Participation of Inmetro in the Regional Comparison of Natural Gas Measurement within the Inter-American Metrology System

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Abstract. Natural gas is formed by light hydrocarbons, which are often associated with CO_2, N_2, O_2, CO, H_2, H_2S and noble gases. Among hydrocarbons, methane (CH_4) represents the main constituent of natural gas, followed by ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), pentane (C_5H_{12}) and their respective isomers. Natural gas is mainly used in electricity generation (thermoelectric plants) and industrial consumption. In the generation of electricity, it is favoured by good energy efficiency and lower CO2 emission rate. Inmetro is one of the Metrology institutes of South America. NMIs have the mission to establish globally uniform measurement systems for important gases and to support energy priorities, as well as to ensure reliable measurements for the country's production chain. Carrying out regional comparisons is essential to ensure metrological traceability in the production chain of their countries. Inmetro has participated in the last regional key-comparison of natural gas coordinated under the auspices of the inter-American metrology system, SIM-QM-S5, and this work presents Inmetro´s results.

1. Introduction

Natural gas (NG) is a fossil fuel, essentially composed of methane hydrocarbons (CH_4), with levels above 70%, it is used mainly in electric generation (thermoelectric plants) and industrial consumption. In the generation of electricity, it is favoured by good energy efficiency and a lower rate of carbon dioxide emissions, which makes its use less harmful to the environment compared to other fossil fuels. Its economic value per unit volume or mass is mainly determined by its calorific value. The according to ISO-6976[1] calorific value is the amount of heat that is released by the complete combustion with oxygen of a known quantity of fuel gas under specific conditions and depends on the composition of the gas. The calculation of the price of natural gas is based on the energy consumed, which is the product of the volume by the calorific value. To calculate the calorific value of natural gas, all the components present in this energy source must be determined. The main method for determining the components of natural gas used in the calculation of the calorific value of the gas is the gas chromatography (GC) technique. Therefore, this chromatographic technique is used in the fiscal measurements involved in the commercialization of natural gas in the country. To assess the quality of

NG are necessary: accurate flow and correct calculation of energy, reliable and traceable measurement methods and reference materials (BIPM, 2015). To obtain traceable measurement results, these methods and reference materials must be supported by metrology.

Metrology is fundamental in the development of reliable measurement methods that are traceable to the International System of Units. To support participating Metrology Institutes in the South American region to develop technical capacity and apply for their results to the CIPM MRA to be (peer-reviewed) and obtain international recognition of their calibration and measurement capability (CMCs) from the institutes, this supplementary comparison SIM.QM-S5 in natural gas of components of NG up to n-hexane was performed in the Interamerican Metrology System (SIM) region. This additional comparison of natural gas in the SIM was carried out within the scope of the triangular cooperation Project "Natural Gas in Latin America and the Caribbean" planned since September 2012, supported by the technical cooperation of the PTB. This comparison involves synthetic natural gas mixtures containing nitrogen, carbon dioxide and alkanes up to n-hexane with a total of 10 components. Among the participating laboratories in the SIM region, only two NMIs have existing CMCs for natural gas mixtures: CENAM and INMETRO.

The importance of demonstrating natural gas metrologically assessment is because measurement of the composition of natural gas mixtures is commonly used for calculating their calorific value and other natural gas properties, and natural gas prices are based on calorific value.

2. Metodologia

2.1 Participants

Table 1 lists the participants in this comparison.

Table 1. List of participants

Acronym	Country	Institute
INACAL	Peru	Instituto Nacional de Calidad
INTI	Argentina	Instituto Nacional de Tecnología Industrial
INM	Colombia	Instituto Nacional de Metrología
INMETRO	Brazil	Instituto Nacional de Metrología, Qualidade e Tecnologia
IBMETRO	Bolivia	Instituto Boliviano de Metrología
CENAM	Mexico	Centro Nacional de Metrología
KRISS	Republic of Korea	Korea Research Institute of Standards and Science

2.2 Measurement standards

A set of synthetic mixtures of natural gas under pressure contained in aluminum cylinders were prepared by an external party.

Table 2 shows the nominal composition of the mixtures (expressed as amount of substance fraction).

Table 2. Nominal composition of the mixture

Component	Value / $cmol \cdot mol^{-1}$
n-hexane	0.04
n-pentane	0.04
i-pentane	0.04
n-butane	0.025
i-butane	0.025
propane	2
ethane	8
carbon dioxide	2
nitrogen	4
methane	83.83

The mixtures were verified, and value assigned prior to shipment to the participant NMIs using the specially configured natural gas GC-FID/TCD, Wasson 326-D0 with an Agilent 6890. After the completion of measurements by participants, the mixtures were re-analyzed for stability.

The quantifications were realized by interpolation of a calibration curve using 5 primary reference materials gravimetrically prepared in CENAM according to ISO-6142 [2]. The sample and standards were analyzed at least three times each with six replicates. The first measurement of each cylinder has been removed to render five replicates. The ISO-6143 [3] data analysis procedure was used to evaluate the data.

Each cylinder had its own reference values and associated expanded uncertainties.

2.3 Measurement protocol

Participants were requested to use their normal procedure for the measurement of the composition of the gas mixtures. The participants were asked to perform at least three measurements, on different days with independent calibrations.

The participants were also requested to describe their methods of measurement, and the models used for evaluating the measurement uncertainty. The report of the evaluation of measurement uncertainty should at least address which components have been included in the evaluation, and what their quantitative impact is on the uncertainty of the reported results, i. e. the uncertainty budget.

2.4 Measurement equation

The reference value used in this comparison was determined to be the analytical value of the initial verification before shipment of each cylinder measured by CENAM). The estimation of the uncertainty associated with this value included the initial verification uncertainty based on ISO-6143 that includes the propagation of the measurement model uncertainty, sample measurement signals and the primary gas mixtures from CENAM, plus a tentative bias factor for each component calculated using the difference between the value assigned by the KRISS and by CENAM to the same cylinder. See later in this report the stability of travelling standards as support of these decisions.

$$x_{\mathrm{i,ref}} = x_{\mathrm{i,ver}} + x_{\mathrm{i,stab}} + b_{\mathrm{i}}$$

Where

$x_{i,ref}$ is the reference value of mixture i, (cmol/mol or µmol/mol)

$x_{i,ver}$ is the amount of substance fraction from verification before shipment of cylinders to participants, (cmol/mol or µmol/mol)

$x_{i,stab}$ is amount of substance fraction from the stability after return of cylinders, (cmol/mol or µmol/mol)

b_i is an effect uncertainty component due to the differences between CENAM and KRISS values, as consequence of the lower performance of the measurement system presented at CENAM (see stability of travelling standards).

Long-term stability is considered

$$\Delta x_{i,\text{stab}} = 0$$

Summarizing, the model of the reference value reduces to

$$x_{i,ref} = x_{i,ver}$$

2.5 Measurement methods

A summary of the Inmetro calibration methods and metrological traceability is given in Table 3:

Table 3. Summary of calibration methods and metrological traceability.

Laboratory	**Date of measurement**	**Calibration**	**Traceability**	**Measurement technique**
INMETRO	20 oct 2016 and 01, 07, 17,22, 28 nov 2016	Calibration curves with 5 primary standards and 6 primary standards for the measurement of propane. Polynomial degree of 2.	VSL/NPL/ INMETRO	GC-TCD/FID

2.6 Supported CMC claims

The results of this comparison can be used to support CMC claims for natural gas mixtures containing n-hexane, n-pentane, i-pentane, n-butane, i-butane, propane, ethane, methane, carbon dioxide and nitrogen within the following amount of substance fraction ranges ('how far the light shines' (HFTLS) of table 4.

Table 4. Nominal amount of substance fraction

I.	Component	II.	Amount-of-substance fractions / $cmol \cdot mol^{-1}$
III.	n-hexane	IV.	0.02 – 0.1
V.	n-pentane	VI.	0.02 – 0.1
VII.	i-pentane	VIII.	0.02 – 0.1
IX.	n-butane	X.	0.02 – 0.5
XI.	i-butane	XII.	0.02 – 0.1
XIII.	propane	XIV.	0.2 - 4
XV.	ethane	XVI.	1 - 14
XVII.	carbon dioxide	XVIII.	0.5 - 4
XIX.	nitrogen	XX.	1 - 16
XXI.	methane	XXII.	60 - 98

3 Results from participants

Participant performance is shown in the figures.

3.1Degrees of equivalence

A degree of equivalence (D_i) in the comparison is determined by the following equation:

$$\Delta x_i = D_i = x_{i,lab} - x_{i,ref}$$

Where $x_{i,lab}$ is the reported value by each participant and $x_{i,ref}$ is the reference value.

The standard uncertainty of the difference is determined by the following equation.

$$u_{D_i}^2 = u_{i.lab}^2 + u_{i,ref}^2$$

Where $u_{i,lab}$ is the standard uncertainty of $x_{i,lab}$ and $u_{i,lab}$ is the uncertainty of of $x_{i,ref}$.
The uncertainty of the degree of equivalence (D) is expressed as the expanded uncertainty of the difference at approximately 95 % level of confidence with a coverage factor (k) of 2.
In Fig. 1 to 9, the degrees of equivalence for all participating laboratories are given relative to the reference value. The uncertainties are given as 95 % level of confidence. For the evaluation of uncertainty of the degrees of equivalence, the normal distribution has been assumed, and a coverage factor $\boldsymbol{k} = \mathbf{2}$ was used. For obtaining the standard uncertainty of the laboratory results, the expanded uncertainty provided by the laboratories (stated at a 95 % level of confidence) from the laboratory was divided by the reported coverage factor.

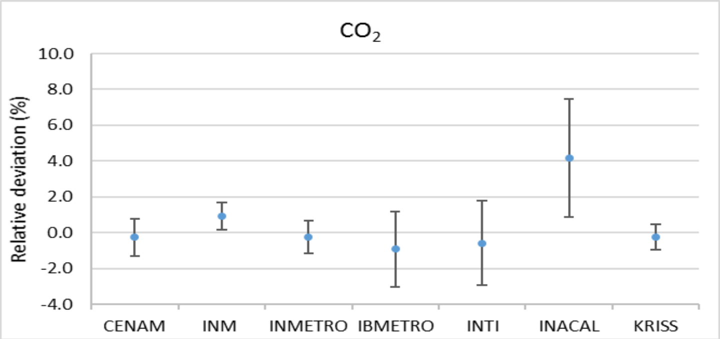

Figure 1. Degree of equivalence for carbon dioxide

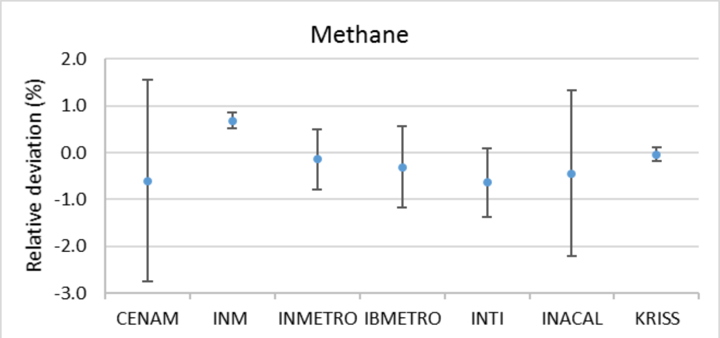

Figure 2. Degree of equivalence for methane

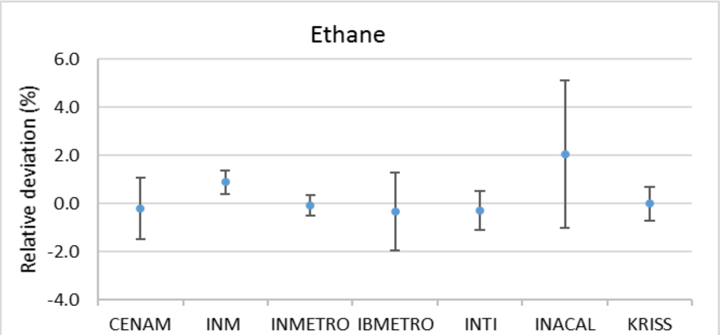

Figure 3. Degree of equivalence for ethane

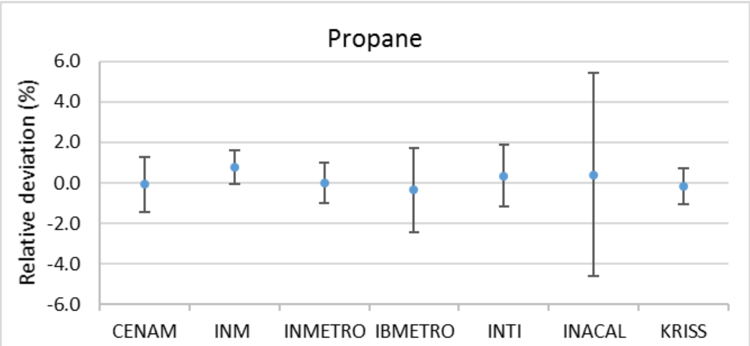

Figure 4. Degree of equivalence for propane

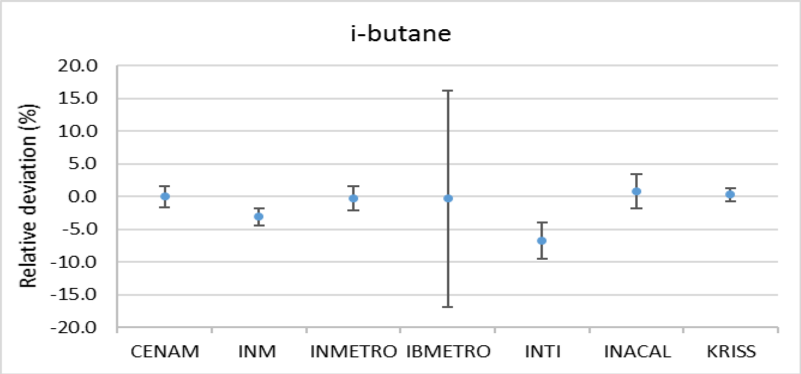

Figure 5. Degree of equivalence for i-butane

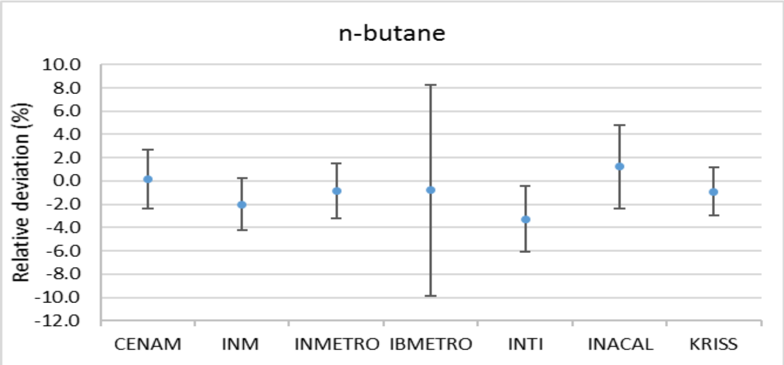

Figure 6. Degree of equivalence for n-butane

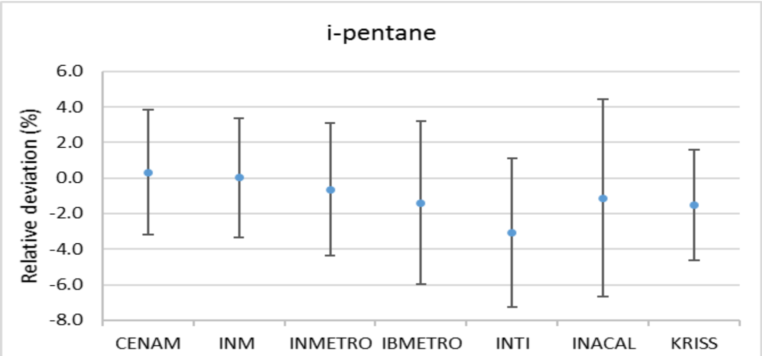

Figure 7. Degree of equivalence for i-pentane

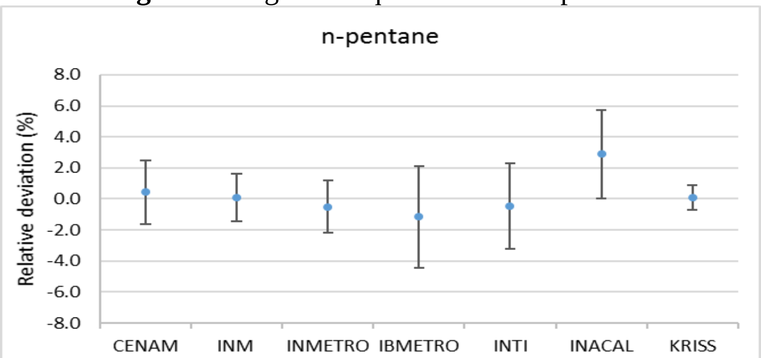

Figure 8. Degree of equivalence for n-pentane

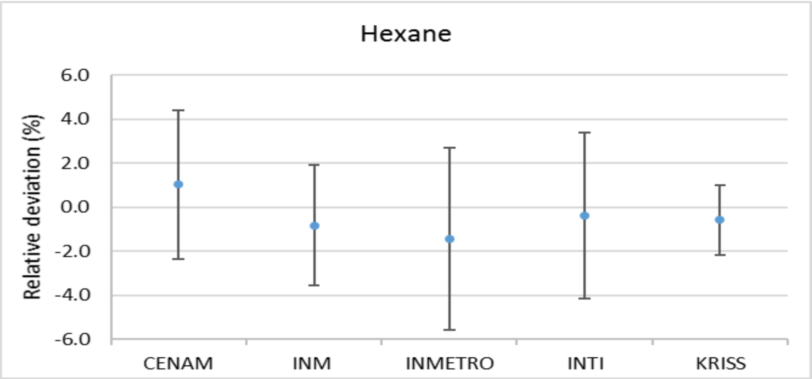

Figure 9. Degree of equivalence for n-hexane

Conclusions

According to the results presented at the figures above, the results obtained by Inmetro were successful for all 09 (nine) compounds of the natural gas sample part of the SIM-QM-S5. The uncertainties presented were under the same level from the coordinated laboratory and also in the same level from Inmetro´s CMCs published and available in the KCDB data base from the BIPM webpage, which means that Inmetro´s measurement capacity for natural gas analysis is still satisfactory.

Some participating laboratories did not consider normalizing their results and did not apply all appropriate corrections. For the reference value, all normalized quantity fractions were used and uncertainties propagated accordingly. The inexperience of some of the participating laboratories in participating in high-level comparisons may also have continued these greater uncertainties. The comparison results are, however, an official starting point to support the participating Metrology Institutes in the South American region to develop technical capacity and apply their results to the CIPM MRA to obtain international recognition (CMC) and to disseminate traceability well such as quality and reliability in its production chain.

References

[1] ISO ISO 6976:2016 Natural gas — Calculation of calorific values, density, relative density and Wobbe indices from composition.
[2] ISO 6142:2015 - Gas analysis — Preparation of calibration gas mixtures — Gravimetric method.
[3] ISO 6143:2001 Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures.
[4] ISO 16664:2004 Gas analysis — Handling of calibration gases and gas mixtures — Guidelines.
[5] https://www.bipm.org/en/gas-metrology.