



Screening analysis of natural gas with respect to methane content by near-infrared spectrometry



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ABSTRACT

This paper proposes a method for fast, non-destructive screening analysis of natural gas (NG) with respect to methane content by using near-infrared (NIR) spectrometry. A total of 55 NG samples were collected from vehicle fueling stations in north-eastern Brazil by using a *lab-made* high-pressure sampling cylinder with a purpose-built admission system. In addition, a gas mixing system was specifically developed for use in this investigation in order to simulate NG samples with methane content smaller than 85.0% mol/mol, which is the lower limit specification established by the Brazilian National Fuel Authority. A total of 23 simulated samples were prepared by mixing NG with nitrogen, compressed air, lighter fluid (commercial propane–butane mixture) and ethane. The NIR screening analysis was then carried out by using a SIMCA (soft independent modelling of class analogies) model. For this purpose, samples with methane content above and below the 85.0% mol/mol specification were considered negative and positive cases, respectively. At a confidence level of 95%, all test samples were correctly classified, i.e. no false positives or false negatives were obtained. These findings indicate that the use of NIR spectrometry can be of value for routine quality control of NG with respect to methane content.

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1. Introduction

Natural gas (NG) is a mixture of light hydrocarbons (C1 – C5) obtained primarily from the processing of crude oil. It has been widely used as an alternative to other fossil fuels for domestic, commercial, industrial and vehicular use [1], with the advantage of providing a cleaner combustion [2,3]. The role of NG as an important world energy source was emphasized in a recent report by the International Energy Agency [4], which forecasts an increase in the consumption of this fuel over the next 20 years.

In order to support the growing use of NG in the energy matrix, appropriate mechanisms must be developed to control the quality of this fuel in the production, storage and distribution stages [5–7]. At present, quality control involves the determination of several physicochemical parameters, with bounds established by the fuel authorities in each country [7,8]. The content of methane is of particular importance, as it accounts for more than 80% (mol/mol) of the NG composition and is directly related to the calorific value of the fuel [9–11].

Gas chromatography (GC) is the standard method for determining the parameters related to chemical composition of NG according to

the ASTM D1945 [12] and ABNT NBR 14903 [13] standards. However, GC involves substantial equipment, operation and maintenance costs. Moreover, the analyses are destructive and generate large amounts of chemical waste. Such inconveniences have motivated the development of new analytical technologies for quality control of NG [2,8]. Among these technologies, a promising alternative is the use of near-infrared (NIR) spectrometry [14–16].

Generally, the use of NIR spectrometry is of value to carry out non-destructive and non-invasive analyses with large analytical speed and minimal (or even without) sample preparation. Moreover, NIR instruments are suitable for use in portable equipment sets or in the production line [17,18]. However, the spectral data in the NIR range are usually complex and call for some type of chemometrics treatment [19–24]. In the case of quality control, a possibility consists of using multivariate classification methods for the purpose of screening analysis. The result of such an analysis consists of a binary (yes/no) indication as to whether the sample satisfies a given acceptance criterion [21,24–30].

This work proposes an NIR screening analysis method for verifying whether an NG sample is in conformity with the specification of methane content. More specifically, the present investigation is concerned with vehicular NG supplied in the north-eastern region of Brazil, which must have a minimum of 85.0% (mol/mol) of methane [7]. The NIR screening analysis is carried out by using a SIMCA (soft independent modelling of class analogies) model [31].

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2. Experimental

2.1. Samples

This investigation involved 55 samples of NG, which were acquired at 220 bar from vehicle fuelling stations in three cities in the north-eastern region of Brazil (João Pessoa—Paraíba, Recife—Pernambuco and Natal—Rio Grande do Norte). In addition, 23 gas mixtures were prepared in order to simulate NG samples with methane content outside the specification. For this purpose, NG was mixed with either nitrogen (10.0 or 50.0%), compressed air (10.0 or 20.0%), lighter fluid (10.0 or 20.0%) or ethane (10.0 or 20.0%). All gas contents indicated herein are expressed in % mol/mol. The nitrogen (99.9%) and ethane (99.0%) gases employed in the mixtures were acquired from Linde Gas. Lighter fluid is a commercial propane–butane mixture. Methane (Linde Gas, 99.9%) was employed in the calibration of the GC analysis.

2.2. Apparatus

The NG samples were collected by using a *lab-made* sampling cylinder (Fig. 1) capable of withstanding pressures in excess of 500 bar, for safety purposes. The cylinder was made with seamless chromium–molybdenum steel (AISI 4130) and internal Teflon lining, and was fitted with NG input/output and valve taps. The admission system was designed to allow the collection of samples directly from the NG dispenser at the vehicle fuelling stations.

The NIR measurements were carried out by using the gas sampling apparatus proposed in [30]. A novel gas mixing system (GMS) was employed to prepare the mixtures of NG with nitrogen, compressed air, lighter fluid and ethane. The overall apparatus is presented in Fig. 2A. The NIR spectrophotometric analyses were carried out by using an FT-NIR spectrophotometer (Perkin Elmer, Spectrum GX). In addition, a gas chromatographer (*Shimadzu, modelo CG, série 2014*) was employed to determine the methane content in the original NG samples, as well as in the gas mixtures. The chromatographer was fitted with a 30-m capillary column (GC-GASPRO) with an internal diameter of 0.32 mm. The GC injections were performed in split mode (1:100) at a temperature of 240 °C by using a sampling valve (Valco E60) with a 25 microliter loop. Helium was used as carrier gas with a flow rate of 1.4 mL/min. All analyses were carried out in isothermal mode with the column temperature at 90 °C. A flame ionization detector was employed with temperature set at 250 °C. The total analysis time per run was 10 min.

A schematic diagram of the apparatus is presented in Fig. 2B, with indication of the GMS designed for use in this work. The remaining components are the same as those of the gas flow system employed in [30].

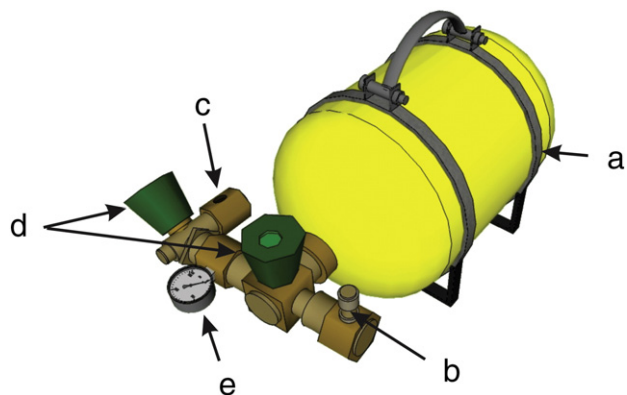


Fig. 1. High-pressure sampling cylinder: (a) steel strap and trestle with carrying handle, (b) NG input with locking pin, (c) NG output, (d) valve taps, (e) and internal pressure gauge.

The component symbols and tags in the diagram are depicted according to the ISA-5.1 standard [32]. In what follows, the analytical procedure will be described with reference to the schematic diagram in Fig. 2B.

2.3. Purging and cleaning

Prior to any measurements, the entire system was purged with compressed air followed by nitrogen using the corresponding gas supplies (b), (c) and their respective valves and pressure regulators.

2.4. Analysis of the commercial NG samples

Initially, the gas line between (e) and (h) was filled with the NG sample, and an aliquot of the sample was admitted in the intake pipe (i) by opening second valve (e). The sample was transferred to the NIR cell (m) by adjusting the rotameter (k) to keep the flow rate smaller than 5 mL min⁻¹ until the pressure indicated by the digital manometer (n) reached 4.0 bar. The NIR/MIR spectrum was then acquired in the range 2700–15,000 cm⁻¹ as the average of 16 scans with resolution of 2.0 cm⁻¹. Room temperature and relative air humidity during the measurements were approximately 23 °C and 55%, respectively.

Finally, the sample was transferred to the GC sampling valve, and the chromatographic analysis was carried out in triplicate.

2.5. Preparation and analysis of the gas mixtures

The gas mixtures were prepared by using pressure indications, since the partial pressures of the components of a gas mixture are directly related to the corresponding molar fractions (Dalton's law). Initially, an aliquot of the commercial NG sample was transferred to the NIR cell (m) as described above until the digital manometer indication (n) reached the pressure corresponding to the desired fraction of NG in the mixture. The other gas (nitrogen, compressed air, lighter fluid, or ethane) was then introduced by following a similar procedure until the total pressure reached 4.0 bar. After acquiring the NIR spectrum, the mixture was transferred to the GC sampling valve for chromatographic analysis.

2.6. Pre-processing of the spectral data

After inspecting the NIR spectra of the commercial NG samples and gas mixtures, the regions with poor signal-to-noise ratio or very large absorbance (close to saturation) were excluded from the data set. As a result, the spectral range 9100–4800 cm⁻¹ was chosen for the chemometrics analysis. This region contains several NIR spectral features of methane, as described elsewhere [33].

Minor misalignments of the spectra along the wavenumber axis were corrected by using iCoshift, which is a recently proposed algorithm for the alignment of instrumental signals [34,35]. Such misalignments may occur in NIR spectra because of imperfections in the mechanical parts of the interferometer, as discussed elsewhere [36].

Principal component analysis (PCA) was initially employed for an exploratory analysis of the overall spectral data set. Afterwards, a SIMCA model was developed for the screening analysis. A SIMCA class model is developed on the basis of the principal components (PCs) of a training data set (which corresponds to NG samples within the methane specification in the present work). The similarity of an unknown sample with respect to the class is evaluated by projecting the sample onto the PC subspace of the class and comparing the resulting residual variance with the average residual variance of the samples in the training set. For this purpose, two measures are usually employed, namely the space distance H_i (distance to the center of the model within the PC subspace, expressed as a leverage value) and the orthogonal distance S_i (distance to the PC subspace, expressed as a residual standard deviation). The classification is then carried out by comparing these distances with critical values corresponding to the adopted confidence level [37], which is set to 95% in the present work.

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