



Mid- infrared uncooled sensor for the identification of pure fuel, additives and adulterants in gasoline



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ABSTRACT

The aim of the present study is to test the ability of a low-cost and portable middle infrared spectrometer based on a linear array of 1×128 of PbSe, coupled with a linear variable optical filter in the wavelength range of 3–4.5 μm , for the differentiation of pure chemical substances and quality control of fuels. Potential additives and adulterants for gasoline were tested, considering the alcohols ethanol, n-butanol, n-propanol and n-hexanol as potential additives and methanol and diesel oils as adulterants. Multivariate analysis of variance (MANOVA) applied to the scores obtained in the Principal Component Analysis (PCA) was conducted to analyze the spectral data and distinguish between the individual components. For the purposes of classifying anonymous samples, the centroid of each pure substance in the canonical variables was calculated, followed by the distance calculated between new samples to such centroids, assigning the individual to the most proximate category. The results demonstrated that the technique was able to discriminate between gasoline, diesel oils and the alcohols methanol, ethanol, n-propanol, n-butanol and n-hexanol and that it had the potential to be applied in the fuel industry.

1. Introduction

The means of transport currently in use are based on fossil fuels (petrol and diesel) which are non-renewable. Moreover, the increase in per capita energy use and improvements in the standard of living in developed and developing countries are enhancing this fuel dependency, with transport being a major contributor. In fact, the transport sector experienced an increase in the share of energy demand from 26% in 1990 to 32% in 2013 in the EU (Eurostat, simplified energy balance sheets, 2015 annual data) [9]. In recent years, fuel quality has become increasingly important, not only for its role in vehicle performance, but also for its impact on their emissions [21]. Fuel composition will continue to grow in importance as governments continue their strategy to achieve near-zero-emission vehicles. The removal of alkyl-lead compounds as an additive in gasoline, for environmental and public health reasons, has led oxygenated compounds to become increasingly important components in the formulation of automotive gasoline [3]. ETBE (ethyl tert-butyl ether) and alcohols (ethanol and butanol) are the oxygenated compounds most commonly added to gasoline [8,17,18]. Among the various alcohols, ethanol (100% renewable as bioethanol) is known as the most suitable, renewable, bio-based and eco-friendly fuel for spark-ignition engines [5,10]. In parallel, butanol

has good prospects as gasoline blend stock ([10,17]), since it presents better blending features compared to ethanol, but on the other hand some properties are better in ETBE. Nevertheless, it is not as renewable as alcohols ([5,10]). These issues are shown in Table 1. Higher chain alcohols (C3–C5) contain a high energy density, and are compatible with the current infrastructure as they are less hygroscopic [10]. These alcohols can be blended with gasoline. They also have the potential to be used as replacements, as butanol has already been shown to perform well in conventional gasoline engines [10,17].

Normally fuels are adulterated by mixing them with comparatively lower-priced adulterants which are chemically similar and necessarily easily miscible with them, such as industrial organic solvents, waste lubricants or kerosene [14]. Another kind of adulteration practice is frequent in countries where bioethanol is currently used as a common biofuel, mixed with gasoline in its dehydrated form (Hydrated Ethyl Alcohol Fuel, usually known as HEAF). HEAF is commonly adulterated with methanol, as methanol and ethanol present similar physical and chemical properties, and the price of methanol is lower than that of ethanol [14,15]. Fuel quality control has gained interest in many countries owing to the potential damage of low-quality fuel to engines, the environment, and economy. Thus, the application of analytical techniques to verify quality control of fuels has become crucial

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Table 1
Gasoline blendstock comparison: Ethanol vs butanol and ETBE.

PROPERTIES	ETBE	Ethanol	Butanol
Blend octane ⁽¹⁾ (R + M)/2	111	112	102
Blend RVP ⁽²⁾ (psi)	4–6	18–22	4–5
Oxygen content (%)	15.66	34.7	21.6
Net energy (% gasoline)	84.3	65	82
Renewability ⁽³⁾ (%)	47	100	100

[4,6,11].

The fuel industry is constantly on the lookout for sensors to be used for in-situ monitoring of fuel quality and adulteration detection. Vibrational spectroscopy techniques are non-destructive analytical techniques that allow reliable direct and fast determination of several properties at the same time without sample pre-treatment ([7,13]). Infrared spectroscopy using Fourier transform spectrometers (FTIR) is the most common method used to determine the presence of adulterants in oils and petrol [4,7,11]. This is due to the fact that most organic compounds absorb radiation from the Infrared Spectrum [20].

The functional group region goes from 4000 to 1300 cm^{-1} , and it offers general information about the chemical structure of a particular compound. The so-called fingerprint region goes from 909 to 650 cm^{-1} where the absorption of molecules belonging to the same functional group is quite different. The MWIR spectrometer used for this study works only in the functional region [20]. In previous studies, infrared spectroscopy has been used to predict the properties of ethanol as an additive in gasoline blending [12], and for raw ingredients in the production of rocket propellant, as well as for fuel quality control issues [16].

Mathematical analysis is used as a complementary tool for infrared spectroscopy, specifically multivariate techniques ([4,11]). Nevertheless, FTIR spectrometers are expensive and heavy devices, which means that they are suitable for laboratory use but not for in situ applications which may require several devices installed along the product chain.

For this reason there are plans to introduce low-cost spectrometers for some applications.

These have huge potential in systems for chemical analysis by optical absorption, fluorescence and emission line characterization [1]. Such micro spectrometers offer significant advantages over existing instruments, including size reduction, small sample size, and fast data acquisition [2]. However, on the down side, this kind of sensors have a limited signal-to noise ratio and poor resolution (in the case under study, the resolution is 60 nm).

This disadvantage can be proven by the mathematical tools used in Chemometrics [4]. On the other hand, the infrared sensor used in this study is covered by a linear variable filter (LVF). This filter is based on a tapered cavity on top of a linear array of photodetectors, enabling the transfer of the optical spectrum into a lateral light intensity profile over the array of photodetectors. The same concept for this system can be designed and implemented for wavelengths ranging from UV to IR (0.3–5 μm). In previous studies, LVF microspectrometers for UV and visible spectral ranges were presented [1,2].

The sensor used in this study provides a potential solution of portable equipment for fuel identification, using chemometrics as a support for the identification and segregation of gasoline, its additives (ethanol, propanol, butanol and hexanol) and two types of adulterants (methanol and diesel oil).

2. Materials and methods

The instrumentation and set-up consist of an infrared source, a sample chamber and a detector. The mid-infrared (MIR) spectrometer used for this study was based on a nondispersive linear sensor model CORE-HS LUXELL 128, which is manufactured by the company New Infrared Technologies (Boadilla del Monte, Madrid). It is made of vapor phase deposited PbSe (VPD PbSe) and has a coupled linear variable filter (LVF), in the wavelength range between 3 and 4.5 μm . The PbSe detection band ranges between 1 and 5 μm . The peak detection wavelength is 3.7 μm . The integration time ranges between 4 and 20 μs (selectable on the instrument). The acquisition rate is up to 300 spectra per second [18], so it is faster than other kinds of sensors. This spectrometer, with no moving parts, is a rugged, compact and economically affordable device. An image of this sensor and the experimental set-up is displayed in the picture below (fig. 1). The infrared light source consisted of a SiC filament and a parabolic reflector (IR-SiX, Hawkeye Technologies, Inc.).

During the experiments, the intensity was set at 4.5 A, while voltage was fixed at 6.5 V. Liquid samples were allocated between two sapphire windows without any spacer in between, thereby allowing a very thin optical path (around 200 μm).

The 60 nm spectral resolution imposed by the spectrometer LVF + linear array performance levels means that chemometrics have to be used to reveal “hidden” information included in the low-resolution IR spectra obtained and, analyze the chemical species and extract their features.

Samples and chemicals.

The gasoline samples were taken in two different seasons (winter and summer gasoline according to legislation) and from different

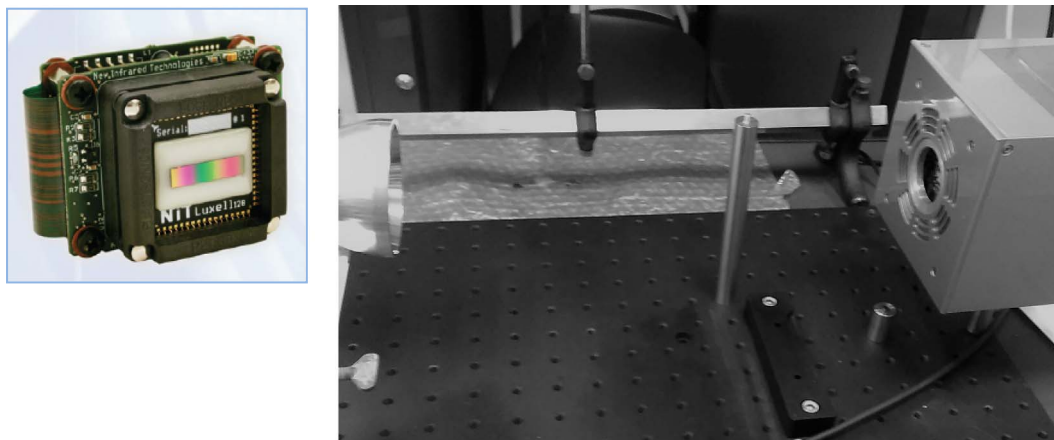


Fig. 1. (left) LUXELL non refrigerated FPA covered by the LVF and assembled to its module; (right) Experimental set up: On the left side there is an IR source lamp made of a SiC filament and a parabolic reflector. The sample was dropped between two sapphire wafers, which are transparent to IR radiation, and put on the path between the source and the detector. On the right side there is the camera containing the IR detector made of PbSe with a coupled LVF.

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