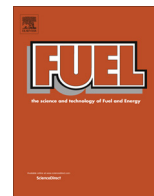




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Gasoline analysis by headspace mass spectrometry and near infrared spectroscopy

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HIGHLIGHTS

- HS–MS and NIRS allow for gasoline samples discrimination.
- No solvents are need for the HS–MS analyses nor for NIRS analyses, no wastes are produced.
- HS–MS method produced similar or better results than NIRS for the discrimination among gasoline samples.

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ABSTRACT

Headspace mass spectrometry and near infrared spectroscopy in combination with chemometric tools, including hierarchical cluster analysis and linear discriminant analysis, have been used for the classification of gasoline according to the research octane number. Volatile components were studied by headspace mass spectrometry whereas the whole gasoline samples were studied by near infrared spectroscopy. Sample pretreatment was not required for either analysis. A set of 60 samples belonging to two different research octane numbers (95# and 98#) was analyzed by both techniques. The best results were obtained on using linear discriminant analysis, which allowed a full discrimination of the gasoline samples using only four *m/z* ratios (46, 59, 95 and 98) in the case of headspace mass spectrometry and three regions (below 1000 nm, 1400–1500 nm and 1600 nm) in the case of near infrared spectroscopy.

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1. Introduction

A typical gasoline is predominantly a mixture of volatile hydrocarbons such as paraffins (alkanes), naphthenes (cycloalkenes) and olefins (alkenes), although it also contains compounds with oxygen, nitrogen or sulfur. Automotive gasoline is one of the most refined products and the specific process involved in gasoline production defines the final chemical composition of gasoline fractions and the resulting gasoline quality [1]. The production of gasoline must meet a variety of specifications and the quality of the resulting gasoline must satisfy the national standard requirements.

Several different gasoline types can currently be found in the market, with at least two different types available in most countries. Different countries use different research octane number

levels and most employ 93–95 for the lowest level and 96–98 for the highest. The gasoline market in Spain and most European countries includes 2 different types of gasoline that are differentiated by the RON: 95# and 98# [2]. RON is a measure of a fuel's resistance to knock or to ignite prematurely and it is determined using the Co-operative Fuel Research (CFR) engine according to ASTM D2699-08 [3].

The identification and discrimination of gasoline types is of primary importance for numerous reasons, the most important of which are quality control, ecological monitoring, and forensic science. In relation to forensic sciences, accelerants such as ignitable liquids are commonly used to start fires in arson attacks. The most commonly used ignitable liquids are petroleum-based products like gasoline because they are easy to obtain. In some cases, traces of gasoline or other ignitable liquids remain at the fire scene and these can be matched to samples that are collected in a database or associated with a particular suspect [4]. From a chemical point of view, gasoline and other ignitable liquids have different fingerprints and these help to discriminate between different

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liquids and allow the investigator to establish links between a suspect and a fire scene [5,6]. For this reason, in some laboratories work is being carried out to develop databases and these include the Ignitable Liquid Reference Collection (ILRC) at NCFS in The United States [7]. In fuel spill investigation it is also important to identify the fuel source – an activity that is not always straightforward [8,9]. It is also worth mentioning that there are several forms of illegal practice within the fuel market. For instance, the addition of lower price components, such as solvents, to gasoline due to the large difference in the taxation of gasoline and solvents [10,11]. As a consequence, there is a strong need to develop analytical techniques for gasoline characterization.

The most widely used analytical methods for the classification of these liquids are gas-chromatography coupled with an FID [12,13] or MS detector [4,14,15]. Indeed, the American Society for Testing and Materials (ASTM) has approved GC–MS as the standard method for the analysis of ignitable liquids even in fire debris [16]. However, the application of numerous different spectroscopic techniques is also described in the literature and these include FT-IR [10,11,17], NIR [18,19] and MIR [20–23] or Raman [24] spectroscopy combined with multivariate analysis for the characterization and quality control of fuels. These spectroscopic methods have several advantages over chromatographic techniques, e.g. the sample requires little or no preparation, the sample is not destroyed, reagents are not required, the equipment is relatively cheap and the analysis is quick.

In contrast to the above, compared with the chromatographic techniques, these spectroscopic techniques do have some drawbacks, mainly because spectroscopic signals cannot be assigned to specific compounds in the gasoline samples, meaning that they provide little information about individual components.

Since gasoline samples and other ignitable liquids contain large amounts of volatile organic compounds, VOCs, headspace-based techniques such as headspace mass spectrometry (HS–MS) have potential in this field. To date, most applications of these techniques are related to food and beverage, cigarette, pharmaceutical and paper industries, biotechnology, medicine, wastewater treatment plants and security companies. In many of these applications this application is also known as an electronic nose (EN).

Primary results on the application of an EN based on sensors for the classification of gasoline, heating oil and diesel oil can be found in the literature [25].

This technique does have specific advantages. Apart from the speed of the analysis, the fact that the sample does not require preparation, the absence of residues because solvents are not used, this technique also has high sensitivity, good accuracy, low cost, it is easy to handle for routine analysis and the required sample volume is very small. Most of these advantages are also provided by the NIRS systems [26], which have previously been applied for gasoline characterization [20,21] and related samples as biodiesel [27].

In the work described here, a total of 60 gasoline samples provided by different Spanish refineries and belonging to 2 different RON (95# and 98#) were analyzed by both HS–MS and NIRS. The results obtained with both techniques were compared. A chemometric study was carried out in order to obtain a discrimination method for both sets of samples.

2. Materials and methods

2.1. Gasoline samples

60 gasoline samples were purchased from different gas stations corresponding to different Spanish refineries. The samples corresponded to two different types characterized by the RON: 30 samples from 95# and 30 samples from 98#.

2.2. Acquisition of HS–MS spectra

Gasoline analysis was performed with an HS–MS Alpha Moss (Toulouse, France) system that consisted of an HS 100 static headspace autosampler and an α Kronos quadrupole mass spectrometer (MS). The samples were contained in 10 mL sealed vials and each sample was placed in the autosampler oven to be heated and agitated in order to generate the headspace. Headspace was finally taken from the vial using a gas syringe and injected into the mass spectrometer detector. The gas syringe was heated above the sample temperature (+5 °C) to avoid condensation phenomenon. Between each sample injection, the gas syringe was flushed with carrier gas (nitrogen) to avoid cross-contamination.

The experimental conditions for the headspace sampler were as follows [28]: sample volume of 80 μ L, incubation temperature 145 °C, incubation time 10 min, agitation speed 500 rpm, syringe type 5 mL, syringe temperature 150 °C, flushing time 120 s, fill speed 100 μ L/s, injection volume 4.5 mL and injection speed 75 μ L/s. The carrier gas was nitrogen and 2 μ L of TBPFA (perfluorotributylamine) were added to all samples as an internal standard. The total time per sample was approximately 10 min. The components in the headspace of the vials were passed directly to the mass detector without any chromatographic separation or sample pre-treatment. In this way, for any given measurement, the resulting mass spectrum gives a fingerprint of the gasoline. MS spectra were recorded in the range m/z 45–200. Instrument control was achieved using RGA (Residual Gas Analysis software package) and Alpha Soft 7.01 software.

2.3. Acquisition of NIR spectra

The 60 samples were also analyzed by NIR spectrometry. NIR spectra were collected in an AvasSpec-NIR 256-1.7 equipped with a tungsten halogen lamp and a transmittance probe with a path length of 10 mm. The spectra were acquired at room temperature. Transmittance values in the range of 891–1812 nm were acquired with a resolution of 3.4 nm.

2.4. Data analysis and software

Multivariate analysis of the data, which included hierarchical cluster analysis (HCA) and linear Discriminant Analysis (LDA), was performed using the statistical computer package SPSS 17.0. (Chicago, IL, USA) [29].

3. Results and discussion

3.1. HS–MS chemometric Study

The whole set of 60 gasoline samples (Gas 95# and Gas 98#) were analyzed by HS–MS. All mass spectra were normalized at an m/z of 131, which is the significant m/z of the internal standard (TBPFA), because previous analyses of the gasoline samples did not produce a signal at m/z 131. The mass spectra of the 60 gasoline samples are shown in Fig. 1. The spectra for gasoline 95# and 98# appear to be quite similar and it is therefore very difficult to distinguish between the two types of gasoline based only on their HS–MS spectra. This finding demonstrates the need to use chemometric techniques for the classification of these samples.

An exploratory chemometric technique was initially carried out in order to check for a general distribution of the gasoline samples. An HCA (hierarchical cluster analysis) was applied using all of the m/z values (45–200 m/z) as variables to form groups. The results of the cluster analysis are shown in a dendrogram in Fig. 2, in which all of the samples are listed, and this indicates the level of

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