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A PLS regression model using flame spectroscopy emission for determination of octane numbers in gasoline

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ABSTRACT

This paper presents a method for the prediction of MON (Motor Octane Number) and RON (Research Octane Number) of automotive gasoline using flame emission spectroscopy and multivariate calibration (partial least squares). We obtained low values of RMSEC (root mean square error of calibration) and RMSEP (root mean square error of prediction), of 0.14 and 0.56, respectively for MON, while these values for RON were 0.34 and 0.9. The technique is simple and fast, does not require pretreatment of samples and still produces low octane rating errors, making it a good alternative to the standard method used in quality control of automotive gasoline.

1. Introduction

Automotive gasoline is a complex mixture of organic substances obtained from the fractional distillation of petroleum. These can be grouped into four classes: aromatic, olefinic, paraffinic and naphthenic hydrocarbons. In Brazil, common gasoline type C also contains oxygenated compounds due to the addition of 25% v/v of ethanol [1]. This fuel has significant importance in the Brazilian energy mix, with annual sales of 44 billion liters in 2014 according to the National Petroleum, Natural Gas and Biofuels Agency (ANP), making it the second leading fuel in the country in terms of volume sold [1].

The ANP [2] sets the characteristics of fuel marketed in Brazil. Among the parameters used for quality control of gasoline include determination of color, relative density, distillation curves, ethanol content, hydrocarbons content and octane numbers, namely MON (Motor Octane Number) and RON (Research Octane Number). According to the ANP [1], the main causes of gasoline nonconformity recorded are deviations in distillation curves, ethanol and octane content outside the specified range and insufficient octane number.

The octane number (ON) is a practical measure of auto-ignition resistance of fuel compared with a mixture range of reference fuels [3]. The method used for determining MON is described by ASTM D2700 and assesses the fuel's resistance to detonation when the engine operates under severe conditions, keeping rotation of ±9900 rpm, with lube oil temperature maintained at 58 ± 8 °C and cooling fluid kept at 100 ± 2 °C [4]. In turn, ASTM D2699 describes the method to determine RON, which measures how the fuel resists detonation when the motor is under full load at low rpm. In this case, the test conditions consider rotation equal to 600 ± 6 rpm with oil temperature of 58 ± 8 °C and cooling fluid maintained at 100 ± 2 °C [5].

The octane number is calculated by interpolation of the average intensity values of detonation of three samples, which must present values within the range of octane numbers of the surrogate used [3]. For common gasoline, Brazilian regulations determine a minimum value of 82.0 for MON and 87.0 for Octane Anti-knock Index (IAD), which is the arithmetic mean of the MON and RON values [2].

Although the control of gasoline quality is done according to standard laboratory tests, there is a general consensus concerning some intrinsic problems: the standard engines used are extremely expensive, consume large simulacrum sample amounts (approximately 500 mL per test); the engines are noisy; the exhaust gases produced require frequent cleaning and maintenance periods; and the analysis is slow (approximately 30 min per sample).

To overcome these problems, the literature has reported several alternative methods to determine gasoline octane numbers [6–14] using conventional methods associated simulation and also with chemometric methods. These alternative methods allow extracting more information and thus favor better results with high repeatability and reproducibility.

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Detailed kinetics and engine simulations allow a clearer understanding of the physical meaning parameters related with octane number measurement. They also help to have a best understand about differences and similarities between different hydrocarbon fuels [15].

Badra et al. [16] provide a methodology to associate MON and RON analysis in fuels with homogenous gas-phase ignition delay times through the use of chemical kinetic simulations. The authors presented results predicting MON and RON errors using four different conditions stablished that resulted in uncertainties that are lower than the repeatability and reproducibility limits of the measurements in the CFR engine.

Knop et al. [17] used a linear-by-mole computation method for octane number prediction based on pure compound values. Measurements demonstrated that a linear computation method is accurate for ternary mixtures of n-heptane, iso-octane and toluene, with a very high level of accuracy for RON, MON and sensitivity.

Similarly, chemometrics tools is been used to provide important information related alternative methods to determine octane numbers in fuels. The PLS models allow determination of several parameters and specific properties using indirect measures [18]. However, for the model to be robust, it is necessary to mimic as best as possible a real situation, taking into account the greatest possible number of variations, using samples for calibration similar to those that will be used for future analyses. Based on these principles, automatic analyzers employing near infrared (NIR) spectroscopy with multivariate calibration are available commercially for this application.

Among the techniques described in the literature, one can highlight the efficiency of multivariate calibration for estimating octane numbers in gasoline. Kelly et al. [8] associated NIR spectrometry with PLS for prediction of octane numbers, obtaining RMSEC values of 0.355 and 0.383 for MON and RON, respectively. Leeuwen et al. [9] associated results obtained by gas chromatographic analysis with non-linear regression techniques to determine gasoline octane numbers. Pasadakis et al. [10] used models with artificial neural networks (ANN) to predict RON values. PLS models have also been employed to correlate spectral data obtained using Raman spectroscopy to measure MON and RON values of petroleum-derived fuels [11,12]. Mendes et al. [13] determined the octane numbers of gasoline through the association of data obtained from distillation curves with PLS, obtaining RMSEP values of 0.063 and 0.085 for MON and RON, respectively.

Another technique that has been widely used in the study of fuels and that can be associated with chemometric methods is flame emission spectroscopy (FES). In this technique, the detection of radicals formed during the burning of fuels through the emission spectra is used to determine the flame temperature and kinetic mechanisms involving combustion [19–21].

Recently, Barbeira et al. [22,23] highlighted the possibility of using spectral data obtained from FES and chemometric tools to predict adulteration of gasoline with different solvents. The proposed method enables distinguishing differences in the compositions of gasoline through the detection of the radicals formed during burning. These data were used in chemometric models capable of determining the type of adulterant and its amount added to gasoline.

This article describes the use of flame emission spectra of the radicals resulting from the combustion of automotive gasoline in conjunction with multivariate analysis for the prediction of octane numbers. The results show this technique is advantageous because it is practical, fast and inexpensive, so it can be used as an alternative to the standard method commonly used in quality control of automotive gasoline.

2. Experimental

2.1. Materials and methods

The gasoline samples used in this study were obtained from the Fuel Quality Monitoring Program (PMQC) of Minas Gerais Federal University (UFMG) in partnership with the ANP, which is monitoring the quality of fuels marketed in the eastern region of the state of Minas Gerais. This region is supplied with gasoline from seven refineries, providing variability to the chemometric models. The samples were selected to improve the maximum extension of the MON and RON ranges for the Brazilian gasolines and kept cooled from receipt until time of analysis. For this reason, only some samples were used in both models (MON and RON ones).

The analytical signals were obtained from a manufactured system that provides signals from the continuous emission spectra recorded by an EPP 2000 spectrometer (StellarNet, Inc.), in the 200–860 nm range. The emission spectra were obtained by burning the samples in a nebulizer combustion system of a Varian AA-6 atomic absorption spectrometer, using synthetic air as oxidant and methane as fuel, which operational conditions are described in Table 1.

For prediction of MON, 50 samples (from 82.8 to 85.2) were used, 34 for model calibration and 16 for validation. For RON, other 50 samples (from 92.2 to 100.0) were used, 34 for calibration and 16 for validation. Initially, the two parameters (MON and RON) were determined experimentally using a Petrospec GS1000 automatic analyzer based on mid-infrared spectroscopy associated with multivariate calibration methods, namely PLS, PCR (principal components regression) and MLR (multiple linear regression), according to ASTM E1655 [24]. The equipment's database contains data on samples whose octane numbers were obtained using engine tests and is periodically updated with the introduction of new samples. The accuracy of the values obtained with a commercial spectrometer is usually evaluated by the ANP's inter-laboratory testing program, which has more than 20 participants and holds three annual testing rounds.

2.2. Procedures

The samples were introduced in the nebulizer/combustion system and the analytic signals were obtained through the continuous emission spectra recorded by the detector from an average of five spectra.

In the determination of MON and RON values about 20 mL of the sample was transferred to the device's sample bottle of the automatic analyzer. The results were obtained in an average of 30 s. After experimental determination of MON and RON, the same samples were analyzed using flame emission spectroscopy (FES). The numerical data obtained from these analyses were imported to the Matlab 7.9 R2009b program (MathWorks, Inc., Natick, MA).

For each sample (n), the spectra obtained were organized into an array of data to construct a row vector ($n \times 1219$) for each sample. The PLS algorithm was performed using PLS_Toolbox for

Table 1
Experimental conditions of flame emission spectrometer.

Parameter	Condition
Air flow rate[a]	1.25 NLPM
Fuel flow rate[b]	11.00 NLPM
Sample flow rate	1.0 mL min^{-1}
Air pressure	1.25 bar
Fuel pressure	5.50 bar

[a] Synthetic air (79% v/v N_2 and 21% v/v O_2).
[b] CH_4 (89% v/v).