Interlaboratory Comparison to determine the majority composition of Biomethane

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Abstract. With the energy transition, many studies have been carried out on biogas, as it is considered a renewable energy source. For its use as fuel, a purification process is necessary, becoming biomethane, with a higher concentration of methane and calorific value. The quality control of biomethane from landfills intended different uses is established by ANP Resolution No. 886 of 2022. To comply with this Resolution, it is necessary to correctly measure the composition of the components using high-precision analytical methods. Therefore, the analytical methods were adapted so that they can determine the composition of the major components present in biomethane. A collaborative interlaboratory comparison study was conducted in order to improve and compare measurements composition results for mixtures of biomethane with major components (methane around 90%mol/mol and carbon dioxide around 1.75%mol/mol) with the purpose to assess technical competence of the participants. The study aimed to provide evidence for validated methods using alternative analytical techniques for the proposed measurement using traceable standards, and verify whether the results are in accordance with the parameters reported in the resolution. Through the results, it was possible to conclude that the methods are suitable for their intended use for methane, but for carbon dioxide, there were divergences from the reference value when it was used the portable sensor analysers.

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1 Introduction

The increase in energy consumption, together with the limitation of fossil resources, brings to light the need to reduce emissions of pollutants into the atmosphere. In this sense, the debate on the preservation of natural resources, the development of stricter environmental legislation, and even the establishment of global treatments, were responsible for the growth of sustainable appeal. Currently, the use of renewable sources and the diversification of the national energy matrix have become the subject of debates and the focus of research [1],[2]-[3].

In recent years, many studies on the use of renewable energy sources for power generation are being carried out. Biogas is considered a renewable energy source and has gained interest mainly because it is considered low pollutant [4].

The product generated from raw biogas consists of methane, carbon dioxide and other gases such as oxygen, nitrogen, hydrocarbons and siloxanes. It can be produced from agricultural waste, urban solid waste contained in sanitary landfills or from sewage in sewage treatment plants, being, in all cases, under the action of bacteria by anaerobic digestion. After stages of purification of biogas, biomethane is the result, a renewable energy source with a high methane content in its composition [5].

The production and use of biomethane in the world has been growing over the years. It is important to emphasize that several measures to encourage the production of biomethane were launched in Brazil [6].

1.1 Biogas and biomethane scenario in Brazil

The Brazilian biogas market for energy applications has expanded significantly. Brazil has 1,365 biogas production plants, and between 2022 and 2023, 338 new units were implemented, representing a 32% growth in the total number of plants and a 21% increase in biogas volume, reaching 4.15 billion Nm³/year. Regarding its application, 86% is destined for electricity generation, 3% for biomethane, and 9% for thermal energy. The plants that started operating in 2024 have an average installed capacity 54% greater than those that started operating in 2023 [7].

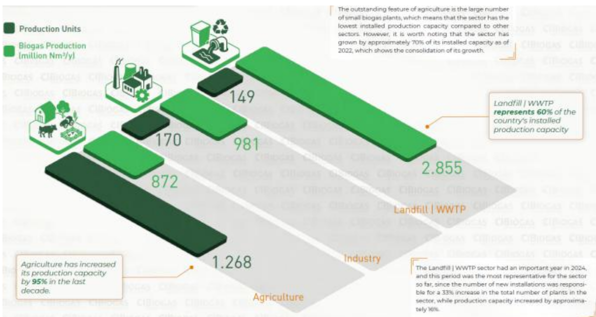

Fig. 1. Biogas origin (source: CIBiogas, 2024)

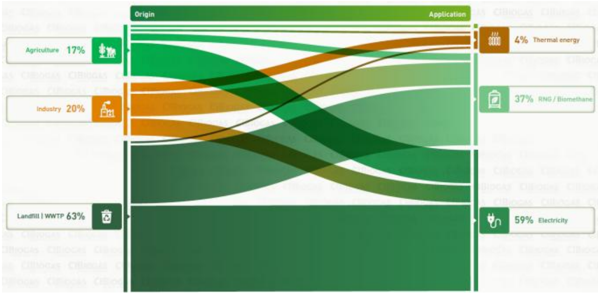

Fig. 2. Biogas relation between origin and demand (source: CIBiogas, 2024)

In order to guarantee the quality of biomethane, the Brazilian Oil and Gas Agency (Agência Nacional de Petróleo, Gás Natural e Biocombustíveis -ANP) through Resolution No. 886 of September 29, 2022, established the criteria for approval of quality control and the specification of this energy source from landfills and sewage treatment stations for vehicular use and residential, industrial and commercial installations to be sold throughout the Brazilian territory [8].

However, complying with industry regulatory specifications can prove challenging for laboratories, as there is no specific analytical method to determine the composition of biomethane, suggesting the use of methods described in standards for natural gas analysis, such as: NBR 14903, ASTM D 1945, and ISO 6974 [9]-[11]. Nevertheless, the composition of these gases is not similar to biomethane gas, nor are the concentration limits. Despite this, the analytical methodologies described in the current resolutions, similar to those established for natural gas, with additional parameters such as halogenated compounds and siloxanes, can represent technical and economic challenges for medium and small-scale producers, due to the need for high-cost equipment and specialized labor. Furthermore, there is a limitation in the number of national laboratories capable of performing these analyses in Brazil. Currently, there are no laboratories accredited for biomethane testing; there is only one accredited laboratory for natural gas, which can partially perform some methodologies.

Therefore, as biomass represents almost one-third of Brazil's domestic energy supply, giving Brazil the cleanest energy matrix, the application of gas metrology is essential to ensure reliable and competitive quality control results for this energy input [12].

1.2 The importance of scientific metrology in biomethane regulatory resolutions

In this context, pilot-scale laboratory applied research is necessary to demonstrate the possibility of adjustments to the analytical parameters of the aforementioned resolutions, in relation to both quality requirements and the use of simpler and more agile alternative methodologies that guarantee the required technical safety. This regulatory improvement is essential to consolidate biomethane as a strategic fuel, boosting investments and strengthening the low-carbon economy in Brazil.

Inmetro, the Brazilian Metrology Institute (Inmetro), through its Gas Analysis Laboratory (Lanag), develops and validates analytical methodologies in the areas of energy and environmental control, being the main entity responsible for disseminating metrological knowledge of gases in Brazil. It produces certified reference materials, works on the transfer of metrological traceability, and coordinates laboratory comparison programs. It stands out for its highly complex equipment park, accessible to external users, and operates in accordance with the ISO 17025 and ISO 17034 standards [13],[14]. The experience in developing traceability service and products for biogas and biomethane measurements will drive technical and scientific advances, market growth, professional qualification, and the transfer of metrological knowledge, contributing to national development and increasing the reliability of measurements.

The study presented in this paper aims to ensure the reliability of research through rigorous evaluation of performance parameters, complying with current regulatory resolutions and proposing new, more agile and effective analytical methodologies. These methodologies will serve as a basis for proposing regulatory changes.

1.2.1 Biogas Key-comparison

One of the tools for control and guarantee of the validity of analytical results is the use of certified reference materials (CRMs), which are essential for validation of methods, as well as in the calibration of instruments ensuring the metrological traceability, reliability and comparability of results in order to guarantee the quality of measurements carried out. In order to evaluate the confidence of these standards, National Metrology Institutes, including Inmetro, are required to participate in international key-comparisons (KC). The first biogas KC, CCQM-K112, was conducted in 2020, with the following amount of fraction of 7 components gravimetrically prepared (Fig. 3).

Component	Amount fraction x (cmol mol^{-1})
Methane	40 – 56
Carbon dioxide	36 – 42
Nitrogen	12 – 16
Hydrogen	0.8 – 1.2
Oxygen	0.3 – 0.6
Ethane	0.02 – 0.08
Propane	0.005 – 0.020

Fig. 3. Specification of standards

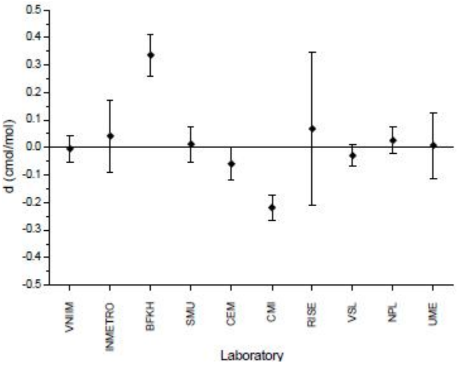

Fig. 4. Degree-of-equivalence for Methane

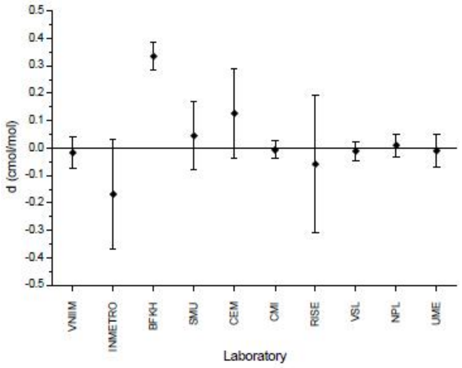

Fig. 5. Degree-of-equivalence for Carbon dioxide

Inmetro´s results were satisfactory for all biogas components, according to results presented for some of the main components of biogas at Figure 4 and 5 [15].

1.2.2 Biomethane collaborative interlaboratory comparison study

An Interlaboratory Comparison (IC) aims to compare measurement results obtained under similar conditions from two or more laboratories and to evaluate the technical competence of the participants. Generally, it assesses laboratory performance, highlights problems related to testing procedures, and enables corrective and/or preventive actions to be taken, with the specific objective to contribute to the improvement of measurements focused on the renewable energy sector.

A collaborative interlaboratory comparison study was conducted in order to improve and compare measurements composition results for mixtures of biomethane with major components (methane around 90% mol/mol and carbon dioxide around 1.75% mol/mol) with the purpose to assess technical competence of the participants.

That way, specific methods for determining the composition of biomethane will make it possible to properly verify the composition of the fuel, making it of high quality, that is, high calorific value, generating more energy. The methodology will also contribute to generating benefits for industrial development, the environment, the economy and society.

2 Methods and Development

Ten cylinders containing synthetic mixtures of methane (approximately 90 mol/mol concentration) and carbon dioxide (approximately 1.75 mol/mol concentration)

were available. Inmetro was responsible for the reference value of the samples and data compilation, through the calibration of each gravimetric standard of biomethane acquired from an accredited body industry against Inmetro´s own PRM. The analytical technique used by Inmetro in calibrating the standards was micro GC-TCD (model Agilent 490), according to ISO 6143:2024 [16]. Inmetro´s certified reference material from biomethane were produce according to ISO 6142:2001 [17].
The participants used their own analytical methodology (Table 1) to determine the majority composition of biomethane. This study was conducted in order to provide evidence for the development of national standards using alternative analytical techniques for the proposed measurement.

Table 1. Analythical techniques.

Lab ID	Technique
1	GC-TCD
2	GC-TCD
3	Micro GC-TCD
4	Micro GC-TCD
5	GC-TCD
6	NDIR
7	NDIR
8	Portable analyser - Electrochemical sensor
9	Portable analyser - Electrochemical sensor

The tolerance limit for methane and carbon dioxide was established following National ISO Standard for natural gas [9], which states that for components with concentrations of 1 to 10 %mol/mol, the limit is 10%, and for components with concentrations of 50 to 100 %mol/mol, it is 3%. We have decided to use half of the tolerance limit from the Standard.

3 Results and discussion

The results of the comparative study of analytical methodologies are summarized in Tables 2 and 3, followed by the graphical results showing the degrees of equivalence (Figures 6 and 7) [18].

Table 2. Methane results.

	Inmetro/ Methane (%mol/mol)	Lab/ Methane (%mol/mol)	Absolute deviation
Lab 1	90,59	90,97	0,38
Lab 2	90,65	90,46	-0,19
Lab 3	90,65	90,97	0,32
Lab 4	90,71	91,98	1,27
Lab 5	90,55	90,79	0,24
Lab 6	90,54	90,53	-0,01
Lab 7	90,66	91,10	0,44
Lab 8	90,62	90,86	0,24
Lab 9	90,07	89,91	-0,16

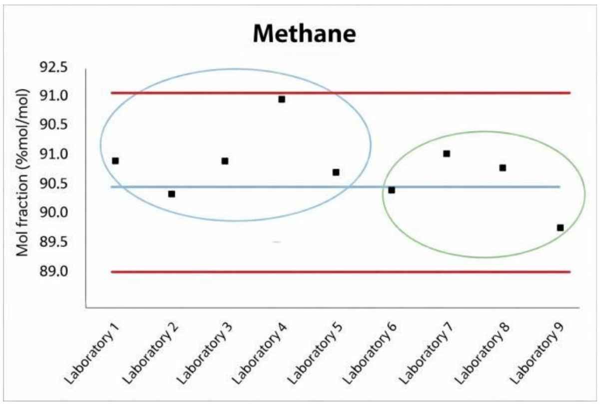

Fig. 6. Degree-of-equivalence for Methane

The results of the comparison of methodologies for the component methane, whose concentration is around 90 %mol/mol, proved satisfactory. All laboratories (Fig. 6) obtained satisfactory performance, both using the gas chromatography analytical technique and the portable and fixed analyzer techniques.

Table 3. Carbon dioxide results.

	Inmetro/ CO_2 (% mol/mol)	Lab/ CO_2 (%mol/mol)	Absolute deviation
Lab1	1,75	1,76	0,01
Lab 2	1,76	1,74	-0,02
Lab 3	1,75	1,68	-0,07
Lab 4	1,75	1,73	-0,02
Lab 5	1,76	1,75	-0,01
Lab 6	1,75	1,80	0,05
Lab 7	1,74	1,70	-0,04
Lab 8	1,75	1,56	-0,19
Lab 9	1,71	1,91	0,20

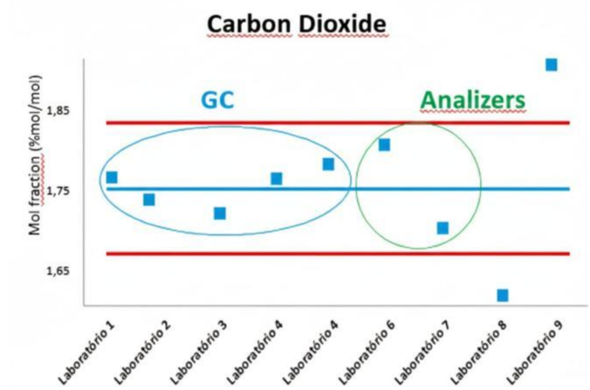

Fig. 7. Degree-of-equivalence for Carbon dioxide

The results of the comparison of methodologies for the component Carbon dioxide, whose concentration is around 1.75 %mol/mol, showed satisfactory performance for all 05 laboratories that used the gas chromatography analysis technique. For the laboratories that used the fixed analyzer technique, 02 laboratories had satisfactory performance, while the 02 laboratories that used the portable analyzer technique had unsatisfactory performance.
The reason for this could be evaluated as:

- Absence of a certified reference material (CRM) close to the sample measurement range during instrument calibration;
- Use of expired CRMs or CRMs from manufacturers without recognized competence;
- Lack of experience in performing auto zero gas monitoring.

4 Conclusion

The use of biomethane aims to promote an energy transition aligned with Brazil's potential and competitive advantages, consolidating the country as a protagonist in the national and international energy scenario.
All results for methane were satisfactory. However, the participants that measures carbon dioxide using portable analyzers had unsatisfactory results, which can be explained by misuse or even lack of certified reference materials in the calibration of the sensors.
A proficiency test is being organized in order to evaluate a major number of laboratories including the estimative of the uncertainty of the measurements with the use of Inmetro´s primary reference gas mixtures of biomethane.

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References

1. International energy agency, Outlook for biogas and biomethane - a global geospatial assessment, IEA, March 2025. Online [Accessed January 16, 2026]
2. Programa de Energia para o Brasil (PEB), Biogás no Brasil - Potencial de descarbonização a curto prazo, Technical report 01-2022. São Paulo: Instituto 17, 2022. Online [Accessed January 16, 2026] [In Portuguese].
3. World BiogasAssociation-WBA, GlobalPotential of Biogas, 2019.
4. Fernandes, G.; Mariani, L. O alto potencial de produção e uso fará do biogás a próxima fronteira da energia renovável no Brasil? FGV Energia, 2019.
5. Van der Veen, A. M. H.; Brown, A. S.; Li, J.; Murugan, A.; Heinonen, M.; Haloua, F.; Arrhenius, K. Measurement requirements for biogas specifications. EDP Sciences, 2015. DOI: https://doi.org/10.1051/metrology/20150008006
6. Government of Brazil. Incentive to the production and sustainable use of biomethane, 2022. [Accessed August 5, 2022] [In Portuguese].
7. Centro Internacional de Energias Renováveis – Biogás Panorama do Biogás no Brasil 2024. CIBiogás (Brasil) Relatório Técnico nº 001/2024 – Foz do Iguaçu, CIBiogás, 2024. Online [Accessed January 16, 2026] [In Portuguese].
8. National Agency of Petroleum, Natural Gas and Biofuels (ANP), Biomethane, 2017. [Accessed April 7, 2021] [In Portuguese].
9. ABNT NBR 14903:2014 - Gás natural – Determinação da composição química por cromatografia em fase gasosa.
10. ASTM D1945-14:2019 - Standard Test Method for Analysis of Natural Gas by Gas chromatography.
11. ISO 6974-1:2012 - Natural gas — Determination of composition and associated uncertainty by gas chromatography - Part 1: General guidelines and calculation of composition.
12. Energia e Biogás. Panorama of electric power generation from biogas sources, 2021. [Accessed August 27, 2022] [In Portuguese].
13. ABNT NBR ISO/IEC 17025:2017 – Requisitos Gerais para a competência de laboratórios de ensaio e calibração.
14. ABNT NBR ISO/IEC 17034:2017 - Requisitos gerais para a competência de produtores de material de referência.
15. Adriaan M H van der Veen *et al*. International comparison CCQM-K112 biogas. Metrologia, Volume 57, Number 1A, 2020. DOI: 10.1088/0026-1394/57/1A/08011
16. ISO 6143:2025 - Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures. Ed.3.
17. ISO 6142-1:2015 - Gas analysis — Preparation of calibration gas mixtures, Part 1: Gravimetric method for Class I mixtures, Ed.1.
18. Inmetro. Technical report R-0786/2024 - Estudo Colaborativo de Comparação de Metodologias Analíticas de Determinação de Composição de Biometano, 2024.