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Short communication

An automatic flow system for NIR screening analysis of liquefied petroleum gas with respect to propane content

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ABSTRACT

This paper proposes a NIR spectrometric method for screening analysis of liquefied petroleum gas (LPG) samples. The proposed method is aimed at discriminating samples with low and high propane content, which can be useful for the adjustment of burn settings in industrial applications. A gas flow system was developed to introduce the LPG sample into a NIR flow cell at constant pressure. In addition, a gas chromatographer was employed to determine the propane content of the sample for reference purposes. The results of a principal component analysis, as well as a classification study using SIMCA (soft independent modeling of class analogies), revealed that the samples can be successfully discriminated with respect to propane content by using the NIR spectrum in the range 8100–8800 cm^{-1}. In addition, by using SPA-LDA (linear discriminant analysis with variables selected by the successive projections algorithm), it was found that perfect discrimination can also be achieved by using only two wavenumbers (8215 and 8324 cm^{-1}). This finding may be of value for the design of a dedicated, low-cost instrument for routine analyses.

1. Introduction

Liquefied petroleum gas (LPG) is a mixture of hydrocarbon gases obtained as a by-product of petroleum refinement and natural gas processing, which is widely used for heating, cooking and refrigeration, as well as motor fuel. LPG is usually supplied in pressurized cylinders, which can be conveniently stored, transported and distributed. As compared to other fossil fuels, the combustion of LPG generates very little particulate matter and sulfur emissions [1,2].

LPG mainly consists of propane and butane, with a smaller proportion of propene, butene, odorants and other gases, which may vary according to the petroleum/natural gas source and production process. A larger propane content is associated to a higher calorific value [3–5] (energy per unit mass — J kg^{-1}), i.e. a "rich" LPG. Conversely, a smaller propane content characterizes a "poor" LPG, with lower calorific value. However, commercial LPG is often distributed without an associated chemical analysis report. Therefore, the availability of a simple and fast screening method would be of value to determine whether the LPG product is rich or poor so that the user can adjust the burning process accordingly. Indeed, if the burning process is set for use with a poor LPG feed and a rich LPG is employed, then too much fuel will be unnecessarily delivered to the burner. In contrast, if the burning process is set for use with a rich LPG feed, and a poor LPG is employed then the resulting heat production may be insufficient [3].

The chemical composition of LPG can be determined by gas chromatography (GC), which is the standard method for gas analysis. However, GC is expensive in terms of equipment, maintenance and operation costs. In the present context, a simpler, less expensive method that could provide a classification of the LPG feed into rich or poor categories may be sufficient. Within this scope, the use of near-infrared (NIR) spectrometry may be a convenient alternative [6,7]. Indeed, as compared to GC, NIR spectrometry involves a less costly instrumentation, which can be more easily deployed in the production line and has less stringent maintenance and operation requirements [8,9]. Moreover, the NIR method is fast and non-destructive, making on-line measurement easier.

With the dissemination of NIR spectroscopy for analytical purposes, several authors have discussed the possibility

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of applying this technique to gas matrices [10,11]. Applications have included the analysis of liquefied alcanes [12,13] and fuel gases such as natural gas [14,15] and LPG [16,17]. More specifically, Ryan and collaborators [16,17] suggested the possibility of estimating the composition of LPG with respect to propane, butane and 2-methylpropane content by using broad-band detectors (10,750–11,500 cm^{-1}), LED-based (10,640–11,360 cm^{-1}) or filter wheel (8700–9040 cm^{-1}) instruments in the NIR range. However, the reported investigations were preliminary and a study involving a representative set of LPG samples was not carried out. Moreover, an automatic system for manipulating the gas samples and carrying out the analyses was not described.

This paper presents a gas flow system for NIR spectrometric analysis of LPG samples. The apparatus was designed for automatic manipulation of the sample, including sampling from a commercial cylinder, introduction into a flow cell at constant pressure for NIR spectrum acquisition, purging and cleaning. In the present work, the proposed system was employed for screening analysis of LPG in terms of low or high propane content. The class labels (“rich” or “poor”) for each sample were assigned on the basis of the propane content measured by a gas chromatographer. However, it is worth noting that the chromatographic results are only used to build and test the NIR classification models. After the models are constructed, routine screening analyses of unknown samples can be carried out by using the NIR spectrometer alone.

The classification models were obtained by employing SIMCA (soft independent modeling of class analogies) [18–20], as well as SPA-LDA (linear discriminant analysis with variables selected by the successive projections algorithm) [21,22]. The SIMCA models were built on the basis of the entire spectral working range. The use of SPA-LDA was aimed as selecting a reduced subset of wavelengths that could possibly be monitored by a dedicated, low-cost instrument (NIR photometer) [23,24].

2. Experimental

2.1. Samples

The 57 samples employed in this study were provided in pressurized cylinders by an LPG supplier from the city of João Pessoa (Paraíba, Brazil) over a period of 12 months. The calibration of the GC analyses was carried out by using pure propane (Linde-Aga, 99.5% mol/mol).

2.2. Apparatus

Fig. 1A and B present the gas flow system employed in the study, which comprises an FT–NIR spectrophotometer (Perkin Elmer, Spectrum GX), a gas chromatographer (Shimadzu, CG 2014) and a lab-made gas sampling system. As compared to solid and liquid matrices, the manipulation of gas samples requires a more sophisticated apparatus, with hermetical sealing as well as pressure and volume control. The sampling system was designed to transfer the LPG sample directly from the commercial cylinder to the NIR flow cell and the gas chromatographer, with monitoring of the pressure throughout the entire process. All procedures, including purging and cleaning, are carried out in an automatic manner, thus reducing the chance of contamination and human error.

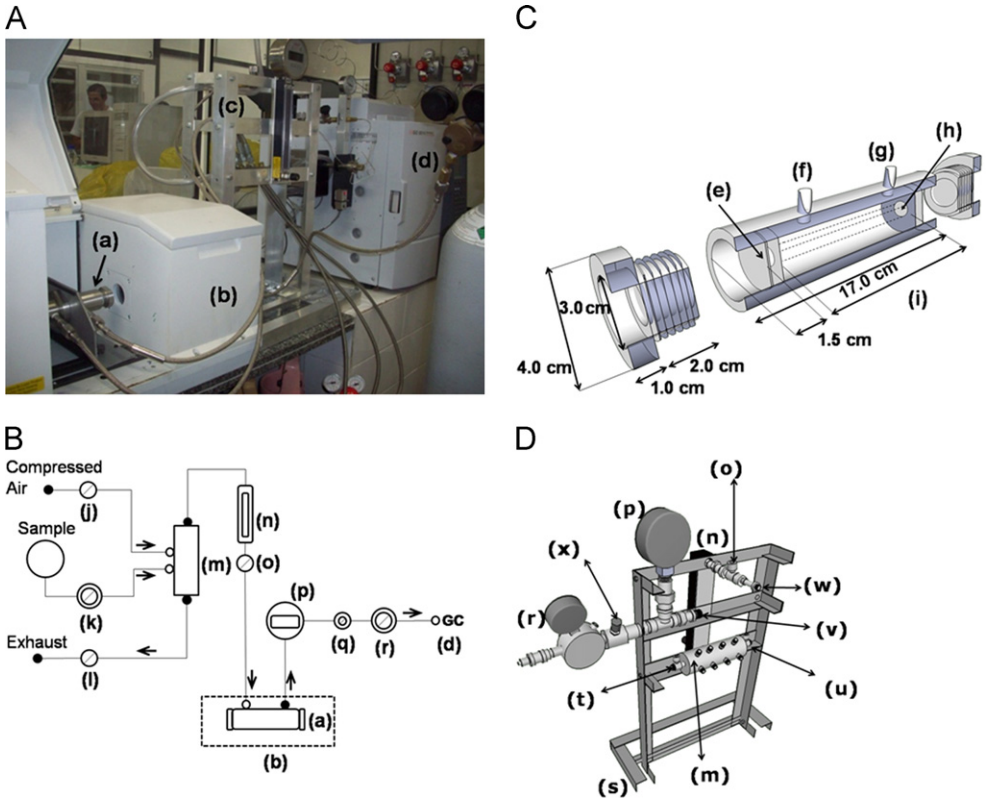

Fig. 1. (A) Photograph of the gas flow system for NIR and GC analyses, and schematic diagrams of (B) gas flow system, (C) NIR flow cell (lab-made), and (D) gas sampling system (back view). (a) NIR flow cell (lab-made), (b) FT-NIR spectrophotometer, (c) gas sampling system, (d) gas chromatographer, (e) quartz window (0.5 cm thickness), (f) gas inlet, (g) gas outlet, (h) NIR beam diameter (1.0 cm), (i) optical path (10.0 cm), (j), (l) and (o) ball valve (3/8″ BSP screw-stainless steel), (k) and (r) pressure gauge (regulator type), (m) gas intake pipe (lab-made), (n) local flow gauge (rotameter), (p) pressure equipment (digital manometer), (q) needle valve (3/8″ BSP screw-brass), (s) support structure of the injection system, (t) connection for air intake system cleaning, (u) exhaust valve or purping of the confluence, (v) output connection of the flow cell, (w) input connection to the flow cell, and (x) shutoff valve injection system.

The chromatographer was fitted with a flame ionization detector (FID) and a 30 m capillary column (GC-GASPRO) with an internal diameter of 0.32 mm. The GC injections were performed by using a sampling valve (Valco E60) with a 25 μL loop. The connecting tubes were made of Teflon covered with stainless steel braid. The lab-made NIR flow cell and gas sampling system are depicted in Fig. 1C and D, respectively.

2.3. Procedure

In what follows, the analytical procedure will be described with reference to the schematic diagram presented in Fig. 1B. Prior to the analysis of each GLP sample, the gas flow system was purged by using compressed air followed by the sample itself. The gas intake pipe (m) was initially purged by opening valve (j) for 5 s. The remaining elements of the system were then purged by opening valves (j), (o), (q) and (r) for 55 s. Afterwards, a similar procedure was employed by opening valve (k) instead of (j) in order to fill the system with the GLP sample. The sample was left to flow through the gas intake pipe during 5 s and the remainder of the system during 25 s. At the end of this procedure, all valves were closed.

The NIR and CG analysis were carried out as follows. An aliquot of the sample was admitted in the gas intake pipe (m) through a gradual opening of valve (k). Valve (o) was then opened until the manometric pressure reached 4.00 bar in (p). Ten seconds later, the NIR spectrum was acquired. The sample was then released through valve (q) and valve (r) was slowly opened in order to fill the sampling loop for the CG analysis (d).

The NIR spectrum was acquired in the range 2700–15,000 cm^{-1} as the average of 16 scans with a resolution of 2.0 cm^{-1}. Temperature and relative humidity remained around 23 °C and 55%, respectively. The overall time required by the NIR analysis was three minutes per sample.

In the CG analysis, the injection was carried out at 240 °C in Split 100:1 mode. The analysis was performed in isothermal mode, with column temperature at 90 °C and detection at 250 °C. The overall time required by the CG analysis was ten minutes per sample.

2.4. Software

Principal Component Analysis (PCA) was initially applied for exploratory analysis of the NIR spectra. Afterwards, a classification study was carried out to investigate the possibility of discriminating the poor and rich GLP samples on the basis of the NIR measurements. For this purpose, the samples were divided into training, validation and test sets by using the Kennard–Stone (KS) algorithm [25]. Classification was then accomplished by using SIMCA and SPA-LDA. The training and validation sets were employed in the SIMCA and SPA-LDA modeling procedures, whereas the test set was only used in the final assessment of classification performance.

SIMCA is a full-spectrum classification technique in which a separate PCA is applied to the samples of each class, in order to build a model for that class [26]. In the present study, the number of principal components to be used in each SIMCA class model was optimized by using the validation data set. In contrast, SPA-LDA is aimed at classifying the samples on the basis of a reduced number of spectral variables (i.e. wavenumbers), rather than the full-spectrum. These variables are selected in order to minimize a cost function associated to the risk of incorrect classification over the validation set [27,28].

PCA, KS and SPA-LDA were carried out in Matlab R2008a (Mathworks), whereas SIMCA calculations were accomplished in The Unscrambler 9.7 (CAMO S.A.).

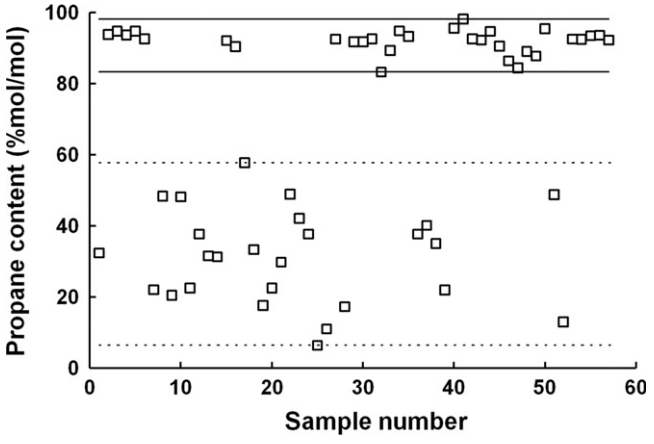

Fig. 2. Propane content values resulting from the chromatographic analysis of the 57 LPG samples. The joint standard deviation of the replicate measurements was calculated as 0.55% mol/mol. The solid and dashed lines indicate the minimum and maximum values of propane content for the rich and poor samples, respectively.

3. Results and discussion

3.1. Chromatographic analysis

Fig. 2 presents the propane content values resulting from the chromatographic analysis of the 57 LPG samples. As can be seen, there is a clear distinction between 31 samples with high (83.29–98.16% mol/mol) and 26 samples with low (6.39–57.74% mol/mol) propane content. These two groups of samples will be treated as separate classes, which need to be discriminated in the proposed screening analysis procedure. In what follows, the possibility of carrying out such a discrimination on the basis of NIR measurements will be investigated, with the aim of offering a simpler, less costly alternative to the use of gas chromatography.

3.2. Spectrometric analysis

After inspecting the NIR spectra of the LPG samples, 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 working region 8100–8800 cm^{-1} was chosen, as shown in Fig. 3a. Due to the large number of possible combinations of the fundamental frequencies, the assignment of bands within this region is not straightforward [12]. However, the bands observed in Fig. 3a are consistent with the findings of Rest et al. [12], who reported the presence of spectral peaks at 8302, 8398, 8513 and 8695 cm^{-1} for propane and 8286, 8410, 8513 and 8680 cm^{-1} for butane.

As can be seen in Fig. 3a, the rich and poor LPG samples are markedly separated from each other, which confirms that the NIR spectra can be employed for screening analysis purposes. Such a finding is corroborated by the PC1 × PC2 score plot in Fig. 3b. It is interesting to note that the rich samples exhibit substantially smaller dispersion as compared to the poor samples (Fig. 3a and b). Indeed, the composition of the rich samples is dominated by the propane content (at least 83.29% mol/mol, as indicated in Fig. 2), whereas the poor samples present a less uniform composition, with propane content varying within a wider range (6.39–57.74% mol/mol).

3.3. Screening analysis

In order to carry out the classification study, the samples were divided into training (15 rich+13 poor), validation (8 rich+6 poor) and test (8 rich+7 poor) sets by applying the KS algorithm

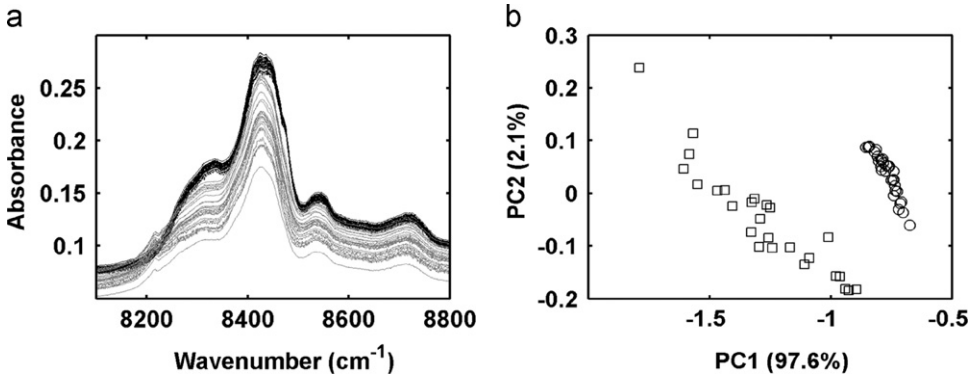

Fig. 3. (a) NIR spectra of the rich (black lines) and poor (gray lines) LPG samples, and (b) PC1 × PC2 score plot obtained from the NIR spectra. The percent explained variance is indicated within parenthesis at each axis. The rich and poor LPG samples are indicated by circle and square markers, respectively.

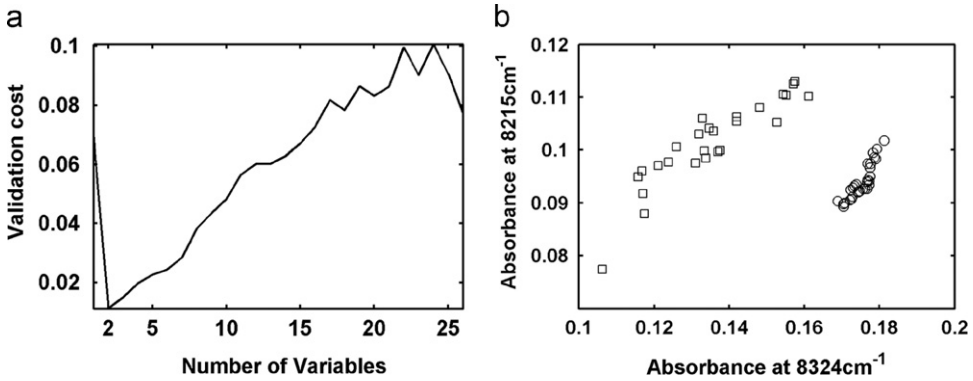

Fig. 4. (a) Validation cost in SPA-LDA as a function of the number of selected wavenumbers, and (b) absorbance values of the 57 LPG samples at the two selected wavenumbers. The rich and poor LPG samples are indicated by circle and square markers, respectively.

to the NIR spectra of each class separately. The training set was employed to develop a SIMCA model for each of the two classes. The validation set was adopted to establish an appropriate number of principal components for each model, whereas the test set was only used to evaluate the final classification performance. As a result, all samples in the test set were correctly classified at the default significance level (5%). These results indicate that a screening analysis involving the discrimination of rich and poor LPG samples can be successfully carried out by using the NIR spectra with the SIMCA models.

Finally, the SPA-LDA algorithm was employed to explore the possibility of discriminating the two classes by using a reduced subset of wavenumbers, instead of the full working range used in SIMCA. For this purpose, the same training, validation and test sets described above were adopted. As shown in Fig. 4a, the smallest value of the SPA-LDA validation cost was achieved by using only two spectral variables. These variables correspond to the wavenumbers 8215 and 8324 cm^{-1} (which correspond to 1217 and 1201 nm, respectively). By applying the resulting SPA-LDA model to the test set, all samples were correctly classified. The separation between rich and poor samples at these two wavenumbers is illustrated in the scatter plot presented in Fig. 4b.

Interestingly, one might question the need for using the absorbance at 8215 cm^{-1}, since the spectra of the rich and poor samples overlap at this wavenumber, as seen in Fig. 3a. Indeed, an inspection of Fig. 4b reveals that the absorbance values at 8215 cm^{-1} alone are insufficient to separate the two classes. However, they are useful to improve the discrimination provided by the absorbance values at 8324 cm^{-1}. It may be argued that the joint use of these two wavenumbers in the SPA-LDA model was necessary to account in a multivariate manner for the variations in the baseline of the spectra. In fact, Fig. 4b shows that the poor samples generally exhibit a smaller absorbance at 8324 cm^{-1}, as compared to the rich samples. However, a smaller absorbance at this wavenumber could also be associated to a downward fluctuation in the baseline. Since the absorbance at 8215 cm^{-1} is mainly related to baseline fluctuations (rather than differences between the two classes), it can be used as an internal standard in the SPA-LDA model to correct for this effect. Such a finding is also in agreement with the PCA score plot presented in Fig. 3b. In fact, the separation between rich and poor samples is mainly associated to PC1, but the discrimination can be further improved by considering PC2. It may be argued that the variability explained by PC1 encompasses baseline features in addition to the difference between the composition of the samples, whereas PC2 is mainly related to the baseline variations.

4. Conclusion

The results presented in this paper demonstrate that liquefied petroleum gas (LPG) samples can be screened with respect to propane content by using a simple NIR spectrometric method. More specifically, it was shown that spectral measurements in the range 8100–8800 cm^{-1} can be successfully used to discriminate samples with high and low propane content, which may be of value to adjust burn settings in industrial applications. In addition, by using SPA-LDA for variable selection, it was possible to obtain a suitable classification by using only two wavenumbers (8215 and 8324 cm^{-1}). Such a finding may be of value for the design of a dedicated, low-cost instrument for routine analyses.

In principle, the experimental data set employed in this work could also be used for a quantitative analysis study, involving the NIR spectrometric determination of propane content in LPG.

However, due to the heterogeneous nature (i.e. the presence of two clearly different sample groups) of the data set and the wide range of variation of propane content, the construction of a multivariate calibration model may not be a straightforward task. Therefore, such a possibility is left as a suggestion for future research.

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