Final Report of the Proficiency Testing in Cachaça Measurement – 4th Round Organic Parameters

Inmetro
Instituto Nacional de Metrologia, Qualidade e Tecnologia

PEP-Inmetro

Programa de Ensaios de Proficiência do Inmetro

PROFICIENCY TESTING IN CACHAÇA MEASUREMENT – 4ª ROUND – ORGANIC PARAMETERS

Registration Period: 19/10/16 to 28/10/16

FINAL REPORT Nº 005/2017

PROFICIENCY TESTING ORGANIZATION

Instituto Nacional de Metrologia, Qualidade e Tecnologia - Inmetro
Diretoria de Metrologia, Científica e Tecnologia - Dimci
Endereço: Av. Nossa Senhora das Graças, 50 – Xerém – Duque de Caxias
RJ – Brasil – CEP: 25250-020
E-mail para contato: pep-inmetro@inmetro.gov.br

ORGANIZING COMMITTEE

Adelcio Rena Lemos (Inmetro/Dimci)
José Ricardo Bardellini da Silva (Inmetro/Dimci)
Paulo Roberto da Fonseca Santos (Inmetro/Dimci) - Coordenador PEP-Inmetro
Neivaldo Silva Nonato (Inmetro/Dimci)
Valnei Smarçaro da Cunha (Inmetro/Dimci/Dimqt)
Chang Hoon (Phillip) Shin (KTR)

TECHNICAL COMMITTEE

Eliane Cristina Pires do Rego (Inmetro/Dimci/Dimqt/Labor)
Fernando Gustavo Marques Violante (Inmetro/Dimci/Dimqt/Labor)
Janaína Marques Rodrigues Caixeiro (Inmetro/Dimci/Dimqt)
Lucas Junqueira de Carvalho (Inmetro/Dimci/ Dimqt/Labor)
Rodrigo Vivarelli Poggi Leal (Inmetro/Dimci/Dimqt/Labor)
Tânia Maria Monteiro (Inmetro/Dimci/ Dimqt/Labor)

SUMMARY

1. Introduction

Cachaça is the second most commonly consumed alcoholic beverage in Brazil and has been conquering markets due to the efforts of the productive sector in conjunction with governmental actions at various levels.

According to Normative Instruction nº 13, dated June 29th, 2005, of the Brazilian Ministry of Agriculture, Livestock and Food Supply - MAPA, cachaça is the typical and exclusive denomination of cane brand produced in Brazil, with alcoholic graduation of thirty eight to forty eight per cent in a 20 ºC volume obtained by fermented sugar cane most distillation with peculiar sensorial characteristics and may be added with sugars up to six grams per liter, expressed in sucrose [1]. The referred Normative Instruction also provides for a series of requirements such as standardization, classification, register, inspection, production and surveillance for the Brazilian produced cachaça.

Cachaça chemical-physical analysis is one of the necessary requirements for the certification (conformity assessment) of cachaça. Cachaça certification provides written guarantee that a certain cachaça brand is in conformity with all the requirements specified by the Ordinance nº 276 dated September 24th, 2009 [2].

To promote the enhancement of reliability and quality to laboratory measurement results, Inmetro performs Proficiency Testing (PT). PT participation is one of the necessary tools for calibration and testing laboratories for the maintenance of accreditation according to the ABNT NBR ISO/IEC 17025 Standard [3]. Achieving satisfactory results in proficiency testing is, for the laboratory, an evidence of its analytical competence in a determined measurement.

Therefore, a PT has the purpose to compare measurement results of different laboratories, performed under similar conditions, and thus obtain a technical competence evaluation of participant laboratories, supplying an adequate mechanism for evaluating and demonstrating the reliability of their measurement [4]. Laboratories, at their turn, have the opportunity of reviewing their analysis procedures, as well as to implement improvements in the different activities they act, if it's necessary.

This report presents the performance evaluation of participant laboratories in the Cachaça Proficiency Testing – 4th round.

The objectives of this PT scheme were:

- To determine the performance of laboratories for the proposed tests;
- To contribute for the confidence increase in laboratory measurement results;
- To contribute for the continuous improvement of the measurement techniques of each laboratory;

- To aggregate value to the Brazilian cachaça in order to increase the health protection of consumers and to conquer international markets.

2. Test Item

2.1. Test Item Preparation

The test item corresponds to a commercial cachaça sample (batch 1) and an ethyl carbamate sample in water-alcohol solution (batch 2). In batch 1 the parameters methanol, 1-butanol, 2-butanol, isobutanol e propanol were evaluated and in batch 2 the parameter ethyl carbamate was evaluated.

The reference material for the ethyl carbamate in water-alcohol solution was gravimetrically prepared from the ethyl carbamate standard and from water-alcohol solution prepared in alcoholic degree similar to cachaça.

The reference material to the other organic parameters in cachaça was prepared gravimetrically by means of addition of contaminant organic standards to commercial cachaça. The addition was only carried out if the contaminant presence was not in the desired range in the selected commercial cachaça.

Both materials were packed in glass bottles containing approximately 6 mL (batch 1) and 10 mL (batch 2) solution. Each bottle was properly identified, containing in its label the PT name, the corresponding batch and the round number.

The concentration ranges of each analyte in the materials, as well as the recommended analysis methodology, are presented in Table 1.

Table 1: Concentration ranges for the parameters in test items and recommended methodologies for analysis

Batch	Parameter	Concentration Range	Recommended Analytic Technique	Reference Standards
1	Methanol	2 a 30 mg/100g	Gas chromatography with flame ionization detection (GC-FID) or Gas chromatography with mass spectrometry (GC-MS)	AOAC Official Method 972.11 (CG-DIC): methanol. AOAC Official Method 968.09 (CG-DIC) or 972.10 (CG-DIC): other alcohols.
	2-butanol	1 a 20 mg/100g		
	1-butanol	0,1 a 10 mg/100g		
	isobutanol	5 a 100 mg/100g		
	1-propanol	5 a 100 mg/100g		
2	Ethyl Carbamate	50 a 300 ng/g	Gas chromatography with mass spectrometry (GC-MS)	AOAC Official Method 994.07 (CG-ME)

2.2. Test Item Characterization, Homogeneity and Stability

The Organic Analysis Laboratory of the Chemical and Thermal Metrology Division of Inmetro was responsible for the preparation, bottling, characterization and stability and homogeneity studies (according to ABNT ISO Guide 35[5]) of the samples supplied as test items.

The test item bottles were used in long term homogeneity, characterization and stability studies were selected randomly. All these study bottles were stored at 4 °C ± 3 °C.

In the characterization study of test item of ethyl carbamate batch in water-alcohol solution it was used a gas chromatography technique coupled to mass spectrometry (GC-MS), with isotopic dilution quantification. In the test items characterization of the other batch for the cachaça organic parameters it was used the gas chromatography technique with flame ionization detection (GC-FID)[1] and gas chromatography coupled to mass spectrometry (GC-MS)[2], both using an internal standardization technique, whose measurement methodologies are published [6]. Five bottles of each batch were used for the characterization study.

In the homogeneity and stability study it was employed the gas chromatography technique coupled to the mass spectrometry. It was applied the Grubbs Test for the identification of dispersed values or outliers among the acquired results. In the homogeneity study, the measurement results were evaluated by means of the variance analysis (ANOVA) with one factor [5]. In the stability study, the measurement results of each parameter were evaluated through the linear regression as a function of the storage time [5].

2.3. Test Item Characterization Results

The prepared material, batch 1 and batch 2, was considered homogeneous as well as presented adequate stability through this entire PT.

The obtained characterization value for batches 1 and 2 represents the reference value for this PT.

Table 2 presents the characterization value and its uncertainty, which has the material characterization and the homogeneity and stability studies as sources for this PT test item.

[1] GC-FID, Agilent Technologies, model 6890N

[2] GC-MS, Agilent Technologies, models 6890N (GC) and 5975B (ME)

Table 2 - Results in mg/kg

Batch 1	Concentration	Combined standard uncertainty (u)	Coverage Factor (*k*)	Expanded Uncertainty (U)
methanol	82.4	3.59	2	7.2
1-butanol	35.8	0.84	2	1.7
2-butanol	62.1	4.11	2	8.2
isobutanol	209.6	4.42	2	8.8
1-propanol	268	12.6	2	25
Batch 2	**Concentration**	**Combined standard uncertainty (u)**	**Coverage Factor (*k*)**	**Expanded Uncertainty (U)**
Ethyl Carbamate	0.2010	0.0022	2	0.0044

3. Methods for Statistical Analysis of Results

3.1. Z-score

It represents a distance measure of the result presented by a specific laboratory in relation to the reference value of the proficiency testing and, therefore, is used to check if the measurement result of each participant is in conformity to the assigned value. The z-score [4, 6, 8, 9] is calculated according to Equation 1.

$$z_i = \frac{x_i - X}{\hat{\sigma}} \quad (1)$$

Where,

x_i: is the mean value of the six measurements of the i-th participant;

X: is the assigned value by the Reference Laboratory: Labor;Dimqt/Inmetro;

$\hat{\sigma}$: is the standard deviation for the proficiency testing, which in this PT will be considered the combined standard uncertainty value of the test item (u_X).

The interpretation of z-score value is described as follows:

$|z| \leq 2{,}0$ - Indicates “satisfactory” performance and generates no signal;

$2{,}0 < |z| < 3{,}0$ - Indicates “questionable” performance and generates a warning signal;

$|z| \geq 3{,}0$ - Indicates “unsatisfactory” performance and generates an action signal.

3.2. Normalized Error

For the evaluation of laboratories that informed the measurement uncertainty value and the coverage factor *(k)*, which were optional, it was also applied the normalized error. Similar to the z-score, such parameter is also used to check if the measurement result of each participant is in conformity to the

reference value, but taking into consideration not only the measurement results, but also the respective uncertainties [6]. The normalized error is calculated according to Equation 2.

$$E_{ni} = \frac{y_i - y_{ref}}{\sqrt{U_i^2 + U_{ref}^2}} \quad (2)$$

Where:

y_{ref} is the reference value, assigned by Labor/Dimqt/Inmetro;

y_i is the mean value of the six measurements of a specific i-laboratory;

U_{ref} is the reference value expanded uncertainty assigned by Labor/Dimqt/Inmetro;

U_i is the expanded uncertainty value informed by a specific i-laboratory.

The normalized error acceptance criteria is:

$|E_n| \leq 1$ Satisfactory result

$|E_n| > 1$ Unsatisfactory result

4. Results and Discussion

4.1. Participants Results

4.1.1 Methanol

The results for methanol analyte, as well as the applied analytical techniques are presented in Table 3.

Table 3: Reported results by participant laboratories for methanol analyte

Laboratory Code	Bottle	Concentration (mg/kg)					Technique
		Measurement			Mean	Expanded Uncertainty (U)	
		1	2	3			
Me017	1	98.658	97.681	92.027	93.57	4.80	GC-FID external calibration
	2	86.142	92.046	94.891			
Me045	1	83.936	81.093	81.959	81.436	Not reported	GC-FID not reported
	2	82.177	80.960	78.493			
Me058	1	70.889	75.619	72.749	73.937	5.127	GC-FID internal calibration
	2	72.486	77.574	74.305			
Me133	1	71.406	70.932	71.484	71.082	4.46793	GC-FID standard addition
	2	71.172	70.988	70.511			
Me156	1	85.764	90.850	88.307	87.872	2.54	GC-FID external calibration
	2	86.554	88.319	87.436			
Me161	1	87.700	85.959	86.928	87.919	17.584	GC-ME external calibration
	2	88.989	89.057	88.881			

Laboratory Code	Bottle	Concentration (mg/kg)					Technique
		Measurement			Mean	Expanded Uncertainty (U)	
		1	2	3			
Me199	1	145.602	153.093	142.877	154.164	Not reported	GC-FID external calibration
	2	160.596	172.763	150.051			
Me201	1	77.235	77.710	78.722	80.063	23.653	GC-ME external calibration
	2	80.339	85.877	80.494			
Me218	1	85.226	84.676	83.946	84.487	7.407	GC-FID external calibration
	2	85.426	85.046	82.602			
Me290	1	65.821	55.342	58.439	61.600	Not reported	GC-FID external calibration
	2	56.674	76.303	57.024			

For all uncertainty values, the coverage factor (*k*) is 2.00.

Figure 1 presents the mean values and uncertainties reported by participants for methanol measurements. The error bars represent the measurement expanded uncertainty. The black line in the graph represents the reference value (Ref) and the green line represents the reference value with respect to once the expanded uncertainty (Ref ± U). The continuous blue line represents the dispersion of the reference value with respect to twice the expanded uncertainty (Ref ± 2U) and the continuous red line represents the dispersion of the reference value with respect to three times the expanded uncertainty (Ref ± 3U).

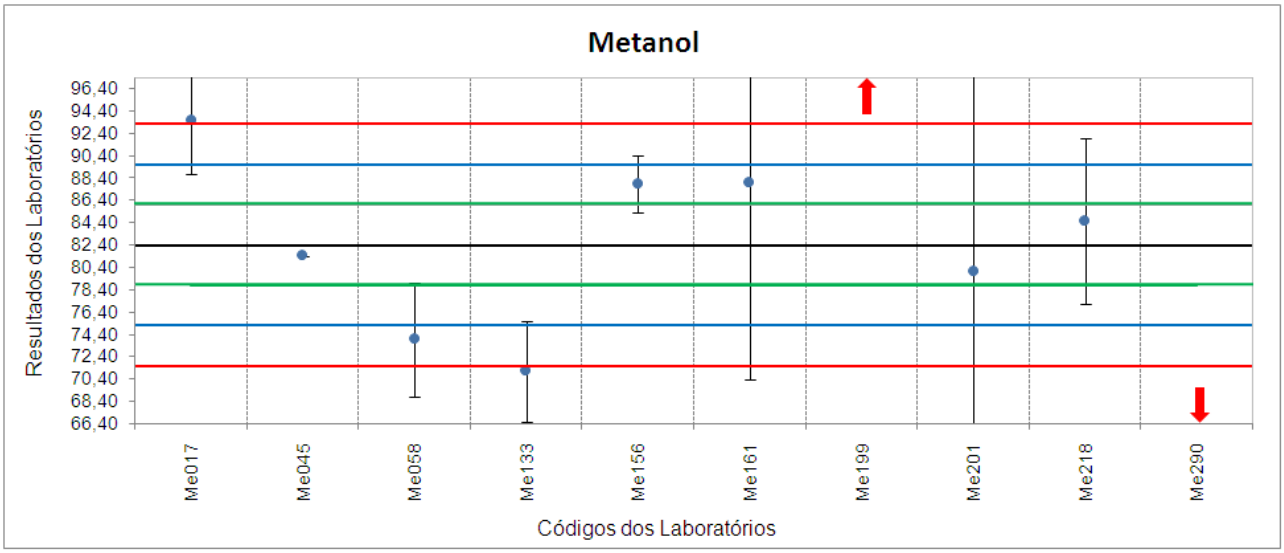

Figure 1: Methanol measurements performed by PT participants.

4.1.2. 1-butanol

The results for 1-butanol analyte, as well as the employed analytical techniques are presented in Table 4.

Table 4: Reported results by participant laboratories for 1-butanol analyte

Laboratory Code	Bottle	Concentration (mg/kg)					Technique
		Measurement			Mean	Expanded Uncertainty (U)	
		1	2	3			
1b018	1	63.557	64.106	63.693	64.075	Not reported	GC-FID external calibration
	2	63.660	65.100	64.331			
1b024	1	32.891	31.435	33.376	32.806	3.14675	GC-FID standard addition
	2	31.908	31.858	35.369			
1b032	1	30.745	31.811	31.654	31.373	1.265	GC-FID external calibration
	2	31.771	32.012	30.242			
1b059	1	37.234	38.268	36.860	37.412	21.103	GC-ME external calibration
	2	34.631	39.450	38.027			
1b073	1	34.421	34.098	34.273	34.218	2.02	GC-FID external calibration
	2	33.889	34.706	33.923			
1b079	1	61.711	63.561	60.469	67.516	Not reported	GC-FID external calibration
	2	71.179	72.763	75.412			
1b096	1	29.130	26.435	31.141	28.288	Not reported	GC-FID external calibration
	2	24.053	28.290	30.678			
1b106	1	29.793	32.707	32.915	32.338	1.29	GC-FID external calibration
	2	32.107	33.127	33.380			
1b175	1	36.609	36.352	36.131	36.452	0.24	GC-FID external calibration
	2	36.337	36.333	36.947			
1b231	1	31.355	30.872	30.515	30.988	2.213	GC-FID internal calibration
	2	31.240	30.767	31.177			
1b283	1	37.840	38.401	38.281	37.937	3.414	GC-ME external calibration
	2	37.687	37.787	37.623			

For all uncertainty values, the coverage factor (*k*) is 2.00.

Figure 2 presents the mean values and uncertainties reported by participants for 1-butanol measurements. The error bars represent the measurement expanded uncertainty. The black line in the graph represents the reference value (Ref) and the green line represents the reference value with respect to once the expanded uncertainty (Ref ± U). The continuous blue line represents the dispersion of the reference value with respect to twice the expanded uncertainty (Ref ± 2U) and the continuous red line represents the dispersion of the reference value with respect to three times the expanded uncertainty (Ref ± 3U).

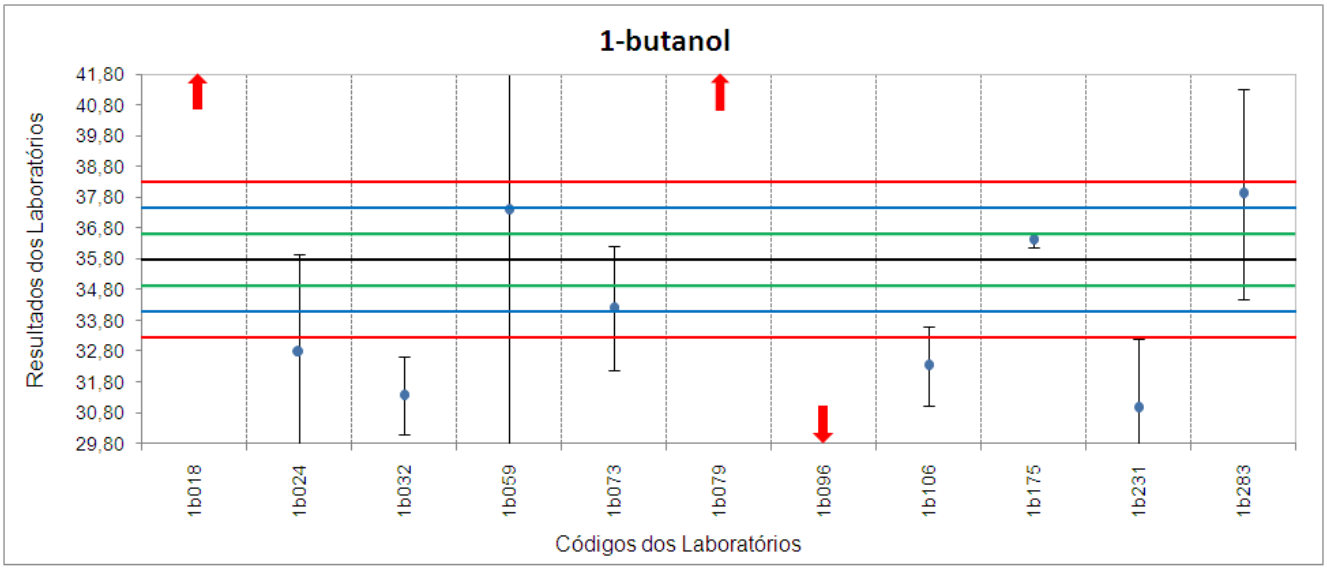

Figure 2: 1-butanol measurements performed by PT participants.

4.1.3. 2-butanol

The results for 2-butanol analyte, as well as the employed analytical techniques are presented in Table 5.

Table 5: Reported results by participant laboratories for 2-butanol analyte

Laboratory Code	Bottle	Concentration (mg/kg)					Technique
		Measurement			Mean	Expanded Uncertainty (U)	
		1	2	3			
2b035	1	64.610	65.565	64.452	64.334	5.147	GC-ME external calibration
	2	63.638	63.960	63.780			
2b047	1	35.782	35.472	36.719	36.871	7.76	GC-FID external calibration
	2	38.675	37.623	36.958			
2b048	1	56.255	57.489	58.604	57.223	3.704	GC-FID external calibration
	2	57.093	58.171	55.725			
2b076	1	54.297	62.498	51.767	55.821	Not reported	GC-FID external calibration
	2	50.305	54.634	61.426			
2b108	1	64.202	63.332	64.210	63.288	24.277	GC-ME external calibration
	2	59.817	64.310	63.854			
2b150	1	69.212	69.746	68.874	69.025	Not reported	GC-FID external calibration
	2	69.683	68.072	68.562			
2b267	1	110.748	113.891	110.279	119.799	Not reported	GC-FID external calibration
	2	128.213	127.896	127.769			
2b272	1	43.748	46.187	45.031	45.392	3.134	GC-FID internal calibration
	2	45.830	47.249	44.305			
2b279	1	60.384	60.532	56.472	59.93	2.30	GC-FID external calibration
	2	61.869	60.403	59.917			
2b294	1	63.733	63.861	63.947	63.599	2.36283	GC-FID standard addition
	2	63.504	63.566	62.981			

For all uncertainty values, the coverage factor (*k*) is 2.00.

Figure 3 presents the mean values and uncertainties reported by participants for 2-butanol measurements. The error bars represent the measurement expanded uncertainty. The black line in the graph represents the reference value (Ref) and the green line represents the reference value with respect to once the expanded uncertainty (Ref ± U). The continuous blue line represents the dispersion of the reference value with respect to twice the expanded uncertainty (Ref ± 2U) and the continuous red line represents the dispersion of the reference value with respect to three times the expanded uncertainty (Ref ± 3U).

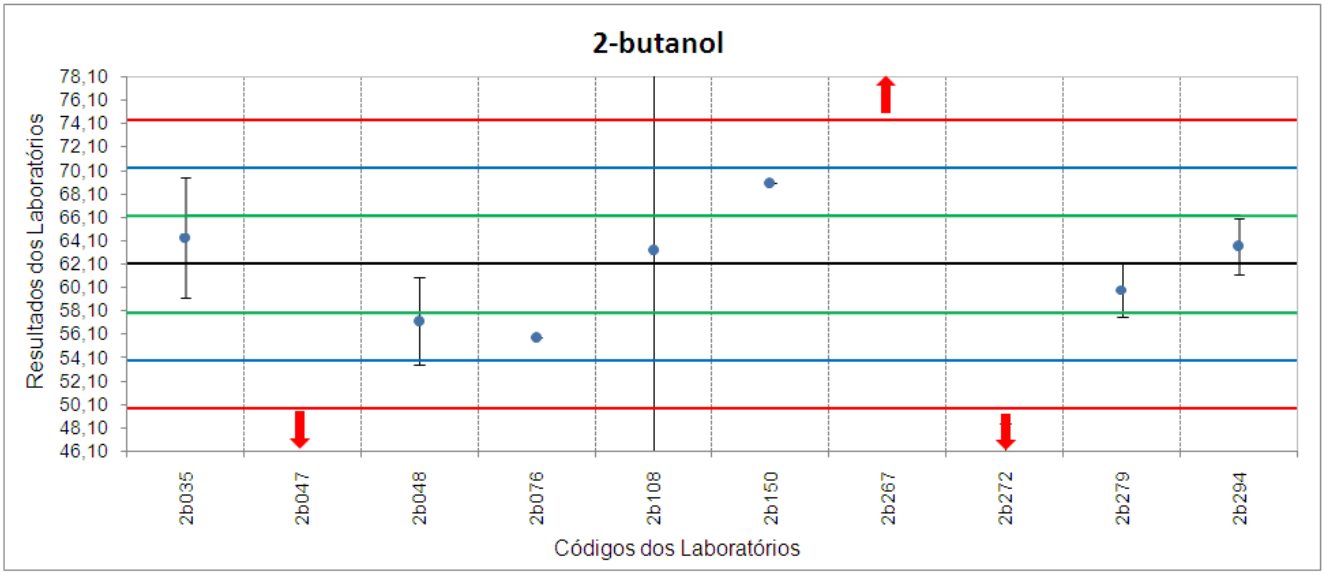

Figure 3: 2-butanol measurements performed by PT participants.

4.1.4. Isobutanol

The results for isobutanol analyte, as well as the employed analytical techniques are presented in Table 6.

Table 6: Reported results by participant laboratories for isobutanol analyte

Laboratory Code	Bottle	Concentration (mg/kg)					Technique
		Measurement			Mean	Expanded Uncertainty (U)	
		1	2	3			
Is038	1	210.907	212.729	216.326	210.534	18.948	GC-ME external calibration
	2	210.702	205.204	207.319			
Is056	1	227.334	229.370	227.931	224.356	Not reported	GC-FID external calibration
	2	226.414	219.356	215.729			
Is063	1	172.169	169.739	177.041	173.657	8.96	GC-FID external calibration
	2	173.887	177.049	172.058			
Is083	1	379.493	384.880	372.725	406.515	Not reported	External calibration
	2	433.612	432.662	435.716			
Is128	1	217.702	217.204	204.576	213.064	7.44	GC-FID external calibration
	2	215.264	217.729	205.910			

Laboratory Code	Bottle	Concentration (mg/kg)					Technique
		Measurement			Mean	Expanded Uncertainty (U)	
		1	2	3			
Is147	1	173.406	173.989	171.514	174.823	12.143	GC-FID internal calibration
	2	176.507	177.926	175.593			
Is163	1	204.213	201.884	202.101	200.701	7.02293	GC-FID standard addition
	2	198.632	199.415	197.958			
Is181	1	227.876	228.324	228.530	229.425	32.529	GC-ME external calibration
	2	225.115	237.542	229.164			
Is277	1	107.489	127.111	127.199	119.373	Not reported	GC-FID external calibration
	2	95.289	126.064	133.085			
Is300	1	198.658	203.110	206.248	202.762	18.996	GC-FID external calibration
	2	203.885	208.366	196.304			

For all uncertainty values, the coverage factor (*k*) is 2.00.

Figure 4 presents the mean values and uncertainties reported by participants for isobutanol measurements. The error bars represent the measurement expanded uncertainty. The black line in the graph represents the reference value (Ref) and the green line represents the reference value with respect to once the expanded uncertainty (Ref ± U). The continuous blue line represents the dispersion of the reference value with respect to twice the expanded uncertainty (Ref ± 2U) and the continuous red line represents the dispersion of the reference value with respect to three times the expanded uncertainty (Ref ± 3U).

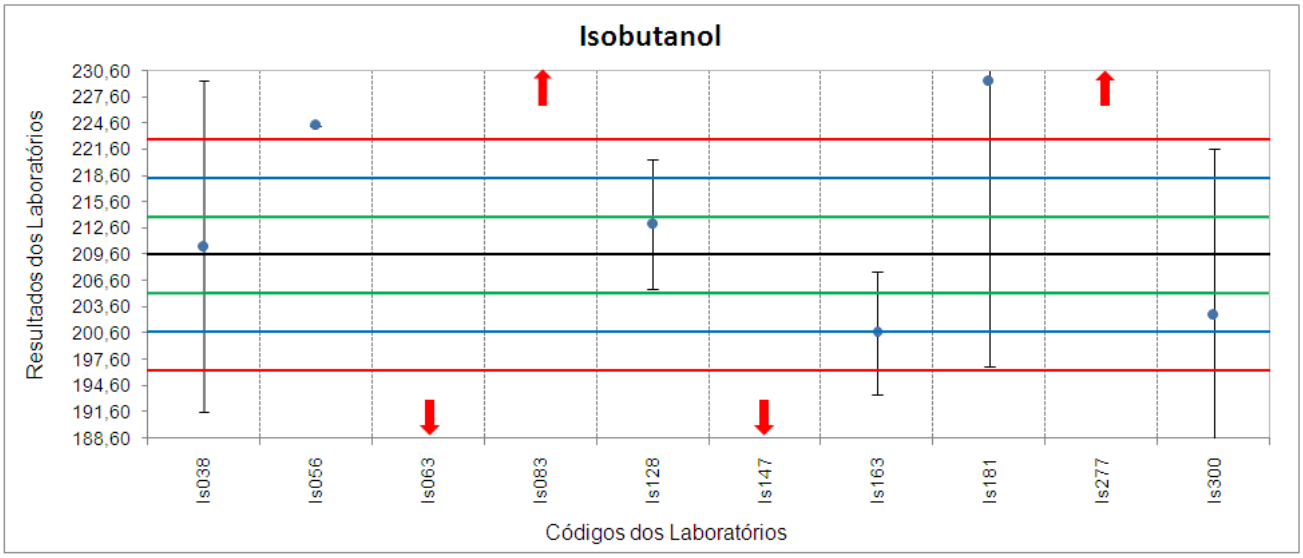

Figure 4: Isobutanol measurements performed by PT participants

4.1.5. 1-propanol

The results for 1-propanol analyte, as well as the employed analytical techniques are presented in Table 7.

Table 7: Reported results by participant laboratories for 1-propanol analyte

Laboratory Code	Bottle	Concentration (mg/kg)					Technique
		Measurement			Mean	Expanded Uncertainty (U)	
		1	2	3			
Pp010	1	321.314	320.725	315.696	316.087	Not reported	GC-FID external calibration
	2	317.284	311.528	309.975			
Pp011	1	265.047	270.649	271.464	268.780	14.713	GC-FID external calibration
	2	270.818	273.878	260.821			
Pp013	1	194.466	202.557	203.312	200.94	9.70	GC-FID external calibration
	2	196.395	203.243	205.638			
Pp016	1	49.187	79.277	73.303	67.924	Not reported	GC-FID external calibration
	2	33.635	89.070	83.074			
Pp036	1	276.682	265.353	263.525	269.650	7.13	GC-FID external calibration
	2	272.487	273.926	265.928			
Pp069	1	485.830	500.177	473.333	519.187	Not reported	External calibration
	2	556.591	567.858	531.331			
Pp099	1	206.523	207.360	209.781	204.086	13.8	GC-FID external calibration
	2	197.506	202.265	201.083			
Pp101	1	313.581	309.496	313.213	307.425	30.743	GC-ME external calibration
	2	303.021	303.142	302.095			
Pp187	1	265.129	264.116	262.124	262.155	9.17333	GC-FID standard addition
	2	263.666	259.337	258.558			
Pp192	1	225.553	233.489	226.720	230.607	15.957	GC-FID internal calibration
	2	234.099	233.920	229.863			
Pp202	1	293.318	292.308	296.234	293.310	39.613	GC-ME external calibration
	2	288.340	296.641	293.016			

For all uncertainty values, the coverage factor (*k*) is 2.00.

Figure 5 presents the mean values and uncertainties reported by participants for 1-propanol measurements. The error bars represent the measurement expanded uncertainty. The black line in the graph represents the reference value (Ref) and the green line represents the reference value with respect to once the expanded uncertainty (Ref ± U). The continuous blue line represents the dispersion of the reference value with respect to twice the expanded uncertainty (Ref ± 2U) and the continuous red line represents the dispersion of the reference value with respect to three times the expanded uncertainty (Ref ± 3U).

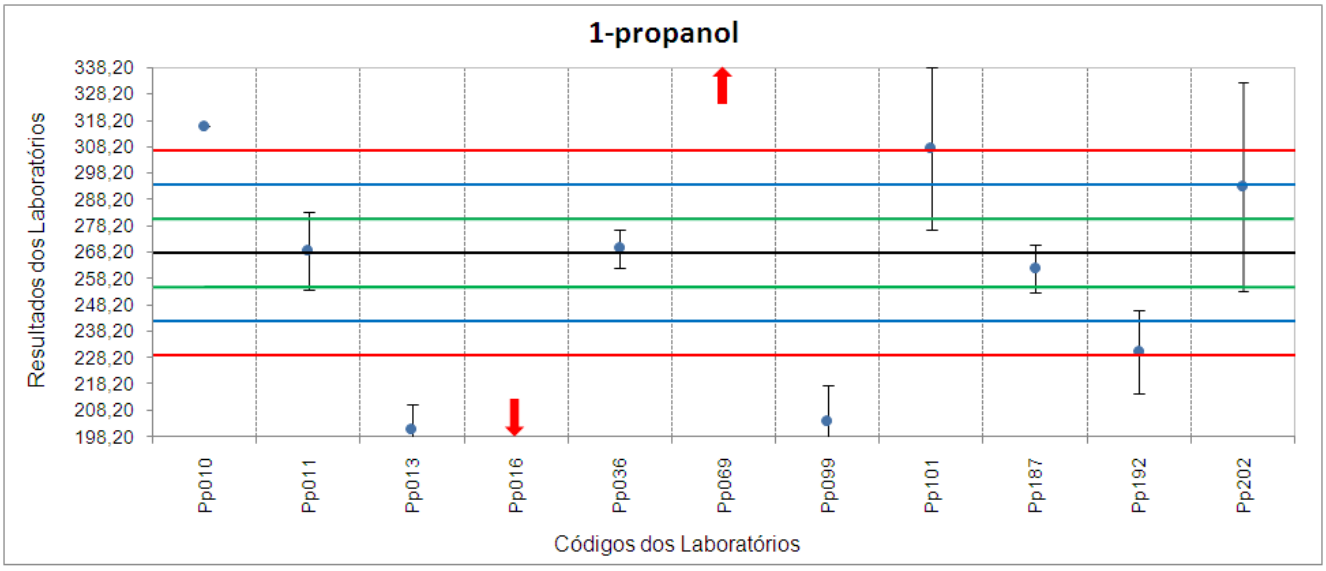

Figure 5: 1-propanol measurements performed by PT participants

4.1.6. Ethyl Carbamate

The results for ethyl carbamate analyte, as well as the employed analytical techniques are presented in Table 8.

Table 8: Reported results by participant laboratories for ethyl carbamate analyte

Laboratory Code	Bottle	Concentration (mg/kg)					Technique
		Measurement			Mean	Expanded Uncertainty (U)	
		1	2	3			
Ec043	1	0.179	0.177	0.166	0.176	0.032	GC-ME com SPME injection external calibration
	2	0.183	0.179	0.169			
Ec115	1	0.284	0.284	0.281	0.250	0.01125	GC-ME – external calibration
	2	0.216	0.220	0.218			
Ec144	1	0.202	0.201	0.199	0.200	0.010	GC-ME – external calibration
	2	0.198	0.203	0.196			
Ec174	1	0.268	0.258	0.241	0.230	0.01961	GC-ME – standard addition
	2	0.211	0.200	0.199			
Ec222	1	0.197	0.198	0.192	0.196	0.011	GC-ME – external calibration
	2	0.195	0.197	0.198			
Ec280	1	0.197	0.192	0.195	0.192	0.030	GC-ME – external calibration
	2	0.198	0.180	0.189			

For all uncertainty values, the coverage factor (*k*) is 2.00.

Figure 6 presents the mean values and uncertainties reported by participants for ethyl carbamate measurements. The error bars represent the measurement expanded uncertainty. The black line in the graph represents the reference value (Ref) and the green line represents the reference value with respect to once the expanded uncertainty (Ref ± U). The continuous blue line represents the dispersion of the reference value with respect to twice the expanded uncertainty (Ref ± 2U) and the

continuous red line represents the dispersion of the reference value with respect to three times the expanded uncertainty (Ref ± 3U).

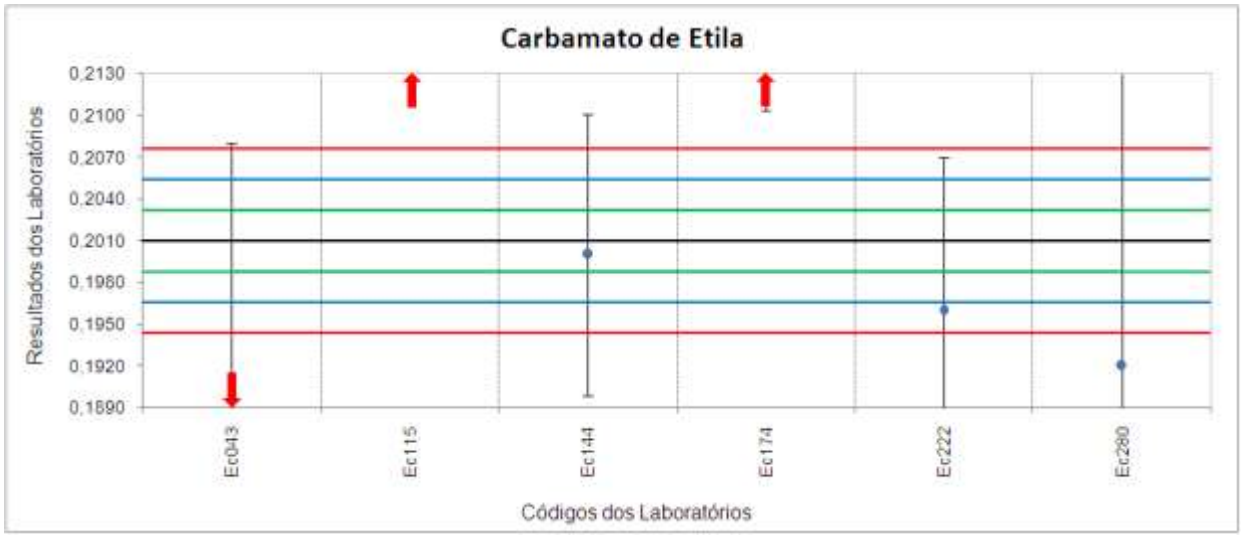

Figure 6: Ethyl carbamate measurements performed by PT participants

4.2 Participants Evaluation Performance

4.2.1. Z-score

All participants had the performance evaluation performed by calculating the z-score.

Tables 9 and 10 present participating laboratories z-score values.

Table 9: Z-score values for metanol, 1-butanol and 2-butanol analytes (*) (**)

Metanol		1-butanol		2-butanol	
Código do Laboratório	Índice *z*	Código do Laboratório	Índice *z*	Código do Laboratório	Índice *z*
Me017	1.55	1b018	16.63	2b035	0.27
Me045	-0.13	1b024	-1.76	2b047	-3.08
Me058	-1.18	1b032	-2.60	2b048	-0.59
Me133	-1.57	1b059	0.95	2b076	-0.77
Me156	0.76	1b073	-0.93	2b108	0.14
Me161	0.77	1b079	18.66	2b150	0.84
Me199	9.97	1b096	-4.42	2b267	7.04
Me201	-0.32	1b106	-2.04	2b272	-2.04
Me218	0.29	1b175	0.38	2b279	-0.26
Me290	-2.89	1b231	-2.83	2b294	0.18
		1b283	1.26		

* Highlighted in blue: questionable values
** In red: unsatisfactory values

Table 10: Z-score values for isobutanol, 1-propanol and ethyl carbamate analytes (*) (**)

Isobutanol		1-propanol		Etyl Carbamate	
Laboratory Code	Z-score	Laboratory Code	Z-score	Laboratory Code	Z-score
Is038	0.11	Pp010	1.92	Ec043	-5.68
Is056	1.68	Pp011	0.03	Ec115	11.14
Is063	-4.08	Pp013	-2.68	Ec144	-0.23
Is083	22.38	Pp016	-8.00	Ec174	6.59
Is128	0.39	Pp036	0.07	Ec222	-1.14
Is147	-3.95	Pp069	10.05	Ec280	-2.05
Is163	-1.01	Pp099	-2.56		
Is181	2.25	Pp101	1.58		
Is277	-10.25	Pp187	-0.23		
Is300	-0.78	Pp192	-1.50		
		Pp202	1.01		

* Highlighted in blue: questionable values
** In red: unsatisfactory values

Figures 7 to 12 present Z-score results obtained from participant laboratories for the cachaça contaminants.

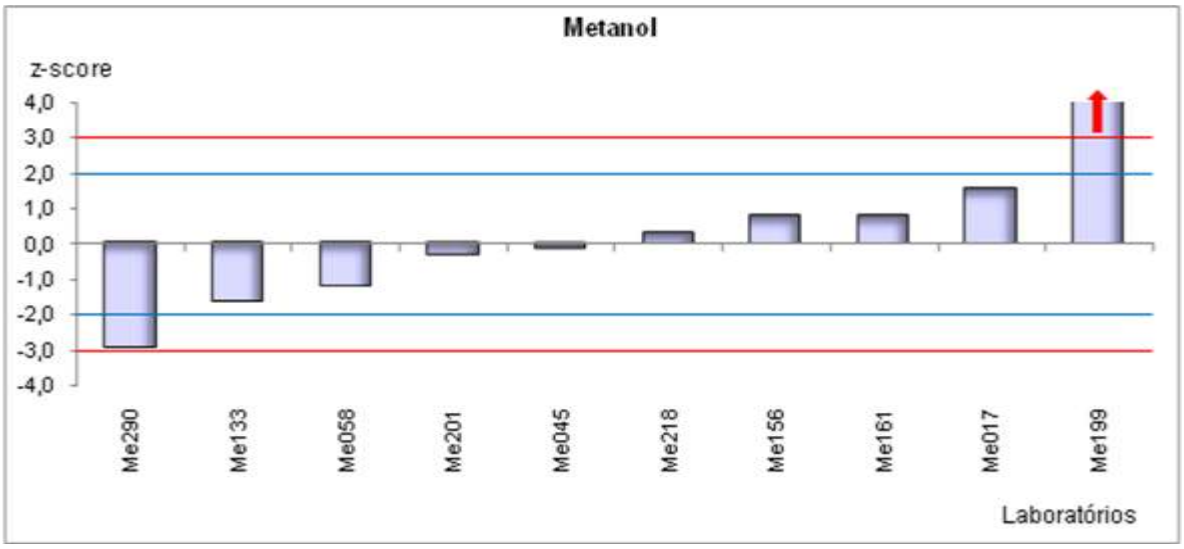

Figure 7 – Z-score for Methanol

The performance evaluation through z-score regarding methanol measurement showed that:

- 8 (eight) participants presented satisfactory performance;
- 1 (one) participant presented questionable performance;
- 1 (one) participant presented unsatisfactory performance.

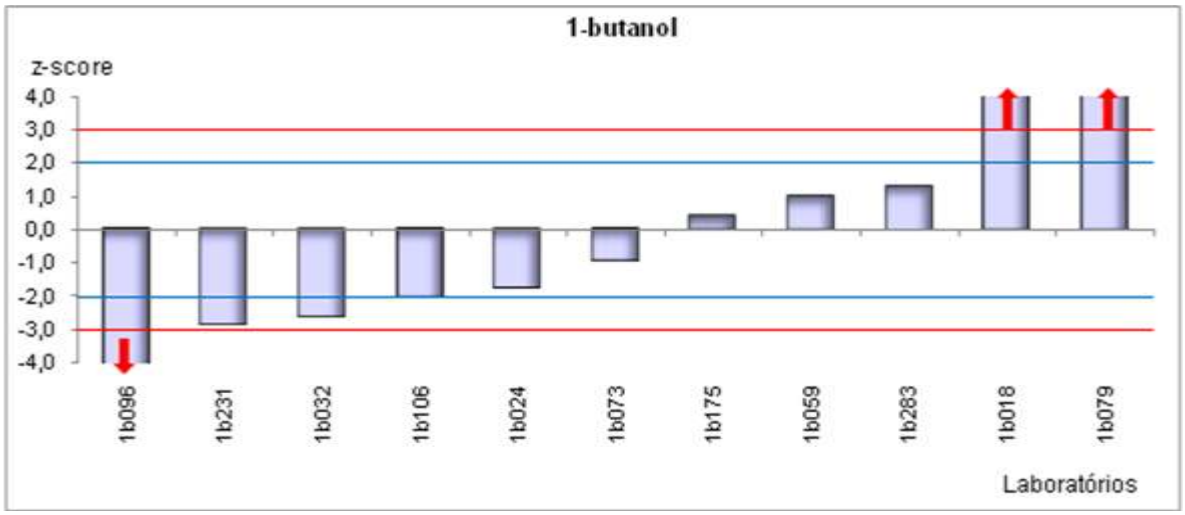

Figure 8 – Z-score for 1-butanol

The performance evaluation through z-score regarding 1-butanol measurement showed that:

- 5 (five) participants presented satisfactory performance;
- 3 (three) participants presented questionable performance;
- 3 (three) participants presented unsatisfactory performance.

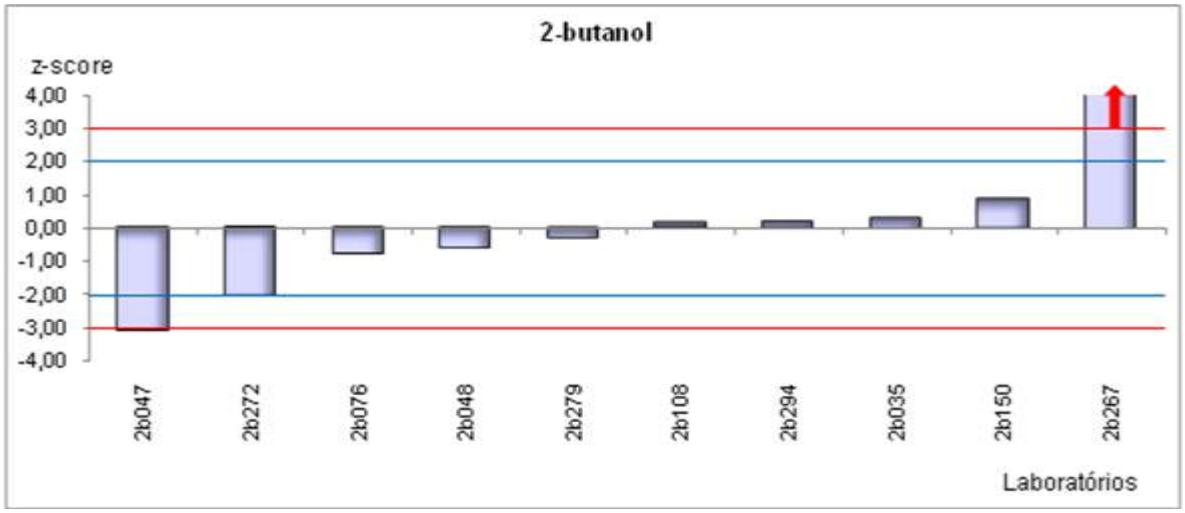

Figure 9 – Z-score for 2-butanol

The performance evaluation through z-score regarding 2-butanol measurement showed that:

- 7 (seven) participants presented satisfactory performance;
- 1 (one) participant presented questionable performance;
- 2 (two) participants presented unsatisfactory performance.

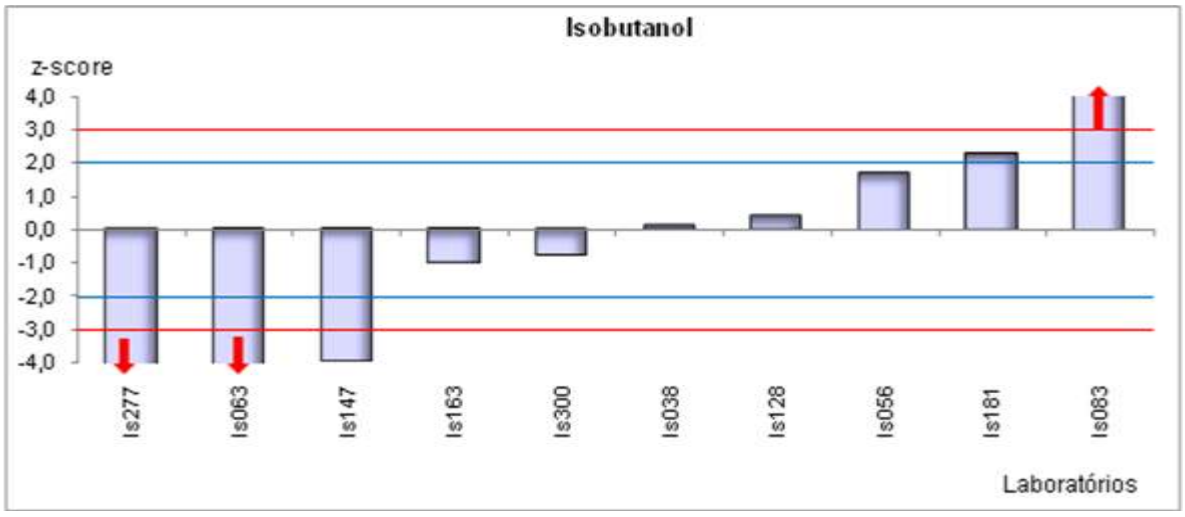

Figure 10 – Z-score for Isobutanol

The performance evaluation through z-score regarding isobutanol measurement showed that:

- 5 (five) participants presented satisfactory performance;
- 1 (one) participant presented questionable performance;
- 4 (four) participants presented unsatisfactory performance.

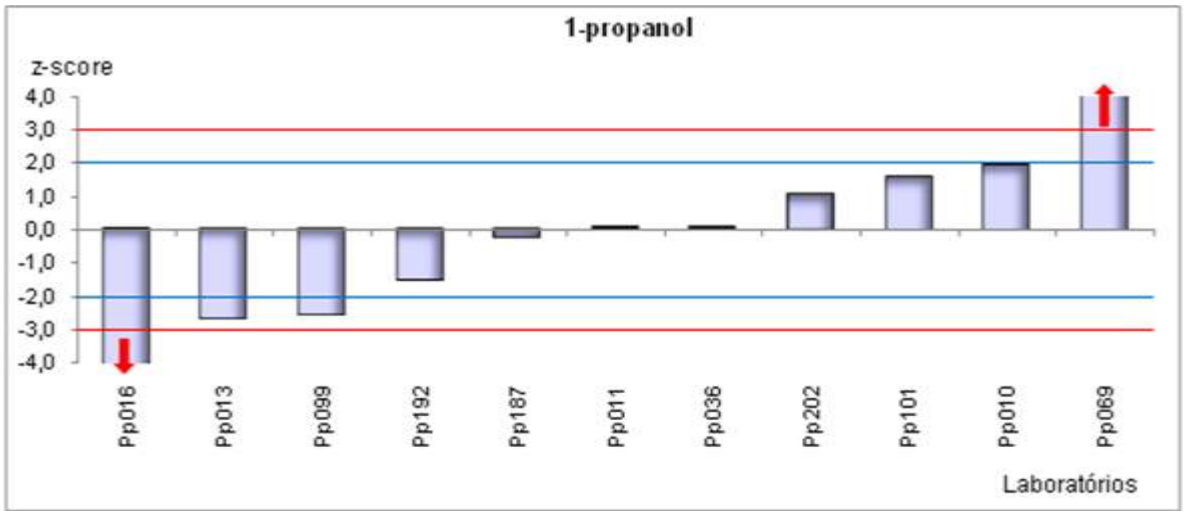

Figure 11 – Z-score for 1-propanol

The performance evaluation through z-score regarding 1-propanol measurement showed that:

- 7 (seven) participants presented satisfactory performance;
- 2 (two) participants presented questionable performance;
- 2 (two) participants presented unsatisfactory performance.

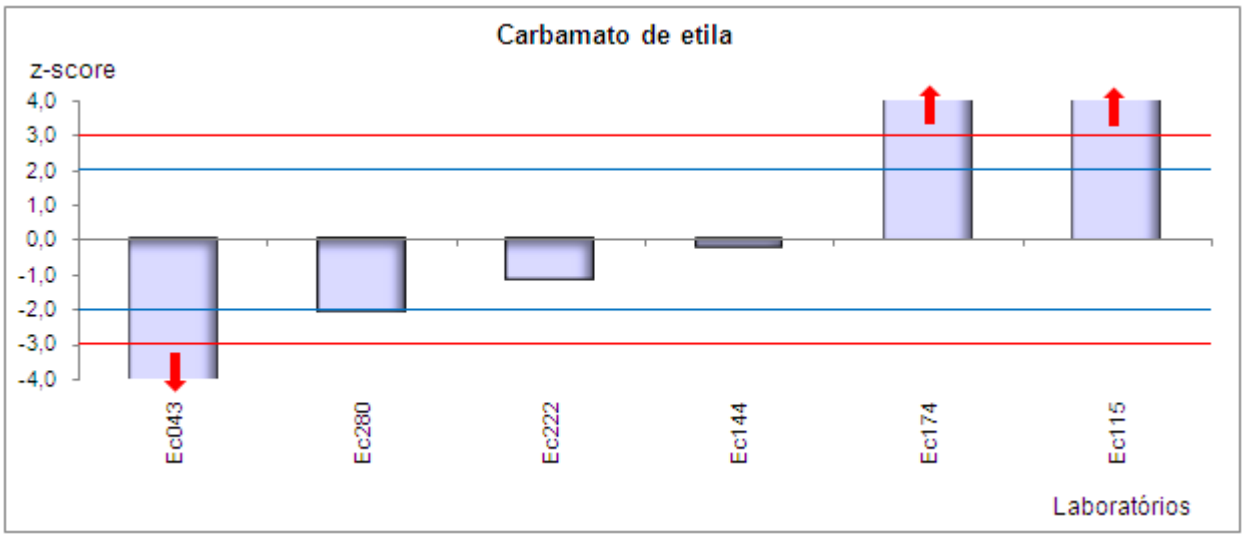

Figure 12 – Z-score for Ethyl Carbamate

The performance evaluation through z-score regarding ethyl carbamate measurement showed that:

- 2 (two) participants presented satisfactory performance;
- 1 (one) participant presented questionable performance;
- 3 (three) participants presented unsatisfactory performance.

4.2.2. Normalized Error

Laboratories that informed measurement uncertainties with the respective coverage factors had also their performance evaluated through the normalized error calculation. The normalized error values for each participant are presented in tables 11 to 16. Figures 13 to 18 present graphically participants performance.

Table 11: Normalized error results for methanol, 1-butanol, 2-butanol and isobutanol analytes (*)

Methanol		1-Butanol		2-Butanol		Isobutanol	
Laboratory Code	E_n	Laboratory Code	E_n	Laboratory Code	E_n	Laboratory Code	E_n
Me133	-1.3	1b032	-2.1	2b047	-2.2	Is063	-2.9
Me058	-1.0	1b106	-1.6	2b272	-1.9	Is147	-2.3
Me201	-0.1	1b231	-1.7	2b048	-0.5	Is163	-0.8
Me218	0.2	1b024	-0.8	2b279	-0.3	Is300	-0.3
Me161	0.3	1b073	-0.6	2b108	0.05	Is038	0.0
Me156	0.7	1b059	0.1	2b294	0.2	Is128	0.3
Me017	1.3	1b175	0.4	2b035	0.2	Is181	0.6
		1b283	0.6				

* Highlighted in red are unsatisfactory values

Table 12: Normalized error results for 1-propanol and ethyl carbamate analytes (*)

1-Propanol		Carbamato de etila	
Laboratory Code	**E_n**	**Laboratory Code**	**E_n**
Pp013	-2.5	Ec043	-0.8
Pp099	-2.2	Ec222	-0.4
Pp192	-1.3	Ec280	-0.3
Pp187	-0.2	Ec144	-0.1
Pp011	0.0	Ec174	1.4
Pp036	0.1	Ec115	4.1
Pp202	0.5		
Pp101	1.0		

* Highlighted in red are unsatisfactory values

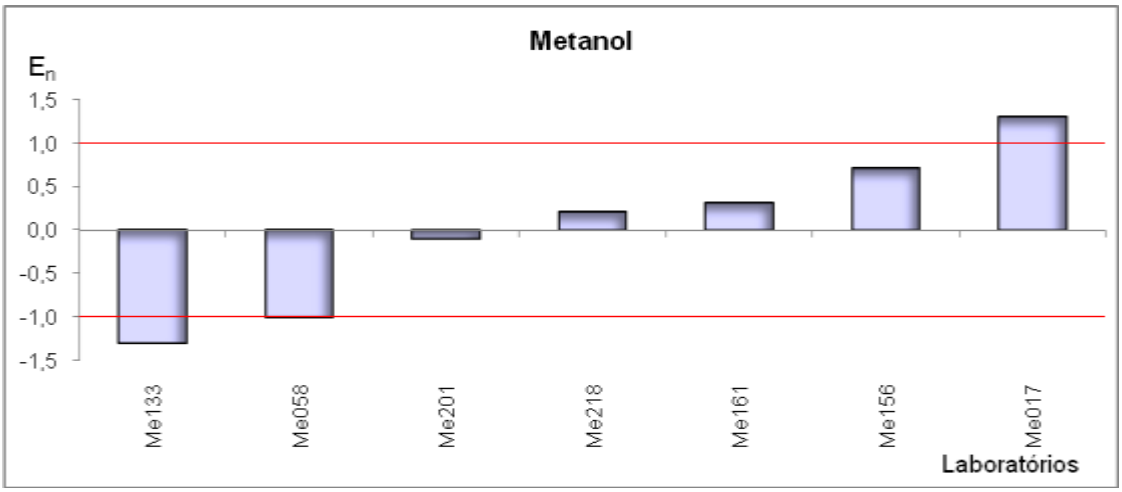

Figure 13 – Performance evaluation by normalized error - Methanol analyte

The performance evaluation through the normalized error regarding methanol measurement showed that:

- 5 (five) laboratories presented satisfactory results, i.e., $|E_n| \leq 1$;
- 2 (two) laboratories presented unsatisfactory results, i.e., $|E_n| > 1$.

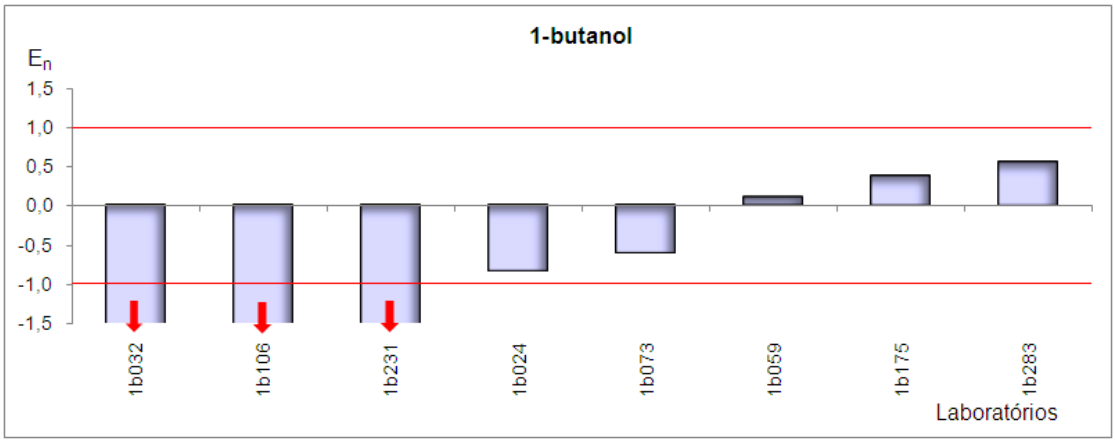

Figure 14 - Performance evaluation by normalized error - 1-butanol analyte

The performance evaluation through the normalized error regarding 1-butanol measurement showed that:

- 5 (five) laboratories presented satisfactory results, i.e., $|E_n| \leq 1$;
- 3 (three) laboratories presented unsatisfactory results, i.e., $|E_n| > 1$.

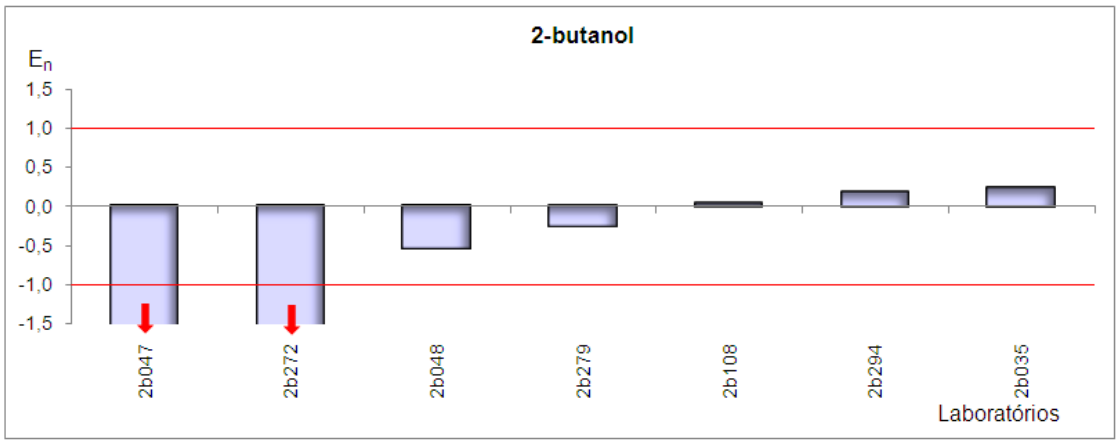

Figure 15 - Performance evaluation by normalized error - 2-butanol analyte

The performance evaluation through the normalized error regarding 2-butanol measurement showed that:

- 5 (five) laboratories presented satisfactory results, i.e., $|E_n| \leq 1$;
- 2 (two) laboratories presented unsatisfactory results, i.e., $|E_n| > 1$.

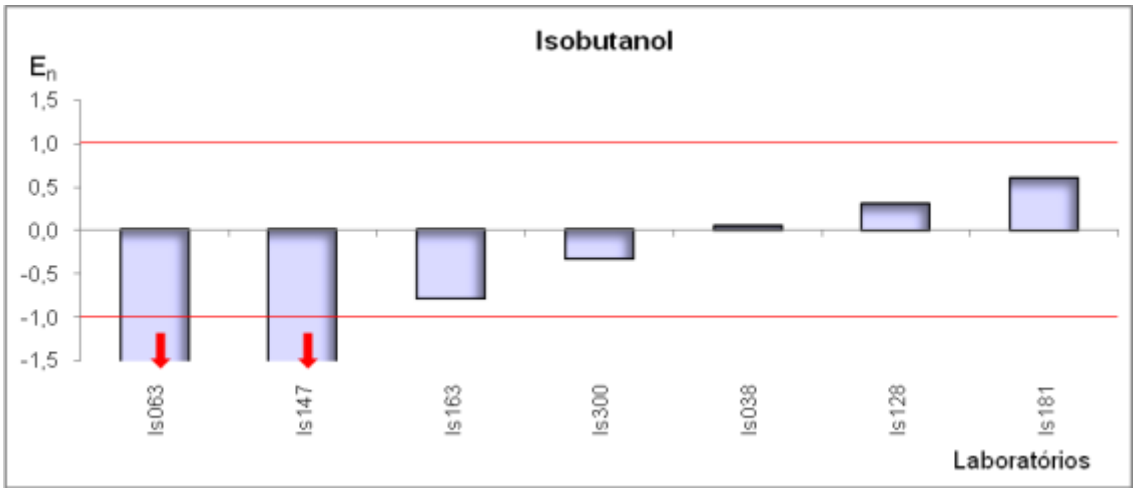

Figure 16 - Performance evaluation by normalized error - isobutanol analyte

The performance evaluation through the normalized error regarding isobutanol measurement showed that:

- 5 (five) laboratories presented satisfactory results, i.e., $|E_n| \leq 1$;
- 2 (two) laboratories presented unsatisfactory results, i.e., $|E_n| > 1$.

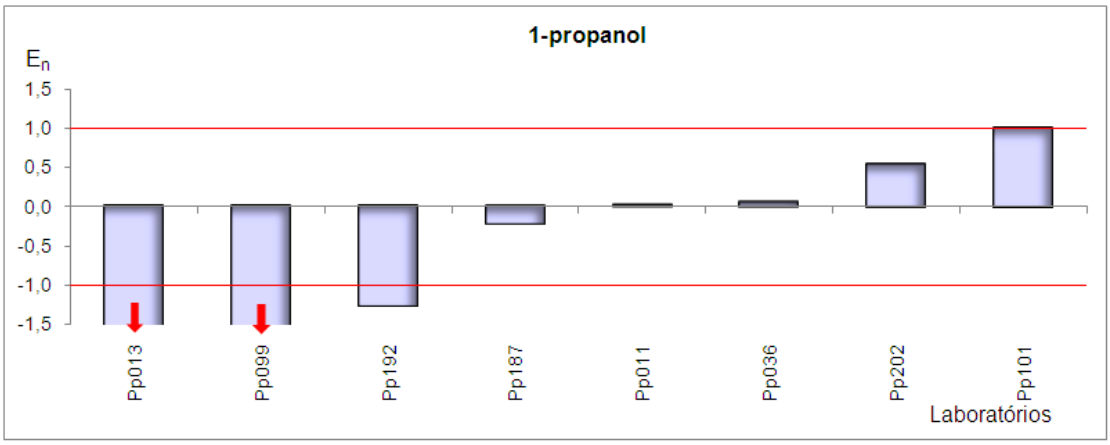

Figure 17 - Performance evaluation by normalized error - 1-propanol analyte

The performance evaluation through the normalized error regarding 1-propanol measurement showed that:

- 5 (five) laboratories presented satisfactory results, i.e., $|E_n| \leq 1$;
- 3 (three) laboratories presented unsatisfactory results, i.e., $|E_n| > 1$.

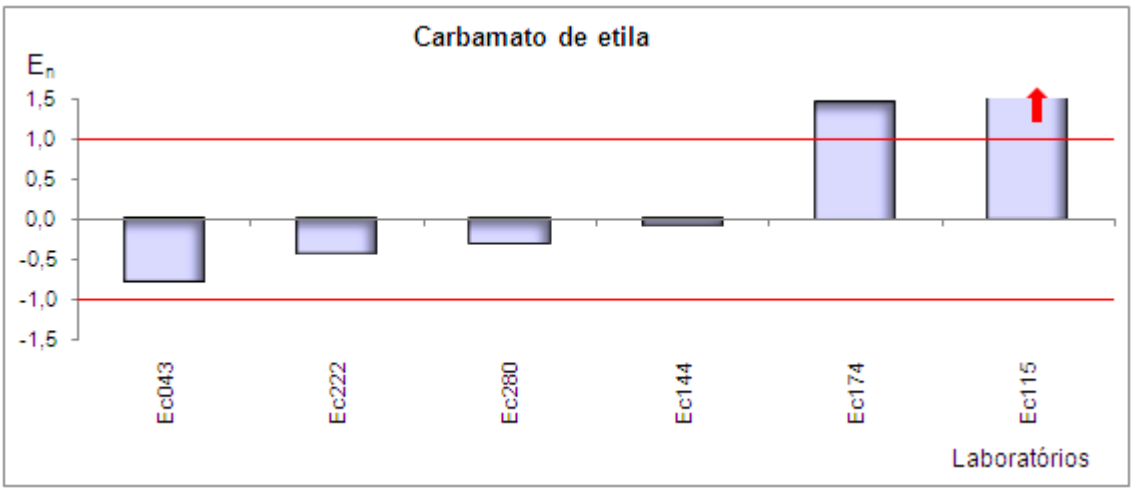

Figure 18 - Performance evaluation by normalized error - ethyl carbamate analyte

The performance evaluation through the normalized error regarding ethyl carbamate measurement showed that:

- 4 (four) laboratories presented satisfactory results, i.e., $|E_n| \leq 1$;
- 2 (two) laboratories presented unsatisfactory results, i.e., $|E_n| > 1$.

It should be noted that the normalized error and z-score are just an indicator of the participant performance and it's up to each one to make its interpretation and to implement corrective actions, if deemed necessary.

5. Confidentiality

Each participant was identified by an individual code that is only known by the participant and the PT coordination. The participant received, by e-mail, its identification code corresponding to the PT participation. This code was used as identification in filling in the results registration. The results may be used in studies and publications by Inmetro respecting the confidentiality of each participant.

As established in section 4.10.4 of ABNT ISO/IEC 17043:2011, in exceptional circumstances, a regulatory authority may require the results and the identification of the participants to the PT provider. If this occurs, the provider will notify the PT participants about this action.

6. Conclusion

The results presented by participant laboratories is this Proficiency Testing demonstrate the necessity of the confidentiality enhancement in measurements for the organic contaminants in cachaça for the majority of laboratories. The analysis performed through the dispersion graphs (Figures 1, 2, 3, 4, 5 and 6) demonstrate that the mean of the laboratories reported values for methanol, 1-butanol, 2-butanol, isobutanol, 1-propanol and ethyl carbamate, respectively, are dispersed in relation to the reference value determined by Inmetro.

Among the 10 results for methanol evaluated by z-score, 80 % (8 laboratories) present satisfactory performance against 10 % (1 laboratory) with questionable performance and 10 % (1 laboratory) with unsatisfactory performance. Among 11 1-butanol results evaluated by z-score, 45.4 % (5 laboratories) presented satisfactory performance against 27.3 % (3 laboratories) with questionable performance and 27.3 % (3 laboratories) with unsatisfactory performance. Among 10 2-butanol results evaluated by z-score, 70 % (7 laboratories) presented satisfactory performance against 10 % (1 laboratory) with questionable performance and 20 % (2 laboratories) with unsatisfactory performance. Among 10 isobutanol results evaluated by z-score, 50 % (5 laboratories) presented satisfactory performance against 10 % (1 laboratory) with questionable performance and 40 % (4 laboratories) with unsatisfactory performance. Among 11 1-propanol results evaluated by z-score, 63.6 % (7 laboratories) presented satisfactory performance against 18.2 % (2 laboratories) with questionable performance and 18.2 % (2 laboratories) with unsatisfactory performance. Among 6 ethyl carbamate results evaluated by z-score, 33.3 % (2 laboratories) presented satisfactory performance against 16.7 % (1 laboratory) with questionable performance and 50 % (3 laboratories) with unsatisfactory performance.

Among 7 methanol results evaluated by the normalized error, 71.4 % (5 laboratories) presented satisfactory performance against 28.6 % (2 laboratories) with unsatisfactory performance. Among 8

1-butanol results evaluated by the normalized error, 62.5 % (5 laboratories) presented satisfactory performance against 37.5 % (3 laboratories) with unsatisfactory performance. Among 7 2-butanol results evaluated by the normalized error, 71.4 % (5 laboratories) presented satisfactory against 28.6 % (2 laboratories) with unsatisfactory performance. Among 7 isobutanol results evaluated by the normalized error, 71.4 % (5 laboratories) presented satisfactory performance against 28.6 % (2 laboratories) with unsatisfactory performance. Among 8 1-propanol results evaluated by the normalized error, 62.5 % (5 laboratories) presented satisfactory performance against 37.5 % (3 laboratories) with unsatisfactory performance. Among 6 ethyl carbamate results evaluated by the normalized error, 66.7 % (4 laboratories) presented satisfactory performance against 33.3 % (2 laboratories) with unsatisfactory performance.

The z-score evaluation and normalized error evaluation are independent. Each laboratory has to carry out a critical analysis of the results, including those who reported the measurement result uncertainty, how this uncertainty is under or overestimated. It is recommended that laboratories that didn't present satisfactory performance in the z-score criteria make a critical analysis of its measurement method and, besides, laboratories that didn't present satisfactory performance in the normalized error evaluation review its calculation for the estimation of the measurement uncertainty.

Among 12 laboratories that submitted valid results for organic contaminants, only 3 laboratories (corresponding to 25 % of them) presented satisfactory results for all analytes. Among 12 laboratories that submitted results, one laboratory (corresponding to 8 % of them) didn't present satisfactory result for any parameter. Among those that submitted all results, two laboratories (corresponding to 20 % of them), only had satisfactory result for one analyte, with lower unsatisfactory or questionable results than the assigned value to the other parameters, which may be attributed to the use of negative biased methods. Three laboratories among those that submitted all results (corresponding to 30 % of laboratories) presented questionable results only for one analyte.

Following the disclosure of the preliminary report, the laboratory that didn't present any satisfactory result informed that they were reported erroneously in mg/100mL unit, but the proficiency test Organization Committee, for not being able to change the content that had been reported in the results registration form, as foreseen in the PT protocol, preserved the original data in the final report. It's important to emphasize that the measurement unit is part of the result. Thus, it is the laboratory responsibility to report the correct unit.

The differences between the laboratories reported results and the reference values show the importance of the use of samples with certified values in proficiency testing. In case it was used the consensus value as a reference, this value would certainly be displaced and would not reflect the reality of the measurement.

For the improvement of the measurements performed by the laboratories, it's recommended that the establishment of corrective actions and the continuous participation in proficiency testing of this nature are tools of great contribution. The results reported here also show the lack in the use certified reference materials for this kind of analysis that certainly would imply in a greater measurement reliability and accuracy, generating better results.

7. Participants

Fourteen laboratories signed up for this PT to measure at least one parameter. Among them, two laboratories didn't send their results. Thus the effective number of participants is effectively 12. Upon registration, laboratories informed if they would take part of the PT analyzing batch 1 and/or batch 2.

The list of laboratories that sent their results to the coordination of the PT program is presented in Table 13. It's important to emphasize that the table numbering is just an indication of the number of PT participating laboratories and, under no circumstances it is associated to laboratory identification in presenting their results.

Table 13 – Cachaça PT participating laboratories – 4th round

	Institution
1.	Companhia Müller de Bebidas
2.	Instituto de Pesquisas Energéticas e Nucleares - Laboratorio de Caracterização Química
3.	Serviço Nacional de Aprendizagem Industrial - CTS Ambiental
4.	Centro de Inovação e Tecnologia SENAI FIEMG - Campus CETEC - Instituto Senai de Tecnologia em Química - Laboratório de Ensaios Orgânicos
5.	Food Intelligence Laboratório de Análise de Alimentos Ltda.
6.	Laboratório Nacional Agropecuário - LANAGRO/RS - Laboratório de Análises de Bebidas e Vinagres - LABV
7.	Laboratório Amazile Biagioni Maia Ltda - EPP - LABM
8.	Serviço Nacional de Aprendizagem Industrial - Laboratório de Ensaios em Bebidas
9.	Laboratório Nacional Agropecuário em Goiás - Laboratório de Análises Físico-Químicas de Bebidas e Vinagres
10.	Korea Testing & Research Institute - KTR - Beauty Industry Team
11.	Korea Testing & Research Institute - KTR - Environment and Health Team
12.	Kemidas

Total participants: 12.

8. Bibliographic References

[1] Normative Instruction nº 13, June 29th, 2005 - Brazilian Ministry of Agriculture, Livestock and Food Supply (MAPA), available in: http://sistemasweb.agricultura.gov.br/sislegis/action/detalhaAto.do?method=consultarLegislacaoFederal

[2] Ordinance nº 276, September 24th 2009 – National Institute of Metrology, Quality and Technology – Inmetro, available in: http://www.inmetro.gov.br/legislacao/rtac/pdf/RTAC001497.pdf

[3] ABNT NBR ISO/IEC 17025, Requisitos gerais para a competência de laboratórios de ensaio e calibração, ABNT, Rio de Janeiro, 2005.

[4] M. Thompson, S.L. Ellison, R. Wood, *The International Harmonized Protocol for the Proficiency Testing of Analytical Chemistry Laboratories*, Pure Appl. Chem. 78 (2006) 145-196.

[5] ABNT ISO GUIA 35, Materiais de referência – Princípios gerais e estatísticos para certificação, ABNT, Rio de Janeiro, 2012.

[6] Monteiro, T.M., Rodrigues, J.M., Rego, E.C.P., Carvalho Rocha, W.F., Mattos, J.S., Nunes, F.F., Cunha, V.S., de La Cruz, M.H.C., Souza, V. *Development of a certified reference material for cachaça: an effective material for quality assurance*. *Accred Qual Assur*18:197–206, 2013. DOI 10.1007/s00769-013-0985-8.

Programa de Ensaio da Proficiência do Instituto Nacional de Metrologia, Qualidade e Tecnologia - PEP-Inmetro
Av. Nossa Senhora das Graças, 50 - Xerém - Duque de Caxias - RJ - Brasil CEP: 25250-020
Tel/Fax: +55 21 2679-9745 - www.inmetro.gov.br - E-mail: pep-inmetro@inmetro.gov.br