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Methods improvements for determining the composition of biomethane

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ABSTRACT
As part of energy transition, many studies have been carried out on biogas, as it is considered a renewable energy source. To use it as a fuel, a purification process is necessary, so that it becomes biomethane, with a higher concentration of methane and calorific value. The quality control of biomethane from landfills intended for vehicle use 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. This work sought to adapt and validate analytical methods to subsequently evaluate the composition of a biomethane sample, produced by the gas industry, containing methane, dioxide, and oxygen, and to verify whether the results are in accordance with the parameters reported in the Resolution. Metrological tools were used to quantify biomethane, such as certified reference materials, calibrated instruments, and a validated method. Based on the results, it was possible to conclude that the methods are suitable for their intended use, and that the methane composition does not comply with the limit established in the resolution.

Section: RESEARCH PAPER

Keywords: biogas; biomethane; gas chromatography; method validation

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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 the 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 treaties, such as the Kyoto Protocol, signed in 1997, and the Paris Agreement, signed in 2015, were responsible for the growth of sustainable appeal. Since 2012, studies have been carried out with the aim of evolving the process of obtaining reliable information that could collaborate with the sustainable appeal, such as a mobile measurement system for real-time monitoring of environmental pollution in urban areas. 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 have been carried out. Biogas is considered a renewable energy source and has gained interest mainly because it is considered low pollutant. After the stages of the purification of biogas, biomethane is the result: a renewable energy source with a high methane content in its composition [4]-[5].

The production and use of biomethane in the world has been growing over the years. Through research, it was possible to observe that in global terms, Europe has been standing out in relation to the use of biomethane as a source of renewable energy. Since 2014, there has already been a need to use "clean" energy and awareness for the environment. However, it is important to emphasize that several measures to encourage the production of biomethane have been launched in Brazil [6].

The use of biomethane as vehicle fuel or as an injection into natural gas networks has provoked growing interest due to its potential and the various environmental benefits, especially

because its use as a 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 the approval of quality control and the specifications 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 [5]. However, complying with the industry regulatory specifications can be 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. Nevertheless, the composition of these gases is not similar to biomethane gas, nor are the concentration limits.

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

2. DEVELOPMENT

2.1. Biogas and biomethane

The need for the use of renewable energy sources is increasing every day. Biogas and biomethane are considered great bioenergetic sources and biofuels, and their production and use in the world has been growing over the years [7].

In Brazil, the scenario has also been developing. In 2022, several measures were launched to encourage the production of biomethane, and their use 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 emission of almost 2 million tonnes of carbon into the atmosphere will be avoided, which is equivalent to the planting of 14 million trees in terms of carbon capture [6].

Biogas consists of 50–75 % methane, 25–50 % carbon dioxide, and 2–8 % other gases, such as oxygen, nitrogen, hydrocarbons, siloxanes, and 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, through, in all cases, the action of bacteria by anaerobic digestion [5]-[8].

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 [9].

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 [8], [10], [11].

After the biogas purification stage, resulting in biomethane, the analysis and determination of the composition of the resulting biofuel are carried out using a specific analytical method in order to verify the efficiency of the purification process. In this study, the analytical technique used was gas chromatography, which is an efficient technique for the detection, separation, and quantitative determination of a mixture of volatile organic compounds. Quantitative determination was performed using certified reference materials.

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 its own regulations with specifications and concentration limits that must be met [12]. In addition, the methods developed through the project have different parameters to those of the methods appropriate 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 No. 886 of September 29, 2022, established by the ANP. According to this Resolution, the determination of the composition of biomethane must be carried out using, by similarity, the method ABNT NBR 14903: 2014- Natural gas - Determination of chemical composition by gas chromatography [5]. 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 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 biomethane composition, a specific method for this analysis is required. Therefore, the development and application of metrological tools is indispensable.

One of the tools to control and guarantee the validity of analytical results is the use of certified reference materials (CRMs), which are essential for the 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 the development and adequacy of analytical methods, which are demonstrated in this scientific study.

3. RESULTS AND DISCUSSION

3.1. Method adjustment using a thermal conductivity detector

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 to adjust this method was the selection of the concentration range for each gaseous component of the mixture according to the limits established in the ANP Resolution No. 886/2022. Then the cylinders of the primary gaseous standards used in the calibration curve were selected,

besides the cylinder of the standard mixture used as a 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 fitted 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 an 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 also consists of a TCD (thermal conductivity detector), and the oven temperature was 80 °C.

After initial tests for the 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 adaptation of analytical methods. In this study, certified gas reference materials (CRM) containing the components under study (methane, carbon dioxide, and oxygen) were used as standards for obtaining the calibration curve, using calibrated equipment. Another metrological tool employed was the validation of the analytical method, with the aim of ensuring, through experimental studies, that the method meets the requirements of analytical applications, ensuring the reliability of the results.

In method validation, the validation parameters studied were selectivity, linearity, limit of detection, limit of quantification, trueness, and precision. Acceptance criteria were established for each parameter, and the results obtained must meet these criteria.

The first study parameter was selectivity, with the analysis of the chromatograms mentioned in Figure 1 and Figure 2, and the acceptance criteria established were the following: the peak of each component in the chromatogram must be separated from the others, with adequate resolution ($Rs \geq 1.5$), selectivity ($\alpha \geq 1$) and asymmetry ($0.9 \leq As \leq 1.2$). For the three components, all results were approved in relation to the established acceptance criteria, that is, the method is in accordance with its intended use. The results obtained were as follows:

- methane $Rs = 1.5; \alpha = 1.4; \ As = 0.7$,
- carbon dioxide $Rs = 1.8; \alpha = 1.6; As = 1.2$, and
- oxygen $Rs = 2.4; \alpha = 1.5$.

The methane component peak is not symmetrical, and the asymmetry calculation result does not meet the acceptance criteria, as the mixture contains a very high concentration of the component under study, resulting in a concentration overload. Corrective action is not possible because the equipment used has a configuration limitation. Furthermore, it is a chromatograph with only a thermal conductivity detector, which is not the most appropriate detector for determining the composition of the methane component at high concentrations. The results obtained revealed adequate selectivity in the method.

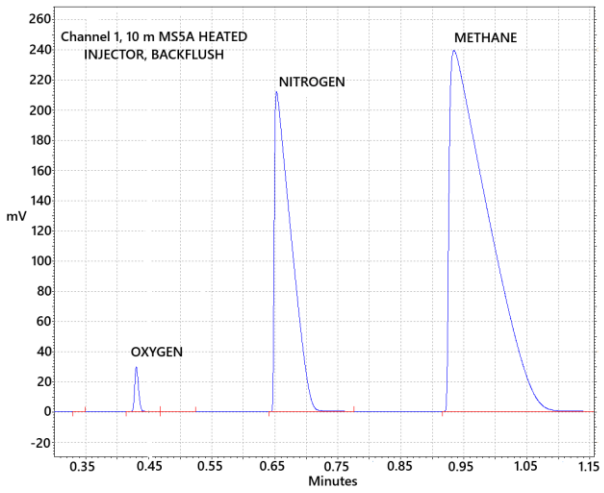

Figure 1. Channel 1 chromatogram of the CMR.

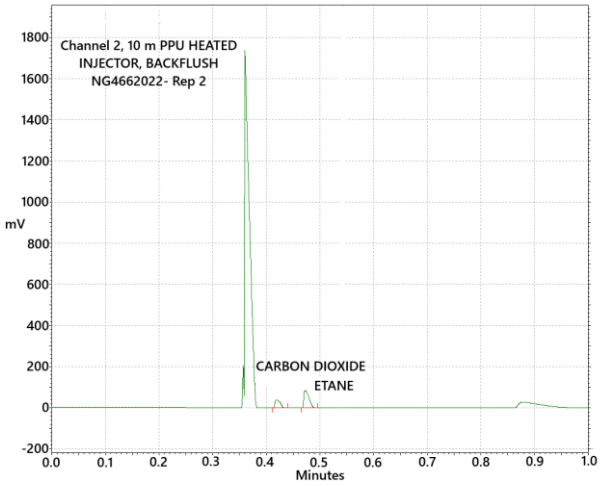

Figure 2. Channel 2 chromatogram of the CMR.

Linearity was assessed through repeated injections of standards of varying concentrations. The chromatographic peak areas of the components present in the reference standards were used to analyse the linearity of the calibration curves. To assess the adequacy of the regression equation, tests should be performed to verify the fit of the linear model, the validity of the regression, its efficiency, and its maximum efficiency.

Verifying the absence of outliers and verifying the homoscedasticity of the data (equality of variances) are part of the first step to assess linearity. Grubbs' test was used to verify the absence of outliers, and Cochran's test was used to verify homoscedasticity. In the process of verifying outliers, any values identified as outliers must be removed from the study.

In this case, no measurement result was considered an outlier, therefore, all values resulting from the measurement process were retained in the study. In Cochran's test, the calculated values

- for methane $Ccalc = 0.365$,
- for carbon dioxide $Ccalc = 0.499$, and
- for oxygen $Ccalc = 0.403$

were lower than the tabulated values

- for methane $Ctab = 0.506$,
- for carbon dioxide $Ctab = 0.590$, and
- for oxygen $Ctab = 0.480$,

demonstrating the homoscedasticity of the analytical curve, enabling the calculation of simple linear regression equations and the identification of correlation coefficients (r) and determination coefficients (r^2).

The acceptance criterion established for the correlation coefficient and for the coefficient of determination were $r \geq 0.991$ and $r^2 \geq 0.991$, and the results obtained were the following:

- methane $r = 0.998$ and $r^2 = 0.997$,
- carbon dioxide $r = 0.999$ and $r^2 = 0.999$ and
- oxygen $r = 0.998$ and $r^2 = 0.996$,

in accordance with the established acceptance criteria. Figure 3, Figure 4, and Figure 5 demonstrate the analytical curves.

The limit of detection (LOD) and limit of quantification (LOQ) were calculated from the estimated analytical curve, using the standard deviation of the concentration of the lowest concentration standard that constitutes the analytical curve. The results obtained were as follows:

- methane
  $LOD = 0.13\ \%\ \mathrm{mol/mol},\ LOQ = 0.36\ \%\ \mathrm{mol/mol},$
- carbon dioxide
  $LOD = 0.0006\ \%\ \mathrm{mol/mol},\quad LOQ = 0.002\ \%\ \mathrm{mol/mol},$
  and
- oxygen
  $LOD = 0.003\ \%\ \mathrm{mol/mol}, LOQ = 0.009\ \%\ \mathrm{mol/mol}.$

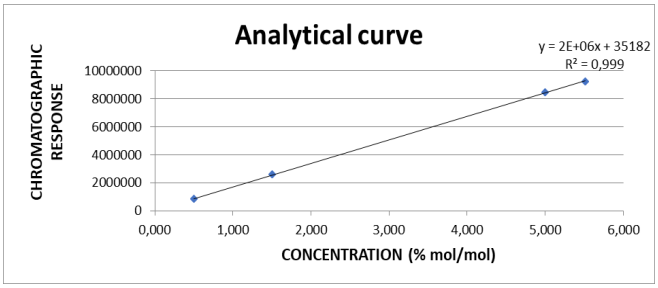

Figure 3. Analytical curve linearity parameter – methane component – TCD.

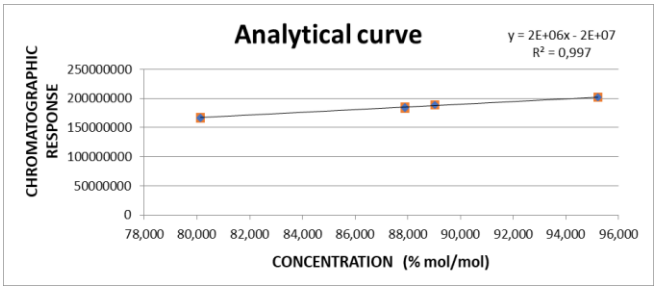

Figure 4. Analytical curve linearity parameter – carbon dioxide component – TCD.

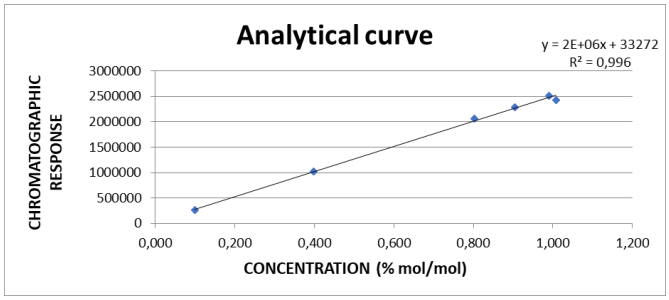

Figure 5. Analytical curve linearity parameter – oxygen component – TCD.

The acceptance criterion established was that the concentrations of the samples to be analysed in this method must be greater than or equal to the calculated limit of quantification. After calculating the LOD and LOQ, for these parameters to be tested, it would be necessary to use gas mixtures with concentrations equivalent to the results obtained. Therefore, it was not possible to verify these parameters because the concentration range established for compliance with this method is greater than the results obtained in the LOD and LOQ. It is important to highlight that the LOQs are below the first point of the calibration curve of each component, namely:

- methane: $80.1\ \%\ \mathrm{mol/mol}$;
- carbon dioxide: $0.5\ \%\ \mathrm{mol/mol}$; and
- oxygen: $0.1\ \%\ \mathrm{mol/mol}$.

To assess the trueness parametron, CMRs were used, as well as sample concentration values were calculated using Xlgenline, a software for determining polynomial calibration functions by generalized least, v1.1/2010, developed at the National Metrology Institute (VSL). This software is based on ISO 6143: Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures. This software determines the concentration of each sample using the results of the areas emitted by the method and estimates the standard uncertainty of the mole fraction of each sample component using the propagation of the measured responses and checking the appropriate function models. It estimates the measurement uncertainty and calculates the concentration of each mixture, which is then compared with the reference value. The concentration values obtained by the method under study are compared with the concentration values of the reference material used. When the laboratory calculates the expanded uncertainty of its result (U_{lab}), the true value (Xv) must be within the interval ($X_{\mathrm{lab}} \pm U_{\mathrm{lab}}$). If this does not occur, this interval may be underestimated, therefore, the concept of normalized error (E_{n}) is used.

The acceptance criteria established were Xv between $(X_{\mathrm{lab}} - U_{\mathrm{lab}})$ and $(X_{\mathrm{lab}} + U_{\mathrm{lab}})$.

If $|E_n| \leq 1$, the laboratory result is considered adequate. The results for relative error, normalized error and degree of truthfulness, to evaluate the method's truthfulness were the following: methane (normalized error = 0.8; relative error = 0.04; degree of truthfulness = $99.96\ \%$), carbon dioxide (normalized error = 1; relative error = 0.5; degree of truthfulness = $100.5\ \%$), and oxygen (normalized error = 0.8; relative error = 0.5; degree of truthfulness = $99.5\ \%$).

Regarding the results obtained, it can be observed that they are in accordance with the established acceptance criteria, and the degree of veracity of the method was greater than $99\ \%$.

The precision parameter was evaluated under repeatability and intermediate precision conditions, being verified by the repeatability standard deviation (Sr), intermediate precision standard deviation (Spi), and relative standard deviation (RSD) of these parameters. In the repeatability study, repeated injections of the sample were performed on the same day. For the evaluation of intermediate precision, the same conditions were used regarding sample, equipment, and analyst; the only variation being the day of analysis, occurring on three different days. The results obtained in the evaluation of repeatability and intermediate precision were the following:

- methane
  $Sr = 0.018$; $RSD = 0.021$ % and
  $Spi = 0.162$; $RSD = 0.179$ %,
- carbon dioxide
  $Sr = 0.002$; $RSD = 0.034$ % and
  $Spi = 0.001$; $RSD = 0.075$ %, and
- oxygen
  $Sr = 0.001$; $RSD = 0.020$ % and
  $Spi = 0.001$; $RSD = 0.056$ %.

The acceptance criteria were established in accordance with ABNT NBR 14903 and DOQ-Cgcre-008, and the value of the relative standard deviation (RSD) of the repeatability (Sr) cannot be greater than 0.1 for CH_4, 0.07 for CO_2, and 0.04 for O_2; in relation to the RSD of the intermediate precision (Spi), it cannot be greater than 1.3 for CH_4, 1.9 for CO_2, and 2.0 for O_2. Therefore, it can be concluded that the method presented good repeatability and intermediate precision to quantify the components under study.

After method validation, a sample of biomethane produced externally by the industry was verified, evaluating the concentration of methane, carbon dioxide, and oxygen, and their associated uncertainties. In this analysis, the calibration curve remained the same as the one 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 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 the certified values of the applied calibration curve standards.

The sample was analysed in one day, and the results are mentioned in Table 1 and Table 2.

As already mentioned, the concentration limits of each component were established in accordance with Resolution No. 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 limit established by the Resolution, and the concentrations of carbon dioxide and oxygen are in accordance.

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.

Figure 6 and Figure 7 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.

3.2. Adjustment of the methodology using the flame ionization detector

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

Table 1. Control sample results.

	Methane	Carbon dioxide	Oxygen
Concentration CRM (% mol/ mol)	90.03	1.5	0.5
Concentration Xlgenline (% mol/ mol)	90	1.51	0.498
Standard Uncertainty (%mol/mol)	0.05	0.005	0.002
Expanded Uncertainty (% mol/mol), (k = 2; 95 %)	0.1	0.001	0.004

Table 2. External sample results.

	Methane	Carbon dioxide	Oxygen
Concentration Xlgenline (%mol/mol)	89.59	1.705	0.616
Standard Uncertainty (% mol/mol)	0.04	0.006	0.001
Expanded Uncertainty (% mol/mol), (k = 2; 95 %)	0.08	0.012	0.002

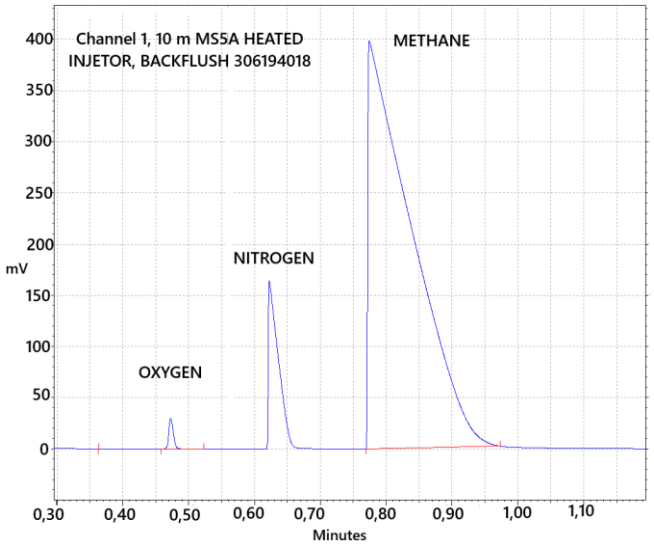

Figure 6. Channel 1 chromatogram of the external sample.

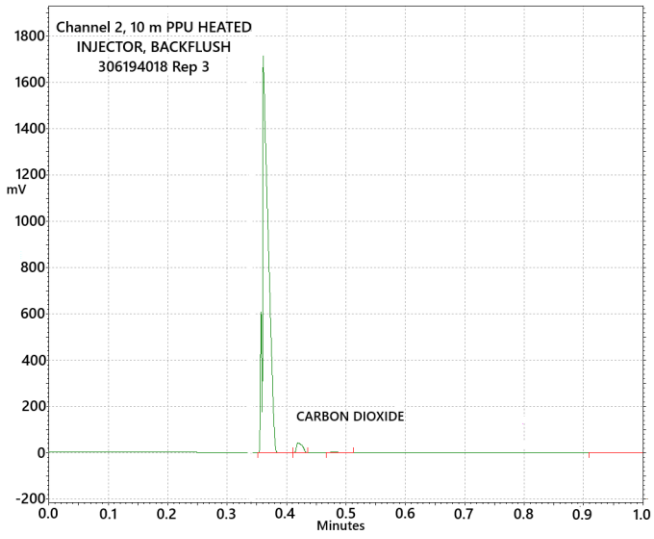

Figure 7. Channel 2 chromatogram of the external sample.

methane component (detected by the FID, flame ionization detector), since the TCD, 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 by the 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 fitted 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 analyses were carried out in two days due to the longer time spent to complete the analyses, 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, the metrological tools were also used in the adaptation procedure of the CP-3800sp, using reference material certificates both as standards to obtain the calibration curve and as samples. Calibrated equipment was used and the validation of the method was performed.

In method validation, the validation parameters studied were selectivity, linearity, limit of detection, limit of quantification, trueness, and precision. The acceptance criteria for each validation parameter remained the same as those established for the method using the thermal conductivity detector.

The first study parameter was selectivity, with the analysis of the chromatogram mentioned in Figure 8, through peak resolution and selectivity. The results obtained were: methane ($Rs = 1.5; \alpha = 1.1$).

The linearity assessment occurred through repeated injections of standards of different concentrations, and for the process of analysing the linearity of the calibration curves obtained, the areas of the chromatographic peaks of the components present in the reference standards were used.

Verifying the absence of outliers and verifying the homoscedasticity of the data (equality of variances) are part of the first step to assess linearity. The Grubbs test was used to check for the absence of outliers, and the Cochran test to check for homoscedasticity. In the process of checking for outliers, any values identified as outliers should be removed from the study.

In this case, no measurement result was considered an outlier, so all values resulting from the measurement process were retained in the study. In the Cochran test, the calculated value ($Ccalc = 0.439$) is lower than the tabulated value ($Ctab = 0.478$), demonstrating the homoscedasticity of the analytical curve, allowing the calculation of simple linear regression

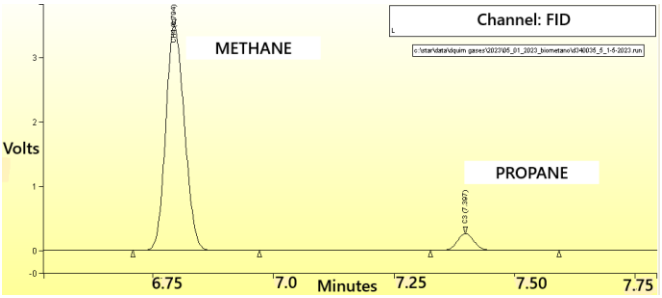

Figure 8. CRM chromatogram.

equations and the identification of correlation coefficients and determination coefficients. The results obtained were: methane ($r = 0.995$ and $r^2 = 0.997$). Figure 9 shows the analytical curve.

The limit of detection (LOD) and limit of quantification (LOQ) were calculated from the estimate of the analytical curve, using the standard deviation of the concentration of the lowest concentration standard that constitutes the analytical curve. The results obtained were as follows: methane ($LOD = 0.57$ % mol/mol, $LOQ = 1.73$ % mol/mol).

After calculating the LOD and LOQ, these parameters would have required the use of gas mixtures with concentrations equivalent to the results obtained. Therefore, these parameters could not be verified because the concentration range established for this method was wider than the results obtained in the LOD and LOQ. It is important to note that the LOQ is below the first point on the methane analytical curve (80.1 % mol/mol).

To evaluate the veracity parameter, the CMRs were used, as well as the sample concentration values that were calculated using the Xlgenline software.

The results obtained were the following: normalized error 0.5; relative error 0.08; degree of truthfulness 100.08 %. It can be observed that they are in accordance with the established acceptance criteria, and the degree of truthfulness of the method was greater than 99 %.

The precision parameter was evaluated under repeatability and intermediate precision conditions, verified by the repeatability standard deviation (Sr), intermediate precision standard deviation (Spi), and relative standard deviation (RSD) of these parameters. In the repeatability study, repeated injections of the sample were performed on the same day. For the intermediate precision evaluation, the same conditions were used regarding sample, equipment, and analyst; only the day of analysis varied, occurring on three different days. The results obtained in the repeatability and intermediate precision evaluation were as follows: $Sr = 0.09$; $RSD = 0.10$ %; and $Spi = 0.29$; $RSD = 0.33$ %. Therefore, it can be concluded that the method demonstrated good repeatability and

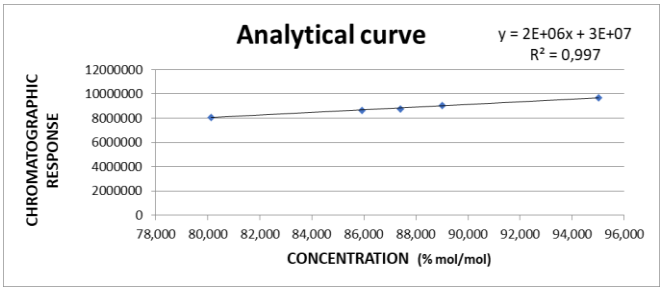

Figure 9. Analytical curve linearity parameter – methane component – FID.

intermediate precision for quantifying the component under study.

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 as the one used in the verification of the method by a TCD.

The biomethane sample was analysed in 1 day, and only the concentration of the methane component was determined due to equipment limitations, as mentioned earlier. It is important to emphasize that, just as in the validation and verification of the method by a TCD, with the FID method, the software that assists in calculating the component concentration from the chromatographic area results provided by the method was also used.

In this analysis, the calibration curve remained the same as the one 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 Table 3 and Table 4 respectively.

The concentration limit established for the method was in accordance with ANP Resolution No. 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 limit established by the Resolution, as well as the result obtained in the verification of the previously validated method using the TCD.

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

Figure 10 shows the chromatogram of the methane component referring to the external sample.

4. CONCLUSION

The results obtained in this study demonstrate that the adapted chromatographic methods are suitable for determining the main components of biomethane, ensuring reliable, accurate, and traceable measurements.

The TCD method has better repeatability, as it obtained lower repeatability standard deviation and RSD results compared to the FID method. Regarding the accuracy comparison, it was possible to verify that the TCD method presented a lower relative error value, however, this difference was not significant. Therefore, it was concluded that the methods have compatible veracity. In the evaluation of chromatographic peak asymmetry, the CP-3800 chromatograph with FID presented better results, as it has the most appropriate detector for identifying methane at high concentrations.

Table 3. Control sample results.

Methane	
Concentration CRM (% mol/mol)	90.03
Concentration Xlgenline (% mol/mol)	90.1
Standard Uncertainty (% mol/mol)	0.22
Expanded Uncertainty (% mol/mol), (*k* = 2; 95 %)	0.44

Table 4. External sample results.

Methane	
Concentration Xlgenline (% mol/mol)	89.6
Standard Uncertainty (% mol/mol)	0.31
Expanded Uncertainty (% mol/mol), (*k* = 2; 95 %)	0.62

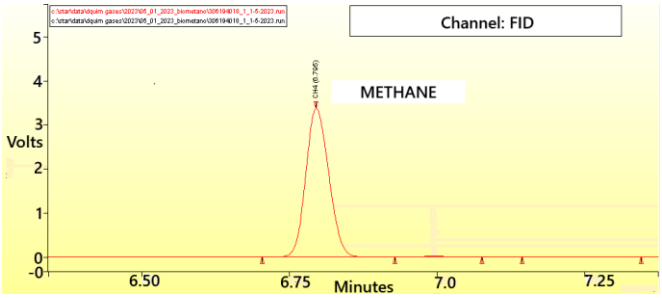

Figure 10. External sample chromatogram.

The implementation of analytical methods developed and metrologically validated can directly support biomethane producers in meeting the requirements established by national regulations, such as the ANP Resolution No. 886/2022, thus contributing to the commercialization of a safe, high-quality, and sustainable energy source.

However, this study also highlights certain limitations. The methods applied primarily focused on methane, carbon dioxide, and oxygen, which are the main components specified by regulation. However, biomethane often contains other critical impurities—such as nitrogen, hydrogen, sulfur compounds, and siloxanes—that were not addressed here. Future research should therefore focus on extending these validated methodologies to multicomponent analysis, as these species can affect safety, performance, and environmental impact.

AUTHORS' CONTRIBUTION

Conceptualization: Isabela de Melo Mostranges Alves, Vanderléa de Souza, Cristiane Rodrigues Augusto Chelles Iglesias, Andreia de Lima Fioravante, Viviane Fernandes Mello, Claudia Cipriano Ribeiro. Data curation: Isabela de Melo Mostranges Alves. Formal analysis: Isabela de Melo Mostranges Alves. Funding acquisition: Vanderléa de Souza. Investigation: Isabela de Melo Mostranges Alves. Methodology: Isabela de Melo Mostranges Alves, Vanderléa de Souza, Cristiane Rodrigues Augusto Chelles Iglesias, Andreia de Lima Fioravante, Viviane Fernandes Mello, Claudia Cipriano Ribeiro. Project administration: Vanderléa de Souza, Cristiane Augusto. Resources: Vanderléa de Souza, Cristiane Rodrigues Augusto Chelles Iglesias. Validation: Isabela de Melo Mostranges Alves. Vizualization: Isabela de Melo Mostranges Alves. Writing – original draft: Isabela de Melo Mostranges Alves, Andreia de Lima Fioravante, Cristiane Rodrigues Augusto Chelles Iglesias, Vanderléa de Souza. Writing – review and editing: Isabela de Melo Mostranges Alves, Andreia de Lima Fioravante, Cristiane Rodrigues Augusto Chelles Iglesias, Vanderléa de Souza.

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