4
INMETRO	K27.2019	237.8	2.0	2.0	4.0	386.8	2.0	2.0	4.0
FTMC	K27.2019	242.5	1.9	2.0	3.9	389.4	6.9	2.0	13.7
INTI	K27.2019	241.20	0.80	2.0	1.6	387.3	1.7	2.0	3.4
LATU	K27.2019	237.0	4.8	2.1	10	390.2	2.7	2.1	5.7
ISP	K27.2019	241.0	5.5	2.0	11	393.0	8.9	2.0	18
IBMETRO	K27.2019	243.0	2.0	2.0	5.0	390.0	4.0	2.0	7.0
NMISA	K27.2019	237.8	2.6	2.0	5.2	391.0	1.9	2.0	3.7
INACAL	K27.2019	242.1	1.7	2.0	3.4	391.1	2.0	2.0	4.0
IMBIH	K27.2019	241.52	1.42	2.0	2.84	389.10	1.43	2.0	2.86
NIMT	K27.2019	242.0	1.7	2.06	3.6	394.4	2.6	2.04	5.3
DMDM	K27.2019	238.8	1.7	2.0	3.36	390.7	2.73	2.0	5.46
CENAM	K27.2019	242.5	2.16	2.0	4.3	391.1	3.7	2.0	7.4
n		13				13			
$\bar{x}$		240.28				390.33			
s		2.36				2.03			
CV		0.98%				0.52%			

n = number of results included in summary statistics; $\bar{x}$ = mean; s = standard deviation;
CV = $100 \cdot s/\bar{x}$, the coefficient of variation


SIM.QM-S17 - Low Level Ethanol in Aqueous Matrix
Reported Values /(mg/kg)
255
250
245
240
235
230
225
CENAM
DMDM
FTMC
IBMETRO
IMBIH
INACAL
INM
INMETRO
INTI
ISP
LATU
NIMT
NMISA

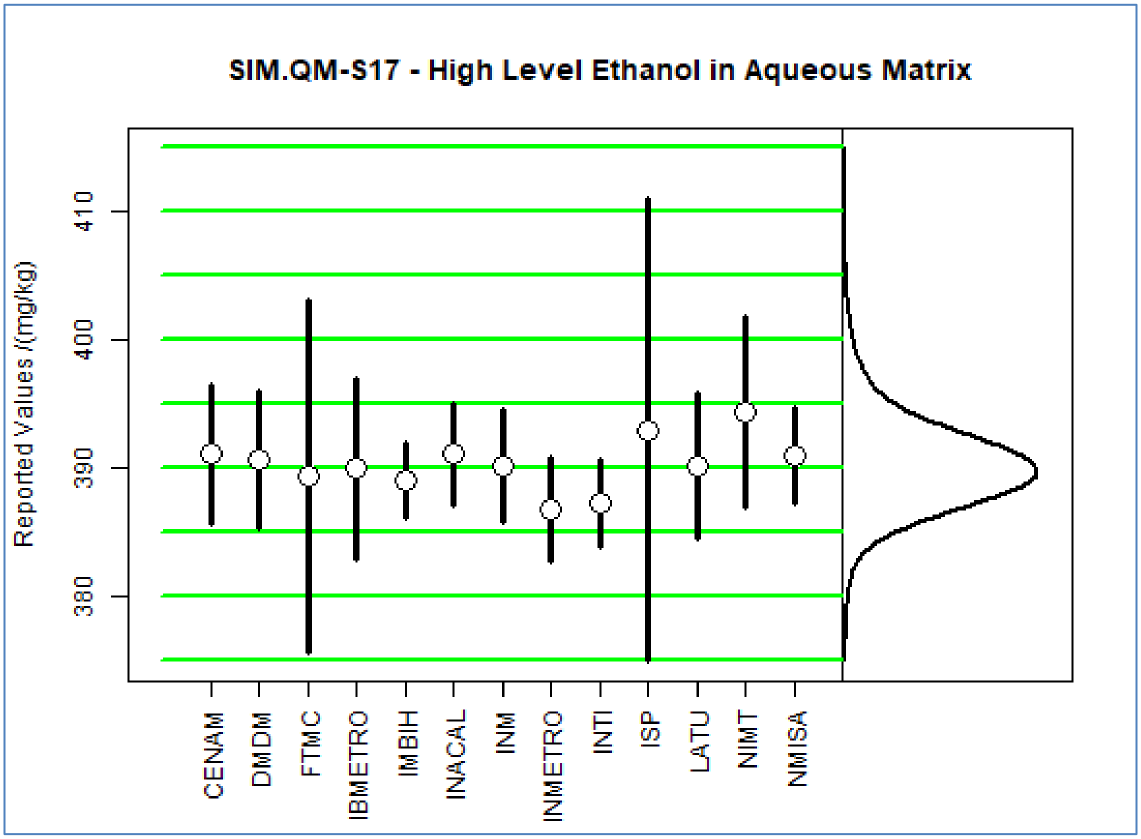

SIM.QM-S17 - High Level Ethanol in Aqueous Matrix
Reported Values /(mg/kg)
410
400
390
380
CENAM
DMDM
FTMC
IBMETRO
IMBIH
INACAL
INM
INMETRO
INTI
ISP
LATU
NIMT
NMISA

Figure 4. Dot-and-Bar chart of reported results for low-level and high-level ethanol in mg/kg

In Figure 4, the top panel displays reported results for low-level ethanol; bottom panel displays results for high-level ethanol. Dots represent the reported mean values, x; bars their 95 % expanded uncertainties, U(x). The thin horizontal gridlines are provided for visual guidance.

TEST MATERIAL CHARACTERIZATION

The test material was characterized by CENAM, and the initial gravimetric values and standard uncertainties were determined as:

Low level: (242.71 ± 0.24) mg/kg

High level: (390.82 ± 0.39) mg/kg

The further uncertainty sources associated with the preparation of the test materials considered the following components:

1) Heterogeneity standard uncertainty 0.02%, dof = 9
2) Instability standard uncertainty 0.65%, dof = 38
3) Preparation trend standard uncertainty 0.06%, dof = 6

The test material values and expanded uncertainties with a 95% probability coverage approximately were determined as:

Low level: (242.7 ± 3.2) mg/kg

High level: (390.8 ± 5.2) mg/kg

The density of the solutions at 20 °C were determined as:

Low level: (0.998156 ± 0.000052) g/cm^3

High level: (0.998127 ± 0.000051) g/cm^3

CANDIDATE KCRV AND CONSENSUS REFERENCE VALUE

CCQM guidance 22-13 [8] was followed for the determination of the Key Comparison Reference Values (KCRVs). Four KCRV candidate estimates were investigated: mean, median, Der Simonian Laird estimator and Hierarchical Bayes estimator. Computations were conducted by using the NIST Consensus Builder (NICOB) [9] when possible and an independent validation using CENAM's Consensus Constructor (CCC) [10] was carried out. Table 10 shows the numeric value of the KCRV candidates for low and high levels of Ethanol in Aqueous Matrix. Figures 5a and 5b show the confidence intervals for low and high levels of ethanol, respectively.

Table 10. Candidate KCRVs with selected KCRV for low-level and high-level ethanol.

		Low level Ethanol in Aqueous Matrix		High level Ethanol in Aqueous Matrix	
Method	Estimating Tool	Value/(mg/kg)	Standard uncertainty/(mg/kg)	Value/(mg/kg)	Standard uncertainty/(mg/kg)
Mean	CCC[a]	240.3	1.0	390.3	1.2
Median	CCC[a]	241.20	0.97	390.2	1.0
Der Simonian Laird	NICOB[b] CCC[a]	240.91 240.91	0.50 0.42	389.70 389.70	0.65 0.64
Hierarchical Bayes	NICOB[b] CCC[a]	240.92 240.84	0.64 0.59	389.87 389.78	0.76 0.72
Selected KCRV: Hierarchical Bayes	**NICOB[b]**	**240.92**	**0.64**	**389.87**	**0.76**

[a]CENAM Consensus Constructor
[b]NIST Consensus Builder

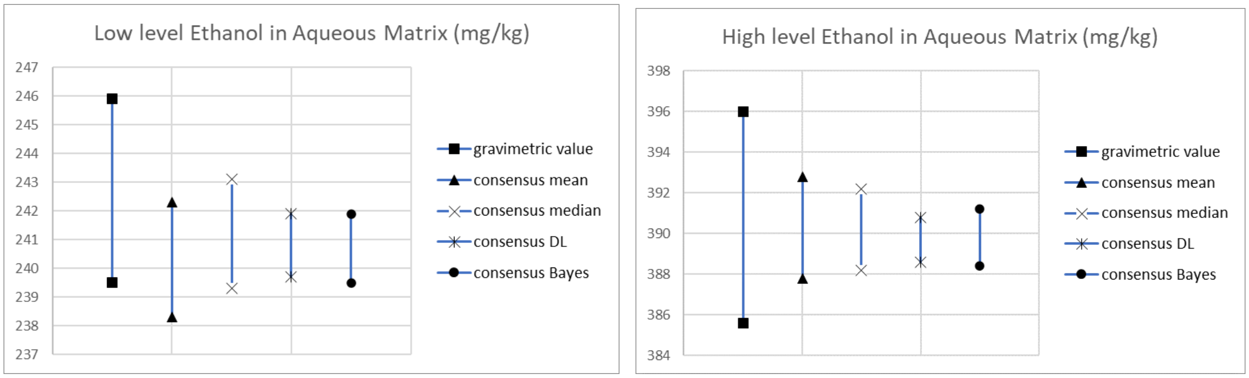


Figure 5. 95% confidence interval chart of candidate consensus reference values for low-level and high-level ethanol in mg/kg.

Estimated consensus reference values using distinct estimators, the gravimetric value, participants mean, participants median, DerSimonian-Laird estimator and the Hierarchical Bayes estimator are shown in Figure 5. Left panel shows the low-level Ethanol estimators, right panel shows the high-level Ethanol estimators. The uncertainty attached to the gravimetric value is clearly larger due to uncertainty components not considered by the participants such as preparation trend, homogeneity, and stability.

This analysis suggests that the gravimetric value can be missing a drift effect and shows a wider uncertainty. The mean and median estimators tend to overestimate the uncertainty. The DerSimonian-Laird and the Hierarchical Bayes estimators use all the information available for the estimation process, and both are slightly similar and statistically superior to the other candidate values. DerSimonian-Laird estimator is easier to compute by hand while the hierarchical bayes estimator is computer intensive by far, however, DerSimonian-Laird uses a simplified model which tends to slightly underestimate the uncertainty. Preliminary results were presented at CCQM meeting on June 6, 2020, it was decided to continue with the Hierarchical Bayesian with Laplacian random effect model for consensus reference value. Figures 6a and 6b show the KCRV for low level Ethanol and for high level Ethanol respectively. We recall the new term considered in the underlying model, the presence of an interlaboratory random effect, characterized by the so-called dark uncertainty τ, for the low-level value the relative standard uncertainty and the standard dark uncertainty represent about 0.3 % and 0.4 % respectively and for the high-level value the relative standard uncertainty and the standard dark uncertainty represent about 0.2 % each.

a) b)

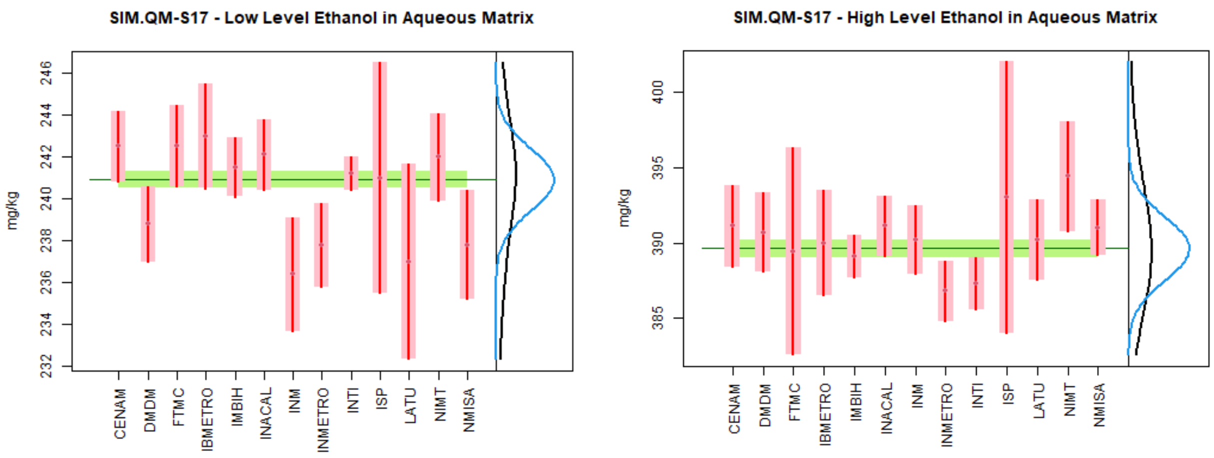


Figure 6. Dot-and-Bar chart of reported results and KCRV in mg/kg

Figure 6 shows the reported results and the Hierarchical Bayes KCRV; (a) panel for low-level results, (b) panel for high-level results. The light green band represent the interval for the estimated KCRV using its standard uncertainty. Thick pink bars represent the standard uncertainty of the reported result (black dot). Thin red bars represent the updated standard uncertainty considering the estimated dark uncertainty component.

DEGREES OF EQUIVALENCE (DoE)

CCQM guidance 22-13 [1] was followed. Computations were conducted by using the NIST Consensus Builder (NICOB) [2] and independent validation using CENAM's own Consensus Constructor (CCC) [3] was carried out. Table 11 shows the numeric value of the DoE for low and high levels of Ethanol in Aqueous Matrix, respectively. For easy assessment, *En* values are included in the last columns respectively, these are calculated as the ratio of the DoE divided by the related expanded uncertainty. Figures 7a and 7b show the respective DoE for low level and high level of Ethanol in Aqueous Matrix.

Table 11. Degrees of Equivalence for low-level and high-level ethanol using the Hierarchical Bayes KCRV.

NMI	**Type**	**Country**	**Low Value (mg/kg)**				**High Value (mg/kg)**			
			DoE	U_{95}	***k***	***En***	**DoE**	U_{95}	***k***	***En***
INM	K27.2019	COLOMBIA	-4.52	7.59	1.96	-0.596	0.32	5.72	1.96	0.057
INMETRO	K27.2019	BRAZIL	-3.12	5.87	2.00	-0.532	-3.07	5.96	2.00	-0.516
FTMC	K27.2019	LITHUANIA	1.60	5.26	2.00	0.304	-0.44	14.17	2.00	-0.031
INTI	K27.2019	ARGENTINA	0.28	3.28	2.00	0.085	-2.57	5.32	2.00	-0.484
LATU	K27.2019	URUGUAY	-3.92	10.84	2.15	-0.362	0.33	6.54	2.14	0.050
ISP	K27.2019	CHILE	0.08	11.43	2.00	0.007	3.13	17.93	2.00	0.174
IBMETRO	K27.2019	BOLIVIA	2.08	5.45	2.00	0.382	0.13	9.02	2.00	0.014
NMISA	K27.2019	SOUTH AFRICA	-3.12	6.21	2.00	-0.503	1.13	4.87	2.00	0.231
INACAL	K27.2019	PERU	1.18	4.85	2.00	0.243	1.23	5.40	2.00	0.227
IMBIH	K27.2019	BOSNIA & HERZEGOVINA	0.60	4.24	2.00	0.142	-0.77	4.42	2.00	-0.175
NIMT	K27.2019	THAILAND	1.08	4.76	2.21	0.227	4.53	7.56	2.05	0.599
DMDM	K27.2019	SERBIA	-2.12	4.89	2.00	-0.433	0.83	6.51	2.00	0.127
CENAM	K27.2019	MEXICO	1.58	5.67	2.00	0.279	1.23	8.27	2.00	0.148

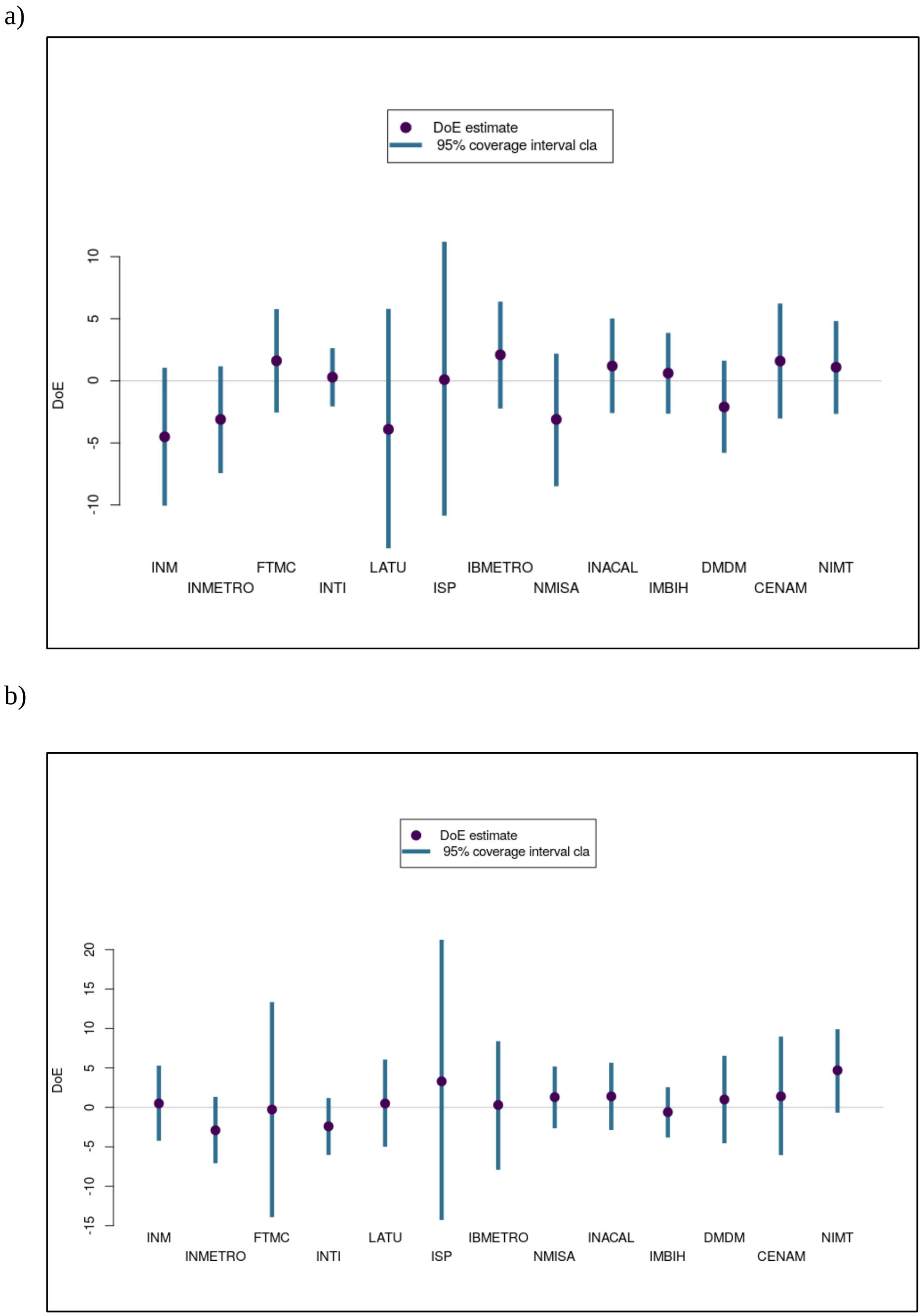


Figure 7. Dot-and-Bar chart of DoEs for low-level and high-level of ethanol in aqueous matrix.

Figure 7 shows the degrees of equivalence of the reported results using the Hierarchical Bayes KCRV; (a) panel for low level, (b) panel for high level. The bars represent the updated expanded uncertainty associated with the degrees of equivalence.

USE OF SIM.QM-S17 IN SUPPORT OF CALIBRATION AND MEASUREMENT CAPABILITY (CMC) CLAIMS

How Far the Light Shines

Participation in the SIM.QM-S17 will demonstrate the laboratory capabilities in determining the mass fraction of ethanol in aqueous matrices in the mass fraction range of 0.1 mg/g to 5 mg/g. The abilities demonstrated by the participants will be indicative of their ability to provide reference measurements for ethanol content in aqueous samples for both forensic and commodities applications.

The completion of a core competency table was not required of the participants as part of the SIM.QM-S17 study. However, the typical competencies that may have been demonstrated by the participants during this study included the following:

- Value assignment of the calibrant
    - Direct use of highly-pure substance or calibration solution CRM (obtained from an NMI)
    - Identity verification of the analyte (i.e., ethanol)
    - In-house value-assignment of the calibration substance
    - Value assignment of the calibration solution
- Sample Analysis
    - Identification of the analyte (i.e. ethanol) in the sample
    - Extraction of analyte (i.e. ethanol) from the sample
    - Transformation/conversion of analyte (i.e. ethanol) to a detectable form
    - Separation and quantification via an analytical system (e.g., GC-FID, LC-MS)
    - Calibration approach for value assignment
    - Any verification methods applied for the value assignment of the analyte (i.e. ethanol) in the sample

The actual competencies demonstrated for each participant depends on how they prepared their calibrants and conducted their sample analysis. Thus, the scope of any future CMC claims that are leveraged from this study may need to consider such details and it may be incumbent of the individual participants to provide such evidence to support their claims.

CCQM is considering the application of “broad-scope” Calibration and Measurement Capabilities (CMCs). Appendix H presents a “broad-scope” CMC table [11], that could be used in claims based on successful participation in SIM.QM-S17 and relevant previous CCQM Key comparisons.

CONCLUSIONS

For both levels of ethanol in aqueous matrix solutions, the DerSimonian-Laird Weighted mean and the Bayesian mean methods seem to give a better estimation of the KCRV ± $KCRU_{95}$ candidate. The rational is that both take advantage of the whole information, obtaining an improved value and uncertainty. This analysis suggests that the mean and median methods tend to slightly overestimate the uncertainty. For this comparison, in June 2020 in the OAWG meeting was agreed to use the Hierarchical Bayes mean as the KCRV ± $KCRU_{95}$ for SIM.QM-S17 regional comparison. The KCRV for SIM.QM-S17 Level 1 (low-level) and Level 2 (high-level) were (240.92 ± 1.28) mg/kg (k =2) and (389.87 ± 1.52) mg/kg (k =2), respectively. All 13 participants result show to be in a good agreement in the SIM.QM-S17 comparison, therefore they all demonstrated their laboratory capabilities in determining the mass fraction of ethanol in aqueous matrices in the mass fraction range of 0.1 mg/g to 5 mg/g, from where they had been supported their ability to provide reference measurements for ethanol content in aqueous samples for both forensic and commodities applications.

ACKNOWLEDGEMENTS

The study coordinators thank all participating laboratories for providing the information requested during this study. Thanks to Dr. Lindsey Mackay, Chair of the OAWG, and Dr. Katrice Lippa, Vice Chair of the OAWG for their guidance and support.

REFERENCES

[1] CCQM-K27a final report. *CCQM K27 (a, b): Determination of ethanol in aqueous matrix,* K S Webb and C S J Wolff Briche, 2004, *Metrologia,* 41, 08002.

[2] CCQM-K27b final report. *CCQM K27 (a, b): Determination of ethanol in aqueous matrix,* K S Webb and C S J Wolff Briche, 2004, *Metrologia,* 41, 08002.

[3] CCQM-K27.1 final report. *CCQM-K27-Subsequent: Key Comparison (subsequent) for the determination of ethanol in aqueous matrix*, Michele M Schantz, David L Duewer, Reenie M Parris, Willie E May, Marcellé Archer, Chris Mussell, David Carter, Leonid A Konopelko, Yury A Kustikov, Anatoli I Krylov and Olga V Fatina, *Metrologia*, 2005, 42, Tech. Suppl., 08005.

[4] CCQM-K27.2 final report. *Final report on CCQM-K27.2: Second Subsequent study: determination of ethanol in aqueous media*, Michele M Schantz, Reenie M Parris, Willie E May, Adriana Rosso, Celia Puglisi, Janaína Marques Rodrigues Caixeiro, Gabriela Massiff, Evangelina Camacho Frías, Melina Pérez Urquiza, Marcellé Archer, *Metrologia*, 2013, 50, Tech. Suppl., 08019.

[5] CCQM-K79 final report. *Final report on CCQM-K79: Comparison of value-assigned CRMs and PT materials: Ethanol in aqueous matrix,* Sebastian Hein, Rosemarie Philipp, David L Duewer, Hugo Gasca Aragon, Katrice A Lippa and Blaza Toman, Metrologia, 2013, 50, Tech. Suppl., 08005.

[6] AFRIMETS.QM-K27, *Final report on AFRIMETS.QM-K27: Determination of ethanol in aqueous matrix*, Marcellé Archer, Maria Fernandes-Whaley, Ria Visser, Jayne de Vos, Sara Prins, Adriana Rosso,

Mariana Ruiz de Arechavaleta, Ibrahim Tahoun, Elias Kakoulides, Caleb Luvonga, *Metrologia*, 2013, 50, Tech. Suppl., 08020.

[7] SIM.QM-K27: *Ethanol in Aqueous Matrix - Final report* , Janaína Marques Rodrigues, Eliane C. P. do Rego, Lucas Junqueira de Carvalho, Tánia Maria Monteiro, and Valnei S. Cunha. June 2019

[8] CCQM Guidance Note: Estimation of a consensus KCRV and associated Degrees of Equivalence. Version 1.0, 2013-04-12.

[9] NIST Consensus Builder, https://consensus.nist.gov

[10] Gasca-Aragon (2020). gconsensus: An implementation of the generalized consensus estimators used to assign the reference value in key comparison exercises and interlaboratory studies. R package version 0.3.0. http://CRAN.R-project.org/package=gconsensus .

[11] CCQM-K95.1 Low-Polarity Analytes in a Botanical Matrix, David L. Duewer, Jacolin A. Murray, Laura J. Wood, and Stephen A. Wise, August 2018.

APPENDIX A: Call for Participation

Dear OAWG colleagues

I wanted to pass on the information for the next JCTLM meeting that will occur in December at BIPM. The details for the meeting and how to register are below.

For our OAWG meeting on 3-4 October please find some further information attached:

- The updated guidelines for OAWG broad claim CMCs. These have been updated by Tang-Lin Teo and John Warren after feedback from our April meeting, all of the changed text is highlighted in yellow. We will be discussing these at the meeting.
- The protocol for the SIM regional comparison for ethanol in water, you can register for this comparison until 7 October.
- The draft protocol for the next comparison coordinated under the BIPM's Mycotoxin Metrology Capacity Building and Knowledge Transfer (MMCBKT) Program. This comparison, CCQM-K154.b, involves calibration solutions for aflatoxin B1 in acetonitrile. It is open to all OAWG members and will commence in 2020.

I will send out the final agenda and further information next, including the final logistical details.
Best wishes
Lindsey

APPENDIX B: Protocol

SIM.QM-S17 Ethanol in Aqueous Matrix: supplement

SIM Key Comparison

Coordinating Laboratory:
CENAM: Marco Ávila Calderón, Victor Serrano Caballero, Hugo Gasca Aragón, Mariana Arce Osuna
INMETRO: Valnei Smarçaro da Cunha / Eliane C. P. do Rego / Bruno Carius Garrido
Study Protocol
August 2019

Introduction

The determination of ethanol in water is important since blood and breath alcohol testing can be imposed on individuals operating private vehicles or operators of commercial vehicles. The various levels of blood alcohol that determine whether these operators are considered legally impaired vary depending on the circumstances, nation, state within the nation, and even month in which the testing is occurring. As a result, practitioners in the field of alcohol testing have a need for reliable and stable standards at many concentrations.

CCQM Organic Analysis Working Group has performed three key comparisons on the determination of ethanol in aqueous matrices (2002: CCQM-K27a for forensic aqueous ethanol and CCQM-K27b for ethanol in wine as a commodity; 2005: CCQM-K27 subsequent studies – four levels of ethanol in water; 2007: CCQM-K27.2 Subsequent 2 for forensic levels). The CCQM-K27 studies establish international measurement comparability between NMIs for the determination of this much traded and forensically important compound. Within the RMOs, both SIM (SIM.QM-K1, SIM.QM-K27) and AFRIMETS (AFRIMETS.QM-K27) have conducted regional key comparisons for the determination of aqueous ethanol solutions. In addition, the Track A Model 2 (formerly known as Track B) Key comparison CCQM-K79 (2010) compared aqueous ethanol certified reference material (CRM) solutions produced and assayed by various NMIs. The CCQM-K79 comparison also supports capabilities demonstrated in the CCQM-K27 comparison series.

Within the SIM RMO, there are NMIs/DIs who have informed of their need to demonstrate measurement capabilities for ethanol measurements in aqueous matrices, even after SIM.QM-K27 (2016), especially across the interval where the alcohol testing requires to be calibrated and verified. This comparison is intended provide to SIM countries an additional opportunity to evaluate their measurements capabilities, other regions are also welcome to participate. SIM CMWG will conduct this supplement regional Key Comparison (SIM.QM-K27.1). Key comparisons performed by regional metrology organizations (RMOs) normally are linked to the CIPM equivalent comparisons through reference to the results from those institutes, which have also taken part in the CIPM key comparison. In this case, the gravimetric preparation value (verified by GC-FID) of the aqueous ethanol solutions will be used to link SIM.QM-K27 subsequent 1 to the CCQM-K27 comparison KCRV. This has been the approach used in the series of comparisons related to aqueous ethanol.

In this SIM.QM-S17 Supplement comparison, as a SIM study, it is expected that all SIM NMIs or DIs who have, or expect to have, services related to the capabilities related to the How Far the Light Shines statement for this key comparison will participate. A parallel pilot study (CCQM-P209) will also be conducted with the same material for interested parties.

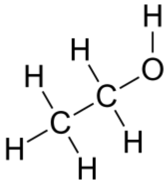
Study Material

The study material will be two batches of solutions of ethanol in water prepared gravimetrically at concentrations between 0.1 mg/g - 5 mg/g by CENAM, dispensed in glass bottles of 50 mL sealed with tear off aluminum crimp seals, with rubber stoppers. The evaporation loss has been evaluated during a period of one year, there was not a significant loss of solution. The purity of the ethanol used to prepare the solution was assessed prior to solution preparation, using the mass balance approach.

Measurand

The measurand of this study is the mass fraction ethanol in each of the two aqueous matrices in mg/g.

Table 1 Information of ethanol

Ethanol	
CAS	64-17-5
Molecular formula	C_2H_5OH
M_W	46.07
Structure	

Methods

Participants are expected to perform measurements by using either gas chromatography with a flame ionization detector (GC-FID) or gas chromatography with mass spectrometry (GC-MS). An isotope dilution quantification approach may be used however it is not required for this study. Other approaches involving internal or external standards are acceptable, and the methods should represent the way the NMI/DI delivers this measurement service.

Homogeneity

Homogeneity analyses for both lots of ethanol in water solutions were performed by gas chromatography with a flame ionization detector (GC-FID), with samples analyzed in duplicate, and three aliquots from each of ten bottles were taken. Three different techniques were used to estimate the probable inhomogeneity. A) The results of the homogeneity assessment based on

ANOVA indicated that standard relative uncertainty due to probable heterogeneity was 0% for the target ethanol. B) A Monte Carlo simulation was conducted in order to estimate an unbiased upper bound for this heterogeneity component, the estimate for probable heterogeneity was 0.02%. C) Using ISO Guide 35 recommendation in section 7.9, we obtain an estimate of 0.12% for this upper bound. In all these cases, the component due to probable inhomogeneity is not significant. One-way ANOVA with F-test in accordance with the requirements as is stipulated in ISO Guide 35 was used to test whether there was significant difference between-bottle of the measurand mass fraction (Table 2). The estimated between-bottle mean squares proved to be smaller than within group mean squares. The value of the relevant F-test ratios, F, is small and p-value is larger than the usual critical 0.05 risk level, which indicates that the heterogeneity of the study material was not significant.

Figure 1 Homogeneity of ethanol

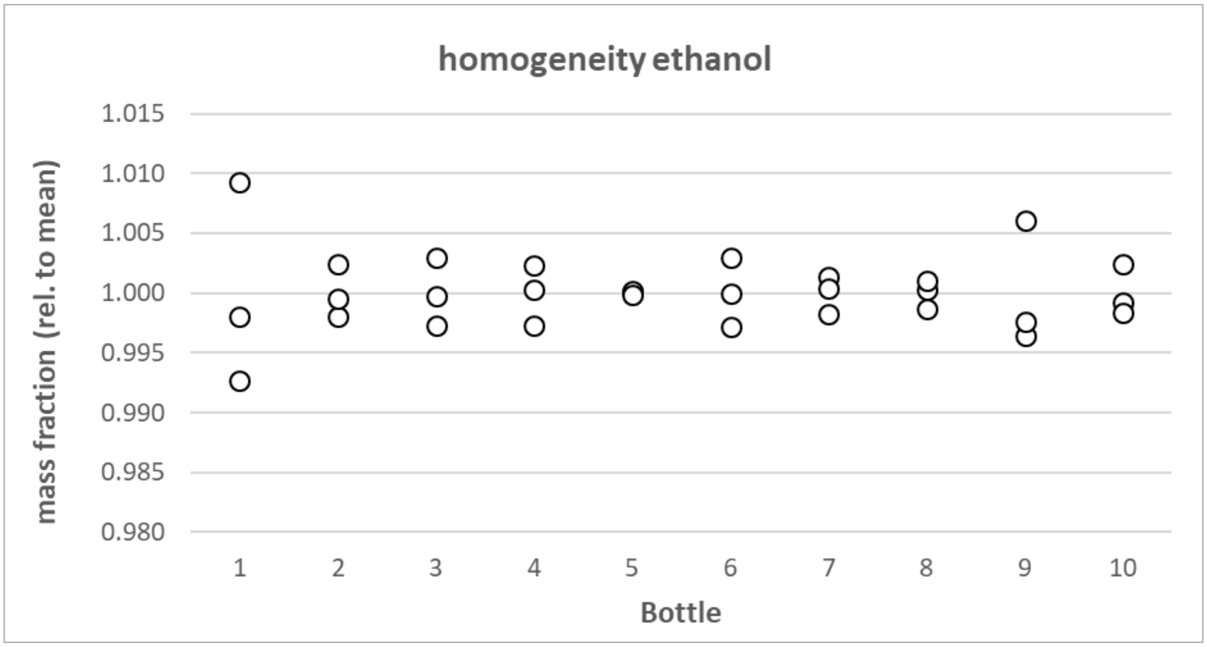


Table 2 Summary of ANOVA for homogeneity test of ethanol

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F $_{crit}$*
Between Groups	5.2228E-05	9	5.80311E-06	0.424	0.90662	2.393
Within Groups	2.7363E-04	20	1.36825E-05			
Total	3.2586E-04	29				

Stability

CENAM has performed formal long-term and short-term stability studies for this solution for one year using the GC-FID method. CENAM had been preparing ethanol solution CRMs in the last 8 years, based on previous experience and from the results of stability studies on both lots of material, no stability problems were observed. Samples were stored at 40 °C for 0, 40, 60, 80, 90 and 100 days for the short-term stability with two bottles being analyzed at each selected date. Duplicate samples were analyzed, and the absolute values were transformed to be relative to the mean. For the long-term stability study, duplicate or triplicate samples were selected randomly at the storage condition of 20 °C for testing at the 0, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, and 14-month time points. Duplicate sub-samples were taken from each bottle to be measured, and the absolute values were transformed to be relative to the mean. The trend graphs of stability are shown in Figures 2 and 3. The results of the stability assessment indicated that standard relative uncertainty due to possible instability was 0.65% for the target ethanol under both circumstances. Therefore, we anticipate that the ethanol would be stable in the solution material during the period of the study. The trend-analysis technique proposed by ISO Guide 35 was applied to assess the stability. The effect of time on the stability was evaluated using linear approximation model by fitting linear regression lines to the data set. The statistical results indicated that no significant trend at 95% confidence level was detected. Hence, the instability of the material was insignificant at the study temperature over the study period. CENAM has used this measurand in similar materials in the past as part of a PT study and the results showed good stability for more than two years.

The stability of the study material was also evaluated through ANOVA test on the regression with results summarized in Tables 3 and 4. The obtained respective p-value for the test is greater than 0.05, indicating that the instability was insignificant at 95% confidence level.

Figure 2 Short-term stability of ethanol

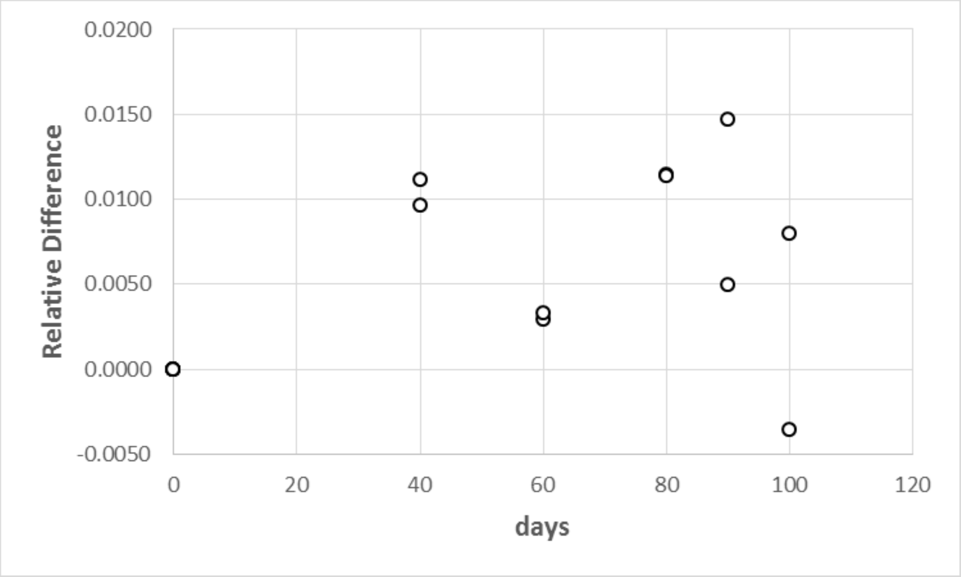


Table 3 Summary of ANOVA test for the short-term stability study of ethanol

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	F_{crit}
Regression	1.1035E-4	1	1.1035E-4	4.2329	0.0603	4.6672
Within Groups	3.3890E-4	13	2.6069E-5			
Total	4.4925E-4	14				

Figure 3 Long-term stability of ethanol

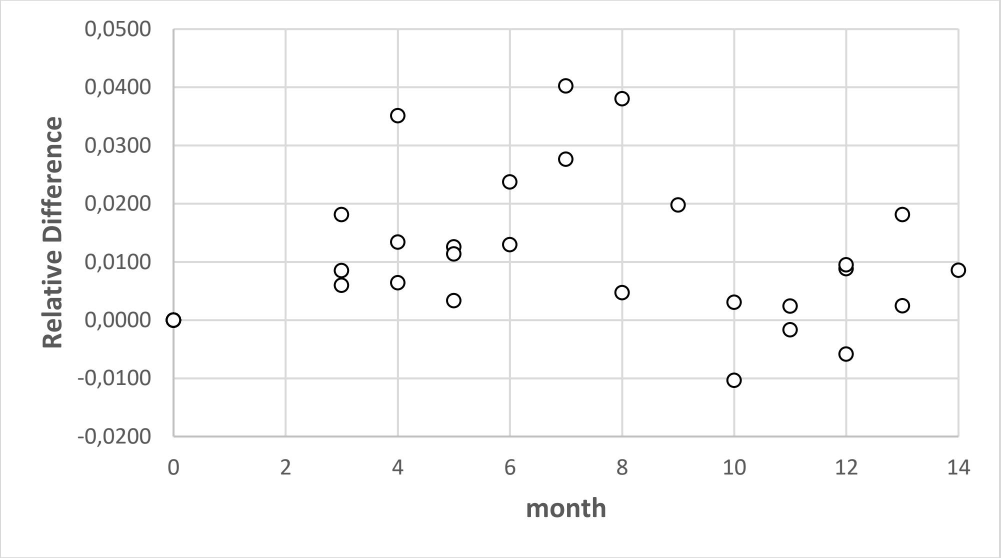


Table 4 Summary of ANOVA test for the long-term stability study of ethanol

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Regression	0.000052	1	0.00005236	0.33076	0.5695	4.1709
Within Groups	0.004749	30	0.0001583			
Total	0.004801	31				

Reference Standards Available

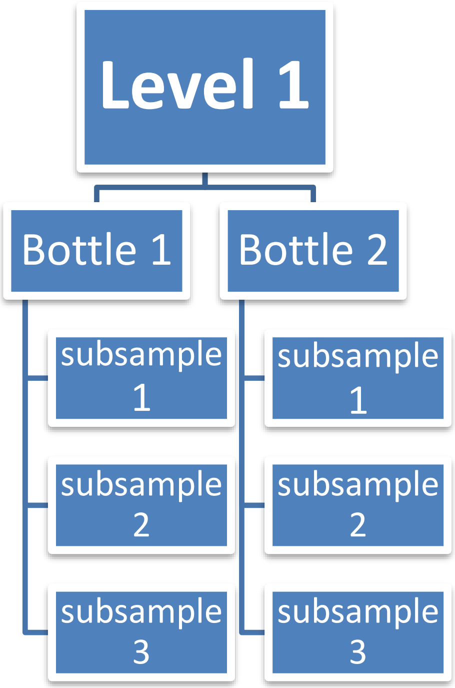
Solution CRMs for the target Ethanol for use as calibrants are available from CENAM (CMR95 c Ethanol, CMR381b aqueous ethanol at 5% in volume, CMR464a Aqueous solution of ethanol to 30% in mass, CMR466a Aqueous solution of ethanol to 49% in mass). In the SIM RMO it is also possible to source from NIST (SRM 1828c - Ethanol-Water Solutions (Six Levels) and from INMETRO (MRC 8848 to 8852 - Five Levels of Ethanol-Water Solutions with Nominal Mass Fraction 0.0509, 0.0814, 0.1069, 0.400, 0.500 %). There are other suitable CRMs from other NMIs on the market, if you wish to use one of them please contact the coordinators so that they could review their certificates and check that they meet the CIPM traceability requirements.

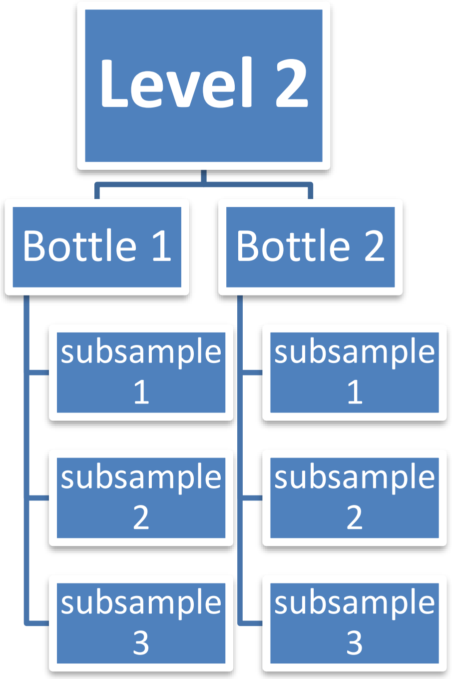
If participating laboratories opt to use their own in-house standards, then they will be responsible for demonstrating SI traceability for the purity values they assign to them. This can be accomplished by using capabilities that have been demonstrated in CIPM-level activities (Key comparisons) or appropriate CMC claims. For NMIs/DIs that do have such evidence, then they may need to provide more direct evidence and provide this information in the reporting sheet.

Study Guidelines

Each participant will receive four 50 mL bottles in total, which correspond to two bottles from each of two solutions at different mass fraction levels. The comparison material samples can be stored at room temperature. Participants can apply their preferred laboratory procedures.

Participants are requested to report a single estimate of the mass fraction (mg/g) for the two solutions based on measurements for three (3) individual subsamples of minimum 1 mL from each bottle of the solution as is showed in the following illustration.





Reporting of Results

At the time of sample dispatch, a sample receipt form will be provided electronically to all participants and must be filled in and returned to the study coordinator on receipt of the shipment. The results reporting form and core competency template will be provided to each participant and must be completed and returned to the study coordinators via email (marce@cenam.mx; vscunha@inmetro.gov.br) before the submission deadline, December 31, 2019.

Submitted results are considered final and no corrections or adjustments of analytical data will be accepted unless approved by the OAWG. The results must include: (1) mass fractions of the each of the two solutions in the units of mg/kg, and (2) the standard and expanded uncertainties with detailed description of the full uncertainty budget. A description of the analytical procedure (GC column; chromatographic conditions, quantification approach) should be provided in the reporting forms. Details should also be provided concerning calibration and internal standards used with appropriate purity statement and/or laboratory assessment and SI traceability.

Evaluation of Results

All the results of the pilot and key comparison will be evaluated against the key comparison reference value (KCRV). The CENAM gravimetric preparation value verified by GC-FID analysis of the aqueous ethanol solutions will be used to link SIM.QM-K27 subsequent 1 to the KCRV of CCQM-K27 comparison. The Draft A report will provide candidate estimates of the KCRV and its uncertainty for review and discussion by the OAWG.

How Far Does the Light Shine?

Participation in the SIM.QM-S17 will demonstrate the laboratory's capabilities in determining the mass fraction of ethanol in aqueous matrices in the mass fraction range of 0.1 mg/g to 5 mg/g. The abilities demonstrated by the participants will be indicative of their ability to provide reference measurements for ethanol content in aqueous samples for both forensic and commodities applications.

Timeline for SIM.QM-S17

Date	Action
September 2018	Proposed to OAWG
October 2018	Draft proposal presented to OAWG
Nov 2018	SIM approved SIM.S17
April 3, 2019	OAWG approved SIM.S17
September 18, 2019	Approval of protocol and call for participation to OAWG members
October 7, 2019	Deadline to confirm participation
October 15,2019	Study samples shipped to participants. The range in shipping times reflects delays from shipping and customs.
December 31, 2019	Results due to coordinating laboratory

APPENDIX C: REGISTRATION FORM

SAMPLE RECEIPT FORM

SIM.QM-S17 Ethanol in Aqueous Matrix: supplement.

SIM Key Comparison

ORGANIZATION / DEPARTMENT / LABORATORY:

NMI/DI:

I hereby acknowledge receipt of four 50 mL bottles of ethanol in aqueous matrix packed in metallic bag in good conditions. Each amber bottle was sealed with rubber caps and tear off aluminium seals.

***Level 1, bottle 1:**	**Yes**	**NO**	***Level 2, bottle 1:**	**Yes**	**NO**
***Level 1, bottle 2:**	**Yes**	**NO**	***Level 2, bottle 2:**	**Yes**	**NO**

* Please circle or mark as appropriate

Remark(s) :

NAME: **email:**

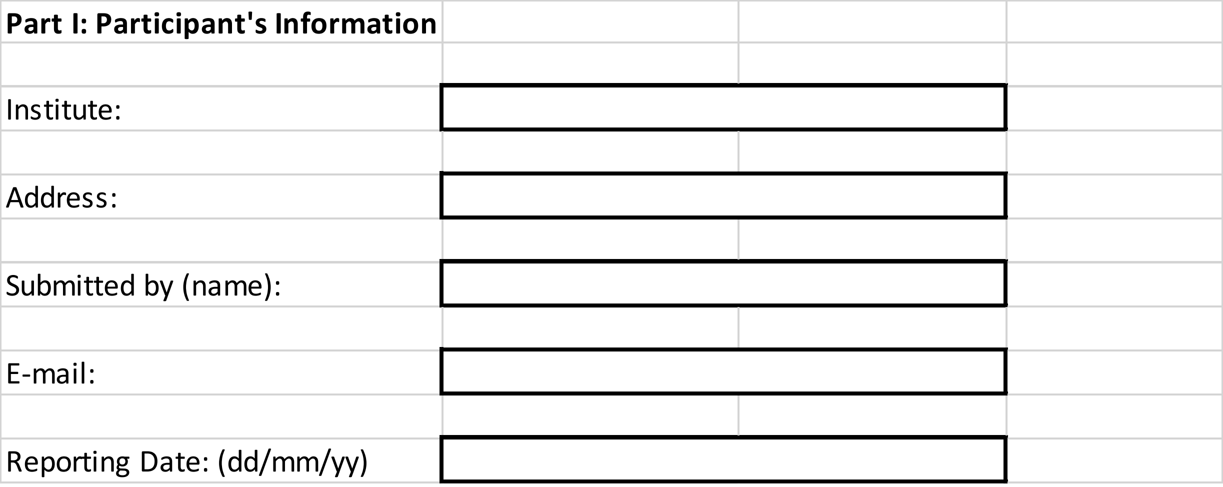
SIGNATURE (S):

RECEIPT DATE: **2019/ /**

APPENDIX D: REGISTRATION FORM

The original form was distributed as an Excel workbook. The following are pictures of the relevant portions of the workbook's three worksheets.

"Participant Details" worksheet



Part I: Participant's Information

Institute:

Address:

Submitted by (name):

E-mail:

Reporting Date: (dd/mm/yy)

“Results” Worksheet

Part II: Results

Level	**Level 1**		**Level 2**	
Bottle code				
Mass Fraction Subsample 1 (mg/kg)				
Mass Fraction Subsample 2 (mg/kg)				
Mass Fraction Subsample 3 (mg/kg)				
Mean (mg/kg)				
Combined Standard Uncertainty (mg/kg)				
Coverage Factor (k)				
U - Expanded Uncertainty (mg/kg) 95% conf.				

“Analytical Information” Worksheet

Part III: Technical Details of Methodology Used

Sample amount used for analysis		g; or	
Calibrant (“pure material” or "calibration solution")			
Source, purity and traceability of calibrant			
Extraction method, if any (e.g., hydrolysis, liquid/liquid (Please briefly describe the extraction procedures)			

“Analytical Information” Worksheet (Continued)

Post extraction clean-up method and derivatization procedures, if any (Please briefly describe the procedures)	
Analytical method used (e.g., GC-MS, GC-FID, Titrimetry, etc.)	
Model of instrument used	
If gas chromatography used:	
Column Phase	
Col. Length, m	
Col. i.d., mm	
Col. film thickness, µm	
The chromatographic condition(s) (e.g., GC oven temperature program, injection mode, injection volume, flow rate, etc)	
The mass spectrometer conditions, if used	
Method of quantification (e.g., IS = Internal Standard, ES = External Standard, IDMS, etc)	

“Analytical Information” Worksheet (Continued)

Type of calibration (e.g., single point, bracketing, calibration curve, etc.)	
Number of points and concentration range of calibration curve, if used	
Internal standard used (Please specify the compound, and at which stage of analysis was the internal standard added.)	

The measurement equation used to calculate the mass fraction of ethanol. Please provide details of all the factors listed in the equation and indicate

Part IV: Uncertainty Calculation

Discuss uncertainty sources and estimation of uncertainties for each factor. Give a complete description of how the estimates were obtained and combined to calculate the overall uncertainty. Please provide a table detailing the full uncertainty budget.

Part V: Addition information

Other information, observations or evidences, if any, that can further support your results, or any problems encountered.

APPENDIX E: Summary of Participants' Analytical Information

The following Tables E-1 to E-3 summarize the detailed information about the analytical procedures each participant provided in their "Analytical Information" worksheets. The presentation of the information in many entries has been consolidated and standardized.

The participant's measurement uncertainty statements are provided verbatim in Appendix F.

Disclaimer

Certain commercial equipment, instruments, or materials are identified in these Tables to specify adequately experimental conditions or reported results. Such identification does not imply recommendation or endorsement by the National Center of Metrology (CENAM) or other participant in this Key Comparison, nor does it imply that the equipment, instruments, or materials identified are necessarily the best available for the purpose.

Table E-1: Summary of Analytical Techniques for SIM.QM-S17

Institute	Analytical Technique	Chromatographic Column	Chromatographic Conditions
CENAM	GC-FID	100% Polyethylen glycol (60 m*0.25 mm*0.25 µm	Inlet temperature: 240 ºC Injection mode: Split: 75:1 Column Flow: 1.0 mL/min. GC oven 50°C; 0 min. to 20°C/min at 220 °C, 1 min. Post run 3 min. Detector temp 240 ºC Hydrogen flow: 40 mL/min Air flow: 450 mL/min Makeup Flow (nitrogen): 35 mL/min
FTMC	GC-FID	Nitroterephthalic acid modified polyethylene glycol (HP-FFAP) (50 m*0.32 mm*0. 5 µm)	Split injection 20:1 / 1µl injection at 240ºC // Hydrogen Gas flow 1ml/min // Initial temperature 70ºC - Hold 7 min // Temperature rate 30ºC/min until 220ºC

Institute	Analytical Technique	Chromatographic Column	Chromatographic Conditions
IBMETRO	GC-FID	DB-WAX (60 m*0.25 mm*0.25 µm)	INJECTION SYSTEM: Temperature: 240 °C, Injection mode Split 100:1, Injection Volumen: 1µL CARRIER GAS. Helium OVEN TEMPERATURE PROGRAM: 6 minutes at Initial Temperature 70 °C , increment of 10 °C/min to 160 °C and keep for 1 minute DETECTOR (FID). Temperature: 240 °C
IMBIH	GC - FID	HP-FFAP(50 m*0.32 mm*0. 5 µm)	Injection: 0.5 µl, autosampler, cool on column (700C); Carrier gas: H2; Oven: 8.5 min at 700C; 300/min to 1800C; 3 min at 1800C;FID: 2500C; H2 40 ml/min, synthetic air 450 ml/min, make up gas N2 45 ml/min

Institute	Analytical Technique	Chromatographic Column	Chromatographic Conditions
INACAL	GC - FID	HP-FFAP (50 m*0.32 mm*0. 5 µm)	Oven temperature program: i. Keep at 35 ° C for 3 minutes, ii. Increase the temperature from 35 ° C to 140 ° C at a rate of 40 ° C / min, iii. Keep at 140 ° C for 5 minutes. Injection temperature: 180 °C Detector temperature: 220 °C Injection mode: Split 100:1 Injection volume: 1 µL Carrier: Helio Flow rate: 2 mL/min
INM	GC-FID	HP-INNOWax (30 m*0.25 mm*0.25 µm)	Temperatures: -oven 65°C -inlet: 210°C -detector 300°C, injection mode: split 1:10, pulsed 35 Lb 0.2 min. Isothermic, run time: 3.50 min
INMETRO	GC-FID	CP-Wax 58 (FFAP) (50 m*0.5 mm*1 µm)	Flow rate: 5.86 mL/min He 5.0; splitless PTV injection: 85 °C; 30 °C/min to 130 °C (8 min); injection volume: 1.0 µL; GC oven: 85 °C (4 min); 15 °C/min to 120 °C (4 min); FID make up: 25 mL/min He 5.0; 40 mL/min H2 5.0; 400 mL/min synthetic air

Institute	Analytical Technique	Chromatographic Column	Chromatographic Conditions
INTI	CG-FID	DB-WAXETR (60m * 0.32 mm * 0.5 µm)	Inlet temp: 220°C; pressure 35 psi; split ratio: 55:1. Direct injection: 1 µL Flow: 6.4 mL/min; Oven: 40°C hold for 9 min Detector temp: 300°C.
ISPCH	GC-FID coupled to Headspace (HS)	DB-BAC1 (30m * 0.32 mm * 1.8 µm)	Gas carrier: Helium, constant flow 2 mL/min Oven temperature 40 °C (6 min); inlet 240 °C; Split ratio 100:1; FID temperature 270°C
DMDM	HSGC–FID	Capillary column InterCap® FFAP,GL Sciences Inc, Tokyo, Japan (30 m*0.25 mm*0.25 µm)	Pre-treatment (Headspace autosampler parameters): heat the GC-vial with sample (10 ml of CRM sample and 100 µ of internal standard) for 3 minutes at 70 °C with constant agitation (Agitation speed 500 rpm).The column temperature program: holds at 70 °C for 1 minutes, afterwards linearly increase temperature from 70 to 120 °C at 15 °C / min., holds 120 °C for 3 min. The injection temperature: 150 °C, Injection speed 500 µL/s, Sample volume: 500 µL. The carrier gas: nitrogen with total flow of 50 mL/min and purge flow 3 ml/min. The detector temperature: 250 °C

Institute	Analytical Technique	Chromatographic Column	Chromatographic Conditions
LATU	GC-FID	Polyethylene glycol (50 m*0.53 mm*1 µm)	Cool On-column injection. Oven: 85°C(6 min) to 120°C at 25 °C/min, 1 µl injection volume, flow 5.9 mL/min, carrier gar: N2. Detector temperature: 220°C, 40ml/min H2 + 400 ml/min air.
NIMT	GC-FID	Fused silica capillary column HP-FFAP (50 m*0.2 mm*0.33 µm)	GC condition Inlet temperature : 100 oC, Injection mode : split ratio 40:1, He carrier gas flow rate: 0.7 mL/min, oven temperature: 60 °C hold time 13 min, FID detector tempereture: 240 °C, Hydrogen flow rate: 30 mL/min, Air flow rate: 350 mL/min, Makeup flow rate: 5 mL/min HS condition Oven temperature : 80 °C, Loop temperature : 90 °C, Transfer line temperature : 100 °C, Vial equilibation time: 5 min, Injection duration time: 0.5 min, GC cycle time: 16 min, Vial shaking: 250 shakes/min
NMISA	Titrimetry	NA	NA

Table E-2: Summary of Calibrants and Standards for SIM.QM-S17

Institute	Type of Calibration	Calibrants	Internal Standards
CENAM	Calibration curve	DMR-95c-Ethanol; CENAM (99.8462 g/100g 0.0084 g/100g)	DMR-418a-1-propanol (CENAM)
FTMC	Calibration curve	CRMs obtained from Bundesanstalt fur Materialforschung und - prufung (BAM) Germany // Ethanol in Water BAM-K003 (Concentration 0,6099 ± 0,0006 g/l) // Ethanol in Water BAM-K006 (Concentration 1,8201 ± 0,0018 g/l)	n-propanol
IBMETRO	Calibration curve	CENAM, Etanol acuoso al 5% en volumen DMR-381b	
IMBIH	Calibration curve	Ethanol in water solution - 1.0293 g/l; BAM K-001 No. 19101816	n-propanol
INACAL	Bracketing	Ethanol 99.97 %, Merck (in house purity assessment	3-pentanol
INM	Bracketing	NIST. Ethanol-water solution SRM 2899a, certified mass fraction: 24.95% ± 0.52%	1-propanol
INMETRO	Calibration curve	Ethanol Lichrosolv Merck®, determined in-house: 99.813 % ± 0.011 g/100 g	1-propanol
INTI	Calibration curve	Ethanol (99.948 %, (in house purity assessment	Methyl Ethyl ketone

Institute	Type of Calibration	Calibrants	Internal Standards
ISPCH	Calibration curve	J.T. Baker, purity 0.99939%, (in house purity assessment	2-propanol
DMDM	Calibration curve	Standard refrence material 2895, Ethanol in water solution, (nominal mass fraction 0.2 %), NIST, ID160419	1-propanol
LATU	Calibration curve	Commercial ethanol (LiChrosolv/Merck) with in-house purity determination	1-propanol
NIMT	Calibration curve	SRM ®-2900 (ethanol-water solution) NIST, 95.6 % ± 1.9 %,	1-propanol
NMISA	NA	Potassium Dichromate used was NIST SRM 136f-4 and for sample 9 and 18 it was NMIJ CRM 3002-a	

Table E-3 Assessment and Verification Methods for SIM.QM-S17

Institute	Purity Assessment	Result Verification
CENAM	CENAM CRM	DMR381 "Ethanol solution 5%" was used as quality control samples
FTMC	CRMs obtained from Bundesanstalt fur Materialforschung und - prufung (BAM) Germany	
IBMETRO	CRM CENAM	
IMBIH	CRM BAM	
INACAL	Ethanol in house purity assessment by GC-FID, two columns and KF. Calibration solution obtained from pure material (99,97%) by gravimetric dilution / impurity determination	
INM	NIST CRM	
INMETRO	Ethanol Lichrosolv Merck®, purity determined in-house by GC-FID with two columns of different polarities, and water content by Karl Fischer	CRMs from Nist (SRM 2896 and SRM 2897a) were used as quality control samples in the same sequence of chromatographic analysis of the samples. They were diluted with water prior to addition of IS solution because their mass fractions were higher than the comparison materials.
INTI	Mass balance : water content, organico impurities (CG-FID using 2 diferents columns; inorganic impurities (XRF)	

Institute	Purity Assessment	Result Verification
ISPCH	J.T. Baker, purity 0.99939%, lot T49C56, traceable to the International system of units through gravimetry, the primary method used to prepare the calibration curve. In addition, traceability is given by the determination of the purity of ethanol, which was determined by coulombimetry by the Karl Fisher technique and Gas Chromatography - Head Space with flame ionization detector (HS-GC / FID) with 2 columns of different polarity.	
DMDM	Standard refrence material 2895, Ethanol in water solution, (nominal mass fraction 0.2 %), NIST, ID160419	Besides the calibrabrants with stated traceability, mentioned above, the results were compared with the in-house made calibrants: Calibrant: ≥ 99.9 % Ethanol G CHROMASOLV®, absolute, for gradient elution, HONEYWELL, Riedel-de Haen, USA, Lot number J069C . The purity of ethanol is determined via Karl-Fisher titration. The received data from both methods were in good agreement.
LATU	Commercial ethanol (LiChrosolv/Merck) with in-house purity determination consisting of GC-FID analysis using two columns of different polarity, coulombimetric Karl-Fischer determination of water content and inorganic impurity determination through evaporation of samples.	
NIMT	NIST, 95.6 %± 1.9 %, the certified value is metrologically traceable to the SI unit of mass, expressed as a percent.	

Institute	Purity Assessment	Result Verification
NMISA	Potassium Dichromate Certified reference Material from NIST and NMIJ	

APPENDIX F: Summary of Participants' Uncertainty Estimation Approaches

The following are pictures of the uncertainty-related information provided by the participants in the "Analytical Information" worksheet of the "Reporting Form" Excel workbook. Information is grouped by participant and presented in alphabetized acronym order.

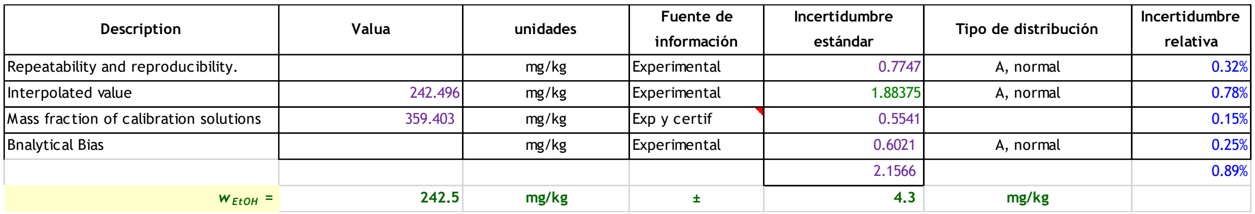
Uncertainty Information from CENAM

$$w_a = \frac{RR_s - \beta_o}{\beta_1}$$

Where:
w_a: mass fraction of the measurand in the sample;
RR_s:Response ratio of sample ;
β_0: intercept of the calibration curve;
β_1: slope of the calibration curve

The uncertainty was estimated according to the GUM and Euachem guide; using as the main source the interpolated value of in the calibration curve that uses the response ratio as the ratio of areas multiplied by the mass fraction of the internal standard.

Additionally, ANOVA was performed with the three subsamples of each bottle and the two bottles; with these results uncertainty was added for repeatability and reproducibility. A source of uncertainty for analytical bias is included when comparing a certified reference material; that although the statistician indicates that it is not significant, it is decided to include it. On the other hand, Because the mathematical model does not include the uncertainty of calibration solutions as a source, this is included as the weighted uncertainty of the calibration levels



Description	Valua	unidades	Fuente de información	Incertidumbre estándar	Tipo de distribución	Incertidumbre relativa
Repeatability and reproducibility.		mg/kg	Experimental	0.7747	A, normal	0.32%
Interpolated value	242.496	mg/kg	Experimental	1.88375	A, normal	0.78%
Mass fraction of calibration solutions	359.403	mg/kg	Exp y certif	0.5541		0.15%
Bnalytical Bias		mg/kg	Experimental	0.6021	A, normal	0.25%
				2.1566		0.89%
w_{EtOH} =	242.5	mg/kg	±	4.3	mg/kg	

Uncertainty Information from FTMC

[EtOH]=(Ae/AIS -0.00207)·(([IS]·mIS)/(0.80239·me))

where
[EtOH] = Concentration of Ethanol
me = Mass of ethanol
[IS] = Concentration of Internal standard
mIS = Mass of Internal Standard
Ae = Area of ethanol
AIS = Area of Internal Standard

Therefore

Eq. => Ae/AIS = a·([EtOH]·me)/([IS]·mIS) + b
Equation obtained from calibration curve: y=0,80239x + 0,00207 // r2= 0,99991

The combined uncertainty (uC) is the combination of the Reproducibility (uR), CRM uncertainty (uCZ) and weighing uncertainty (uW). (Results are showed for Level 1, the same calculation was applied for Level 2) // Reproducibility (Type A uncertainty):
Pooled standard deviation (sp) is used for 2 different series (2 different bottles) (uR)= sp/ẋ = 0,0079
CRM uncertainty (uCZ): uCZ=Uref/(k·Cref) = 0,0006/(2·0,6099) = 0,00049
Uncertainty of weighing (uW): instrument calibration(from certificate) + weighing repeatability: u(W)=√(u(relWc)^2+u(relWr)^2)=√(〚(2,79·10^-5)〛 ^2+ 〚(1,51·10^-6)〛 ^2)=2,794·10^-5
Combined standard uncertainty

(uC): uC=CX*√((uCZ)^2 +(uW)^2 +(uR)^2)=242,04*√(0,0079^2 + 0,00049^2 + (2,794·10^-5)^2) = 1,9229 mg/kg
Expanded uncertainty (95% confidence level, k=2): U=uC·k =1,9229·2 = 3,8457 mg/kg

Uncertainty Information from IBMETRO

The measurement equation used to calculate the mass fraction of ethanol.

$$C_{\text{EtOH}} = \frac{\text{Area} - \text{Interception}}{\text{Slope}}$$

C = Concentration Ethanol
Area = Response obtained from the measurement of sample
Interception = Interception of the regresion line
Slope = Slope of the regresion line

Uncertainty Calculation

Quantities		**Source**
Instrument readings from Chromatograph	Repetibility from readings	Measurements
Calibration curve	lineal regresion	Measurements
Standards weighing	Lineality	Calibration Certificate of balance
	Resolution	
Calibrant Reference Material	U RMC	RMC Certificate

Uncertainty Information from IMBIH

The measurement equation used to calculate the mass fraction of ethanol.

$c_x = [(A_{EtOH}/A_{PrOH}) \times m_{PrOH}] / m_{sample}$
Where: A_{EtOH} is the area of the ethanol peak in the chromatogram

A_{PrOH} is the area of the propanol peak in the chromatogram
m_{PrOH} is the mass of the propanol in mg
m_{sample} is the mass of the sample in g

Uncertainty parameters:
Gravimetric preparations of samples
Gravimetric preparations of calibration solutions
Uncertainty of the CRM used for preparing calibration solutions
Method precision

Uncertainty Information from INACAL

The measurement equation used to calculate the mass fraction of ethanol.

$$C^{x} = C^{x}{}_{ei} \times \frac{m_f}{m_m} \times \left\{ \frac{C^1}{C^1{}_{ei}} + \left(\frac{C^2}{C^2{}_{ei}} - \frac{C^1}{C^1{}_{ei}} \right) \times \frac{(A^x - A^1)}{(A^2 - A^1)} \right\}$$

C^x: Ethanol concentration in the sample

$C^x{}_{ei}$: Concentration of the internal standard in the sample.

m_f : Final mass of the sample aliquot.

m_m: Sample mass

C^1: Concentration of the calibration solution at the low level.

$C^1{}_{ei}$: Concentration of the internal standard at the low level.

C^2: Concentration of the calibration solution at the high level.

$C^2{}_{ei}$: Concentration of the internal standard at the high level.

A^x: Area ratio in the sample.

A^1: Area ratio in the low level.

A^2: Area ratio in the high level

Uncertainty given by:

$$u(y)=\sqrt{(c_1\times u_1)^2+(c_2\times u_2)^2+\ldots\ldots+(c_9\times u_9)^2+(c_{10}\times u_{10})^2}$$

- $u_1 = u_{C^1}$ Uncertainty of the low level calibration solution. Combination of uncertainty of ethanol purity and dilution uncertainty.
- $u_2 = u_{C^1_{ei}}$ Uncertainty of concentration of the internal standard (low level). Combination of uncertainty of 3-pentanol purity and dilution uncertainty.
- $u_3 = u_{C^2}$ Uncertainty of the high level calibration solution. Combination of uncertainty of ethanol purity and dilution uncertainty
- $u_4 = u_{C^2_{ei}}$ Uncertainty of concentration of the internal standard (high level). Combination of uncertainty of 3-pentanol purity and dilution uncertainty.
- $u_5 = u_{C^x_{ei}}$ Uncertainty of concentration of the internal standard (in the sample). Combination of uncertainty of 3-pentanol purity and dilution uncertainty.
- $u_6 = u_{A^1}$

$$u_{A^1} = \sqrt{(\frac{SD_{areas}}{\sqrt{n}})^2+(\frac{SD_{trazado}}{\sqrt{12}})^2}\ ;\ n=3$$

$SD_{trazado}$: Integration by different analysts

- $u_7 = u_{A^2}$

$$u_{A^2} = \sqrt{(\frac{SD_{areas}}{\sqrt{n}})^2+(\frac{SD_{trazado}}{\sqrt{12}})^2}\ ;\ n=3$$

$SD_{trazado}$: Integration by different analysts

- $u_8 = u_{A^x}$

$$u_{A^x} = \sqrt{(\frac{SD_{areas}}{\sqrt{n}})^2+(\frac{SD_{trazado}}{\sqrt{12}})^2}\ ;\ n=3$$

$SD_{trazado}$: Integration by different analysts

- $u_9 = u_{m_f}$ $m_f = m_i - m_j$

$$(u_{mf})^2 = (u_{m_j})^2 + (u_{m_i})^2 + (u_{res})^2$$

- $u_{10} = u_{m_m}$ $m_m = m_k - m_l$

$$(u_{m_m})^2 = (u_{m_k})^2 + (u_{m_l})^2 + (u_{res})^2$$

Level 1

u_1	0.00000039	c_1	0.67115003	$u_1 \times c_1$	0.00000026
u_2	0.00000087	c_2	-0.56814701	$u_2 \times c_2$	-0.00000049
u_3	0.00000043	c_3	0.45469490	$u_3 \times c_3$	0.00000019
u_4	0.00000087	c_4	-0.46414537	$u_4 \times c_4$	-0.00000040
u_5	0.00000088	c_5	1.01902869	$u_5 \times c_5$	0.00000090
u_6	0.00173924	c_6	-0.00023136	$u_6 \times c_6$	-0.00000040
u_7	0.00173694	c_7	-0.00015737	$u_7 \times c_7$	-0.00000027
u_8	0.00292479	c_8	0.00038873	$u_8 \times c_8$	0.00000114
u_9	0.00075287	c_9	0.00004829	$u_9 \times c_9$	0.00000004
u_{10}	0.00075488	c_{10}	-0.00005366	$u_{10} \times c_{10}$	-0.00000004
				u_c (g/g)	0.00000169
				u_c (mg/kg)	1.7

Valor estimado (mg/kg)	**242.1**
U (mg/kg)	**3.4**

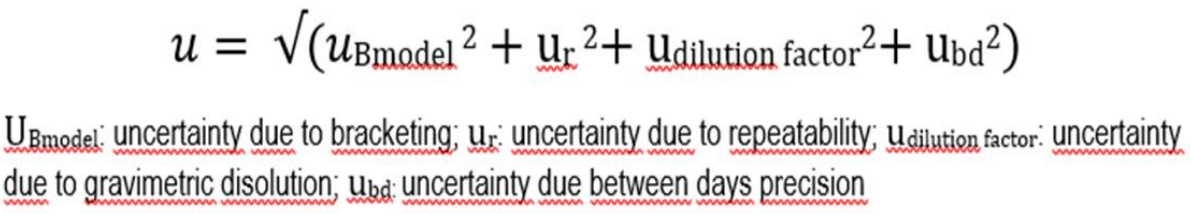
Uncertainty Information from INM

The measurement equation used to calculate the mass fraction of ethanol.

$$mass\ fraction\left(\frac{mg}{g}\right) = \left(mass\ fraction_{low\ level} + \left(R_{a\ sample} - R_{a\ low\ level}\right)\frac{mass\ fraction_{high\ level} - mass\ fraction_{low\ level}}{R_{a\ nigh\ level} - R_{a\ now\ level}}\right) dilution\ factor$$

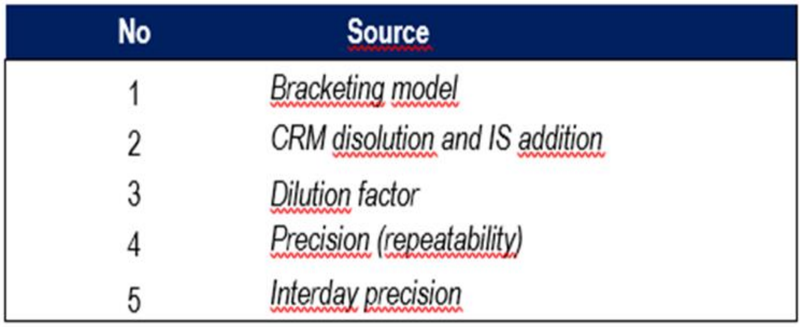
Ra: Ethanol area/n-propanol area; mass fraction (mg/g)

Uncertainty Calculation



$$u = \sqrt{(u_{Bmodel}{}^2 + u_r{}^2 + u_{dilution\ factor}{}^2 + u_{bd}{}^2)}$$

U_{Bmodel}: uncertainty due to bracketing; u_r: uncertainty due to repeatability; $u_{dilution\ factor}$: uncertainty due to gravimetric disolution; u_{bd}: uncertainty due between days precision



No	Source
1	*Bracketing model*
2	*CRM disolution and IS addition*
3	*Dilution factor*
4	*Precision (repeatability)*
5	*Interday precision*

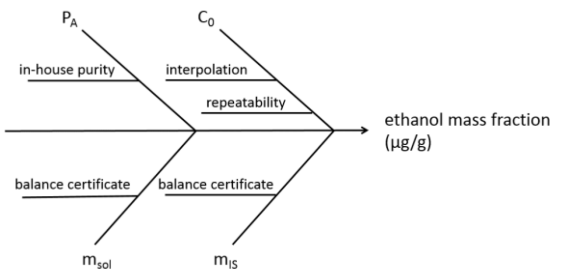
Uncertainty Information from INMETRO

$$w_a = c_0 \times \frac{m_{IS} \times P_a}{m_{sol}} \qquad c_0 = \left(\frac{A - b_0}{b_1}\right)$$

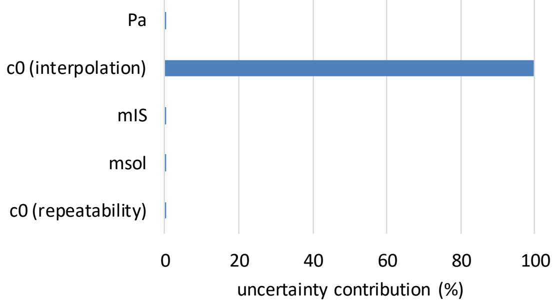
Where: wa: mass fraction of the measurand in the sample; c0: mass fraction of the measurand in the injected solution; mIS: mass of IS solution in the injected solution; Pa: purity of the standard used in the calibration curve; msol: mass of sample in the injected solution; A: area ratio (measurand/IS); b0: intercept of the calibration curve; b1: slope of the calibration curve.

Uncertainty was estimated for individual subsamples and the biggest uncertainty value for the 3 subsamples of each bottle was reported in this form. The uncertainty budget for subsample 2 from bottle 007 (the one with the highest uncertainty for bottle 007) is presented below. As the main contributin source was the interpolation in the calibration curve and the same calibration curve was used for all the samples, the other uncertainty budgets are very similar to this one.

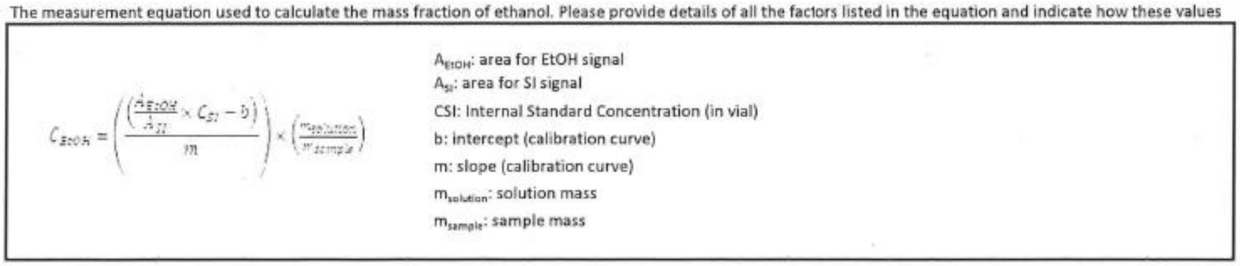
Uncertainty sources	**value**	**type**	**u**	**sensitivity coef.**	**uncertainty component**	**contrib. (%)**
c_0 (repeatability)	240.420289	A	0.058351	0.992333	0.057904	0.083
m_{sol}	1.004000	B	0.000045	-237.626503	0.010693	0.003
m_{IS}	0.998170	B	0.000045	239.014405	0.010756	0.003
b_1	0.000876	A	---	---	---	---
b_0	-0.006025	A	---	---	---	---
c_0 (interpolation)	240.420289	A	2.027762	0.992333	2.012215	99.706
P_a	0.998129	B	0.000383	239.024223	0.091427	0.206
				u_c (mg/kg):	**2.015180**	



Ishikawa diagram



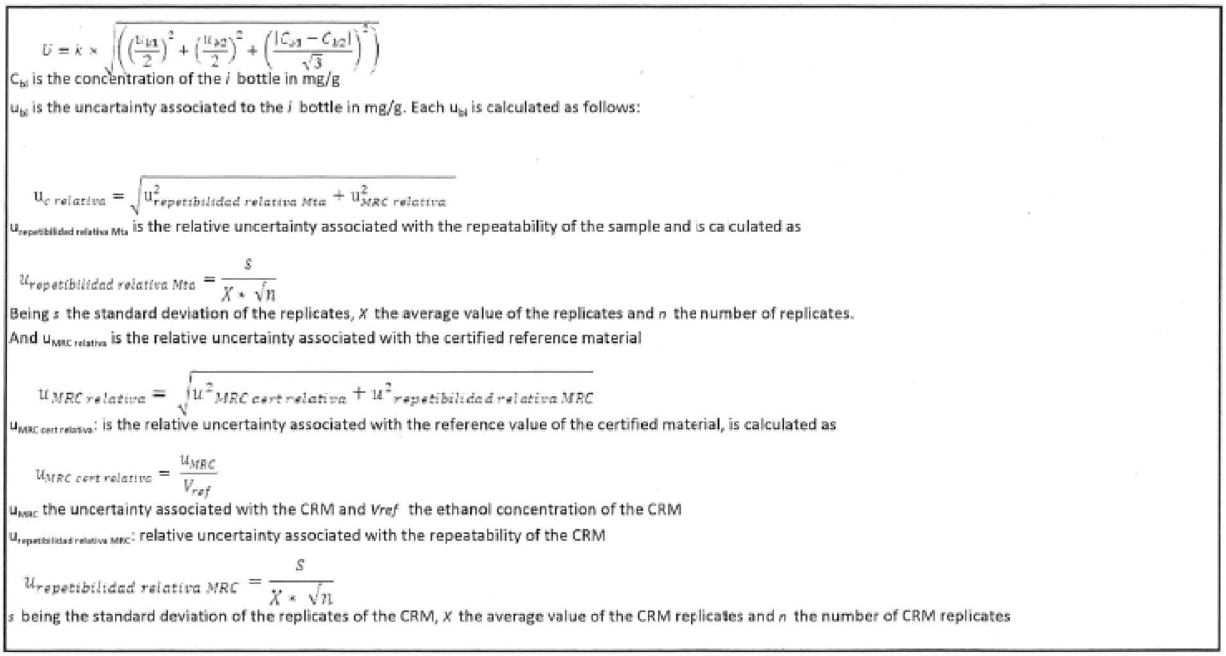
Uncertainty Information from INTI



The measurement equation used to calculate the mass fraction of ethanol. Please provide details of all the factors listed in the equation and indicate how these values

$$C_{EtOH} = \left(\frac{\left(\frac{A_{EtOH}}{A_{SI}} \times C_{SI} - b\right)}{m}\right) \times \left(\frac{m_{solution}}{m_{sample}}\right)$$

A_{EtOH}: area for EtOH signal
A_{SI}: area for SI signal
CSI: Internal Standard Concentration (in vial)
b: intercept (calibration curve)
m: slope (calibration curve)
$m_{solution}$: solution mass
m_{sample}: sample mass



$$U = k \times \sqrt{\left(\left(\frac{u_{b1}}{2}\right)^2 + \left(\frac{u_{b2}}{2}\right)^2 + \left(\frac{|C_{b1} - C_{b2}|}{\sqrt{3}}\right)^2\right)}$$

C_{bi} is the concentration of the i bottle in mg/g

u_{bi} is the uncartainty associated to the i bottle in mg/g. Each u_{bi} is calculated as follows:

$$u_{c\ relativa} = \sqrt{u^2_{repetibilidad\ relativa\ Mta} + u^2_{MRC\ relativa}}$$

$u_{repetibilidad\ relativa\ Mta}$ is the relative uncertainty associated with the repeatability of the sample and is calculated as

$$u_{repetibilidad\ relativa\ Mta} = \frac{s}{X * \sqrt{n}}$$

Being s the standard deviation of the replicates, X the average value of the replicates and n the number of replicates.

And $u_{MRC\ relativa}$ is the relative uncertainty associated with the certified reference material

$$u_{MRC\ relativa} = \sqrt{u^2_{MRC\ cert\ relativa} + u^2_{repetibilidad\ relativa\ MRC}}$$

$u_{MRC\ cert\ relativa}$: is the relative uncertainty associated with the reference value of the certified material, is calculated as

$$u_{MRC\ cert\ relativa} = \frac{u_{MRC}}{V_{ref}}$$

u_{MRC} the uncertainty associated with the CRM and $Vref$ the ethanol concentration of the CRM

$u_{repetibilidad\ relativa\ MRC}$: relative uncertainty associated with the repeatability of the CRM

$$u_{repetibilidad\ relativa\ MRC} = \frac{s}{X * \sqrt{n}}$$

s being the standard deviation of the replicates of the CRM, X the average value of the CRM replicates and n the number of CRM replicates

Uncertainty Information from ISPCH

$A_{EtOH}/A_{IS} = a(C_{EtOH}/C_{IS}) + b$

Where,
A_{EtOH} : Analyte Area
A_{IS} : Internal Standard Area
C_{ETOH} : Concentration of Analyte
C_{IS} : Concentración del Estándar Interno
a : Slope
b : Intercept

The sources of uncertainty in the sample are given by the reproducibility and calibration curve obtained by the validation of the analytical methodology. The uncertainty of the validated test method was estimated considering the standard uncertainty of the internal reproducibility of the validated method and the uncertainty of the calibration curve.

$$u_c = \sqrt{u\ rep^2 + u\ \ st\ Curva^2}$$

Finally, the expanded uncertainty was calculated, with a coverage factor k = 2 at the 95% confidence level.

$$U = k * uc$$

The value of the uncertainty relative to the calibration masses, of the internal standard are not significant with respect to the value of the uncertainty contributed by the value of the calibration cave and the precision, therefore these uncertainties were not considered for the estimation total because they are negligible.

Uncertainty Information from ISPCH

Cx=(Cs*As*fD)/Ac

where:

Cs is the mass fraction of ethanol in the calibration solution in mg g-1; taken from the RM certificate

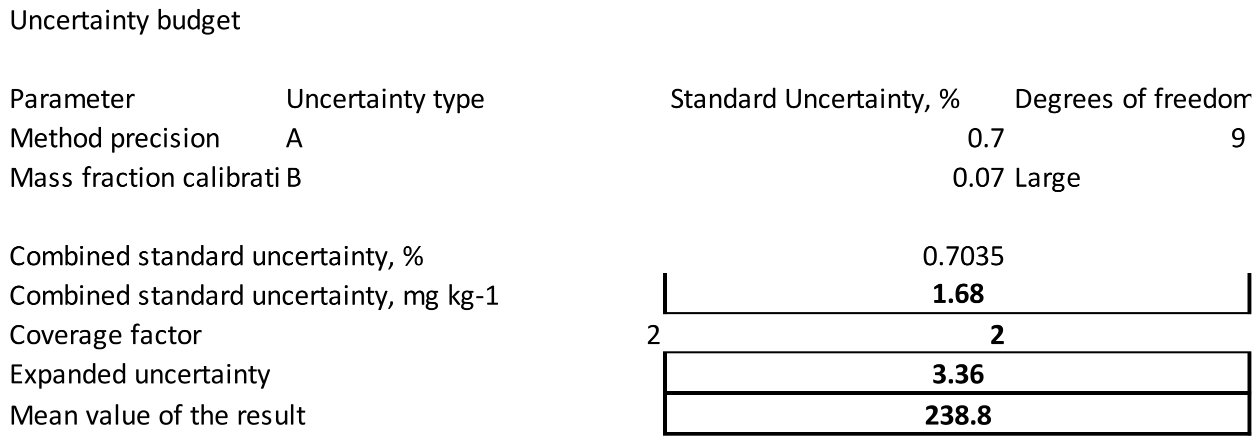
As is the area of the ethanol peak in the chromatogram of the sample; automatic integration by GC solution software

Ac is the area of the ethanol peak in the chromatogram of the calibration;

standard solution; automatic integration by GC solution software

fD is the sample dilution factor

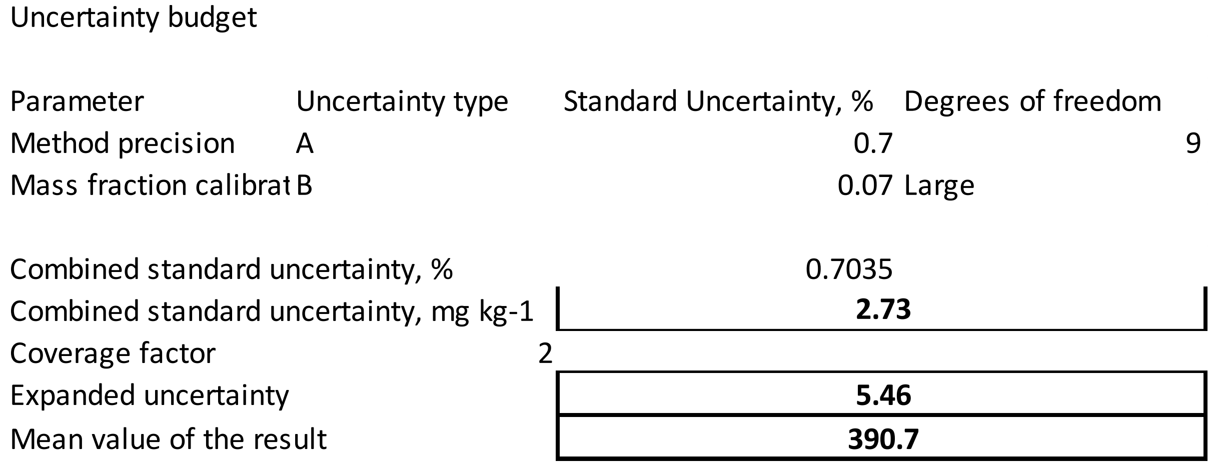
The table with the uncertainty budget for different results, as an exaple is given below.



Uncertainty budget

Parameter	Uncertainty type	Standard Uncertainty, %	Degrees of freedom
Method precision	A	0.7	9
Mass fraction calibrati	B	0.07	Large

Combined standard uncertainty, %		0.7035
Combined standard uncertainty, mg kg-1		**1.68**
Coverage factor	2	**2**
Expanded uncertainty		**3.36**
Mean value of the result		**238.8**



Uncertainty budget

Parameter	Uncertainty type	Standard Uncertainty, %	Degrees of freedom
Method precision	A	0.7	9
Mass fraction calibrat	B	0.07	Large

Combined standard uncertainty, %		0.7035
Combined standard uncertainty, mg kg-1		**2.73**
Coverage factor	2	
Expanded uncertainty		**5.46**
Mean value of the result		**390.7**

Uncertainty Information from LATU

The measurement equation used to calculate the mass fraction of ethanol.

$$w_{Et,mst} = w_{SI,mst} \times \left(\frac{m_{mst} + m_{SI,mst}}{m_{mst}}\right) \times \left\{\frac{w_{Et,cal1}}{w_{SI,cal1}} + \left(\frac{w_{Et,cal2}}{w_{SI,cal2}} - \frac{w_{Et,cal1}}{w_{SI,cal1}}\right) \times \left(\frac{A_{mst} - A_{cal1}}{A_{cal2} - A_{cal1}}\right)\right\}$$

w Et,mst : mass fraction of ethanol in sample. w SI,mst : mass fraction of IS in diluted sample. (wSI,mst= wSI,con×fD , where fD is the corresponding dilution factor). m mst : mass of sample to dilute. m SI,mst : mass of IS added to sample. w Et,cal i: mass fraction of ethanol in the calibrant solution, i=1 low level, i=2 high level. wEt,cal i= wEt,con×fD', where fD' is the correspondig dilution factor. wEt,con=mEt*p*100)/(mEt+mwater, where, mEt is the mass of pure ethanol, p is its in-house purity value and mwater is the mass of added water). m caln,con: is the mass of concentrated calibrant solution. m SI,cal: is the mass of IS solution concentrate added to the calibrant solution. w SI,cal i: mass fraction of IS in the diluted calibrant solution, i=1 low level, i=2 high level, calculated in the same way as wEt,cal i. A mst: average of normalized areas of sample injection. A cal i: average of normalized areas of calibrant injection, i=1 low level, i=2 high level.

	Parameter	Source of uncertainty	Typical value	dard uncerta	Unit	Type	Degrees of Fredom
$w_{Et,cal\ 1}$	Calibrant mass fraction (low level)	Balance calibration uncertainty and purity uncertanty	0.007473	0.000002	g/100 g	B	Large
$w_{SI,cal\ 1}$	IS mass fraction in cal. (low level)	Balance calibration uncertainty	0.043939	0.000002	g/100 g	B	Large
$w_{Et,cal\ 2}$	Calibrant mass fraction (high level)	Balance calibration uncertainty and purity uncertanty	0.012482	0.000002	g/100 g	B	Large
$w_{SI,cal\ 2}$	IS mass fraction in cal. (high level)	Balance calibration uncertainty	0.044075	0.000002	g/100 g	B	Large
$w_{SI,mst}$	IS mass fraction in sample	Balance calibration uncertainty	0.044128	0.000002	g/100 g	B	Large
A_{cal1}	Injection repeatability in cal (low level)	Standard deviation of replicate	0.134098	0.000140	-	A	1
A_{cal2}	Injection repeatability in cal (high level)	Standard deviation of replicate	0.223758	0.000049	-	A	1
A_{mst}	Injection repeatability in sample	Standard deviation of replicate	0.217117	0.000002	-	A	1
m_{tot}	Diluted sample mass	Balance calibration uncertainty	2.005419	0.000010	g	B	Large
m_{mst}	Sample mass	Balance calibration uncertainty	1.005295	0.000008	g	B	Large
Precision	Historic measurement precision	Standard deviation of historical control samples and replicates	0.000000	0.000035	g/100 g	A	5
Bias	Measurement bias	Historical bias	0.000000	0.000042	g/100 g	A	21
					Combined uncertainty=	**0.00005**	**g / 100 g**
					k=	**2.149**	
					Expanded uncertainty=	**0.00012**	**g / 100 g**

Uncertainty Information from NIMT

The measurement equation used to calculate the mass fraction of ethanol.

$$\boxed{w_x = F_{std} \cdot \frac{m_0}{m_x} . F_{pre} . F_{Bias}}$$

w_x= mass fraction of ethanol in the sample (mg/g)
m_0= mass of ethanol obtained from the calibration curve (mg)
m_x= mass of sample
(g)
F_{std}=calibration standard factor, given a value of 1
F_{pre}= method precision factor, given a value of 1
F_{bias}= method bias factor, given a value of 1

$$u(w_x) = w_x \times \sqrt{\left(\frac{u(m_0)}{m_0}\right)^2 + \left(\frac{u(m_x)}{m_x}\right)^2 + \left(\frac{u(F_{pre})}{F_{pre}}\right)^2 + \left(\frac{u(F_{bias})}{F_{bias}}\right)^2 + \left(\frac{u(F_{std})}{F_{std}}\right)^2}$$

where;

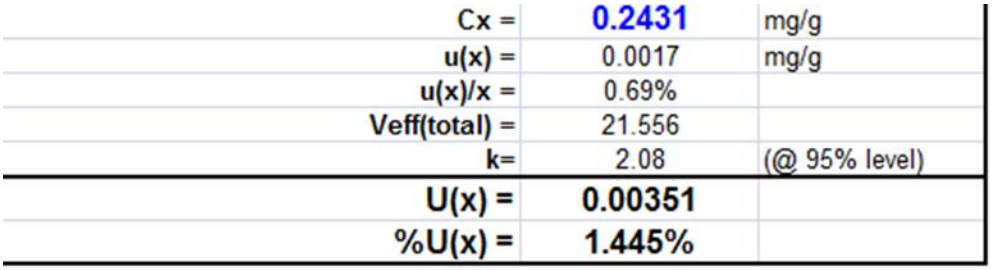
$u(m_0)$ is the standard uncertainty of the calculated mass of ethanol in the sample solution using the calibration curve.

$u(m_x)$ is standard uncertainty of the sample mass. This value was estimated from the bias and precision effect of the balance.

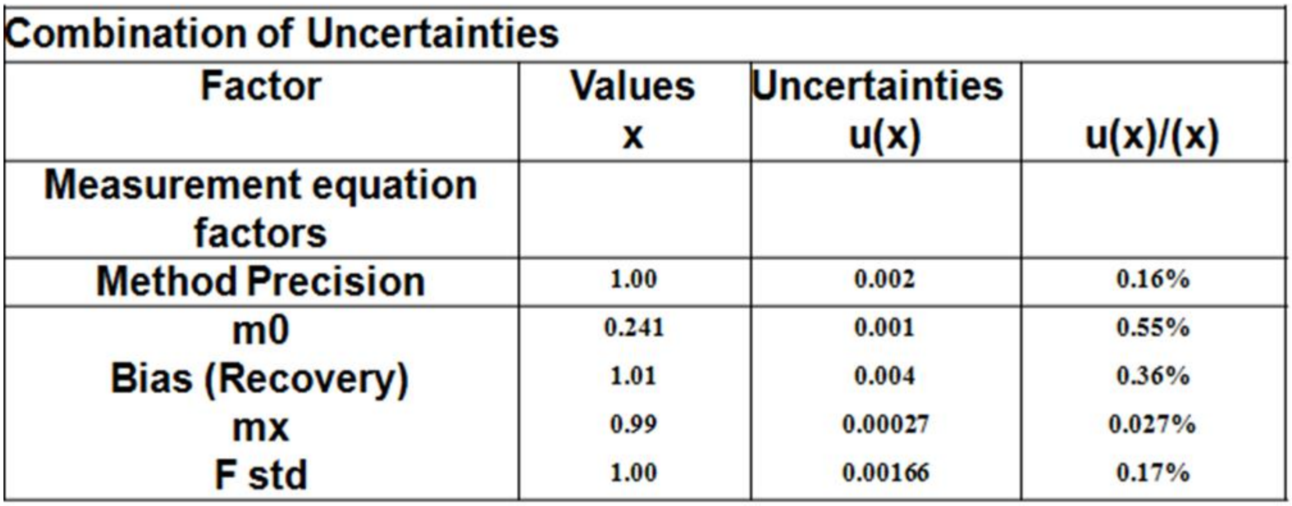
$u\ (F_P)$ is the standard uncertainty of the precision factor. This value was estimated from standard deviation of the multiple results.

$u(F_{bias})$ is the standard uncertainty due to biases. This value was estimated from the recovery of the quality control sample (CRM-used as QC).

$u(F_{std})$ is the standard uncertainty of the calibration standards prepared which was estimated from both bias and random effect. This value was calculated from the uncertainty of stock solution, masses weighed for preparation of stock solutions, dilution and uncertainty using different standard (standard comparision). Example of uncertainty budget of the sample (Level 1, bottle #31) is given below;



Cx =	0.2431	mg/g
u(x) =	0.0017	mg/g
u(x)/x =	0.69%	
Veff(total) =	21.556	
k=	2.08	(@ 95% level)
U(x) =	**0.00351**	
%U(x) =	**1.445%**	



Combination of Uncertainties			
Factor	**Values x**	**Uncertainties u(x)**	**u(x)/(x)**
Measurement equation factors			
Method Precision	1.00	0.002	0.16%
m0	0.241	0.001	0.55%
Bias (Recovery)	1.01	0.004	0.36%
mx	0.99	0.00027	0.027%
F std	1.00	0.00166	0.17%

Uncertainty Information from NMISA

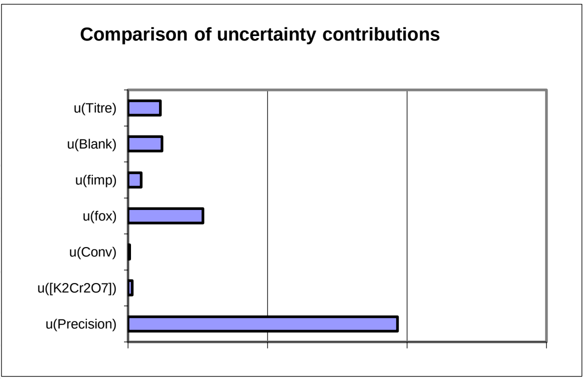
The concentration of the ethanol in aqueous solution is calculated as follows:

[EtOH] = 100 * ([K2Cr2O7] / (4.25718 * MassEtOH soln)) * (MassK2Cr2O7 soln – (Titre(NH4)2Fe(SO4)2/ h))
mg/ 100g
where
[K2Cr2O7] is the concentration of the potassium dichromate solution, calculated by using the certified purity in mg/ g (from Table 3)
MassEtOH soln is the mass of the ethanol solution taken for analysis, in g (From Table 4)
MassK2Cr2O7 soln is the mass of the potassium dichromate solution aliquot added to the ethanol solution, in g (from Table 4)
Titre(NH4)2Fe(SO4)2 is the volume of ammonium iron sulphate titrant used for the aliquot, in ml
the term ‘h’ refers to the blank, the average of the ratio of the ammonium iron sulphate titre to the mass of potassium dichromate titrated (titre(NH4)2Fe(SO4)2/ massK2Cr2O7).

1 gram ethanol reacts with 4.25718 grams K2Cr2O7

Summary of uncertainty contributions

Parameter	x	u(x)	u(x)/x
u(Precision)	38.990	0.15821	0.004058
u([K2Cr2O7])	4.90744	0.000315	6.42E-05
u(Conv)	4.257178	0.000112	2.63E-05
u(f_{ox})	1	0.00113	0.00113
u(f_{imp})	1	0.0002	0.0002
u(Blank)	2.005088	0.001026	0.000512
u(Titre)	18.41014	0.008965	0.000487



To calculate the combined standard uncertainty, u([EtOH]), the square root of the sum of the squares of the relative standard uncertainties is multiplied by the average ethanol concentration.

The expanded uncertainty, U([EtOH]), is calculated by multiplying u([EtOH]) by a coverage factor, k. When the uncertainty is calculated with 95 % confidence, the coverage factor would be 1.96. For ease of use, a coverage factor of k = 2 is used, which gives a confidence of approximately 95 %.

Uncertainty Information from DMDM

Cx=(Cs*As*fD)/Ac

where:
Cs is the mass fraction of ethanol in the calibration solution in mg g-1; taken from the RM certificate

As is the area of the ethanol peak in the chromatogram of the sample; automatic integration by GC solution software
Ac is the area of the ethanol peak in the chromatogram of the calibration; standard solution; automatic integration by GC solution software
fD is the sample dilution factor

The table with the uncertainty budget for different results, as an exaple is given below.

Uncertainty budget

Parameter	Uncertainty type	Standard Uncertainty, %	Degrees of freedom
Method precision	A	0.7	9
Mass fraction calibration solution	B	0.07	Large
Combined standard uncertainty, %		0.7035	
Combined standard uncertainty, mg kg-1		**1.68**	
Coverage factor	2	**2**	
Expanded uncertainty		**3.36**	
Mean value of the result		**238.8**	

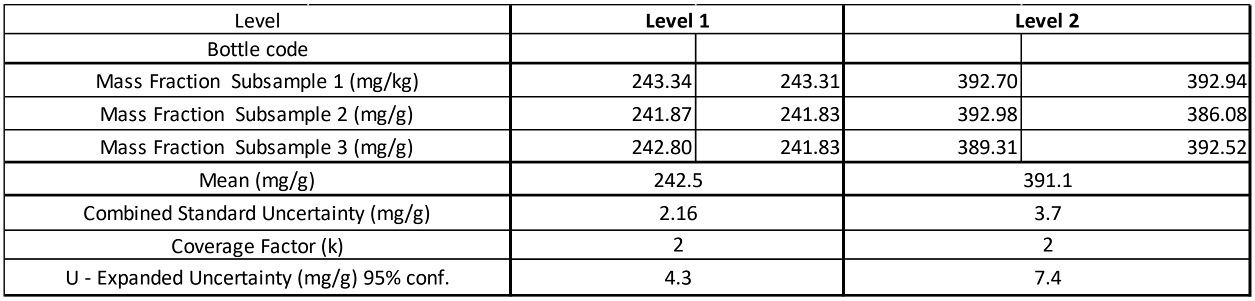
Uncertainty budget

Parameter	Uncertainty type	Standard Uncertainty, %	Degrees of freedom
Method precision	A	0.7	9
Mass fraction calibration solution	B	0.07	Large
Combined standard uncertainty, %		0.7035	
Combined standard uncertainty, mg kg-1		**2.73**	
Coverage factor	2	**2**	
Expanded uncertainty		**5.46**	
Mean value of the result		**390.7**	

APPENDIX G: Participants' Quantitative Results as Reported

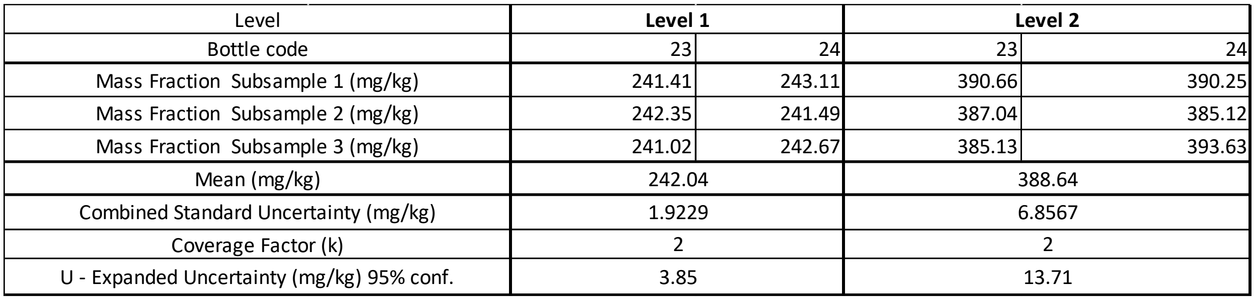
The following are pictures of the quantitative reults as provided by the participants in the "Results" worksheet of the "Reporting Form" Excel workbook. Information is grouped by participant and presented in alphabetized acronym order.

Quantitative Results from CENAM



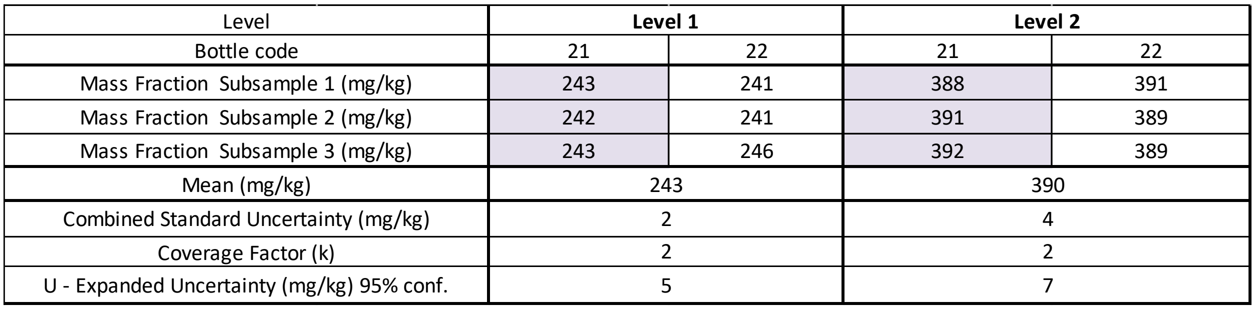
Level	**Level 1**		**Level 2**	
Bottle code				
Mass Fraction Subsample 1 (mg/kg)	243.34	243.31	392.70	392.94
Mass Fraction Subsample 2 (mg/g)	241.87	241.83	392.98	386.08
Mass Fraction Subsample 3 (mg/g)	242.80	241.83	389.31	392.52
Mean (mg/g)	242.5		391.1	
Combined Standard Uncertainty (mg/g)	2.16		3.7	
Coverage Factor (k)	2		2	
U - Expanded Uncertainty (mg/g) 95% conf.	4.3		7.4	

Quantitative Results from FTMC



Level	**Level 1**		**Level 2**	
Bottle code	23	24	23	24
Mass Fraction Subsample 1 (mg/kg)	241.41	243.11	390.66	390.25
Mass Fraction Subsample 2 (mg/kg)	242.35	241.49	387.04	385.12
Mass Fraction Subsample 3 (mg/kg)	241.02	242.67	385.13	393.63
Mean (mg/kg)	242.04		388.64	
Combined Standard Uncertainty (mg/kg)	1.9229		6.8567	
Coverage Factor (k)	2		2	
U - Expanded Uncertainty (mg/kg) 95% conf.	3.85		13.71	

Quantitative Results from IBMETRO



Level	**Level 1**		**Level 2**	
Bottle code	21	22	21	22
Mass Fraction Subsample 1 (mg/kg)	243	241	388	391
Mass Fraction Subsample 2 (mg/kg)	242	241	391	389
Mass Fraction Subsample 3 (mg/kg)	243	246	392	389
Mean (mg/kg)	243		390	
Combined Standard Uncertainty (mg/kg)	2		4	
Coverage Factor (k)	2		2	
U - Expanded Uncertainty (mg/kg) 95% conf.	5		7	

Quantitative Results from IMBIH

Level	**Level 1**		**Level 2**	
Bottle code	017	018	003	004
Mass Fraction Subsample 1 (mg/kg)	241.54	241.59	389.55	389.32
Mass Fraction Subsample 2 (mg/kg)	241.08	241.59	389.09	388.88
Mass Fraction Subsample 3 (mg/kg)	241.82	241.49	388.87	388.88
Mean (mg/kg)	**241.52**		**389.10**	
Combined Standard Uncertainty (mg/kg)	1.42		1.43	
Coverage Factor (k)	2		2	
U - Expanded Uncertainty (mg/kg) 95% conf.	2.84		2.86	

Quantitative Results from INACAL

Level	**Level 1**		**Level 2**	
Bottle code	11	12	13	14
Mass Fraction Subsample 1 (mg/kg)	241.8	242.1	391.3	392.0
Mass Fraction Subsample 2 (mg/kg)	241.6	242.2	390.7	390.4
Mass Fraction Subsample 3 (mg/kg)	242.4	242.3	390.4	392.0
Mean (mg/kg)	**242.1**		**391.1**	
Combined Standard Uncertainty (mg/kg)	1.7		2.0	
Coverage Factor (k)	2		2	
U - Expanded Uncertainty (mg/kg) 95% conf.	**3.4**		**4.0**	

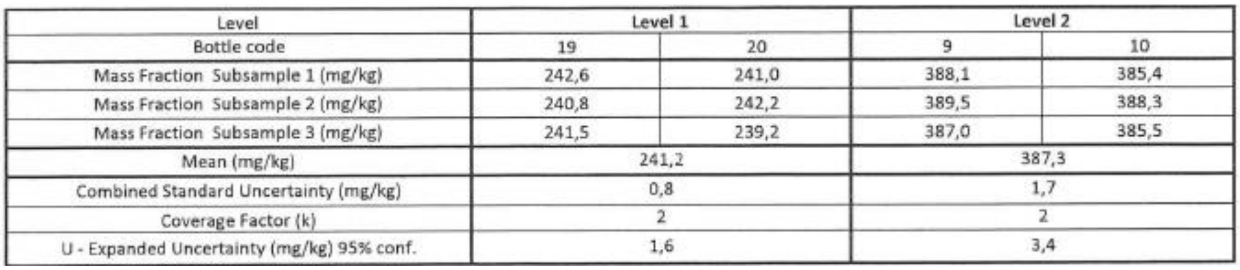
Quantitative Results from INM

Level	**Level 1**		**Level 2**	
Bottle code	15	16	15	16
Mass Fraction Subsample 1 (mg/Kg)	246.0	230.1	390.4	390.5
Mass Fraction Subsample 2 (mg/Kg)	242.7	228.7	390.4	389.9
Mass Fraction Subsample 3 (mg/Kg)	244.6	226.5	389.9	390.7
Mean (mg/Kg)	236.4		390.2	
Combined Standard Uncertainty (mg/Kg)	2.7		2.3	
Coverage Factor (k)	1.96		1.96	
U - Expanded Uncertainty (mg/Kg) 95% conf.	5.3		4.4	

Quantitative Results from INMETRO

Level	**Level 1**		**Level 2**	
Bottle code	007	008	011	012
Mass Fraction Subsample 1 (mg/kg)	238.0	237.5	386.6	386.7
Mass Fraction Subsample 2 (mg/kg)	238.6	237.3	386.5	387.5
Mass Fraction Subsample 3 (mg/kg)	238.2	237.2	386.6	386.7
Mean (mg/kg)	237.8		386.8	
Combined Standard Uncertainty (mg/kg)	2.0		2.0	
Coverage Factor (k)	2		2	
U - Expanded Uncertainty (mg/kg) 95% conf.	4.0		4.0	

Quantitative Results from INTI



Level	Level 1		Level 2	
Bottle code	19	20	9	10
Mass Fraction Subsample 1 (mg/kg)	242,6	241,0	388,1	385,4
Mass Fraction Subsample 2 (mg/kg)	240,8	242,2	389,5	388,3
Mass Fraction Subsample 3 (mg/kg)	241,5	239,2	387,0	385,5
Mean (mg/kg)	241,2		387,3	
Combined Standard Uncertainty (mg/kg)	0,8		1,7	
Coverage Factor (k)	2		2	
U - Expanded Uncertainty (mg/kg) 95% conf.	1,6		3,4	

Quantitative Results from ISPCH

Level	**Level 1**		**Level 2**	
Bottle code	1	2	7	8
Mass Fraction Subsample 1 (mg/kg)	245	242	395	389
Mass Fraction Subsample 2 (mg/kg)	244	236	400	394
Mass Fraction Subsample 3 (mg/kg)	241	238	392	389
Mean (mg/kg)	241		393	
Combined Standard Uncertainty (mg/kg)	5		9	
Coverage Factor (k)	2		2	
U - Expanded Uncertainty (mg/kg) 95% conf.	11		18	

Quantitative Results from DMDM

Level	**Level 1**		**Level 2**	
Bottle code	**3**	**4**	**5**	**6**
Mass Fraction Subsample 1 (mg/kg)	**240.0**	**239.3**	**390.3**	**391.7**
Mass Fraction Subsample 2 (mg/kg)	**237.8**	**237.5**	**390.4**	**389.8**
Mass Fraction Subsample 3 (mg/kg)	**239.7**	**238.3**	**390.9**	**390.9**
Mean (mg/kg)	**238.8**		**390.7**	
Combined Standard Uncertainty (mg/kg)	**1.68**		**2.73**	
Coverage Factor (k)	**2**		**2**	
U - Expanded Uncertainty (mg/kg) 95% conf.	**3.36**		**5.46**	

Quantitative Results from LATU

Level	**Level 1**		**Level 2**	
Bottle code	005	006	019	020
Mass Fraction Subsample 1 (mg/kg)	242	233	390.2	390.0
Mass Fraction Subsample 2 (mg/kg)	242	233	390.1	390.2
Mass Fraction Subsample 3 (mg/kg)	242	233	390.3	390.2
Mean (mg/kg)	237		390.2	
Combined Standard Uncertainty (mg/kg)	4.8		2.7	
Coverage Factor (k)	2.149		2.149	
U - Expanded Uncertainty (mg/kg) 95% conf.	10		5.7	

Quantitative Results from NMIT

Level	Level 1		Level 2	
Bottle code	030	031	031	030
Mass Fraction Subsample 1 (mg/g)	240.2023	242.7334	392.5958	394.0099
Mass Fraction Subsample 2 (mg/g)	240.8200	243.1128	392.4718	396.4656
Mass Fraction Subsample 3 (mg/g)	241.6105	243.4484	394.2982	396.4857
Mean (mg/g)	240.8776	243.0982	393.1219	395.6537
Combined Standard Uncertainty (mg/g)	1.7	1.7	2.6	2.6
Coverage Factor (k)	2.08	2.08	2.04	2.04
U - Expanded Uncertainty (mg/g) 95% conf.	3.6	3.6	5.3	5.3
* the mean of each level (mg/g)	241.9879		394.3878	

Quantitative Results from NMISA

Level	Level 1	
Bottle code	S09	S010
Mass Fraction Subsample 1 (mg/kg)	231.19	244.72
Mass Fraction Subsample 2 (mg/kg)	230.87	244.44
Mass Fraction Subsample 3 (mg/kg)	231.26	243.82
Mass Fraction Subsample 4 (mg/kg)	232.82	243.35
Mass Fraction Subsample 5 (mg/kg)	232.31	243.78
Mass Fraction Subsample 6 (mg/kg)	233.27	245.96
Mass Fraction Subsample 7 (mg/kg)	233.33	
Mass Fraction Subsample 8 (mg/kg)		
Mean (mg/kg)	237.8	
Combined Standard Uncertainty (mg/kg)	2.6	
Coverage Factor (k)	2	
U - Expanded Uncertainty (mg/kg) 95% conf.	5.2	

Level	Level 2	
Bottle code	S018	S017
Mass Fraction Subsample 1 (mg/kg)	395.42	393.45
Mass Fraction Subsample 2 (mg/kg)	389.82	392.36
Mass Fraction Subsample 3 (mg/kg)	389.77	392.17
Mass Fraction Subsample 4 (mg/kg)	397.34	392.00
Mass Fraction Subsample 5 (mg/kg)	389.33	395.29
Mass Fraction Subsample 6 (mg/kg)	387.25	390.65
Mass Fraction Subsample 7 (mg/kg)	384.25	391.43
Mass Fraction Subsample 8 (mg/kg)	386.02	390.07
Mean (mg/kg)	391.0	
Combined Standard Uncertainty (mg/kg)	1.9	
Coverage Factor (k)	2	
U - Expanded Uncertainty (mg/kg) 95% conf.	3.7	

APPENDIX H: Prototype Broad-Scope Core Competency Claim

Table H-1: Prototype Broad Category 3 Claims
for All Participants

Measurement service	Category 3. Organic solutions
Measurement service sub-category	Others (3.4)
Matrix	Water
Measurand	Analyte or Component:high-polarity (pK_{OW} > -2) organic analyte of low molecular mass (0 g/mol to 300 g/mol) Quantity: Mass fraction
Dissemination range of measurement capability	From 0.1 to 5 Unit: mg/g
Range of expanded uncertainties as disseminated	From 0.39 to 0.52 (*to be updated after KCRV/U*) Unit: % Coverage factor: 2 or Student's $t_{1-0.95,n-1}$ Level of confidence: 95 % Expanded uncertainty is a relative one: Yes
Example measurands within this scope	Alcohols, Valine, AAs, SVOCs
Supporting Evidence	Successfully participated in SIM.QM-S17

Table H-2: Prototype Broad Category 1 Claims
for Participants Who Performed In-House Purity Assessment

Measurement service	Category 1. High purity chemicals
Measurement service sub-category	Organic compounds (1.2)
Matrix	High purity [individual primary component]
Measurand	Analyte or Component: high-polarity (pK_{OW} > -2) organic analyte of low molecular mass (0 g/mol to 300 g/mol) Quantity: Mass fraction %
Dissemination range of measurement capability	From 1 to 100 [purity range of calibrant materials] Unit: %
Range of expanded uncertainties as disseminated	From 0.1 to 0.5 (*to be updated after KCRV/U*) Unit: % Coverage factor: 2 or Student's $t_{1-0.95,n-1}$ Level of confidence: 95% Expanded uncertainty is a relative one: Yes
Example measurands within this scope	Alcohols, Valine, AAs, SVOCs
Supporting Evidence	Successfully participated in SIM.QM-S17 and participation in CCQM-K55 series