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Classification of Brazilian and foreign gasolines adulterated with alcohol using infrared spectroscopy

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ABSTRACT

The smuggling of products across the border regions of many countries is a practice to be fought. Brazilian authorities are increasingly worried about the illicit trade of fuels along the frontiers of the country. In order to confirm this as a crime, the Federal Police must have a means of identifying the origin of the fuel. This work describes the development of a rapid and nondestructive methodology to classify gasoline as to its origin (Brazil, Venezuela and Peru), using infrared spectroscopy and multivariate classification. Partial Least Squares Discriminant Analysis (PLS-DA) and Soft Independent Modeling Class Analogy (SIMCA) models were built. Direct standardization (DS) was employed aiming to standardize the spectra obtained in different laboratories of the border units of the Federal Police. Two approaches were considered in this work: (1) local and (2) global classification models. When using Approach 1, the PLS-DA achieved 100% correct classification, and the deviation of the predicted values for the secondary instrument considerably decreased after performing DS. In this case, SIMCA models were not efficient in the classification, even after standardization. Using a global model (Approach 2), both PLS-DA and SIMCA techniques were effective after performing DS. Considering that real situations may involve questioned samples from other nations (such as Peru), the SIMCA method developed according to Approach 2 is a more adequate, since the sample will be classified neither as Brazil nor Venezuelan. This methodology could be applied to other forensic problems involving the chemical classification of a product, provided that a specific modeling is performed.

1. Introduction

Smuggling along the borders of countries is a reality [1–5]. Illicit trade of fuel, especially gasoline, along the borders of Brazil is a problem that concerns the authorities responsible for inspection and surveillance of these areas. This kind of trading occurs more frequently on the borders with Peru, Paraguay, Bolivia and especially, Venezuela. The main cause is the difference between prices in Brazil and in these countries (the difference can be more than 80%). Among the crimes covered in this practice are smuggling, illegal trade, criminal conspiracy and environmental crime (stockpiling harmful environment products). The Brazilian Federal Police is an authority that is often activated in combating this practice through denunciations or previously planned operations. When there is the seizure of fuel, a rapid characterization is required in order to certify its origin (national or foreign), and the result will define if there is a crime. The National Agency of Petroleum, Natural Gas and Biofuels (ANP) is the regulatory body that defines and specifies the physical–chemical quality parameters for the fuels sold in this country. In the case of gasoline, the main difference between Brazilian and the foreign gasoline is the presence of anhydrous ethyl alcohol fuel, currently established at 25% in Brazil [6]. The presence of ethyl alcohol in Brazilian gasoline makes it easily distinguishable from the others through the reference method to determine the content of anhydrous ethyl alcohol fuel (AEAC), established by ABNT NBR 13992 [7]. However, according to the Brazilian Federal Police, ethyl alcohol has been intentionally added to the foreign gasoline confiscated so that quick recognition is difficult. The characterization of Brazilian

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gasoline comprises the determination of physico-chemical quality parameters [8] based on methods that use specific and expensive instruments, require qualified people, and are time-consuming. In the laboratories located at the borders, the Federal Police does not have the kind of tools to perform the necessary analysis. These analyses must be carried out at the National Institute of Criminalistics, located in Brasilia, at least 3000 km away from the regional units. In addition, the transport of seized samples is not a simple procedure. These aspects make the process even more time-consuming and costly. Thus, faster and easier methods to characterize and safely attest to the origin of fuels (national or foreign) would increase the practicality and efficiency in combating this crime. Middle infrared spectroscopy (MIR spectroscopy) can address these demands when combined with multivariate methods of pattern recognition [9–13]. Moreover, MID infrared spectrometers are available in laboratories located in the regional offices of the Federal Police.

The potential of methods based on infrared spectroscopy and multivariate classification to detect and attest to the authenticity of beverages, cigarettes, and pharmaceuticals as well as to identify counterfeit documents, drug origin, and traces of lipstick stains at crime scenes has been reported [11,14–18]. Works using infrared spectroscopy for gasoline classification for different purposes can also be found in the literature. For example, Balabin and Safieva [19] used NIR spectra from three sets of gasoline samples to classify the samples according to the source (refinery and process) and the type (normal, regular and premium). Different methods of multivariate classification (Linear Discriminant Analysis – LDA, Soft Independent Modeling of Class Analogy – SIMCA and Multilayer Perceptron – MLP) were employed. MLP classification achieved the lowest percentage of errors (12% on average) for the three data sets. Classification according to the process provided the highest errors (18 to 35% for MLP and LDA, respectively). In a subsequent work, Balabin and Safieva [20] used the NIR spectra (14,000–8000 cm^{-1}) from a dataset of gasoline samples in order to compare the efficiency of nine different classification methods. The Probabilistic Neural Network (PNN) method was the most effective in performing gasoline classification with errors around 1%. The other methods showed error from 3% to 20%. Guardia et al. [21] proposed a multivariate statistical analysis to perform an automatic test for classification of gasoline samples according to quality (approved or disapproved) using quadratic discriminant analysis (QDA) associated with variable selection (Successive Projections Algorithm – SPA and Genetic Algorithm – GA) in the mid-infrared spectral region. Accuracy values of 93.3% and 95.6% for SPA-QDA and GA-QDA, respectively, were achieved.

Another subject addressed in the present work is instrument standardization. Once a classification model has been developed and validated in one laboratory (which contains the master instrument) is important to transfer the model to different units of the Federal Police strategic locations (where the secondary instruments are situated). However, changes in instrumental responses (spectra), which occur when a sample is measured in different instruments, affect the predictions performed by the model previously established in the master instrument. A procedure used to overcome this drawback can be complete recalibration consisting of performing new measurements for all samples in the secondary instrument and then rebuilding the model. As this procedure is costly and time consuming, an alternative is to use chemometric methods for the calibration transfer of multivariate models. From the various methods for calibration transfer that have been found in the literature [22,23], one widely used is direct standardization – DS [24]. This standardization method transforms the spectra from the secondary instrument to resemble those from the primary instrument. In the DS procedure, the entire spectrum of the secondary instrument is related to each spectral variable (wavelength) recorded in the primary instrument. To perform this transformation, it is necessary to measure a number of representative samples of the data set (transfer samples) with both the primary and secondary instruments. The use of standardization methods for calibration transfer is quite common in cases involving calibration models; in contrast, there are few works that use transfer methods from classification approaches [25,26].

Thus, this work aims to develop a simple, robust, rapid and non-destructive analytical method to classify automotive gasoline as Brazilian or foreign using mid-infrared spectroscopy and multivariate pattern recognition techniques. Additionally the direct standardization method is evaluated in order to transfer the classification models between the instruments located in laboratories that are strategically located: in Brasília and in the units near the borders, where there is this type of demand. Similar strategies could be applied to other forensic problems of smuggling to attest to the origin of products.

2. Materials and methods

2.1. Apparatus

Automotive gasoline samples were analyzed in three mid-infrared spectrometers, all from Thermo Scientific. One of them, the Nicolet FT-IR Model IS10, is located in the Main Laboratory of the Federal Police, in the city of Brasilia (FD). The other two (Nicolet 380 FT-IR) are located in the regional headquarters of the Federal Police in the cities of Boa Vista (Roraima State – RR) and Rio Branco (Acre State – AC). The Horizontal Attenuated Total Reflectance (HATR) accessory was used to perform the measurements in all instruments. The OMNIC™ software, version 8.0.65.0 (Thermo Scientific), was used to acquire the data.

2.2. Samples and reagents

A set of 126 gasoline samples was employed (56 Brazilian, 66 Venezuelan and 4 Peruvian samples). The foreign samples were seized by Federal Police and their ethyl alcohol contents analyzed using the reference method ABNT NBR 13992 [7]. They did not contain ethanol in their composition. The Brazilian samples were acquired in petrol stations located in the states mentioned above. The number of transfer samples was chosen considering the minimum necessary to represent the variability in the data set, due to the difficulties of transporting the gasoline samples to the different localities. Thus, the transfer set had just three samples, one from Venezuela, one from Peru and one from Brazil. Samples from foreign countries do not have ethyl alcohol in their composition. However, in order to simulate adulteration observed in some seized samples, ethyl alcohol was added in a proportion of 20% (v/v) to all foreign samples, according to the *PORTARIA MAPA* N° 678 *de* 31.08.2011 [27], prevailing at the time of sampling. Hence, all spectra used to build the classification models (including the transfer set) were obtained from samples containing ethyl alcohol.

2.3. Spectra acquisition

All absorbance spectra were acquired at room temperature (23 ± 2 °C) in the MIR region (4000–650 cm^{-1}) with 16 scans and resolution of 4 cm^{-1}. From the 126 samples, 18 were analyzed at the National Institute of Criminalistics (INC) of the Brazilian Federal Police Department in Brasilia (Instrument A); 90 samples were analyzed at the Setor Técnico Científico Regional de Roraima (SETEC-RR) in the city of Boa Vista (Instrument B); and the other 18 were analyzed at the SETEC-AC in the city of Rio Branco (Instrument C).