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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.

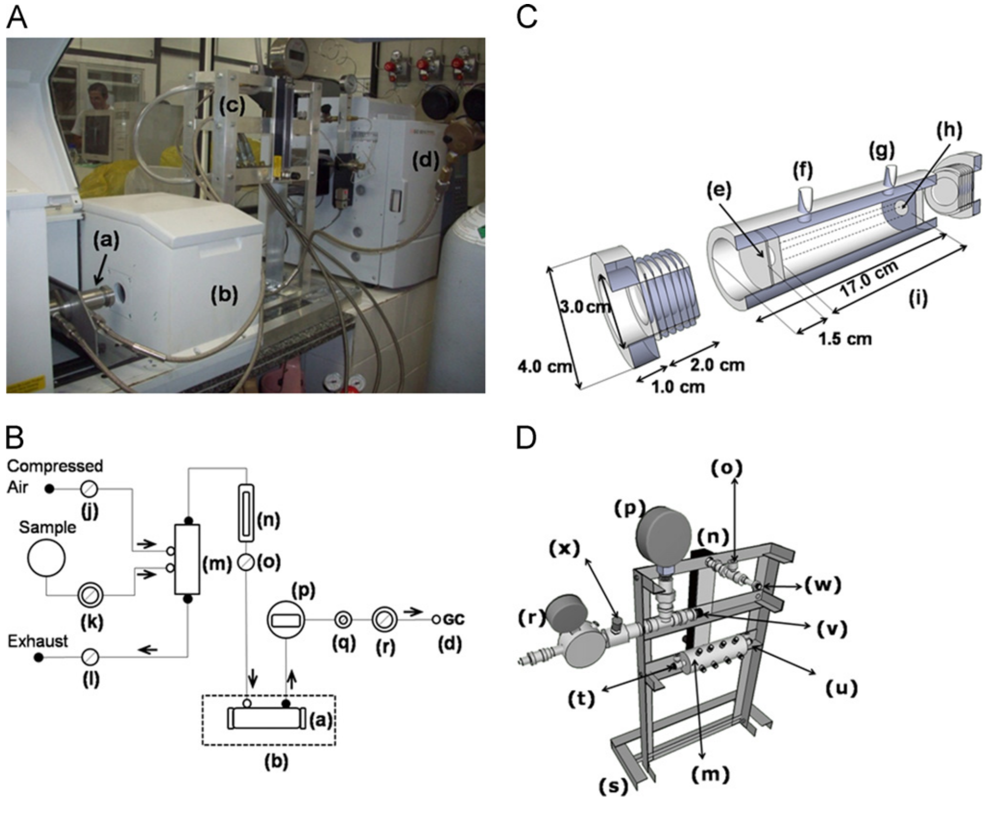

Fig. 1. (A) Photograph of the gas flow system for NIR and GC analyses, and schematic diagrams of (B) gas flow system, (C) NIR flow cell (lab-made), and (D) gas sampling system (back view). (a) NIR flow cell (lab-made), (b) FT-NIR spectrophotometer, (c) gas sampling system, (d) gas chromatographer, (e) 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.