Methods improvements for determining the composition of biomethane

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Abstract. With the increase in pollution and environmental degradation, the need to use renewable energy sources to replace fossil fuels has intensified, and the use of biofuels is an excellent option. In recent years, many studies on biogas have been carried out, as it is considered a renewable energy source. This energy source has several purposes, however, the focus of this work is the use of biogas from landfills as fuel, which can be added to Natural Gas (NG) networks. To add biogas to the NG distribution networks, it needs to go through a purification process, becoming biomethane, with a higher concentration of methane and an increased calorific value. The quality control of biomethane from landfills intended for vehicular use is established by ANP Resolution No. 886 of 2022. To comply with this Resolution, it is necessary to correctly measure the composition of gaseous components with the application of high accuracy and precision methods, in order to perform a reliable measurement with high quality results. In view of this, the adequacy of analytical methods was carried out so that they can determine the composition of the major components (methane, carbon dioxide and oxygen) present in biomethane. Then there was the study of the metrological validation of the methods, and, subsequently, a sample of biomethane produced synthetically by the gas industry was used, and, through the results, it was possible to conclude that the composition of methane is not in accordance with the limit of the Resolution, however, the composition of carbon dioxide and oxygen are in agreement.

1. Introduction

The increase in energy consumption, associated with the limitation of fossil resources, brings to the fore the need for diversification of cleaner energy generation sources, that is, renewable energy sources [1,2].

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 [3].

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 [4].

After stages of purification of biogas, biomethane is the result, a renewable energy source with a high methane content in its composition [4].

The production and use of biomethane in the world has been growing over the years. Through research, it was possible to observe that in world perspectives, Europe has been standing out in relation to the use of biomethane as a source of renewable energy. Since 2014, there was already a need to use “clean” energy and concern for the environment. However, it is important to emphasize that several measures to encourage the production of biomethane were launched in Brazil [5].

The use of biomethane as vehicle fuel or as an injected into natural gas networks, has shown growing interest due to its potential and the various environmental benefits, especially because its use as fuel can substantially reduce greenhouse gas emissions.

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 [4]. However, meeting the specifications of the sector's regulations may prove to be a challenge for laboratories, as there is no specific method for determining the composition of biomethane, suggesting the use of a method for determining the composition of natural gas, however, the composition of these gases is not similar and biomethane, being a bioenergetics.

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. Development

2.1 Biogas e Biomethane

The need for the use of renewable energy sources is increasing every day. Biogas and biomethane are considered great bioenergetic and biofuels, and production and use in the world has been growing over the years [6].

In Brazil, the scenario has been evolving more and more. In 2022, several measures to encourage the production of biomethane were launched, and the inclusion will contribute to the construction of twenty-five new plants. Therefore, production should increase from 400 thousand cubic meters per day to 2.3 million cubic meters per day in 2027, enough to supply more than 900 thousand light vehicles per year.

In addition, the emissions of almost 2 million tons of carbon into the atmosphere will be avoided, which corresponds to the planting of 14 million trees in terms of carbon capture [5].

Biogas consists of 50-75% methane, 25-50% carbon dioxide and 2-8% other gases such as oxygen, nitrogen, hydrocarbons, siloxanes, sulfur, among others. It can be produced from agricultural waste, urban solid waste contained in sanitary landfills or from sanitary sewage in sewage treatment plants, being, in all cases, under the action of bacteria by anaerobic digestion [4, 7].

The ways of using biogas depend mainly on the concentration of the gases that compose it. Through combustion, methane is used to generate energy, making it the biogas component with the highest added value. Therefore, the higher the methane concentration, the higher the added value of biogas [8].

One of the uses of biogas is as a fuel, and it can also be injected into natural gas networks, but for that, it needs to go through a purification process, transforming it into biomethane with 90% or more of its composition being methane [7, 9, 10].

After the purification stage of biogas, obtaining biomethane as a result, the analysis and determination of the composition of the resulting bioenergetic takes place, through the use of a

specific analytical method, in order to verify the efficiency of the purification process. In the literature, there are several techniques that are used in the development of methods for determination of biomethane composition, however, the technique used to adjust the methods for determining the biomethane composition was gas chromatography.

2.2 Methods for determining the composition of biomethane

Through the "Metrology for biogas" project, in a collaboration between the National Physical Laboratory (NPL) and 11 European metrology institutes, analytical methods were developed to determine the composition of the content of critical impurities. However, it is important to note that even with the European Organization for Standardization, each country may have regulations with specifications and concentration limits that must be met [11]. In addition, the methods developed through the project have different parameters from the appropriate methods for determining the composition of the components that were determined in this study and that will be reported in this article, namely: Methane, Carbon Dioxide and Oxygen.

In Brazil, biomethane needs to comply with Resolution N ° 886 of September 29, 2022 established by the ANP. According to this Resolution, the determination of the composition of this gas must be carried out using, by similarity, the method ABNT NBR 14903: 2014- Natural gas - Determination of the chemical composition by gas chromatography [4]. However, the raw materials used to produce biogas differ substantially, as do the adaptation processes to biomethane, the diversity of the raw materials used to produce biogas and biomethane means that it is necessary to specify a greater number of parameters than for the natural gas.

Therefore, the use of the natural gas method does not guarantee the quality and reliability of the measurement results, requiring the use of specific methods that meet the concentration ranges of the biomethane components required by the ANP Resolution.

In order to confirm the adequacy and reliability of the analytical results of the biomethane composition, a specific method for this analysis is required. Therefore, the development and application of metrological tools is indispensable.

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. Therefore, it is essential to emphasize that metrological tools are of significant importance in the process of development and adequacy of analytical methods, which were developed in this scientific study.

3. Results and Discussion

3.1 Method adjustment using the Micro GC 490

In this study, the adaptation of the method developed to determine the composition of biogas using the Micro CG 490 equipment from Agilent was carried out, so that it can determine the composition of methane, carbon dioxide and oxygen present in synthetic mixtures of biomethane.

The first procedure for adjust this method was the selection of the concentration range for each gaseous component of the mixture according to the limit established in ANP Resolution N°. 886/2022, and then the cylinders of the primary gaseous standards used in the calibration curve selected, besides cylinder standard mixture used as sample. As a next step, the parameters and settings of the method were studied.

The carrier gas used was helium gas at a pressure of 70 psi. It should be noted that the equipment is equipped with electronic control of the carrier gas flow, that is, the gas pressure remained constant throughout the analyses.

The sample injection system is made of inert and non-absorbent material, more specifically, stainless steel. A 10-way Vici multiselector valve was used. The injector temperature was set to

110°C, the injection time was 200 milliseconds (ms), and the sample inlet pressure was 200 kPa. This equipment consists of the DCT detector and the oven temperature was 80 °C.

After initial tests for suitability of parameters and method settings, until the aforementioned settings were established, measurements were organized and performed on three different days, and without any intermediate recalibration of the system independently.

The equipment's data acquisition software was programmed to perform 7 readings/repetitions for the methane and carbon dioxide analyses, and 6 readings for the oxygen analyses, due to the pressures in the cylinders. The required calculations (mean, standard deviation and coefficient of variation) were performed with the results of the integrated areas on each measurement day.

It is important to emphasize the importance of metrology and the use of metrological tools in the development or adequacy of analytical methods. In this study, certified reference materials (CRM) were used as standards for obtaining the calibration curve, use of calibrated equipment, and another metrological tool used was the validation of the analytical method, with the objective of guaranteeing, through experimental studies, that the method meets the requirements of analytical applications, ensuring the reliability of the results.

In the validation of the method, in which the validation parameters (selectivity, linearity, limit of detection, limit of quantification, veracity and precision) were studied for the three components, all results were approved in relation to the established acceptance criteria, that is, the method is in accordance with the intended use.

After method validation, a sample of biomethane produced externally by industry Y was verified, evaluating the concentration of methane, carbon dioxide and oxygen, and their associated uncertainties. In this analysis, the calibration curve remained the same used in the validation of the method, and, in addition, the samples used in the validation of the method were inserted as control samples to compare their results with the results of the sample produced externally.

As part of the external sample analysis process, as well as method validation, the software Xlgenline (VERSION 1.1, VSL) was used, which was developed based on ISO Standard 6143:2001 - Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures, which determines the molar fraction/concentration of each sample as well as the standard uncertainty of the molar fraction of each sample component using the propagation of the measured responses and verifying the appropriate function models, through the results of the areas emitted by the method and certified values of applied calibration curve standards.

The sample was analyzed in one day, and the results are mentioned in tables 1 and 2.

As already mentioned, the concentration limits of each component were established in accordance with Resolution N° 886/2022 of the ANP, and, through the results of the external sample mentioned in table 2, it can be seen that the concentration of the methane component is outside the established by the resolution, and the concentration of carbon dioxide and oxygen are in agreement.

Regarding the results obtained by the control samples, this being a CRM, it can be concluded that all results are approved because they are in accordance with the value reported in their respective certificates.

Figures 1 and 2 show the chromatograms of the external sample. In channel 1 it is possible to observe the peak of the methane component and the oxygen component, while in channel 2 it is possible to verify the peak of the carbon dioxide component.

Component	concentration CRM (%mol/mol)	concentration Xlgenline (%mol/mol)	standard uncertainty (%mol/mol)	expanded uncertainty (%mol/mol) (*k*=2, 95%)
Methane	90.03	90	0.05	0.1
Carbon dioxide	1.5	1.51	0.005	0.001
Oxygen	0.5	0.498	0.002	0.004

Table 1. Control sample results.

Component	concentration Xlgenline (%mol/mol)	standard uncertainty (%mol/mol)	expanded uncertainty (%mol/mol) (*k*=2, 95%)
Methane	89.59	0.04	0.08
Carbon dioxide	1.705	0.006	0.012
Oxygen	0.616	0.001	0.002

Table 2 - External sample results.

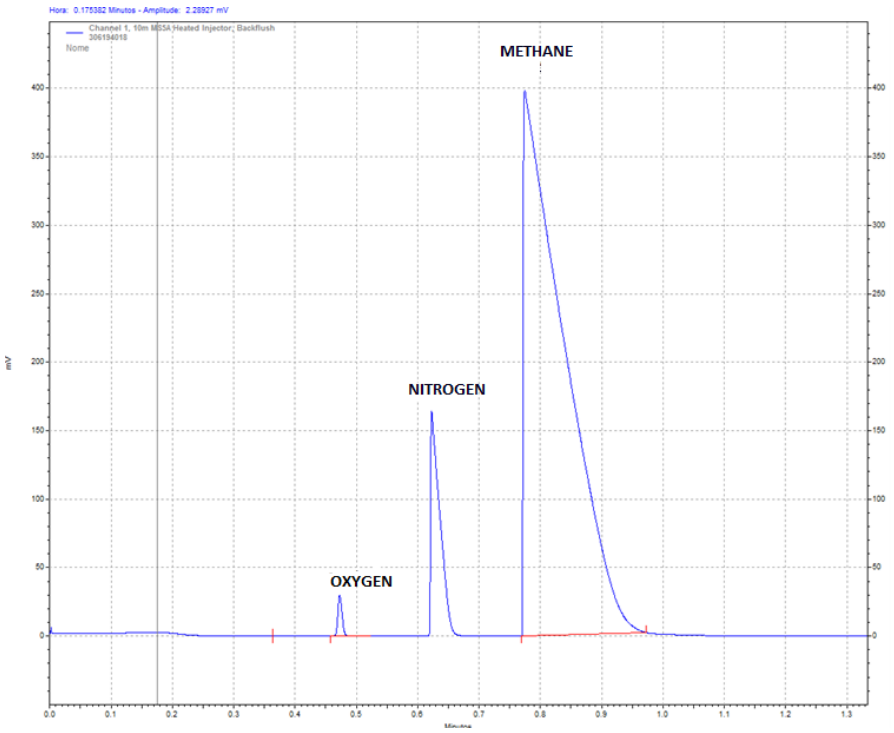

Figure 1. Channel 1 chromatogram.

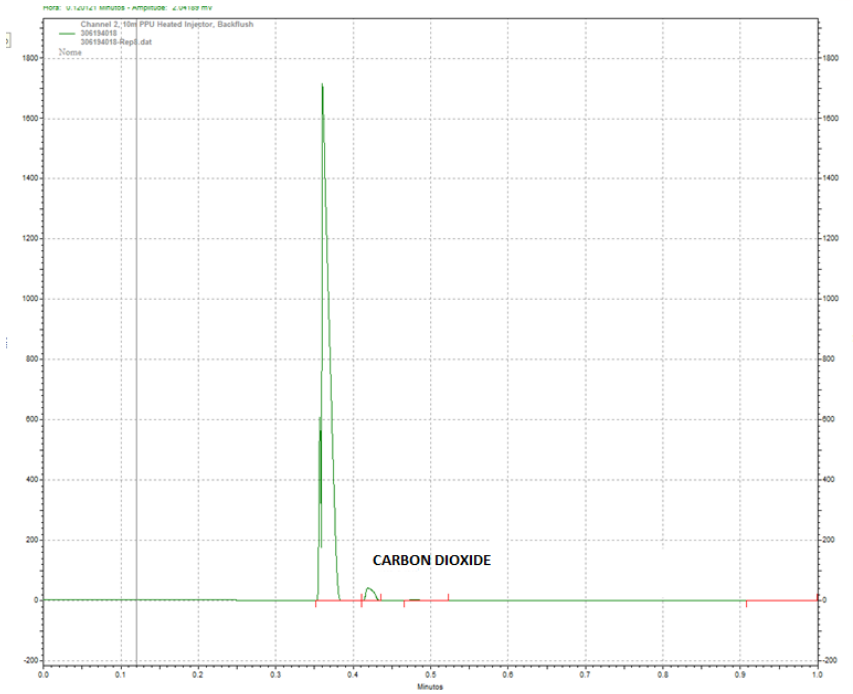

Figure 2. Channel 2 chromatogram.

3.2 Adjustment of methodology using the Gas Chromatograph CP-3800 Special

As with the Micro GC 490 method for determining the composition of methane, carbon dioxide and oxygen, the method developed by Varian's GC CP-3800sp for determining the composition of natural gas was first adapted, so that it can be used to determine the biomethane composition.

However, it is important to mention that with the use of this equipment, it was only possible to carry out the study for the methane component (detected by the FID detector), since the DCT detector, which detects the carbon dioxide and oxygen component, is not suitable for analyses.

The first procedure for method suitability is to establish the concentration range for each component. The concentration range was not modified, remaining the same range established for the method by Micro CG 490 and in accordance with the limit established in ANP Resolution No. 886/2022. Then, the cylinders of the standards used in the calibration curve and the cylinder of the standard used as a sample were selected, all being CRMs. As a next step, the parameters and settings of the method were studied.

The carrier gas used was helium gas at a pressure of 70 psi. The CP-3800 is also an equipment equipped with electronic control of the carrier gas flow, that is, the gas pressure remained constant throughout the analyses.

The sample injection system uses a Vici automatic multiselector valve. The GC system injector was maintained at a temperature of 220°C, the sample inlet pressure was 20 psi, and the injection time for each cylinder (cylinders that make up the calibration curve and sample cylinder) was 1 minute. The temperature of the FID detector was kept constant during the course of all analyses, both on the sample and on the reference standards, at 200°C. The oven temperature was 50°C.

After the experimental tests for the adequacy of the method, the analysis were carried out in two days due to the longer time spent to complete the analyzes, and consequently, greater gas consumption. The CP-3800sp equipment was programmed to perform 7 measurements/repetitions, and the required calculations (mean, standard deviation and coefficient of variation) were performed.

As well as in the adaptation of the method by the Micro CG 490, with the use of the CP-3800sp metrological tools were also used in the adaptation procedure, using reference materials certificates

both as standards to obtain the calibration curve, and as a sample, use of calibrated equipment and validation of the method was performed.

In method validation, in which the validation parameters (selectivity, linearity, detection limit, quantification limit, veracity and precision) were studied for the methane component, where all results were approved in relation to the established acceptance criteria, or that is, the method is in accordance with the intended use. However, a comparison was made between the results of the validation parameters of the two methods, and it was possible to conclude that the method using the micro GC 490 has greater accuracy, as it presented a lower relative error, and was considered the most accurate method, as it presented a lower standard deviation.

In view of the method validation results, a verification of an externally produced biomethane sample was also carried out, in this case, the same sample used in the verification of the method by the Micro CG 490.

The biomethane sample was analyzed in 1 day, and the concentration of only the methane component was determined due to equipment limitations, as previously mentioned. It is important to point out that, just as in the validation and verification of the method by the Micro GC 490, with the method by the CP-3800sp, the software was also used that helps in the calculation of the concentration of the component through the results of the chromatographic areas emitted by the method.

In this analysis, the calibration curve remained the same used in the method validation, and, in addition, the sample used in this method validation was inserted in the verification as a control sample to carry out the comparison of its results with the results of the sample produced externally. The results are presented in tables 3 and 4 respectively.

The concentration limit established for the method was in accordance with ANP Resolution N° 886/2022, and, through the results of the external sample mentioned in table 4, it can be seen that the concentration of the methane component is outside the established by the resolution, as well as the result obtained in the verification of the previously validated method using the Micro CG 490 equipment.

Regarding the results obtained by the control sample, it can be concluded that the result of this analysis is in accordance with what was reported in the method validation.

Figure 3 shows the chromatogram of the methane component referring to the external sample.

Component	Concentration CRM (%mol/mol)	Concentration Xlgenline (%mol/mol)	standard uncertainty (%mol/mol)	Expanded uncertainty (%mol/mol) (k=2, 95%)
Methane	90.03	90.1	0.22	0.44

Table 3. Control sample results.

Component	Concentration Xlgenline (%mol/mol)	standard uncertainty (%mol/mol)	Expanded uncertainty (%mol/mol)
Methane	89.6	0.31	0.62

Table 4. External sample results.

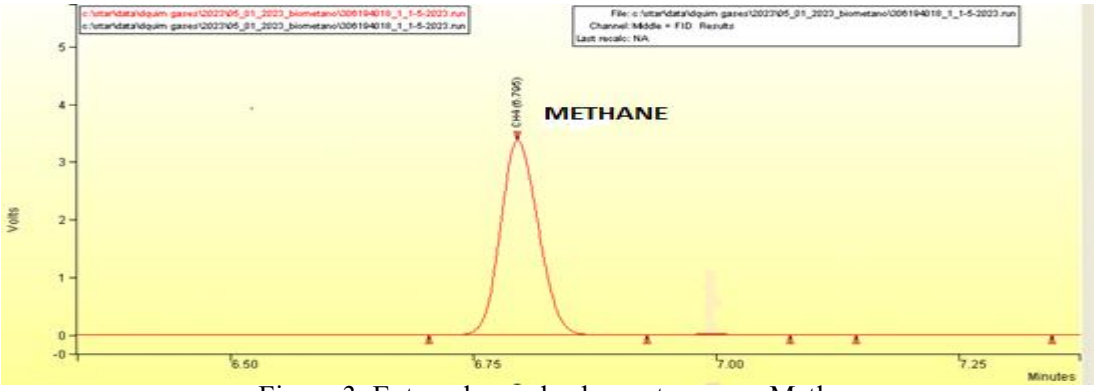

Figure 3. External sample chromatogram – Methane.

4. Conclusion

Through the results presented, it can be concluded that the methods are adequate for the intended use, however the method by the Micro CG 490 is considered a more precise method and with better trueness due to the equipment used.

Regarding the composition of the external biomethane sample, determined in the Micro GC method, it was identified that the methane composition does not comply with the limits required by the sector's regulations, with a concentration lower than the established limit. Therefore, the importance of using specific methods for the determination of biomethane is evident, as well as the great importance of using metrological tools in the process of adjusting and developing methods, as measurements need to be carried out with reliability, precision and trueness, in order not to generate doubts in the final result reported and to make available a quality final product.

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