Final Report of Proficiency Testing of Gas Mixture Composition Analysis
7th Round - Carbon Monoxide in Nitrogen

Inmetro
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PEP-Inmetro

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Proficiency Testing of Gas Mixture Composition Analysis - 7th Round - Carbon Monoxide in Nitrogen

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1. Introduction

Within the framework of the PTB-SIM-COPANT-IAAC project "Promoting innovation in the green economy through the inclusion of quality infrastructure in Latin America and the Caribbean", a pilot project was launched to increase the reliability of atmospheric pollutant measurements in urban centers.

Under the leadership of the National Metrology Institutes (NMI) in Brazil and Mexico, Inmetro and CENAM, cooperation was initiated between NMI from different countries in Latin America and the Caribbean and the competent authorities for air quality monitoring. This cooperative activity foresees that in each country the NMI must establish cooperative contact with a local authority responsible for managing a network of atmospheric pollution measurement stations.

In order to strengthen the cooperation activity between the organisms, a Proficiency Testing was requested to Inmetro to measure the atmospheric component of carbon monoxide. With the implementation of this PT, coordinated by Inmetro, participants have the opportunity to perform their measurements with their routine methods and compare their results with the designated value of the certified gaseous reference material (CRM) of a national metrology institute (Inmetro).

This report presents the results of the Gas Mixture Composition Analysis Proficiency Testing - 7th round. This PT aimed to:

- Determine the performance of laboratories for the proposed test;
- Contribute to increasing confidence in the results of laboratory measurements;
- Contribute to the continuous improvement of the measurement techniques of each laboratory.

2. Materials and Methods

2.1. Test Item Preparation

Test items were prepared by Inmetro's Gas Analysis Laboratory (Lanag) in its own cylinder. The cylinder had a hydraulic volume of 5 L, contained the sample with an approximate initial pressure of 12000 kPa (120 bar), in the concentration range between 5 and 15 μmol/mol.

A DIN 477-1 (ABNT 218-2) cylinder connection and a Concoa double stage stainless steel pressure regulator with two pressure gauges and a ¼" OD outlet for the measuring line were supplied to the cylinder containing the sample tested.

2.2 Characterization, Homogeneity and Test Item Stability

The procedures for characterization and long-term stability studies were performed in accordance with ABNT NBR ISO 17034 [1]. The homogeneity study is not applicable because it is a single batch. It was verified that the batches are stable based on the monitoring of the stability study of the analyzed mixtures, the uncertainty arising from this stability study considered non-significant.

The cylinders of the test item were prepared specifically for this purpose. All measurements were taken at 21 ° C.

2.3 Statistical Analysis of Participants' Results

The z-score (z) statistical test was used for the performance evaluation of the participants, following the ABNT ISO / IEC 17043: 2011 [2]. For laboratories that also reported the measurement uncertainty of the result (Ui) and the coverage factor (k), which are optional, the Normalized Error (E_n) was also used to evaluate its performance. Both the Normalized Error (E_n) and the z-score are described in Annex B of ABNT NBR ISO / IEC 17043: 2011.

2.3.1. *z Score*

It represents a measure of the distance of the presented result by a specific laboratory in relation to the proficiency testing reference value and, therefore, serves to verify if the result of each participant's measurement is in conformity with the designated value. The z-index [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 average of the three measurements of the i^{th} participant;

X: is the designated value of this PT, which will be considered the certified value determined by the reference laboratory (Inmetro);

$\hat{\sigma}$: is the expected standard deviation calculated for this test by the Horwitz method.

The Horwitz deviation was calculated using the equation described below, as described in ISO13528:2015 [3].

$\hat{\sigma} = 0.02\ c^{0.8495}$.

Where the calculated *c* is equal to $c = 9.00503 \times 10^{-6}$.

E $\hat{\sigma}$ = 1.0348

The interpretation of the z-score value is described below:

$|z| \leq 2.0$ indicates "satisfactory" performance;

$2.0 < |z| < 3.0$ - indicates "questionable" performance;

$|z| \geq 3.0$ indicates " unsatisfactory" performance.

2.3.2. Normalized Error (*En*)

This parameter is used to verify if the measurement result of each participant is in conformity with the designated value, taking into account not only the results of the measurements, but also their respective uncertainties. The normalized error is calculated according to Equation 2.

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

Where:

y_i: is the average of the three measurements of the i^{th} participant;

y_{ref}: is the designated value of this PT, which will be considered the certified value determined by the reference laboratory (Inmetro);

U_{ref}: is the value of the expanded uncertainty of y_{ref} obtained by Inmetro;

U_i: value of the expanded uncertainty of y_i obtained by the i^{th} participant.

The interpretation of the value of (E_n) to evaluate the performance of each participant is described below:

$|E_n| \leq 1.0$ indicates "satisfactory" performance and generates no signal;

$|E_n| > 1.0$ indicates "unsatisfactory" performance and generates an action signal.

The results of the normalized error (E_n) and the z-index will be rounded to one decimal place.

3. Results and Discussion

3.1. Characterization, Homogeneity and Test Item Stability

Six (6) primary standard mixtures of carbon monoxide in nitrogen according to ISO 6142:2015 [4] were produced gravimetrically, all in the same period, and then analyzed for the analytical verification

step by gas chromatography (GC) with a flame ionization detector (FID) coupled to a methanizer catalyst. The molar fraction of carbon monoxide used in the characterization of the reference value was the gravimetric concentration obtained from the primary process. The estimated uncertainties for each mixture were the combined standard uncertainties of the gravimetric process and the estimated calibration curve of the analytical verification step, according to ISO 6143:2001 [5]. The final uncertainty presented is the expanded uncertainty (U), with a coverage factor (*k*) equal to 2.

For this type of material, the homogeneity study is not applicable, since each item is produced separately. It was verified that the batches are stable based on the monitoring of the stability study of the analyzed mixtures, the uncertainty arising from this stability study considered non-significant.

Table 1 presents the mixtures composition sent for each participant country.

Table 1 - Characteristics of the reference mixtures.

Manufacturer	Cylinder number	Reference value Lanag µmol/mol	Expanded uncertainty Lanag µmol/mol
Inmetro	D543770	9.009	0.180 (k = 2)
Inmetro	D543737	9.007	0.180 (k = 2)
Inmetro	D958423	9.005	0.180 (k = 2)
Inmetro	D543661	8.970	0.180 (k = 2)
Inmetro	D543669	9.006	0.180 (k = 2)
Inmetro	D248644	9.004	0.180 (k = 2)

3.2. Participants' Results

3.2.1. Methods Used by Participants

PT participants should use their routine method of measurement. For the PT, each participant should perform 3 (three) sample readings for each 3 independent measurements, disconnecting the measuring line where the sample is attached to the equipment (without removing the regulator) and reconnecting it to the next measurement, not performing the readings continuously during the 3 measurements. A total of at most 3 system purges including cylinder connection, pressure regulator and measuring line was recommended.

The total consumption of approximately 1500 kPa (15 bar) per participant was recommended for the accomplishment of the 3 measurements.

Measurements were monitored at all stations by means of a testimony from the NMIs of the participating countries.

3.2.2. Reported Results by Participants

Table 2 shows the results obtained from the average value of the 9 (nine) measurements of each of the 14 (fourteen) participants who reported the measured carbon monoxide concentration. Each laboratory is identified only by the final numbering of its identification code.

Table 2 – Participants' Results.

Laboratory code	Measurements average (μmol/mol)
011	8.93
019	9.42
064	9.94
054	9.59
083	8.29
015	9.02
006	8.96
075	8.81
063	9.00
055	7.85
007	9.40
089	8.97
100	9.57
095	10.09

Table 3 shows the mean values of the 2 (two) single participants who reported the concentration measured with the reported uncertainty estimation and coverage factor.

Table 3 – Participants' results that reported the measurement uncertainty.

Laboratory code	Measurements average (µmol/mol)	Expanded uncertainty (µmol/mol)	Coverage factor (k)
015	9.02	0.17	2
055	7.85	0.17	2

3.2.3. Participants' Performance Evaluation

The z-score (z) statistical test was used for the performance evaluation of the participants and following the ABNT ISO / IEC 17043:2011 [2]. For laboratories that also reported the result measurement uncertainty (U_i) and the coverage factor (k), which were optional, the Normalized Error (E_n) was also used to evaluate its performance.

3.2.3.1. *z* Score

Table 4 and figure 1 present the z-score results, for participants who had their performances evaluated through this index.

Table 4 – *z*-score results for the Carbon Monoxide test item measurement.

Laboratory code	*z*-score
011	-0.07
019	0.40
064	0.90
054	0.57
083	-0.69
015	0.01
006	-0.01
075	-0.16
063	0.03
055	-1.12
007	0.38
089	-0.04
100	0.55
095	1.05

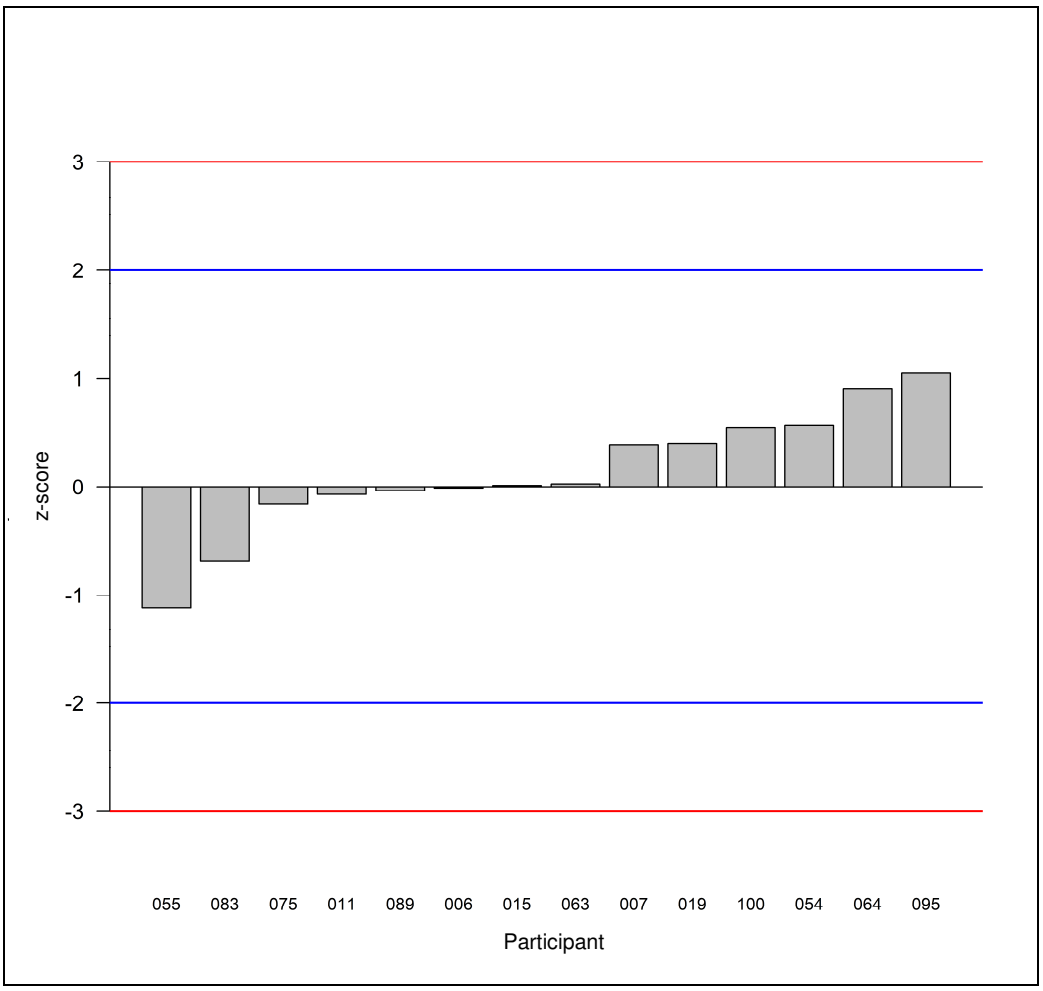

Figure 1 - z-score chart for test item Carbon Monoxide measurement

Through the graph analysis of the z-score, it can be observed that:

- No participant presented an unsatisfactory result, that is, $|z| \geq 3$;
- No participant presented questionable results, that is, $2.0 < |z| < 3.0$; and
- All participants (14 stations) presented satisfactory results, i.e., $|z| \leq 2.0$.

3.2.3.2. Normalized Error

Table 5 and figure 2 present the normalized error results for participants who had reported the measurement uncertainty of the result (U_i) and the coverage factor (k).

Table 5 - Results of the normalized error regarding the test item Carbon Monoxide measurement.

Laboratory code	E_n
015	0.05
055	-2.93

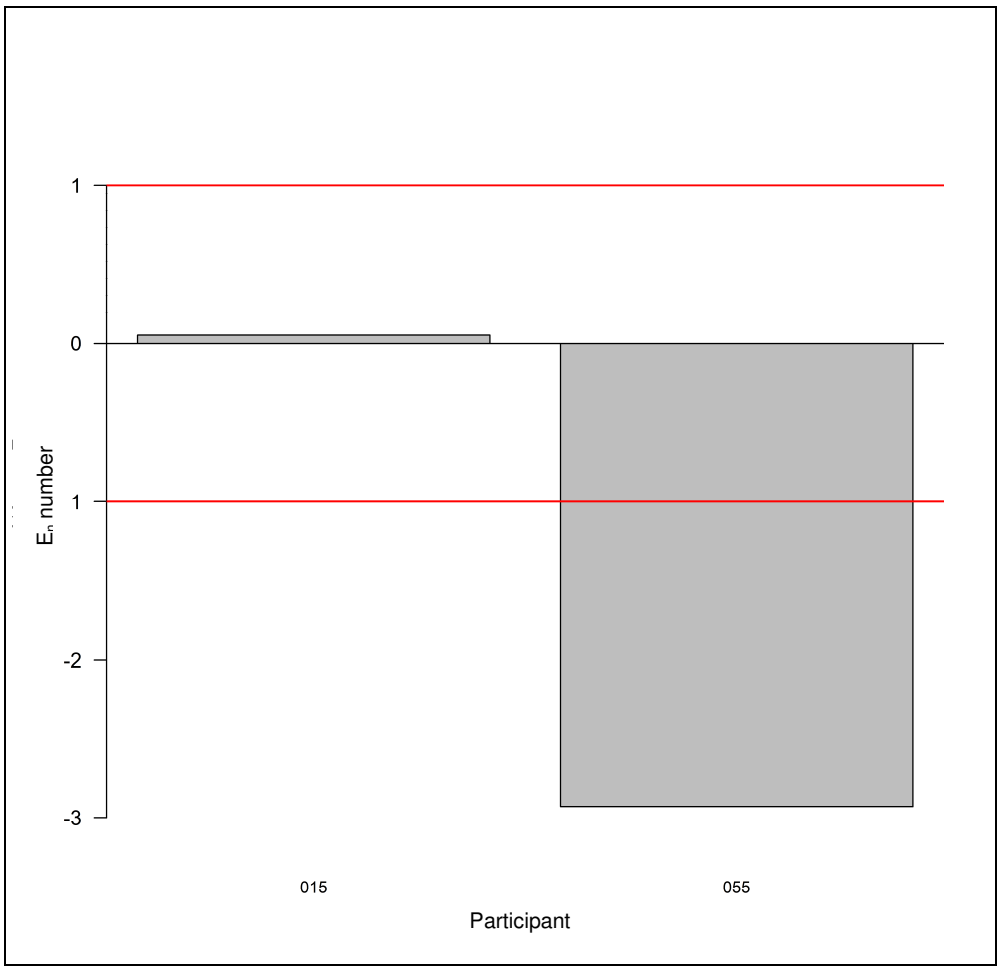

Figure 2 - Normalized error chart for the test item Carbon Monoxide measurement.

By analyzing the graphs of normalized error, we can observe that:

- One participant presented a satisfactory result, i.e. $|En| \leq 1.0$;
- Participant 055 had an unsatisfactory result ($|En| \geq 1$).

4. Confidenciality

Each participant was identified by individual code that is known only by the participant itself and by the coordination of the PT. The participant received, via e-mail, his identification code corresponding to its participation in the PT. This code was used as identification of the participant in the completion of the results record. The results can be used in works and publications by Inmetro respecting the confidentiality of each participant.

As established in paragraph 4.10.4 of ABNT ISO/IEC 17043:2011, in exceptional circumstances, a regulatory authority may request the results of the PT from the provider.

5. Conclusions

All participants presented satisfactory results in the PT through the z-score performance analysis. The objective of determining the performance of the laboratories for the proposed test was reached.

Only one participant presented an unsatisfactory result for the evaluation according to the normalized error. However, this same participant obtained a satisfactory result in the evaluation of the z-score. Therefore, we recommend that the participant assess its uncertainty in the presentation of measurement results.

The establishment of corrective actions and the continuous participation in proficiency testings of this nature are tools of great contribution for the improvement of the measurements made by the participants.

Finally, it is important to highlight the importance of laboratories participation in PT exercises, as it is a useful tool to monitor the routine analysis procedures and to evaluate the results of their measurements, making them able to perform measurements with greater reliability

6. Participants

Eleven participants registered to the 7th round of the Gas Mixture Test with a total of 20 stations, with a maximum of 5 stations per participant allowed.

Two participants did not send any results (001 and 077) and reported their withdrawal to the PT coordination. Other 4 participants did not send at least one result (022, 026, 096 and 098).

Results were reported by 14 stations of 9 participants (006, 007, 011, 015, 019, 054, 055, 063, 064, 075, 083, 089, 095, 100).

Participation in this PT was composed by bodies that carry out air quality measurements invited by the National Metrology Institutes of Argentina (Inti), Brazil (Inmetro), Mexico (Cenam), Trinidad and Tobago (TTBS), Costa Rica (Lacomet) and Guatemala (delegated research institute).

The list of participants who sent the results to the coordination of this PT is presented in Table 6. It is important to note that the numbering of the table is only indicative of the number of participants in the PT and is not, in any case, associated with its identification in the presentation of the results.

Table 6 - Participants (this table only lists the participants who had their results analyzed and published in the report)

	Organization
1.	Agencia de Protección Ambiental- Dirección General de Control Ambiental- G.O. de Determinaciones Ambientales y Laboratorio - Gobierno de la Ciudad de Buenos Aires - Argentina
2.	Centro de Monitoreo de La Calidad Del Aire Del Estado de Querétaro Universidad Autonoma del Estado de Querétaro – UAQ - México
3.	Companhia Ambiental do Estado de São Paulo – CETESB - Brasil
4.	Environmental Management Authority – Trinidad e Tobago
5.	Instituto Estadual do Ambiente – INEA - Brasil
6.	Instituto Nacional de Ecología y Cambio Climático - México
7.	Laboratorio de Análisis Ambiental. Universidad Nacional de Costa Rica – Costa Rica
8.	Lab. Análisis Instrumental – Facultad Ingeniería – Universidad Nacional de Cuyo - Argentina
9.	Laboratorio de Monitoreo del Aire, Facultad de Ciencias Químicas y Farmacia. Universidad de San Carlos de Guatemala –USAC - Guatemala

Total participants: 9.

7. References

[1] ABNT NBR ISO 17034, Requisitos gerais para a competência de produtores de material de referência, 1ª Edição, 2017.

[2] ABNT NBR ISO/IEC 17043, Avaliação de conformidade - Requisitos gerais para ensaios de proficiência, ABNT, Rio de Janeiro, 2011.

[3] ISO 13528, Statistical methods for use in proficiency testing by interlaboratory comparison, ISO, Geneva, 2015.

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

[5] ISO 6143, Gas analysis -- Comparison methods for determining and checking the composition of calibration gas mixtures, 2001.

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