SIM.QM-K27: Ethanol in Aqueous Matrix

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ABSTRACT

Within the SIM RMO, certain NMIs/ DIs have indicated the need to demonstrate their measurement capability for the determination of ethanol in aqueous matrices. Reflecting upon the current situation, the SIM Chemical Metrology Working Group (CMWG) conducted a second regional Key Comparison in 2016 linked to the CCQM-K27, the SIM.QM-K27. The RMO Key Comparison SIM.QM-K27 was coordinated by INMETRO, who demonstrated capability in CCQM-K27.2 Second subsequent study: determination of ethanol in aqueous media. INMETRO also coordinated the first SIM RMO Key Comparison SIM.QM-K1. For SIM.QM-K27, two levels of ethanol in water solutions were gravimetrically prepared by INMETRO with a mass fraction range between 0.5 mg/g and 5 mg/g. The gravimetric value of the aqueous ethanol solutions was used to link SIM.QM-K27 to the CCQM-K27 Key comparison reference value (KCRV). The gravimetric values for SIM.QM-K27 Level 1 and Level 2 were (0.814 ± 0.008) mg/g ($U_{k=2}$) and (3.818 ± 0.038) mg/g ($U_{k=2}$), respectively. The KCRV (Key comparison reference value) was determined using the purity-corrected gravimetric preparation values. The KCRV uncertainty was assigned as 1 % from the reference values in order to get the same uncertainty from the CCQM-K27.2 comparison. Fourteen laboratories took part in this RMO KC, from SIM and other RMOs. One participant (INACAL) did not send results and thus it’s capability was not evaluated. Ten of the thirteen participants in the SIM.QM-K27 demonstrated their ability to measure ethanol in aqueous matrix in the mass fraction range of 0.5 mg/g to 5 mg/g (both levels). Inmetro, the coordinator of this comparison, also measured successfully the ethanol mass fractions in both levels. One participant (ISP) demonstrated its ability to measure ethanol in aqueous matrix only in low level (0.5 to 1.5 mg/g) and another participant (INM) demonstrated its ability to measure ethanol in aqueous matrix only in high level (1.5 to 5.0 mg/g). NIMT has not demonstrated its ability to measure ethanol in aqueous matrix from 0.5 mg/g to 5 mg/g (both levels). The abilities demonstrated by the participants should be indicative of their ability to provide reference measurements for ethanol content in aqueous samples for both forensic and commodities applications. This report presents the results of the SIM Key comparison SIM.QM-K27. Successful participation in SIM.QM-K27 demonstrates the following measurement capabilities in determining mass fraction of ethanol in mass fraction range from 0.5 mg/g to 5 mg/g in an aqueous matrix.

INTRODUCTION

The accurate 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/mass fractions. Additionally, the accurate assessment of the alcoholic content of beverages is an important commercial commodity. As such, ethanol content is determined for the classification, control and taxation of alcoholic beverages.

The CCQM Organic Analysis Working Group had 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 ethanol, which is an important measurand for both commerce and forensic applications. Within the RMOs, both SIM (SIM.QM-K1) and AFRIMETS (AFRIMETS.QM-K27) have conducted regional Key comparisons for the determination of aqueous ethanol solutions. In addition, the (formerly) 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. These comparisons are summarized in Table 1 and their reports can be downloaded from the BIPM KCDB website.

Table 1 Summary of Key comparisons of ethanol in aqueous matrices

Year	Comparison	Description
2002	CCQM-K27a [1]	Ethanol in aqueous matrix Measurand: Mass fraction of ethanol: forensic level
2002	CCQM-K27b [2]	Ethanol in aqueous matrix Measurand: Mass fraction of ethanol, commodity level
2005	CCQM-K27.1 [3]	Key Comparison (subsequent) for the Determination of Ethanol in Aqueous Matrix
2007	CCQM-K27.2 [4]	Second Subsequent Study: Determination of Ethanol in Aqueous Media
2009	SIM.QM-K1 [5]	Ethanol in Aqueous Matrix
2010	CCQM-K79 [6]	Ethanol in Aqueous Matrix Measurand: Value assignment of CRMs and PT materials
2011	AFRIMETS.QM-K27 [7]	Determination of ethanol in aqueous matrix

Within the SIM Regional Metrology Organization (RMO), certain NMIs/DIs have indicated the need to demonstrate their measurement capability for the determination of ethanol in aqueous matrices. Reflecting upon the current situation, SIM CMWG conducted SIM.QM-K27, a second regional Key comparison linked to the CCQM-K27. Key comparisons performed by RMOs normally link 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 was used to link SIM.QM-K27 to the KCRV determined for the CCQM-K27 comparison. This has been the approach used in the series of comparisons related to aqueous ethanol.

INMETRO who demonstrated its capability to determine the mass fraction of ethanol in aqueous solutions in CCQM-K27.2 and CCQM-K79 is the coordinator for this comparison. INMETRO also coordinated the SIM.QM-K1, and currently has calibration and measurement capabilities (CMCs) in the BIPM Key Comparison Database (KCDB) for the measurements and values in reference materials of aqueous ethanol solutions.

STUDY MATERIALS

Preparation of Materials

These solutions were prepared at INMETRO by weighing and mixing known masses of ethanol and organic-free water. Each solution was mixed overnight (a minimum of 16 h). The total mass of each solution was measured, and the mass fraction of each solution was calculated from this gravimetric procedure. These gravimetric mass fractions were adjusted for a chromatographic purity estimation of the ethanol, which was determined using gas chromatography with a flame ionization detector (GC-FID) with two stationary phases of different polarities and Karl Fischer coulometric titration for water content. The purity of the ethanol used to prepare the solutions was assessed prior to solutions preparation, and the purity is 99.943% ± 0.002% ($U_{k=2}$).

Precautions were taken during solution preparation to minimize the evaporation of the ethanol. Following gravimetric preparation and solution stirring, approximately 250 mL was dispensed into 250 mL bottles. These bottles are from silica (boron silicate) glass, with thread caps with an anti-drops ring that also avoid leaks. After being filled with ethanol in water solution, each bottle was immediately closed with its cap.

Homogeneity and Stability Evaluations

The homogeneity of each solution was checked at INMETRO by GC-FID, analyzing in duplicate two aliquots each of six bottles. These analyses confirmed that there was no significant heterogeneity in the pool of samples and that basing the KCRV on the purity-corrected gravimetric value was appropriate. The maximum difference from gravimetric value accepted by INMETRO is 1%. The uncertainty contribution due to batch heterogeneity for level 1 (nominal mass fraction 0.5 mg/g) was 0.43% and for level 2 (nominal mass fraction 5.0 mg/g) was 0.22%.

Previous INMETRO`s studies showed stability of these materials under transport conditions (4 to 60 °C) for 7 days and storage conditions (20 °C) for 13 months. The uncertainty contribution due to short-term stability is less than 0.3% and due to long-term stability is less than 0.7%. More details about stability studies can be obtained from the published report on the development of ethanol in water certified reference material from INMETRO [8].

PARTICIPANTS, INSTRUCTIONS AND SAMPLE DISTRIBUTION

The call for participation was distributed in May 2016 with the intent to distribute samples in July 2016 (but it was distributed in August 2016), receive results in September 2016 (the results were received in December 2016), and discuss results at the (NRC, Ottawa/Canada) SIM meeting, September 2017.

Participants

The following institutes participated in this study:

Country	Institution
Colombia	INM
Uruguay	LATU
Chile	ISP
South Africa	NMISA
Thailand	NIMT
Turkey	UME
Switzerland	METAS
Singapore	HSA
Ukraine	Ukrmetrteststandart
Malaysia	NMIM
Greece	EXHM
Peru	INACAL
Mexico	CENAM

Measurement Protocol and Calculation of Uncertainty

Two bottles of each of the two levels of ethanol in water at mass fractions between 0.5 mg/g and 5 mg/g were sent to the participants by the coordinating laboratory, INMETRO. Each participant was requested to use methods that are used to deliver that laboratory’s measurement services.

In the initial protocol, participants were requested to analyze duplicate subsamples from two bottles of each level. However, due to leakage problems during transportation of some samples to some participants, this procedure was changed. The revised protocol requested all participants to analyze duplicate subsamples from only one bottle of each level, using only bottles received in good condition. A copy of the original protocol and the revised protocol are provided in Appendix A.

The results were reported in mass fraction units of mg/g and corrected for purity of the calibration material used by the participant, together with its expanded uncertainty ($U_{95\%}$). Participants were asked to provide a data summary and an explanation of their uncertainty calculations. A copy of the reporting form is provided in Appendix B and the components of uncertainty are provided in Appendix C.

RESULTS

Measurement Methods and Calibration Solutions

The measurement method used by each participant laboratory is summarized in Table 2. Participants provided the source of their calibrant and/or commercially available high purity materials for which they determined the purity. If the laboratory used their own measurements for a purity assessment, the method used is briefly described in Table 2.

Table 2: Summary of measurement methods, source of calibrants and calibration type.

Laboratory	Source of calibrant	Analytical Technique	Method of Quantitation	Type of Calibration
INM	NIST 2899a Ethanol-water solution	GC-FID and GC-MSD	Internal Standard (n-propanol)	Bracketing
LATU	Pure ethanol CRM: DMR-95c (CENAM)	GC-FID	Internal Standard (1-propanol)	Bracketing
LATU (informative value)	Commercial Ethanol, Merck (in house purity assessment by mass balance - 99.9437 ± 0.0090 %)	GC-FID	Internal Standard (1-propanol)	Bracketing
ISP	NIST SRM 2897a. Solution of Ethanol (ethyl alcohol in water)	GC-FID coupled to Headspace (HS)	Internal Standard (2-propanol)	7 points calibration curve

NMISA	NMIJ Potassium dichromate CRM 3002-a	Titrimetry	Titrimetric back titration	N/A
NIMT	ERM-AC405c : reference spirit - 15% ABV (alcohol by volume)	GC-TOF-Headspace	Internal standard 1,2-$^{13}C_2$-ethanol, IDMS	5 points calibration curve
UME	Pure Ethanol, Merck (102428), with purity performed by qNMR. Traceability to UME CRM 1301 Ethanol (95.15 ± 0.33) %	GC-FID and qNMR	Internal Standard (n-propanol) IS for qNMR: TSP-d4 (3-(Trimethylsilyl)propionic-2,2,3,3-d4 acid sodium)	6 points calibration curve N/A
METAS	Absolute Ethanol puriss, purity 99.99 %, Sigma-Aldrich 02865, H2O ≤ 0.01 %, in ultrapure water (gravimetrically produced). The Ethanol purity has been verified in house by KF.	HPLC-RID	External Standard	Bracketing method with 6 external standard solutions
HSA	Ethanol certified reference material (NMIJ CRM 4001-b) from the National Metrology Institute of Japan (NMIJ) with a purity value of (1.000 ± 0.001) kg/kg	Headspace GC-MS	Exact-matching IDMS. Internal standard $^{13}C_2$-ethanol	Single point calibration

Ukrmetrteststandart	Aqueous ethanol solutions prepared gravimetrically from ethanol become absolute using calcium oxide. The purity was determined in house by GC-FID and KF.	GC-FID	Internal Standard (n-propanol)	Linear calibration function using generalized least-squares method, 3 points in each range (0,74 - 0,82 mg/g and 3,0 - 4,1 mg/g)
NMIM	Pure ethanol, with purity determined in-house by GC-FID and Karl Fisher. NIST SRM 1847 used as quality control.	GC-FID	Internal Standard (1-propanol)	5 points calibration curve
EXHM	EXHM EtOH calibration solutions measured against NIST SRM 2896. EXHM EtOH (Prolabo BDH - 99,89%) - traceability to NIST after exact matching analysis	GC-MS	Exact-matching IDMS. Internal standard ethanol-*d*5	single point (exact matching)
INACAL*	-	-	-	-
CENAM	DMR-95c Ethanol, Reference Certified Material from CENAM	GC-FID	Internal Standard (1-propanol)	5 points calibration curve

INMETRO**	Ethanol 99.9 %, Merck (in house purity assessment by GC-FID and KF)	GC-FID	Internal Standard (1-propanol)	8 points Calibration Curve

* Results not reported. / ** INMETRO was the coordinating laboratory.

The individual laboratory results for SIM.QM-K27: Ethanol in Aqueous Matrix are summarized in Tables 3 and 4. These are graphically displayed in Figures 1 and 2 (for level 1) and Figures 3 to 6 (for level 2). The uncertainty bars in the figures represent 95% expanded uncertainties ($U_{95\%}$) as reported by the participating laboratories.

Key Comparison Reference Value (KCRV)

According to the CIPM MRA document concerning measurement comparisons, only CIPM key comparisons, i.e., those performed by Consultative Committees or the BIPM, may have a KCRV. Key comparisons performed by regional metrology organizations (RMOs) link to the KCRV through reference to the results from those institutes, which have also taken part in the CIPM key comparison. The assigned reference value of the aqueous ethanol solutions will be used to link SIM.QM-K27 to the CCQM-K27 comparison KCRV. The assigned reference values (KCRV) for SIM.QM-K27 are the assigned mass fractions (mg/g) listed in Tables 3 and 4. The KCRV uncertainty was assigned as 1 % from the reference values to attain a comparable uncertainty with the CCQM-K27.2 comparison.

Degrees of Equivalence (DoE)

The degrees of equivalence (in percentage) for the participants in SIM.QM-K27 are estimated as the signed difference between the reported value and the gravimetric value as the KCRV: $\%d_i = x_i - \text{KCRV}$. These are provided in Tables 3 and 4, and graphically displayed in Figures 1 and 2 (for level 1) and Figures 3 to 6 (for level 2).

Table 3: Summary data of reported results - Level 1.

Laboratory	**Mass Fraction (mg/g)**	***u*** **(mg/g)**	**Coverage Factor (*k*)**	$U_{95\%}$ **(mg/g)**	**Difference from gravimetric value (%d$_i$)**
INM	0.77	0.01	1.96	0.01	-5.40
LATU	0.8038	0.0010	2.212	0.0022	-1.25
LATU (informative value)	0.8039	0.0010	2.212	0.0022	-1,24
ISP	0.822	0.016	2.0	0.032	0.98
NMISA	0.81917	0.00124	2.0	0.00248	0.64
NIMT	0.76	0.02	2.06	0.04	-6.63
UME	0.809 *	0.004	2.0	0.009	-0.61
METAS	0.8137	0.0014	2.0	0.0027	-0.04
HSA	0.8051	0.0042	2.0	0.0083	-1.09
Ukrmetrteststandart	0.8161	0.0035	2.0	0.007	0.26
NMIM	0.8132	0.022	2.0	0.044	-0.10
EXHM	0.817	0.009	2.18	0.020	0.37
INACAL	Not reported	Not reported	Not reported	Not reported	-
CENAM	0.8145	0.0058	2.0	0.012	0.07
INMETRO (analytical value)	0.819	0.001	2.0	0.002	0.57
KCRV (gravimetric value)	**0.814**	0.004	2.0	**0.008**	-

* Mean of results from GC-FID and q-NMR methods.

Table 4: Summary data of reported results - Level 2.

Laboratory	**Mass Fraction (mg/g)**	***u*** **(mg/g)**	**Coverage Factor (k)**	**$U_{95\%}$ (mg/g)**	**Difference from gravimetric value (%d_i)**
INM	3.80	0.02	1.96	0.03	-0.48
LATU	3.814	0.0065	2.25	0.015	-0.11
LATU (informative value)	3.817	0.0065	2.25	0.015	-0.04
ISP	3.684	0.045	2.0	0.090	-3.51
NMISA	3.8343	0.0130	2.0	0.0259	0.42
NIMT	2.95	0.05	2.26	0.12	-22.74
UME	3.803 *	0.032	2.0	0.063	-0.40
METAS	3.814	0.006	2.0	0.012	-0.11
HSA	3.800	0.0144	2.0	0.029	-0.47
Ukrmetrteststandart	3.778	0.009	2.0	0.018	-1.05
NMIM	3.8231	0.058	2.0	0.116	0.13
EXHM	3.749	0.044	2.18	0.096	-1.81
INACAL	Not reported	Not reported	Not reported	Not reported	-
CENAM	3.850	0.037	2.0	0.075	0.85
INMETRO (analytical value)	3.826	0.004	2.0	0.008	0.19
KCRV (gravimetric value)	**3.818**	0.019	2.0	**0.038**	-

* Mean of results from GC-FID and q-NMR methods.

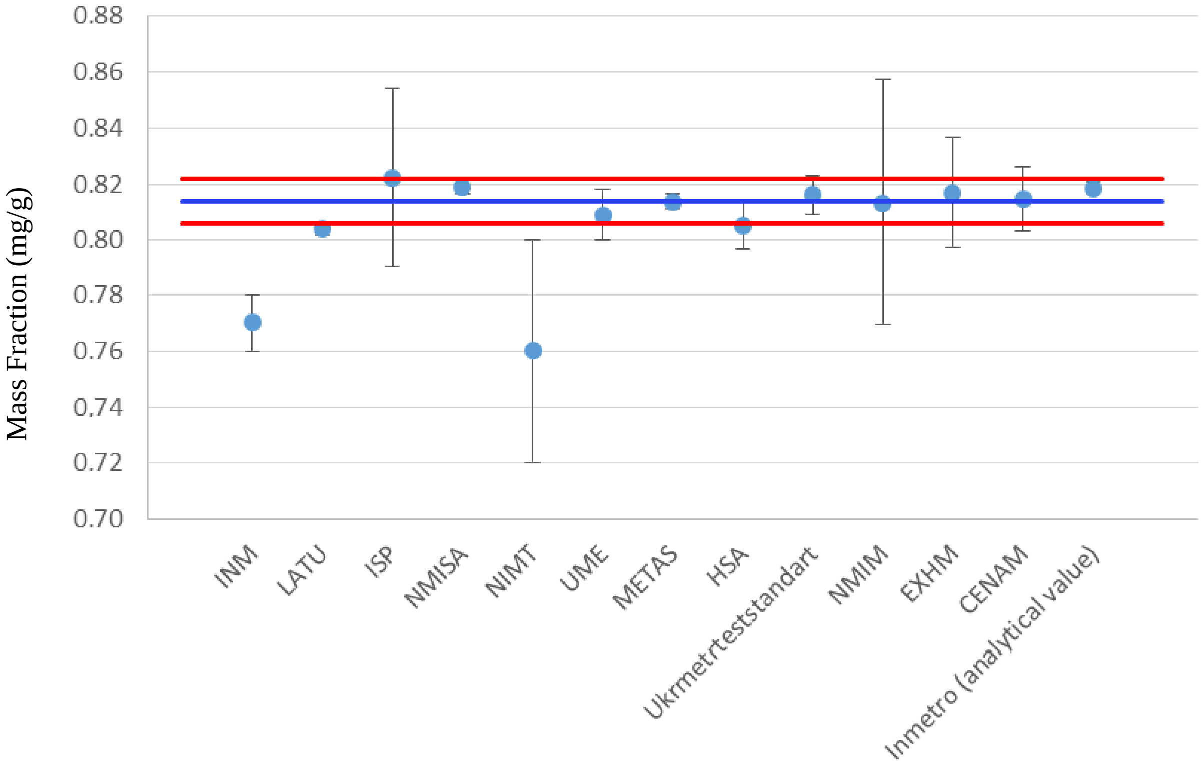

Figure 1. Results of SIM.QM-K27: Ethanol in Aqueous Matrix- Level 1 (absolute values). The red lines represent the expanded uncertainty (**$U_{k=2}$**) of the KCRV (blue line) based on the previous CCQM-K27 studies.

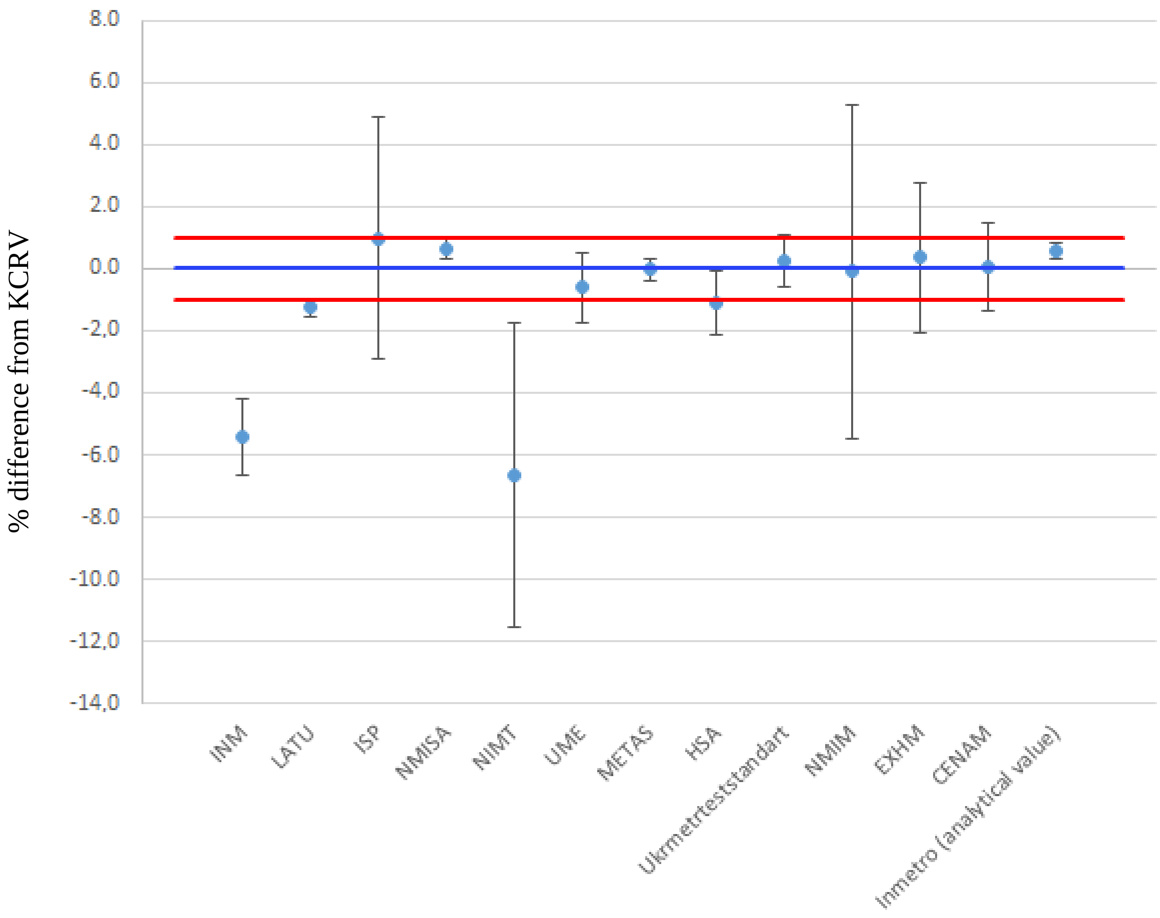

Figure 2. Results of SIM.QM-K27: Ethanol in Aqueous Matrix-Level 1. Percentage deviations (%) from the KCRV (blue line). The red lines represent the expanded uncertainty (**$U_{k=2}$**) of the KCRV based on the previous CCQM-K27 studies.

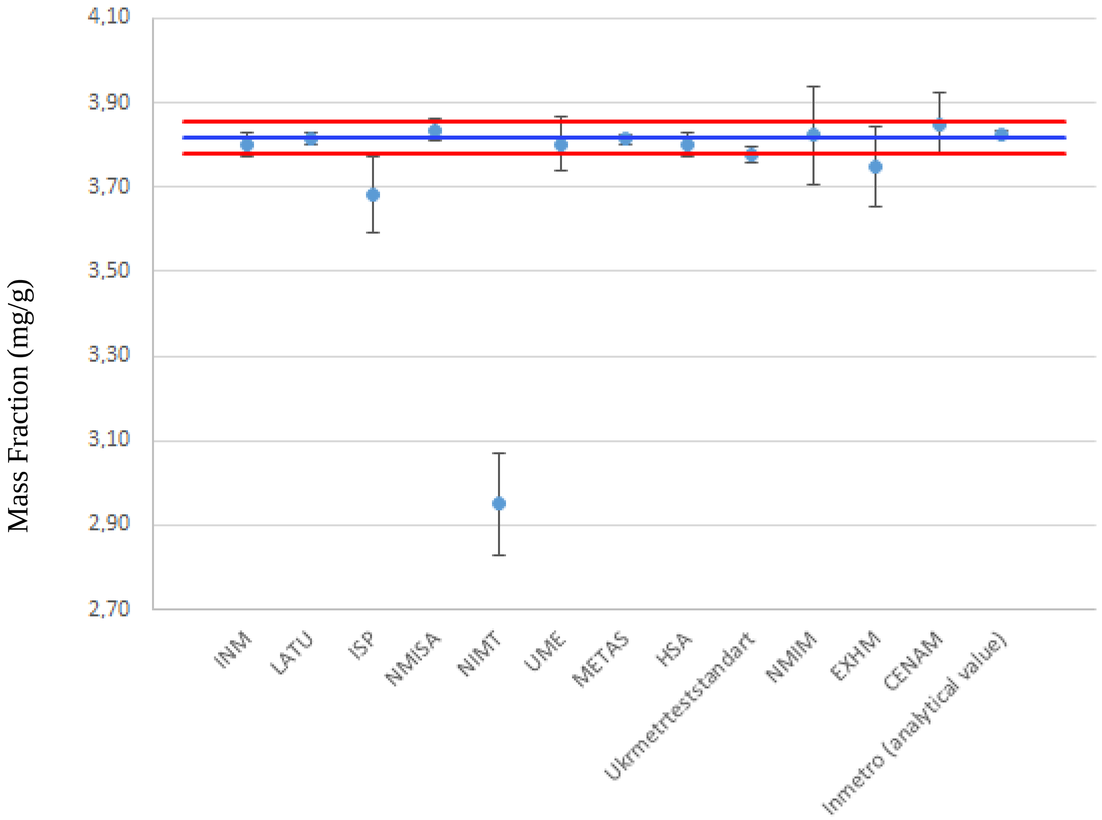

Figure 3. Results of SIM.QM-K27: Ethanol in Aqueous Matrix-Level 2 (absolute values). The red lines represent the expanded uncertainty (**$U_{k=2}$**) of the KCRV (blue line) based on the previous CCQM-K27 studies.

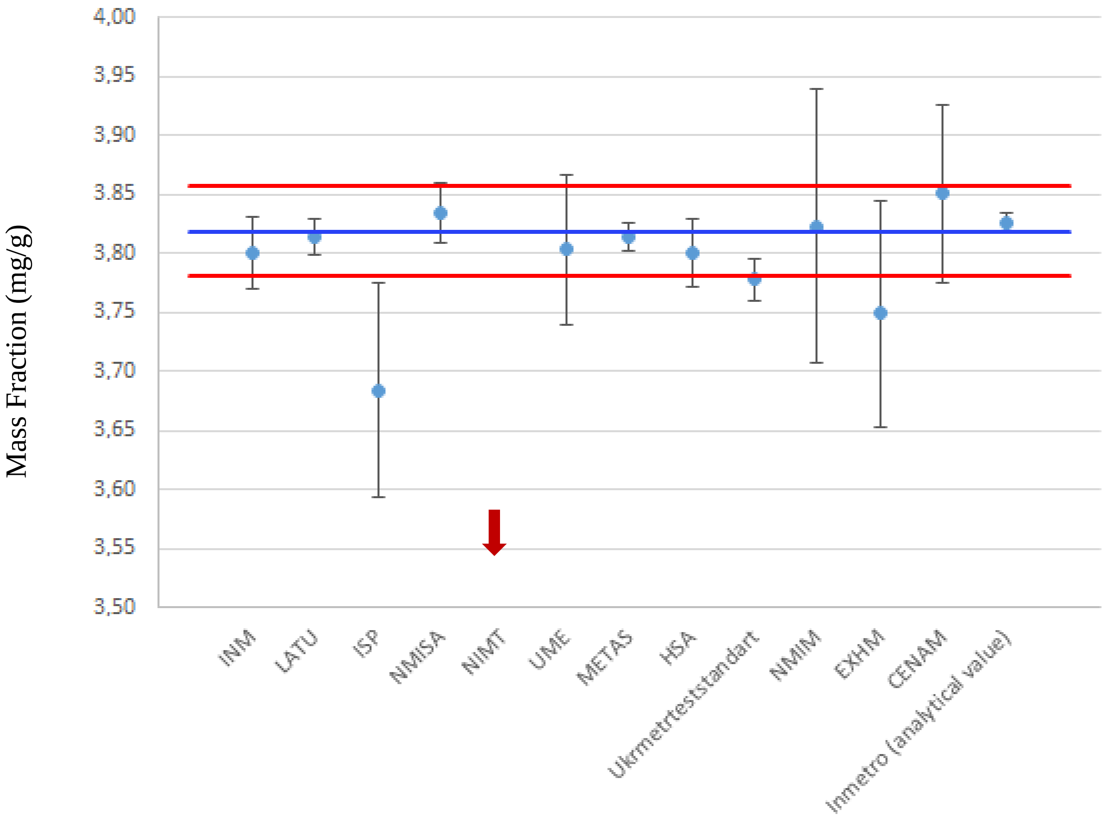

Figure 4. Results of SIM.QM-K27: Ethanol in Aqueous Matrix-Level 2 (absolute values). The red lines represent the expanded uncertainty (**$U_{k=2}$**) of the KCRV (blue line) based on the previous CCQM-K27 studies (zoom view).

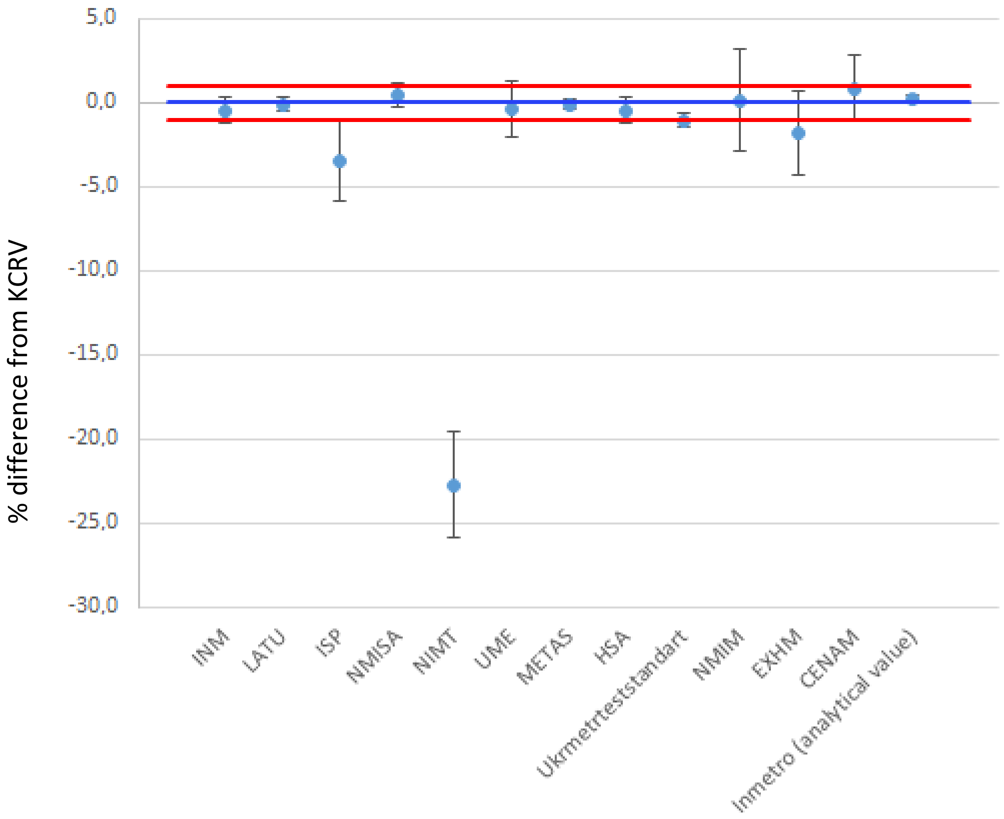

Figure 5. Results of SIM.QM-K27: Ethanol in Aqueous Matrix-Level 2. Percentage deviations (%) from the KCRV (blue line). The red lines represent the expanded uncertainty (**$U_{k=2}$**) of the KCRV based on the previous CCQM-K27 studies.

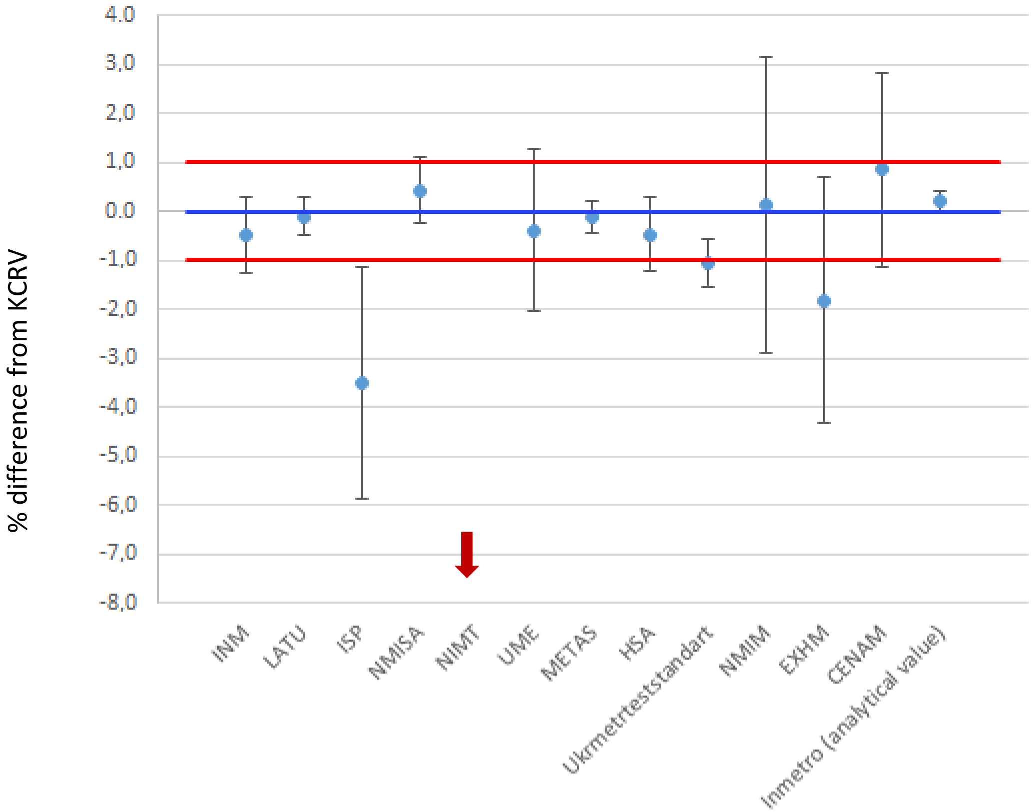

Figure 6. Results of SIM.QM-K27: Ethanol in Aqueous Matrix-Level 2. Percentage deviations (%) from the KCRV (blue line). The red lines represent the expanded uncertainty (**$U_{k=2}$**) of the KCRV based on the previous CCQM-K27 studies (zoom view).

DISCUSSION

In the first subsequent study report (CCQM-K27.1), the expected % RSD of "higher order" measurements of ethanol in aqueous matrices was about 0.85 % (relative). In CCQM-K27.2 four of the five laboratories agreed with the KCRV to within ± 1.5 %. As for the previous key comparison studies for ethanol in aqueous media, the gravimetric mass fraction corrected for the purity of the ethanol used to prepare the samples is the Key Comparison Reference Value (KCRV). As shown in Tables 1 and 2, and Figures 1 to 6, the most participants showed a good agreement with the KCRV considering these reported uncertainties. However, for level 1, INM and NIMT do not agreed with KCRV, and for level 2, and ISP and NIMT do not agreed with KCRV. Figure 7 shows the percentage difference from KCRV of the results of participating institutes of Key comparisons for the determination of ethanol in aqueous matrices.

How Far the Light Shines (HFTLS)

Successful participation in SIM.QM-K27 will demonstrate a laboratory's capabilities in determining ethanol in aqueous matrix in the mass fraction range of 0.5 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 good analytical results performed by Inmetro allow the link of SIM.QM-K27 with CCQM-K27 comparisons.

CONCLUSIONS

Ten of the thirteen participants in the SIM.QM-K27 successfully demonstrated their ability to measure ethanol in an aqueous matrix in the mass fraction range of 0.5 mg/g to 5 mg/g (both levels). One participant demonstrated its ability to measure ethanol in aqueous matrix only in low level (ISP) and another participant demonstrated its ability to measure ethanol in aqueous matrix only in high level (INM). NIMT has not demonstrated its ability to measure ethanol in aqueous matrix from 0.5 mg/g to 5 mg/g (both levels). One participant did not send results and thus it was not evaluated (INACAL). For participant successfully only in low level, it was demonstrated its ability to measure ethanol in an aqueous matrix in the mass fraction range of 0.5 mg/g to 1.5 mg/g. For participant successfully only in high level, it was demonstrated its ability to measure ethanol in an aqueous matrix in the mass fraction range of 1.5 mg/g to 5.0 mg/g.

The Tables in Appendix C list the Core Competencies claimed by the participants in SIM.QM-K27. The information in these tables is as provided by the participants.

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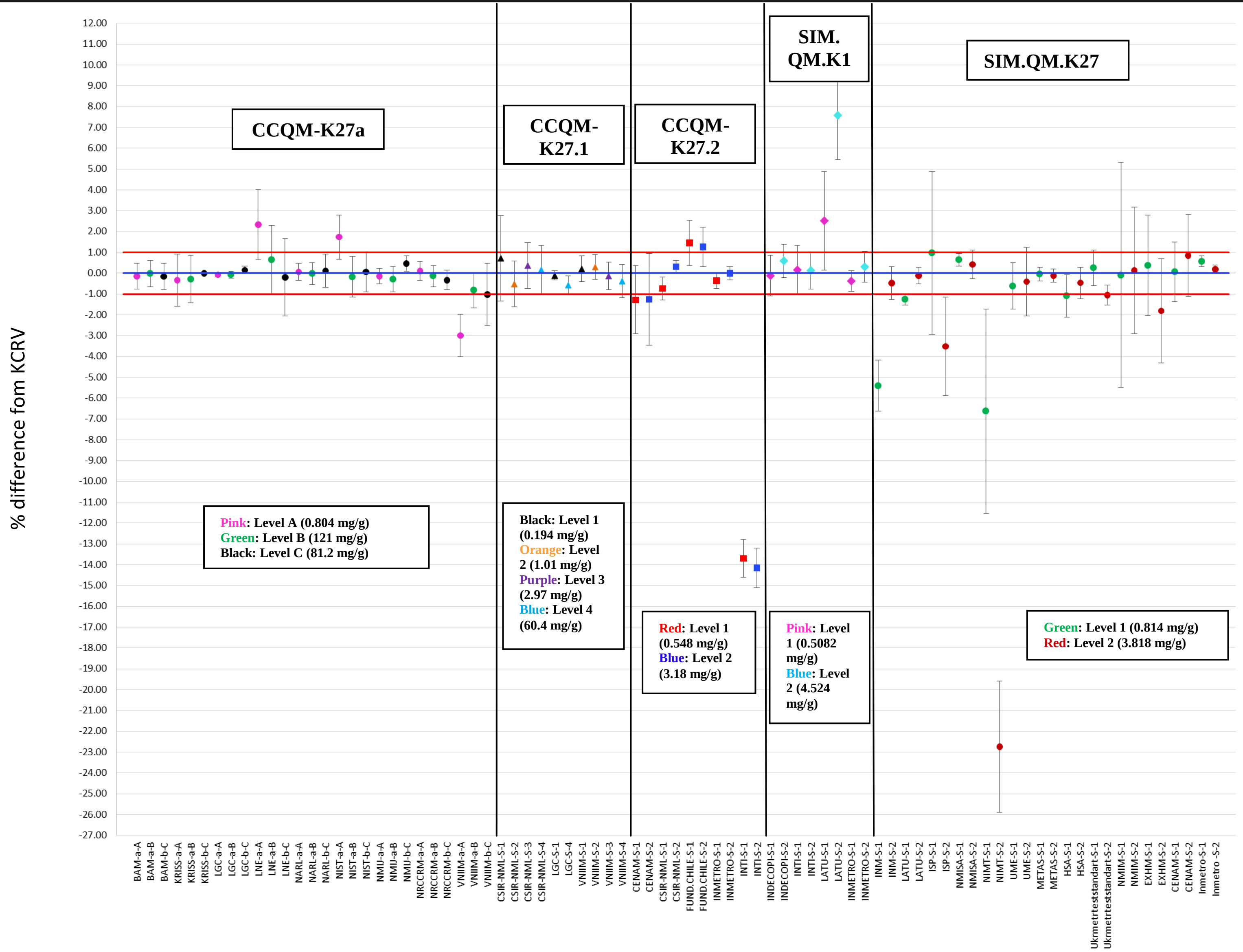

Figure 7. Comparative results in terms of percentage deviations of Key Comparisons for measuring ethanol in aqueous matrices

APPENDIX A: Protocol

National Institute of Metrology, Quality and Technology

SIM.QM-K27: Determination of Ethanol in Aqueous Matrix

Study Protocol

COORDINATING LABORATORY CONTACT INFORMATION

National Institute of Metrology, Quality and Technology (Inmetro)
Organic Analysis Laboratory (Labor) / Chemical Metrology Division (Dquim)
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CEP: 25250-020 - Duque de Caxias/RJ - Brazil

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/mass fractions.

CCQM Organic Analysis Working Group had 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) and AFRIMETS (AFRIMETS.QM-K27) have conducted regional key comparisons for the determination of aqueous ethanol solutions. In addition, the type 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. These comparisons are summarised in Table 1 and their reports can be downloaded from the BIPM KCDB website.

Table 2 Summary of key comparisons of ethanol in Aqueous Matrix

Year	Comparison	Description
2002	CCQM-K27a	Forensic aqueous ethanol
2002	CCQM-K27b	Ethanol in wine as commodity
2005	CCQM-K27.1	Subsequent forensic aqueous ethanol – 4 levels
2007	CCQM-K27.2	Subsequent forensic aqueous ethanol – 2 levels
2009	SIM.QM-K1	Ethanol in Aqueous Matrix – 2 levels
2010	CCQM-K79	Ethanol in Aqueous Matrix – Value assignment of CRMs and PT materials
2011	AFRIMETS.QM-K27	Ethanol in Aqueous Matrix – 2 levels

Within the SIM RMO, certain NMIs/ DIs have indicated the need to demonstrate their measurement capability for the determination of ethanol in aqueous matrices. Reflecting upon the current situation, SIM CMWG will conduct a regional Key Comparison. Key comparisons performed by regional metrology organizations (RMOs) normally link 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 to the CCQM-K27 comparison KCRV. This has been the approach used in the series of comparisons related to aqueous ethanol.
Inmetro who demonstrated its capability in CCQM-K27.2 and CCQM-K79 is coordinating this comparison. Inmetro also coordinated the SIM.QM-K1. The INMETRO currently has calibration and measurement capabilities (CMCs) in the BIPM Key Comparison Database (KCDB) for the measurements and values in reference materials of aqueous ethanol solutions.
The accurate determination of ethanol content in aqueous solutions is critical for regulatory forensic and trade purposes. For forensic purposes, ethanol is determined for the effective regulation of blood alcohol levels (e.g., driving under the influence of alcohol, autopsies, etc.). As a trading commodity, ethanol content is determined for the classification, control and taxation of alcoholic beverages.

Preparation of materials

Two solutions of ethanol in water will be prepared gravimetrically at mass fractions between 0.5 mg/g and 5 mg/g by Inmetro, producing two batches. The purity of the ethanol used to prepare the solution was assessed prior to solution preparation, using the mass balance approach. The purity was assessed a 99.943% ± 0.002% (k=2; 95%). Precautions were taken during solution preparation to minimize the evaporation of the ethanol. Following gravimetric preparation and solution stirring, approximately 250 mL was dispensed into 30 units of 250 mL bottles for each batch. These bottles are from silica (boron silicate) glass, with thread caps with an anti-drops ring that also avoid leaks. After being filled with ethanol in water solution, each bottle was immediately closed with its cap.

Homogeneity and stability testing

The homogeneity of each solution is checked at Inmetro by gas chromatography with a flame ionization detector (GC-FID), analyzing in duplicate two aliquots each of six bottles. These analyses confirm that there is no significant heterogeneity in the pool of samples and that basing the KCRV on the purity-corrected gravimetric value was appropriate. The maximum difference from gravimetric value accepted by Inmetro is 1%. The uncertainty contribution due to batch heterogeneity is less than 0.3%.

Previous Inmetro`s studies showed stability of these materials under transport conditions (4 to 60 °C) for 7 days and storage conditions (20 °C) for 13 months. The uncertainty contribution due to short-term stability is less than 0.3% and due to long-term stability is less than 0.7%. More details about stability studies of ethanol in water certified reference material from Inmetro can be obtained at the article listed on references [1].

Instructions for participants

Each participant will receive two bottles of each of the Ethanol in Aqueous Matrix solutions. Participants should analyze duplicate sub-samples from each of the two bottles at each level. Sub-samples should be taken from each bottle at different times, providing precautions to prevent undue evaporation (having the bottle open for a minimum amount of time, closing it securely and storing it appropriately). It is not recommended that the sample be transferred to another bottle before use.

Storage of Materials:

The sample bottles should be stored away from direct sunlight at ambient temperature (20 °C ± 2 °C). Do not freeze the solutions.

Instructions for Use:

Before opening a bottle, it must stay at least for one hour at the room temperature (20 ± 2 °C). Immediately before opening a bottle, mix it carefully to guarantee that liquid and the vapour phases are in total contact. Please analyze duplicate subsamples from each of two bottles of each level of the study.

Reporting of Results

The measurand for the study is ethanol mass fraction in units of mg/g (mass/mass basis). Please report an overall value and duplicate results for ethanol in each of two bottles of the study materials (four determinations total for each level). For the overall value a standard uncertainty, expanded uncertainty and k factor must be provided.

An electronic result sheet will be distributed by INMETRO. Analytical results that should be reported include:
(i) the mass fraction of ethanol in mg/g;
(ii) detailed technical information describing the methodology used;
(iii) the source and purity of any reference and/or standard materials used;
(iv) a full measurement uncertainty (including all potential uncertainty components for the measurand; combined standard uncertainty; expanded uncertainty and the coverage factor).

Determination of the KCRV:

According to the CIPM MRA document concerning measurement comparisons, only CIPM key comparisons, i.e., those performed by Consultative Committees or the BIPM, may have a KCRV. Key comparisons performed by regional metrology organizations (RMOs), called supplementary comparisons, link to the KCRV through reference to the results from those institutes, which have also taken part in the CIPM key comparison [2]. Inmetro have taken part in the CCQM-K27.2. The gravimetric preparation value of the aqueous ethanol solutions will be used to link SIM.QM-K27 to CCQM-K27 comparison KCRV. INMETRO's capability to gravimetrically prepare ethanol solutions was demonstrated in CCQM K79. The assigned value will be based on the purity-corrected gravimetric value and the uncertainty of the assigned reference value will be a combination of gravimetric preparation and homogeneity uncertainty performed by GC-FID.

How Far the Light Shines (HFTLS)

Participation in the SIM.QM-K27 intended to demonstrate the laboratory's capabilities in determining ethanol in aqueous matrix in the mass fraction range of 0.5 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.

Proposed Schedule

Call for participation	May 2016
Registration Deadline	08 June, 2016
Distribution of the samples	July 2016
Data due to coordinator	16 September 2016
Discussion of results	October/November 2016

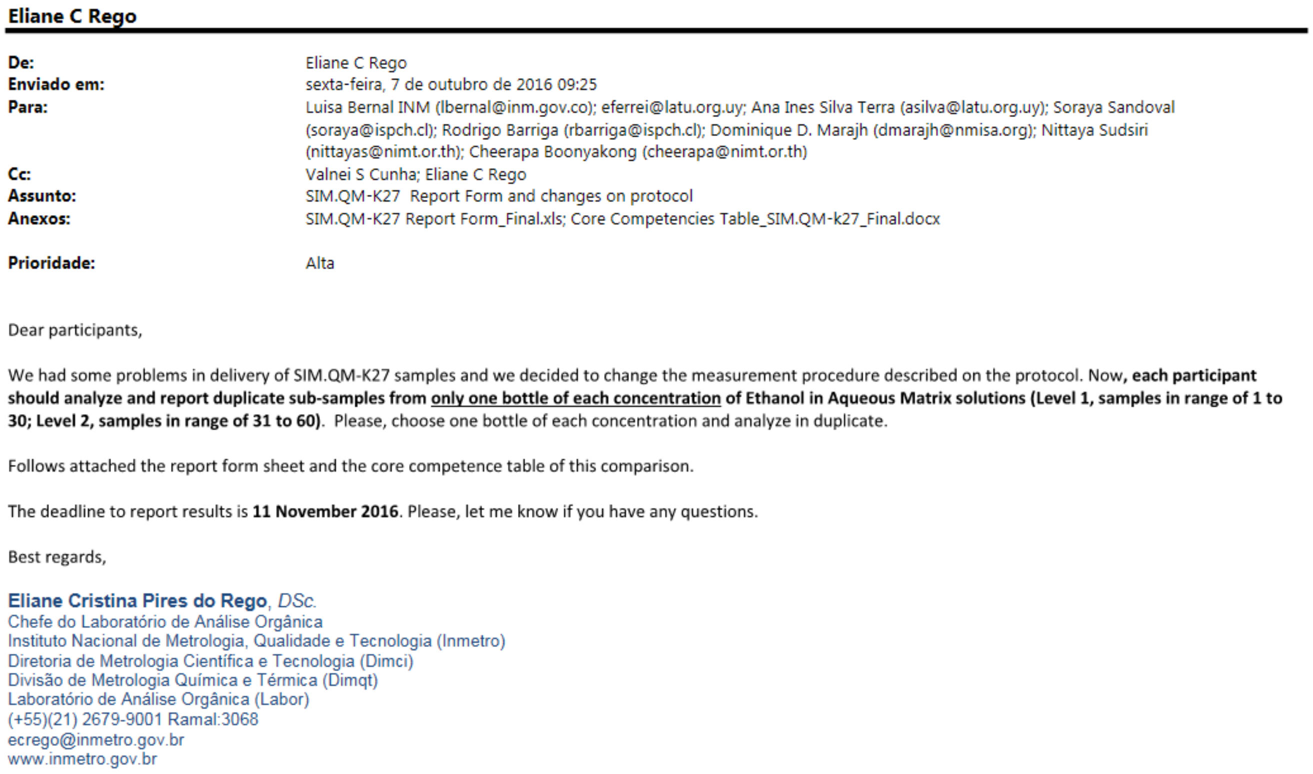
Contact Person:
Valnei Smarçaro da Cunha (vscunha@inmetro.gov.br) and Eliane Cristina Pires do Rego (ecrego@inmetro.gov.br)
Please, registration and report of results by e-mail: ecrego@inmetro.gov.br with a cc to labor@inmetro.gov.br.
Tel/Fax: +5521 2679 9069

REFERENCES

[1] Souza *et al*. Evaluation of the stability of ethanol in water certified reference material: measurement uncertainty under transport and storage conditions. Accred Qual Assur (2008) 13:717–721.

[2] http://www.bipm.org/utils/common/CIPM_MRA/CIPM_MRA-D-05.pdf

APPENDIX A: Revised Protocol



Eliane C Rego

De: Eliane C Rego
Enviado em: sexta-feira, 7 de outubro de 2016 09:25
Para: Luisa Bernal INM (lbernal@inm.gov.co); eferrei@latu.org.uy; Ana Ines Silva Terra (asilva@latu.org.uy); Soraya Sandoval (soraya@ispch.cl); Rodrigo Barriga (rbarriga@ispch.cl); Dominique D. Marajh (dmarajh@nmisa.org); Nittaya Sudsiri (nittayas@nimt.or.th); Cheerapa Boonyakong (cheerapa@nimt.or.th)
Cc: Valnei S Cunha; Eliane C Rego
Assunto: SIM.QM-K27 Report Form and changes on protocol
Anexos: SIM.QM-K27 Report Form_Final.xls; Core Competencies Table_SIM.QM-k27_Final.docx

Prioridade: Alta

Dear participants,

We had some problems in delivery of SIM.QM-K27 samples and we decided to change the measurement procedure described on the protocol. Now**, each participant should analyze and report duplicate sub-samples from only one bottle of each concentration of Ethanol in Aqueous Matrix solutions (Level 1, samples in range of 1 to 30; Level 2, samples in range of 31 to 60)**. Please, choose one bottle of each concentration and analyze in duplicate.

Follows attached the report form sheet and the core competence table of this comparison.

The deadline to report results is **11 November 2016**. Please, let me know if you have any questions.

Best regards,

Eliane Cristina Pires do Rego, *DSc.*
Chefe do Laboratório de Análise Orgânica
Instituto Nacional de Metrologia, Qualidade e Tecnologia (Inmetro)
Diretoria de Metrologia Científica e Tecnologia (Dimci)
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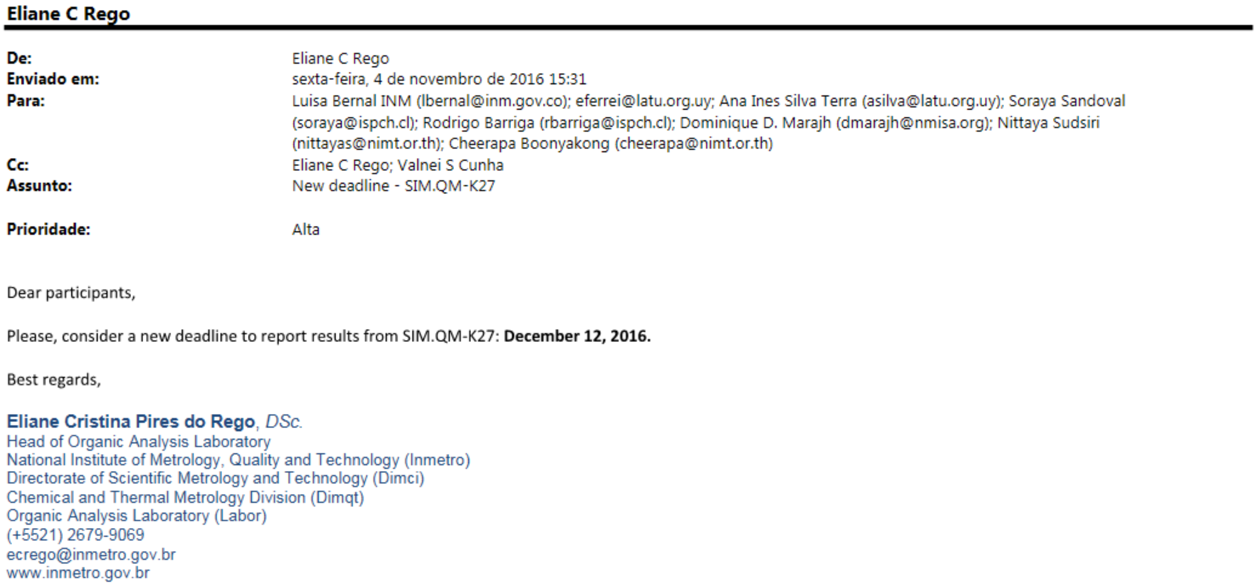

Eliane C Rego

De:	Eliane C Rego
Enviado em:	sexta-feira, 4 de novembro de 2016 15:31
Para:	Luisa Bernal INM (lbernal@inm.gov.co); eferrei@latu.org.uy; Ana Ines Silva Terra (asilva@latu.org.uy); Soraya Sandoval (soraya@ispch.cl); Rodrigo Barriga (rbarriga@ispch.cl); Dominique D. Marajh (dmarajh@nmisa.org); Nittaya Sudsiri (nittayas@nimt.or.th); Cheerapa Boonyakong (cheerapa@nimt.or.th)
Cc:	Eliane C Rego; Valnei S Cunha
Assunto:	New deadline - SIM.QM-K27
Prioridade:	Alta

Dear participants,

Please, consider a new deadline to report results from SIM.QM-K27: **December 12, 2016.**

Best regards,

Eliane Cristina Pires do Rego, *DSc.*
Head of Organic Analysis Laboratory
National Institute of Metrology, Quality and Technology (Inmetro)
Directorate of Scientific Metrology and Technology (Dimci)
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APPENDIX B: Reporting Form

SIM.QM-K27
Ethanol in Aqueous Matrix

Coordinating Laboratory: INMETRO

Results Report Form

Please use this excel sheet for reporting. Do not insert rows or columns within this table. Do not move cells.
The report should be submitted electronically to ecrego@inmetro.gov.br (c/c labor@inmetro.gov.br) before the **November 11th deadline**.
Please fill in all blanks and use requested units of mass fraction.
Please provide any additional information in the comments section or on a separate sheet if necessary.

Part I: Participant's Information

Laboratory Name:	
Submitted by:	
Reporting Date: (dd/mm/yy)	

Part II: Results

Level	Bottle code	Mass Fraction Aliquot 1 (mg/g)	Mass Fraction Aliquot 2 (mg/g)	Mean (mg/g)	Combined Standard Uncertainty (mg/g)	Coverage Factor (k)	U - Expanded Uncertainty (mg/g) 95% conf.
Level 1: samples 1 to 30							
Level 2: samples 31 to 60							

Part III: Technical Details of Methodology Used

Sample amount used for analysis		g; or		mL
Calibrant ("pure material" or "calibration solution")				
Source, purity and traceability of calibrant				

Extraction method, if any (e.g., hydrolysis, liquid/liquid extraction, SPE, etc.) (Please briefly describe the extraction procedures)	
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)	

Type of calibration (e.g., single point, bracketing, calibration curve, etc.)	
Number of points and mass fraction 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 how these values were determined.

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 C: Summary of Participants' Uncertainty Estimation Approaches

The sources of uncertainty in SIM.QM-K27: Ethanol in Aqueous Matrix as noted by the laboratories are summarized below:

Institute	Sources of Uncertainty
INM	Balance error Balance resolution Dilution factor CRM preparation (dissolution and IS addition) Interpolation (bracketing) Repeatability
LATU	Balance calibration uncertainty Purity calibration uncertainty Standard deviation of replicate Standard deviation of historical control samples
ISP	Interpolation of the calibration curve Uncertainty of SRM Repeatability of the sample measurement
NMISA	Precision (repeatability) Potassium dichromate concentration Mass of the ethanol solution Mass of the potassium dichromate solution Factor of reaction Titre, volume of ammonium iron sulphate titrant Blank uncertainty
NIMT	Mass fraction ratio (between unlabeled/labeled) obtained from the calibration curve (ng/ng) estimated from the regression Mass fraction of internal standard Uncertainties due to weighing estimated from bias of balance Uncertainty of mid concentration calibration standard estimated from bias and random effects (type B and type A) Method precision

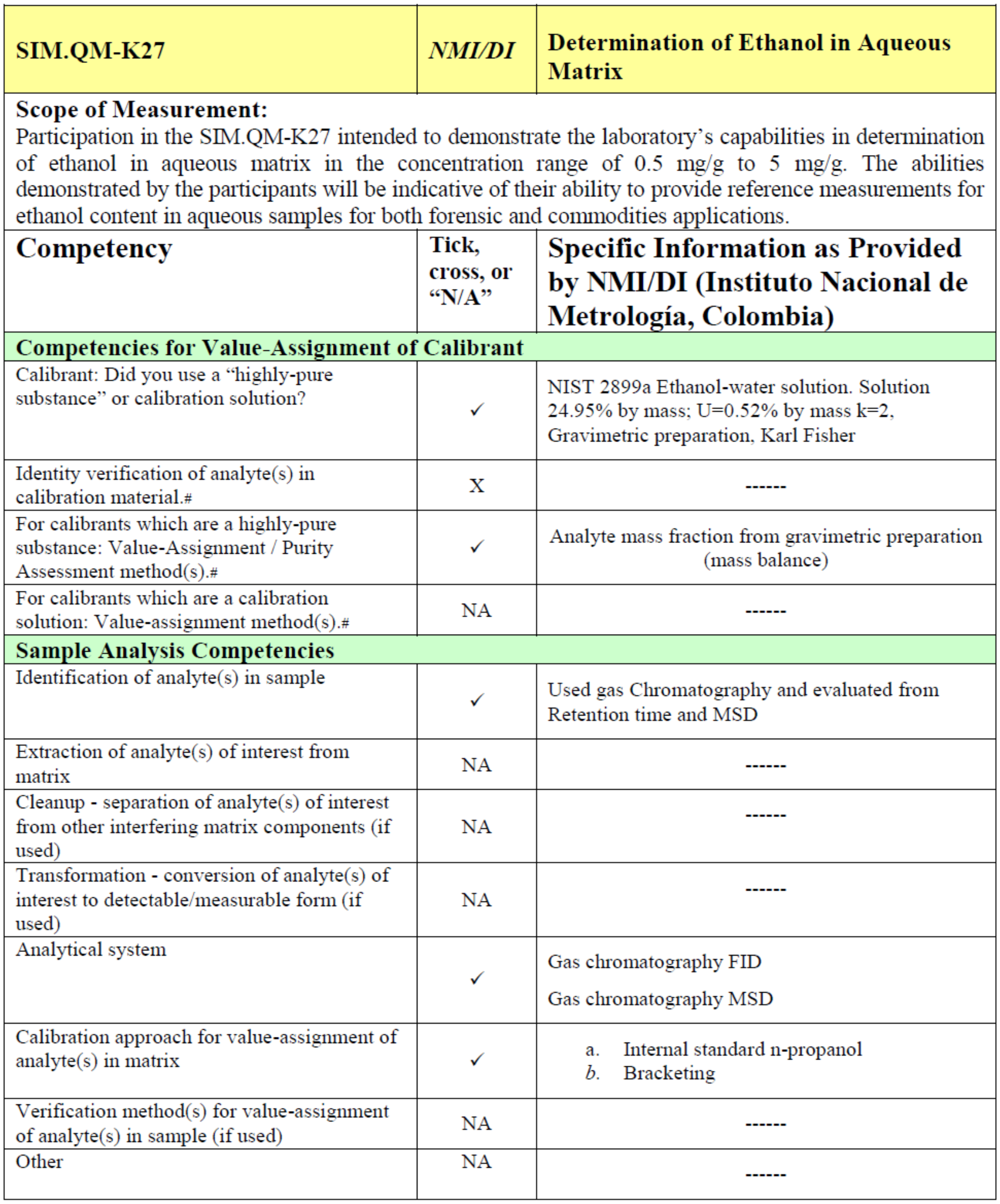
UME	*GC FID method*: Weighing of sample Weighing of IS Standard stock solution Internal stock solution Intermediate precision Recovery Repeatability Calibration graph *qNMR method:* IS purity MW analyte MW IS Mass of analyte Mass of IS
METAS	Standard uncertainty of the calibration solutions, that include: Mass fraction of ethanol in the mixed solution Mass of ethanol Purity of ethanol Correction factor for the evaporation of the ethanol during weighing Mass of water Mass concentration of the solution at 20 ° C Density of the ethanol / water mixture
HSA	Difference between mass fractions from two aliquots. Comparison of results obtained using GC-MS and GC-FID on the same bottle. Comparison of results obtained using different ion pairs on the same subsamples. Comparison of results obtained from different Analysts. Uncertainty in the purity value of ethanol certified reference material (NMIJ CRM 4001-b). Uncertainty in weighing based on balance calibration certificate. Bias in the preparation of calibration blends. Uncertainty in weighing based on balance calibration certificate.

Ukrmetrteststandart	Uncertainty in calibrants values due to uncertainty in masses of ethanol and water used for calibrants preparation by gravimetric procedure and ethanol purity Calibrants verification uncertainty according to the algorithm given in ISO 6142-1 for gravimetrically prepared gas mixtures Standard deviation in ratios of ethanol and n-propanol peak areas Uncertainty in masses of the ethanol solution aliquote and internal standard added to calibrants Uncertainty of calibration function
NMIM	Method precision Sample mass Bias Calibration curve
EXHM	Method precision Ethanol mass fraction in the calibration solution Mass of internal standard solution added to the sample blend Mass of sample in sample blend Mass of the calibration solution in the calibration blend Mass of internal standard solution added to the calibration blend Measured peak area ratio of the selected ions in the sample blend Measured peak area ratio of the selected ions in the calibration blend
CENAM	Predicted value in calibration curve Mass fraction of calibrant (purity) Repeatability between injections Bias with control sample Differences between subsamples
Inmetro (analytical results)	Area ratios Sample mass (gravimetry) IS mass (gravimetry) Repeatability Purity of calibration material Calibration curve

APPENDIX D: Core Competence Tables from participants

Core Competency Table from INM

Note: INM only demonstrated capability in determination of ethanol in aqueous matrix in high level (1.5 to 5.0 mg/g).



SIM.QM-K27	***NMI/DI***	**Determination of Ethanol in Aqueous Matrix**
Scope of Measurement: Participation in the SIM.QM-K27 intended to demonstrate the laboratory's capabilities in determination of ethanol in aqueous matrix in the concentration range of 0.5 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.		
Competency	**Tick, cross, or "N/A"**	**Specific Information as Provided by NMI/DI (Instituto Nacional de Metrología, Colombia)**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	✓	NIST 2899a Ethanol-water solution. Solution 24.95% by mass; U=0.52% by mass k=2, Gravimetric preparation, Karl Fisher
Identity verification of analyte(s) in calibration material.#	X	------
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	✓	Analyte mass fraction from gravimetric preparation (mass balance)
For calibrants which are a calibration solution: Value-assignment method(s).#	NA	------
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	Used gas Chromatography and evaluated from Retention time and MSD
Extraction of analyte(s) of interest from matrix	NA	------
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	NA	------
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	NA	------
Analytical system	✓	Gas chromatography FID Gas chromatography MSD
Calibration approach for value-assignment of analyte(s) in matrix	✓	a. Internal standard n-propanol b. Bracketing
Verification method(s) for value-assignment of analyte(s) in sample (if used)	NA	------
Other	NA	------

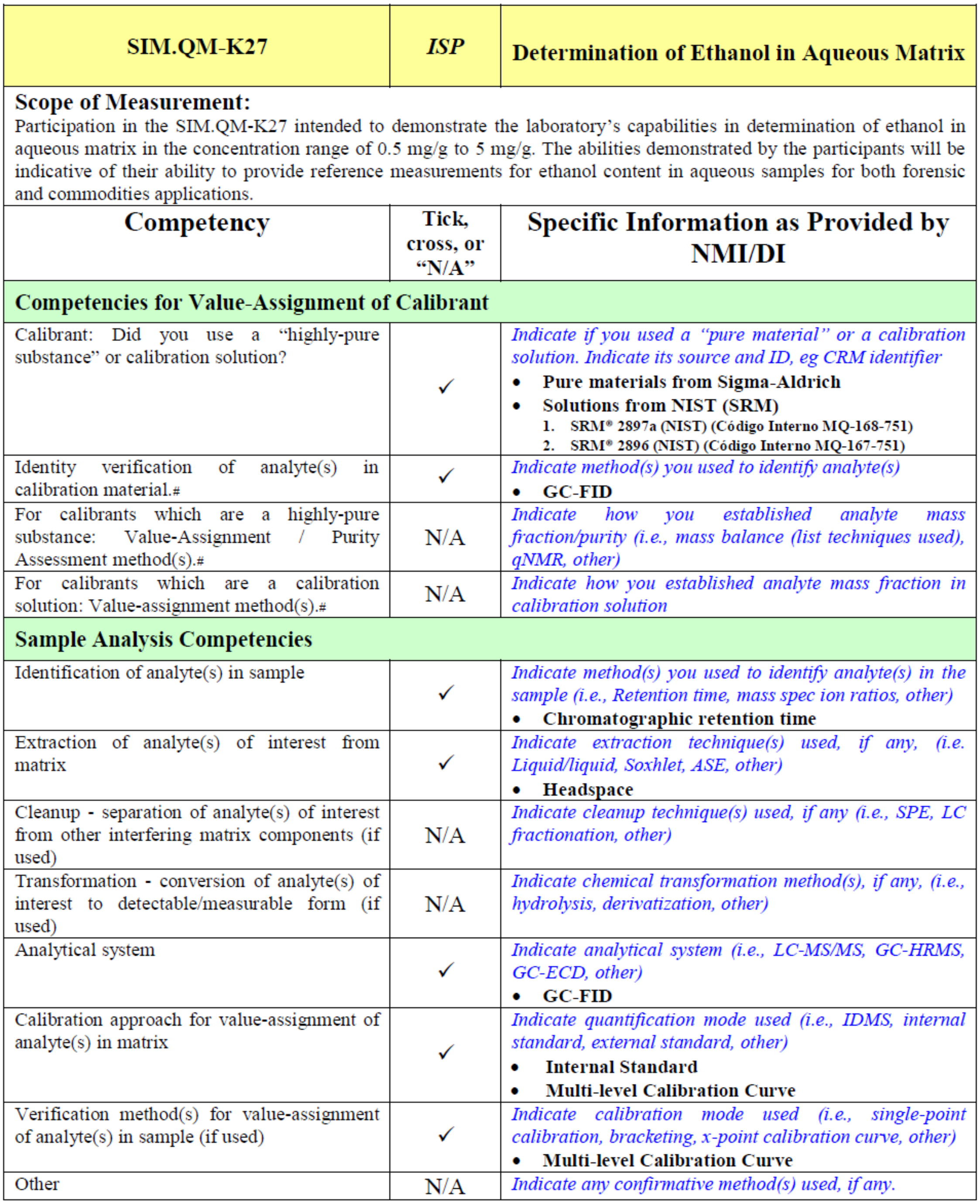
m

Core Competency Table from LATU

SIM.QM-K27	***NMI/DI***	**Determination of Ethanol in Aqueous Matrix**
Scope of Measurement: Participation in the SIM.QM-K27 intended to demonstrate the laboratory's capabilities in determination of ethanol in aqueous matrix in the concentration range of 0.5 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.		
Competency	**Tick, cross, or "N/A"**	**Specific Information as Provided by NMI/DI**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	✓	We used a highly-pure ethanol CRM by CENAM: DMR-95c. We gravimetrically prepared calibrant solutions from these. We also used calibrant solutions prepared from commercially available ethanol, for our informative value. Purity assignment was performed through mass balance approach as described below.
Identity verification of analyte(s) in calibration material.#	✓	This ethanol CRM (DMR-95c) was analyzed by GC-FID using a non-polar phase column (HP-5) and a polar phase column (CP WAX 58) to corroborate identity (through retention time) and purity value (through mass balance approach). The identity and purity of the commercial ethanol used for the informative value was analyzed in the same way.
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	✓	Purity assessment is done through mass balance. The techniques that were used include GC-FID (analysis with polar and non-polar phase columns) and coulombimetric KF analysis.
For calibrants which are a calibration solution: Value-assignment method(s).#	✓	Value assignment is done through gravimetric preparation of calibrant solutions from highly-pure substances.
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	Retention time
Extraction of analyte(s) of interest from matrix	×	-
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	×	-
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	×	-
Analytical system	✓	GC-FID with Cool On-Column injection.
Calibration approach for value-assignment of analyte(s) in matrix	✓	Bracketing with internal standard (1-propanol).
Verification method(s) for value-assignment of analyte(s) in sample (if used)	×	-
Other	×	-

Core Competency Table from ISP

Note: ISP only demonstrated capability in determination of ethanol in aqueous matrix in low level (0.5 to 1.5 mg/g).



SIM.QM-K27	***ISP***	**Determination of Ethanol in Aqueous Matrix**
Scope of Measurement: Participation in the SIM.QM-K27 intended to demonstrate the laboratory's capabilities in determination of ethanol in aqueous matrix in the concentration range of 0.5 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.		
Competency	**Tick, cross, or "N/A"**	**Specific Information as Provided by NMI/DI**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	✓	*Indicate if you used a "pure material" or a calibration solution. Indicate its source and ID, eg CRM identifier* • **Pure materials from Sigma-Aldrich** • **Solutions from NIST (SRM)** **1. SRM® 2897a (NIST) (Código Interno MQ-168-751)** **2. SRM® 2896 (NIST) (Código Interno MQ-167-751)**
Identity verification of analyte(s) in calibration material.#	✓	*Indicate method(s) you used to identify analyte(s)* • **GC-FID**
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	N/A	*Indicate how you established analyte mass fraction/purity (i.e., mass balance (list techniques used), qNMR, other)*
For calibrants which are a calibration solution: Value-assignment method(s).#	N/A	*Indicate how you established analyte mass fraction in calibration solution*
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	*Indicate method(s) you used to identify analyte(s) in the sample (i.e., Retention time, mass spec ion ratios, other)* • **Chromatographic retention time**
Extraction of analyte(s) of interest from matrix	✓	*Indicate extraction technique(s) used, if any, (i.e. Liquid/liquid, Soxhlet, ASE, other)* • **Headspace**
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	*Indicate cleanup technique(s) used, if any (i.e., SPE, LC fractionation, other)*
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	*Indicate chemical transformation method(s), if any, (i.e., hydrolysis, derivatization, other)*
Analytical system	✓	*Indicate analytical system (i.e., LC-MS/MS, GC-HRMS, GC-ECD, other)* • **GC-FID**
Calibration approach for value-assignment of analyte(s) in matrix	✓	*Indicate quantification mode used (i.e., IDMS, internal standard, external standard, other)* • **Internal Standard** • **Multi-level Calibration Curve**
Verification method(s) for value-assignment of analyte(s) in sample (if used)	✓	*Indicate calibration mode used (i.e., single-point calibration, bracketing, x-point calibration curve, other)* • **Multi-level Calibration Curve**
Other	N/A	*Indicate any confirmative method(s) used, if any.*

Core Competency Table from NMISA

SIM.QM-K27	***NMISA***	**Determination of Ethanol in Aqueous Matrix**
Scope of Measurement: Participation in the SIM.QM-K27 intended to demonstrate the laboratory's capabilities in determination of ethanol in aqueous matrix in the mass fraction range of 0.5 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.		
Competency	**Tick, cross, or "N/A"**	**Specific Information as Provided by NMI/DI**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	✓	*NMISA uses titration, a primary method for which the stoichiometry of the chemical reaction is exactly known and traceability to the kilogram and the mole is established*
Identity verification of analyte(s) in calibration material.#	✓	*NMIJ Potassium dichromate CRM 3002-a Sample 020 certified reference material was applied.*
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	✓	*NMIJ Potassium dichromate CRM 3002-a Sample 020 certified reference material was applied.*
For calibrants which are a calibration solution: Value-assignment method(s).#	N/A	*No calibrant used in primary method*
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	*Titrimetric analysis technique involves the oxidation of ethanol with excess potassium dichromate and back-titration of the unreacted potassium dichromate with ammonium iron sulphate.* *Confirmation of ethanol identity was independently confirmed using headspace gas chromatography (HS-GC-FID) through retention time comparison with NMISA and ERM aqueous ethanol CRMs.* *The absence of other alcohols, that may cause a positive bias in the oxidation reaction, was also confirmed using HS-GC-FID.*
Extraction of analyte(s) of interest from matrix	N/A	
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	✓	*Known masses of aqueous ethanol solutions are oxidized to acetic acid with a known mass of standard potassium dichromate solution, in the presence of sulphuric acid:* *Cr2O72- + 8H+ → 2Cr3+ + 4H2O + 3/2O2* *In acidic medium the potassium dichromate will donate 3 atoms of oxygen for oxidation:* *CH3CH2OH + O2 → CH3COOH + 3/2H2O* *3C2H5OH + 2K2Cr2O7 + 8H2SO4 → 3CH3COOH +*

		2K2SO4 + 2Cr2(SO4)3 + 11H2O *The unreacted potassium dichromate is titrated with acidified ammonium iron sulphate solution, and the quantity of ethanol can thus be determined:* *6FeSO4 + 7H2SO4 + K2Cr2O7 = K2SO4 + Cr2(SO4)3 + 3Fe2(SO4)3 + 7H2O*
Analytical system	✓	*Mettler Toledo T70 Autotitrator*
(Quantification) Calibration approach for value-assignment of analyte(s) in matrix	✓	*The concentration of the ethanol in aqueous solution is determined (using equivalence point auto-titration) 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* *MassEtOH soln is the mass of the ethanol solution taken for analysis, in g* *MassK2Cr2O7 soln is the mass of the potassium dichromate solution aliquot added to the ethanol solution, in g* *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*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	✓	*Verification done on Agilent 6890N GC-FID with G1888 Headspace sampler*
Other	N/A	

Core Competency Table from NIMT

Note: NIMT did not demonstrated capability in determination of ethanol in aqueous matrix (0.5 to 5.0 mg/g).

SIM.QM-K27	***NIMT***	**Determination of Ethanol in Aqueous Matrix**
Scope of Measurement: Participation in the SIM.QM-K27 intended to demonstrate the laboratory's capabilities in determination of ethanol in aqueous matrix in the mass fraction range of 0.5 mg/g to 5mg/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.		
Competency	**Tick, cross, or "N/A"**	**Specific Information as Provided by NIMT**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	✓	*Calibration solution obtained from ERM was used*
Identity verification of analyte(s) in calibration material.#	✓	*GC-TOF*
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	N/A	
For calibrants which are a calibration solution: Value-assignment method(s).#	✓	*ERM-AC405c (Reference Spirit) was used in this measurement*
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	*Comparison of analyte retention times and m/z of GC-MS against its calibrant.*
Extraction of analyte(s) of interest from matrix	N/A	
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	✓	GC-Headspace -TOF
Calibration approach for value-assignment of analyte(s) in matrix	✓	*a) IDMS* *b) 5-point calibration curve, the isotope ratio in sample blends were controlled to be closed to 1.0.*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	N/A	
Other	N/A	

Core Competency Table from UME

SIM.QM-K27	***UME***	**Determination of Ethanol in Aqueous Matrix**
Scope of Measurement: Participation in the SIM.QM-K27 intended to demonstrate the laboratory's capabilities in determination of ethanol in aqueous matrix in the mass fraction range of 0.5 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.		
Competency	**Tick, cross, or "N/A"**	**Specific Information as Provided by NMI/DI**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	✓	*Highly pure substance* *Ethanol, Merck(102428)*
Identity verification of analyte(s) in calibration material.#	✓	*GC-FID, HS-GC-FID and qNMR*
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	✓	*Purity of the calibrants were performed by qNMR* *Traceability to UME CRM 1301* *Ethanol (95.15 ± 0.33) %*
For calibrants which are a calibration solution: Value-assignment method(s).#	N/A	
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	*Retention time* *Internal standard, area ratios*
Extraction of analyte(s) of interest from matrix	N/A	
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	✓	*GC-FID and qNMR*
Calibration approach for value-assignment of analyte(s) in matrix	✓	*Internal standard*
Verification method(s) for value-assignment of analyte(s) in sample (if used)		*6 points calibration curve*
Other		*GC-FID; HS-GC-FID and qNMR were used for value assignment*

Core Competency Table from METAS

SIM.QM-K27	***NMI/DI***	**Determination of Ethanol in Aqueous Matrix**
Scope of Measurement: Participation in the SIM.QM-K27 intended to demonstrate the laboratory's capabilities in determination of ethanol in aqueous matrix in the concentration range of 0.5 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.		
Competency	**Tick, cross, or "N/A"**	**Specific Information as Provided by NMI/DI**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?		*The ethanol **calibration solutions** were produced gravimetrically from absolute Ethanol puriss (Sigma-Aldrich 02865,.$H_2O \leq 0.01$ %) in ultrapure water (conductivity$_{25°C} \leq 0.055$ µS/cm) by a two-step dilution.* *The stock solution was produced by the nominal weight of 100 g of ethanol per 5 kg aqueous solution.* *The ethanol calibration solutions with nominal mass fractions of 0.75 mg/g, 0.80 mg/g, 0.85 mg/g, 3.75 mg/g, 3.80 mg/g and 3.85 mg/g Ethanol were obtained by gravimetric dilution of the stock solution with ultrapure water.*
Identity verification of analyte(s) in calibration material.#	*N/A*	-
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	*N/A*	-
For calibrants which are a calibration solution: Value-assignment method(s).#	✓	*Mass fraction from gravimetric preparation process incl. purity information*
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	*HPLC (retention time)*
Extraction of analyte(s) of interest from matrix	*N/A*	-
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	✓	*Filtration of 1.5 mL through a 0.2 µm filter directly in HPLC vials(separation from unspecified particles)*
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	*N/A*	-
Analytical system	✓	*HPLC AGILENT HP 1200* *Aminex HPX-87H Column, Bio-Rad #1250140* *G1362 Refractive Index Detector (RID)*
Calibration approach for value-assignment of analyte(s) in matrix	✓	*Bracketing method with 6 external standard solutions around target values obtained from density measurements.*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	*N/A*	-
Other	✓	*Preliminary testing: density determination*

Core Competency Table from HSA

SIM.QM-K27	***HSA***	**Determination of Ethanol in Aqueous Matrix**
Scope of Measurement: Participation in the SIM.QM-K27 intended to demonstrate the laboratory's capabilities in determination of ethanol in aqueous matrix in the mass fraction range of 0.5 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.		
Competency	**Tick, cross, or "N/A"**	**Specific Information as Provided by NMI/DI**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	✓	*High purity ethanol certified reference material (NMIJ CRM 4001-b) from the National Metrology Institute of Japan (NMIJ) with a purity value of (1.000 ± 0.001) kg/kg.*
Identity verification of analyte(s) in calibration material.#	✓	*The identity of ethanol was verified by comparing the retention time and ions in a GC-MS with the NIST Ethanol-Water Solution SRMs (2893 and 2896).*
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	N/A	
For calibrants which are a calibration solution: Value-assignment method(s).#	N/A	
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	*Retention time and three ions on GC-MS.*
Extraction of analyte(s) of interest from matrix	N/A	
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	✓	*Agilent 7890A/5975C GC-MS with CTC headspace sampler.*
Calibration approach for value-assignment of analyte(s) in matrix	✓	*A single-point calibration, using exact-matching IDMS method.*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	✓	*The NIST Ethanol-Water Solution SRMs (2893 and 2896) were analysed in parallel with each SB (level 1 and level 2) as quality control (QC). The QC was subjected to the same sample treatment as the sample solution. The same calibration blend was used for both the sample blends and QCs. The QC results were all within the expanded uncertainty of the certified values for ethanol.*
Other	✓	*Subsamples from each reporting bottle were also measured with GC-FID (Agilent 7890A GC system with G1888 Headspace), using internal calibration method (1-propanol as the internal standard). The results were used to estimate the uncertainty in the use of different instruments.*

Core Competency Table from Ukrmetrteststandart

SIM.QM-K27	**Ukrmetr-teststandart**	**Determination of Ethanol in Aqueous Matrix**
Scope of Measurement: Participation in the SIM.QM-K27 intended to demonstrate the laboratory's capabilities in determination of ethanol in aqueous matrix in the mass fraction range of 0.5 mg/g to 5mg/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.		
Competency	**Tick, cross, or "N/A"**	**Specific Information as Provided by Ukrmetrteststandart**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	√	*Calibration aqueous solution of ethanol prepared gravimetrically in the laboratory from ethanol that was absolutized using calcium oxide.*
Identity verification of analyte(s) in calibration material. #	√	*GC-FID (retention time)*
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	N/A	
For calibrants which are a calibration solution: Value-assignment method(s).#	√	*By gravimetric procedure and taking into account ethanol purity. Purity of ethanol used for solution preparation was assessed using Karl-Fischer titration and GC-FID.*
Sample Analysis Competencies		
Identification of analyte(s) in sample	√	*GC-FID (retention time)*
Extraction of analyte(s) of interest from matrix	N/A	
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	
Analytical system	√	*GC-FID*
Calibration approach for value-assignment of analyte(s) in matrix	√	*External standard (aqueous ethanol solution) with addition of an internal standard (aqueous n-propanol solution). Linear calibration function using generalized least-squares method.*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	√	*Verification was made using control solutions including those prepared by other personnel from different parent material using different equipment.*
Other	N/A	

Core Competency Table from NMIM

SIM.QM-K27	***NMIM***	**Determination of Ethanol in Aqueous Matrix**
Scope of Measurement: Participation in the SIM.QM-K27 intended to demonstrate the laboratory's capabilities in determination of ethanol in aqueous matrix in the mass fraction range of 0.5 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.		
Competency	**Tick, cross, or "N/A"**	**Specific Information as Provided by NMI/DI**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	✓ /	*Highly pure substance*
Identity verification of analyte(s) in calibration material.#	✓	*GC-FID*
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	✓	*Purity assessment by GC-FID and Karl Fisher*
For calibrants which are a calibration solution: Value-assignment method(s).#		*Indicate how you established analyte mass fraction in calibration solution*
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	*Retention time*
Extraction of analyte(s) of interest from matrix		-
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)		-
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)		-
Analytical system	✓	*GC-FID*
Calibration approach for value-assignment of analyte(s) in matrix	✓	*External standard*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	✓	*5-point calibration curve*
Other		-

Core Competency Table from EXHM

SIM.QM-K27	***EXHM***	**Determination of Ethanol in Aqueous Matrix**
Scope of Measurement: Participation in the SIM.QM-K27 intended to demonstrate the laboratory's capabilities in determination of ethanol in aqueous matrix in the mass fraction range of 0.5 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.		
Competency	**Tick, cross, or "N/A"**	**Specific Information as Provided by NMI/DI**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	✓	*NIST SRM 2896*
Identity verification of analyte(s) in calibration material.#	✓	*GC-MS*
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	✓	*used NIST SRM 2896 to characterise EXHM calibration solutions that were prepared from EtOH characterised by the mass balance approach*
For calibrants which are a calibration solution: Value-assignment method(s).#	✓	*used NIST SRM 2896 to characterise EXHM calibration solutions that were prepared from EtOH characterised by the mass balance approach*
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	*Retention time, mass spec ion ratios*
Extraction of analyte(s) of interest from matrix		*none*
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)		*none*
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)		*none*
Analytical system	✓	*GC-IDMS*
Calibration approach for value-assignment of analyte(s) in matrix	✓	*IDMS at exact matching (single point)*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	✓	*using different calibrants*
Other	✓	*GC-FID*

Core Competency Table from CENAM

SIM.QM-K27	***CENAM***	**Determination of Ethanol in Aqueous Matrix**
Scope of Measurement: Participation in the SIM.QM-K27 intended to demonstrate the laboratory's capabilities in determination of ethanol in aqueous matrix in the mass fraction range of 0.5 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.		
Competency	**Tick, cross, or "N/A"**	**Specific Information as Provided by NMI/DI**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	✓	*Pure material: DMR-95c Etanol CENAM.*
Identity verification of analyte(s) in calibration material.#	✓	*Certified Reference material in purity identifying ethanol as the main compound.*
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	✓	*Mass fraction (998.4620 ± 0.0840) mg/g* *This reference material was certified by quantification of organic impurities with two different columns by GC-FID. In addition, water content was measured by Karl Fischer titration.*
For calibrants which are a calibration solution: Value-assignment method(s).#		*NA*
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	*Retention time of pure material: 6.75 min.*
Extraction of analyte(s) of interest from matrix		*None*
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)		*None*
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)		*None*
Analytical system	✓	*GC-FID*
Calibration approach for value-assignment of analyte(s) in matrix	✓	*internal standard*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	✓	*5-point calibration curve*
Other	✓	*Use of DMR466a "Disolución acuosa de etanol al 49 % en masa" as control in two dilution levels.*

Core Competency Table from INMETRO

SIM.QM-K27	***INMETRO***	**Determination of Ethanol in Aqueous Matrix**
Scope of Measurement: Participation in the SIM.QM-K27 intended to demonstrate the laboratory's capabilities in determination of ethanol in aqueous matrix in the mass fraction range of 0.5 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.		
Competency	**Tick, cross, or "N/A"**	**Specific Information as Provided by NMI/DI**
Competencies for Value-Assignment of Calibrant		
Calibrant: Did you use a "highly-pure substance" or calibration solution?	✓	*Highly pure Ethanol 99.9 %, from Merck, in house purity assessment by mass balance*
Identity verification of analyte(s) in calibration material.#	✓	*GC-FID (retention time)*
For calibrants which are a highly-pure substance: Value-Assignment / Purity Assessment method(s).#	✓	*Ethanol purity: 99.943% ± 0.002% (k=2; 95%)* *In house purity assessment by quantification of organic impurities with two different columns by GC-FID, and water content by Coulometric Karl Fischer titration.*
For calibrants which are a calibration solution: Value-assignment method(s).#	N/A	-
Sample Analysis Competencies		
Identification of analyte(s) in sample	✓	*Retention time*
Extraction of analyte(s) of interest from matrix	N/A	-
Cleanup - separation of analyte(s) of interest from other interfering matrix components (if used)	N/A	-
Transformation - conversion of analyte(s) of interest to detectable/measurable form (if used)	N/A	-
Analytical system	✓	*GC-FID*
Calibration approach for value-assignment of analyte(s) in matrix	✓	*Internal standard (1-propanol)*
Verification method(s) for value-assignment of analyte(s) in sample (if used)	✓	*8-point calibration curve*
Other	N/A	