Analytical Methods for Determining Automotive Fuel Composition

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1. Introduction

Gasoline, a sub-product from the fractional distillation of petroleum, is a mixture of several hundred organic volatile compounds, mainly hydrocarbons, ranged from four to twelve carbon atoms with boiling points in the range of 30 – 225 °C (Fialkov et al., 2008). The physico-chemical properties depend on the origin and method used to obtain the gasoline (Barbeira et al., 2007).

It has been used as fuel for internal combustion engine vehicles for over a century, albeit the possibility of producing alternative sustainable fuels was considered long time ago, as can be learnt from Henry Ford’s statement to the New York Times in 1925 (French & Malone, 2005): “There is fuel in every bit of vegetable matter that can be fermented. There’s enough alcohol in one year’s yield of an acre of potatoes to drive the machinery necessary to cultivate the fields for a 100 years.”

In the last decades, there has been a growing concern with regard to some important environmental aspects as, for instance, the vehicle-generated greenhouse gas emissions leading to air pollution and the need for renewable fuels due to energy shortage. Ethanol has been considered as an attractive alternative fuel, because it can be obtained from domestic crops, such as sugar cane, corn, sorghum, wheat and potatoes and presents higher octane number and faster combustion speed than gasoline (Yao et al., 2009). Interestingly, ethanol, as automotive fuel, started to be used in Brazil as early as the 1930s (Szklo et al., 2007), but it was only after the two major oil shocks of the 1970s that its consumption became significant either as a gasoline additive or as a gasoline substitute. Currently, several other countries such as the USA, Thailand, China and Sweden are using blends of gasoline and ethanol, to fuel vehicles.

Gasohol is gasoline blended with anhydrous ethanol at different percentages expressed by an E-number, which corresponds to the percentage in volume of alcohol present in the fuel (Muncharoen et al., 2009). For instance, E20 contains ethanol at 20% and gasoline at 80%, by volume.

In the last decade, flexible-fuel vehicles (FFV), that can use gasoline, gasohol, hydrated ethanol or any mixture of them, became very popular. Currently, in Brazil, more FFV
vehicles are sold than those powered by gasohol. Since the composition of the fuel in the tank may fluctuate widely depending on the type of fuel a driver decides to buy, and since the optimal air:fuel ratio in the combustion chambers is a function of this composition and is crucial for the smooth operation of the engine, the need for sensors capable to directly or indirectly measure the alcohol:gasoline ratio became very important. Currently, most vehicles are equipped with lambda sensors or universal exhaust gas oxygen (UEGO) sensors (Regitz & Collings, 2008) which do not determine the real fuel composition, but the amount of oxygen present in the exhaust gases. Besides, they are exposed to high temperatures (up to 1000 °C) and high vibrations (up to 50 g), which may lead to fast degradation of the sensor (Hanrieder et al., 1992).

1.1 Environmental aspects
Transport facilities belong to one of the most important sources of air pollutants (Sobanski et al., 2006). One of the crucial parameters that influence the formation of pollutant gases in internal combustion engines is the nature of the fuel and its additives. A recent study comparing the emissions of several pollutants and greenhouse gases when gasoline and gasohol are used as fuels (Zhai et al., 2009) has shown that although the latter may reduce products of incomplete combustion, such as CO (-35–60%), the emission rates of methane are increased (+30–40%), as well as of NOx and especially of acetaldehyde (+60% and +200%, respectively, as the ethanol content was increased to 40%). Besides, gasohol has a higher vapour pressure than gasoline, thus raising concerns about evaporative emissions (Pumphrey et al., 2000).

Anti-knock additives such as tetraethyl lead (TEL), which contributed to increase atmospheric pollution and octane enhancers such as methyl tert-butyl ether (MTBE), which caused contamination of underground waters are no longer required when using gasohol, since ethanol has anti-knock properties and enhances the octane number. On the other hand, its content must be monitored to keep the octane number aligned with the standard (Muncharoen, et al., 2009).

The emission of volatile organic compounds (VOCs) to ambient air is of increasing concern also because of the role of these compounds in the formation of photochemical smog and the toxicity of some individual compounds such as benzene (Winebrake and Deaton, 1999; Leong et al., 2002).

The comprehensive approach to reduce pollution requires the control of automotive fuel composition, which is currently performed by accredited laboratories being costly and time consuming. Hence, inexpensive analytical methods to certify the quality of fuels are important to be developed (Pereira et al., 2006).

1.2 Fuel adulteration
The standards for fuels are usually regulated by governmental agencies. Unfortunately, in many countries, people intentionally add cheaper organic substances in an attempt to raise profit margins. This illicit practice is called adulteration. It affects public coffers through tax embezzlement, since solvents such as mineral spirits, kerosene, rubber solvents, naphta, and thinner are levied at different rates (Pereira et al., 2006). It may also severely damage the engines and produce emissions that increase environmental pollution.

In Greece, for example, three types of diesel fuel are commercialized: automotive, domestic heating and marine diesel fuel. Marine and domestic are cheaper than automotive diesel fuel, and are therefore used to adulterate the latter (Kalligeros et al., 2001).
In the United States of America biodiesel blends are adulterated with soy oil (Mahamuni & Adewuyi, 2009). In Southeast Asia diesel is adulterated with kerosene, cyclohexane, crude hexane and turpentine oil (Bahari et al., 1990; Roy 1999; Patra & Mishara, 2002).

Since 1979 the Brazilian gasoline labelled ‘gasolina C’ or gasohol has been combined with ethanol in different proportions from 19-27% (v/v) that are specified by the Brazilian governmental body ‘Agência Nacional do Petróleo’ (ANP) (De Oliveira et al., 2004). The proportion depends on the national production of ethanol from sugar cane, and is currently 25% (Aleme et al., 2009). The end of the fuel distribution monopoly, opened the road to the criminal practice of adulteration of gasohol (Pereira et al., 2006), which mainly consists increasing the fraction of ethanol outside the range specified by ANP and/or the addition of organic solvents (Ré-Poppi et al., 2009). Since 1975 anhydrous ethanol has been used in Brazil and has been adulterated with methanol and even water (Carneiro et al., 2008; Xiong & Sisler, 2010). Methanol is cheaper and quite similar to ethanol in many physico-chemical properties, but presents high toxicity and may cause temporary or permanent corneal, pancreatic and liver damage or even death by inhalation or skin absorption. (Carneiro et al., 2008; Costa et al., 2005; Treichel, et al., 2003).

Some years ago, ANP begun to introduce tracers in all solvents commercialized in Brazil, which can be detected by specific analytical techniques. Although efficient, this measure is quite expensive (Pereira et al., 2006).

For the purpose of overcoming fuel adulteration practices, it is necessary to develop novel, in situ, low-cost and reliable methods to monitor the fuel composition.

2. Analytical methods

The most traditional methods to qualitatively and quantitatively estimate fuel composition are gas chromatography (GC) (Pedroso et al., 2008) and high-performance liquid chromatography HPLC (Zinbo, 1984). These techniques involve the separation of mixtures of compounds by differential rates of elution by passing through a chromatographic column, governed by their distribution between a mobile and a stationary phase.

Infrared spectroscopy has been reported for quantitative analysis of ethanol and methanol in fuels by using attenuated total reflectance (ATR) (Battiste, 1981) and Fourier transform near infrared (FT-NIR) (Fernandes et al, 2008).

$^{17}$O nuclear magnetic resonance spectroscopy ($^{17}$O NMR) was used for the quantification of oxygenated additives in gasoline (Lonnon & Hook, 2003).

Although these methods are reliable they need trained professionals and costly equipments and cannot be performed in loco. This chapter will focus on modern analytical methods that can be incorporated into vehicles at a reasonable cost.

2.1 Fuel analysis based on electrical conductivity change

There are several types of gas sensors based on the change in electrical dc resistance (or ac impedance) upon exposure to volatile compounds. They are known as chemoresistive sensors and are usually made from metal oxide semiconductors (MOS), MOS field-effect-transistors (MOSFET) or, more recently, from conducting polymers (CP). The oldest and most commonly used chemoresistive sensor is the so-called Taguchi sensor, which consists of ceramic devices made by sintering powdered n-type or p-type MOS. Such sensors have been widely used to detect reducing and oxidizing gases as, for instance, petrol vapours in filling stations, ethanol in exhaled air etc. (Gründler, 2007). These sensors present as
drawbacks the high working temperature (200 to 600 ºC) and the slow change in their performance characteristics over time.

CP based sensors have attracted much interest, specially for electronic noses, which are analytical instruments developed to mimic the human nose, and are basically formed by an array of dissimilar gas sensors, that generate different response patterns for different types of smells, attached to a pattern recognition system (Gardner & Bartlett, 1999). The reasons for using CPs for this purpose are that a huge number of different CPs can be synthesized, they respond to a wide range of volatile compounds and they operate at room temperature, which implies in low power consumption and, hence, portability. The most common CPs used for gas-sensing purposes are polypyrrole (De Melo et al., 2005), polythiophene (Chang et al., 2006), polyaniline (Anitha & Subramanian, 2003) and more recently also poly(p-phenylenevinylene) derivatives (Benvenho et al., 2009) and poly-p-xylylenes (Li et al., 2008; Li et al., 2009). Their chemical structures are shown in Figure 1. Interestingly, although poly-p-xylene is known for its excellent insulating property, aryl-substituted derivatives become conducting upon doping and are highly stable to air and humidity, being very convenient for gas sensors (Li et al., 2008).

![Chemical structures of polypyrrole (PPy), polythiophene (PT), polyaniline (PANI), poly(p-phenylenevinylene) (PPV) and poly-p-xylylene (PPX).](image1)

Fig. 1. Chemical structures of polypyrrole (PPy), polythiophene (PT), polyaniline (PANI), poly(p-phenylenevinylene) (PPV) and poly-p-xylylene (PPX).

The sensors usually consist of thin (1 – 50 μm) doped polymer films deposited by spin-coating, drop-casting or other technique onto interdigitated electrodes. These, depending on the desired distance between digits can be obtained by several methods as, for instance, circuit printing (Li et al., 2008) and graphite line patterning (Venancio et al., 2008) (for distances > 200 μm) or lift-off and conventional lithography (for distances between 1 μm and 200 μm).

![Polymeric gas sensor using a printed circuit interdigitated electrode and interdigitated electrode obtained by conventional lithography.](image2)

Fig. 2. (a) Polymeric gas sensor using a printed circuit interdigitated electrode and (b) interdigitated electrode obtained by conventional lithography.

Reversible changes in the electrical conductance of the CP films, upon exposure to volatile compounds, can be measured using a conductivity meter. The reasons for these changes remain not fully understood but may involve swelling of the polymer and also charge-
transfer interactions caused by the penetrating vapours (Meruvia et al., 2007; Slater et al., 1992). A typical measuring system using a single sensor is shown in Figure 3.

Fig. 3. Block diagram of the measuring system using one gas sensor.

The above-mentioned system was used to detect and discriminate many different types of volatile organic compounds. For instance, Figure 4 shows the response pattern of three similar sensors (differing only in the CP film thickness) when exposed sequentially to air saturated with five different carbonyl compounds, often present in polluted indoor air (Li et al., 2009). As can be seen, the pattern (amplitude, positive or negative response and shape) is different for each volatile compound.

In order to analyse data generated by several sensors (three, in this particular case) three parameters were defined, the relative response (Ra), the half-response time (T1) and the half-recovery time (T2), as follows:

\[ Ra = \frac{(G_2 - G_1)}{G_1} \]  
\[ T_1 = \frac{G_1 + G_2}{2} - T_{G_1} \]  
\[ T_2 = \frac{G_2 + G_3}{2} - T_{G_2} \]

Where \( G_1 \) is the conductance immediately before exposure to a particular vapour, \( G_2 \) is the conductance at the end of the exposure period and \( G_3 \) is the conductance after the recovery period. Figure 5 represents these parameters.

Fig. 4. Response of three CP based gas sensors to five volatile carbonyl compounds. Polymer film thickness (μm): 30 (sensor 1), 15 (sensor 2) and 10 (sensor 3). (Reproduced from Li et al., 2009, with permission of Elsevier ©)
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Fig. 5. Parameters used for calculating $T_1$ and $T_2$. (Reproduced from Li et al., 2009, with permission of Elsevier ©)

A plot of $R_a \times T_1 \times T_2$ (Figure 6) reveals the discrimination power of these sensors. There are five separate clusters of data points corresponding each one to a particular organic compound, i.e. benzaldehyde, propionaldehyde, butanone, acetone and acetaldehyde. It is worth mentioning that the cost of each sensor is less than US$1 and it lasts for at least one year. Besides, they are easy to fabricate, operate at room temperature, have extremely low power consumption (< 1 mW) and are insensitive to humidity.

Fig. 6. Three-dimensional plot of $R_a \times T_1 \times T_2$. (Adapted from Li et al., 2009, with permission of Elsevier ©)
The results above are qualitative, i.e. the sensorial system identifies de volatile compound but does not indicate its concentration. For fuel analysis, this kind of information is important but quantification is crucial. Thinking of flex-fuel vehicles, in which the alcohol-gasoline composition may vary widely, a sensor was developed that is insensitive to hydrocarbons (gasoline) but quite sensitive to ethanol (Benvenho et al., 2009). The sensor was made of a thin (30 μm) film of poly(2-bromo-5-hexyloxy-1,4-phenylenevinylene)-co-(1,4-phenylenevinylene) (BHPPV-co-PPV), doped with dodecylbenzenesulfonic acid (17 % w/w), drop-casted onto an interdigitated electrode having a gap of 0.2 mm between digits and active area of 1 cm². Several sensors were fabricated and tested of over one year. Some of them were kept in closed vessels containing ethanol, gasoline and a 1:1 mixture of both. Figure 7 shows a linear relative response (Ra) of these sensors towards gasohols ranging form E5 to E100.

![Fig. 7. Relative response (Ra) of the sensor in function of the concentration of ethanol in gasoline. (Reproduced from Benvenho et al., 2009, with permission of Elsevier ©)](image)

### 2.2 Fuel analysis based on capacitance change

Gas sensors based on capacitive properties or chemocapacitors (CAP) have been used in the study of organic volatile substances. The CAPs have been constructed in different geometries. The most common structure is planar with interdigitated electrodes having as sensitive layer conducting oxides (Ponce et al., 2009), porous silicon (Tutov et al., 2000) and polymers (Josse et al., 1996; Meruvia et al., 2007), for example. The chemocapacitor is based on the change of capacitance caused by a change of dielectric constant, due the modifications in polarization properties of molecules and/or atoms inside the active layer by external perturbations, such as the interaction with volatile organic compounds (VOC). These layers are permeable for permitting the interaction between the analytes and the sensors (Pearce et al., 2003). For generation of an electrical signal, the method uses alternate current (AC) in the frequency range from a few kHz up to 500 kHz (Pearce et al., 2003).
Matter consists of positive and negative charges that are not completely separated inside a neutral molecule resulting in molecular dipoles or molecule dipole moments that depend on the structure of atoms or molecules and that can be externally perturbed by electrical fields. The molecule polarization is given by:

\[ P = \varepsilon_0 \chi E \]  

(1)

where \( \varepsilon_0 \) is the vacuum permittivity, \( \chi \) is the susceptibility and \( E \) is the electric field.

The study of the physical characteristics by static methods is not very meaningful. More relevant, both experimentally and technologically, are time or frequency dependent methods (Jonscher, 1983).

In the case of gas sensors based on change of dielectric constant, the usual method is the frequency-dependence domain. This method is very useful in systems with a non-linear process.

The frequency method implies the need of a mathematical transformation from time-domain to frequency-domain, which is achieved by a Fourier transform (FT). The frequency dependent polarization is thus given by (Jonscher, 1983):

\[ P(\omega) = \varepsilon_0 \chi(\omega)E(\omega) \]  

(2)

where the electric field is frequency dependent and susceptibility is a complex function

\[ \chi(\omega) = \chi'(\omega) - i\chi''(\omega) \]  

(3)

in which \( \chi'(\omega) \) gives the amplitude in phase with the harmonic driving field and \( \chi''(\omega) \) gives the component of quadrature with field.

The changes of susceptibility can be modelled as changes of dielectric responses that thus can be written in a complex form as

\[ \varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) \]  

(4)

The first term is the contribution of the material susceptibility and the second term is due to dielectric loss.

The geometrical capacitance can be defined by

\[ C = \varepsilon A / d \]  

(5)

where \( A \) is the electrode area, \( d \) is the distance between the electrodes and \( \varepsilon \) is the relative permittivity.

The capacitance which is the scaled device equivalent of the material parameter \( \varepsilon \) becomes

\[ C(\omega) = C'(\omega) - iC''(\omega) \]  

(6)

where \( C'(\omega) \) corresponds to the ordinary capacitance and \( C''(\omega) \) represents the dielectric loss component.

The experimental method used to measure the properties as a function of frequency is called immittance and can be a measure for admittance (\( Y \)) and impedance (\( Z \)). The detailed explanation of these methods can be found in (Jonscher, 1983; Barsoukov, 2006).

In the case of gas sensors the capacitance depends on the relation between the electrical permittivity of the sensor sensitive layer and the analyte; if the permittivity of the analyte is greater than the permissivity of the sensitive layer the capacitance increases, if opposite the capacitance decreases (Pearce et al., 2003).
This method has been used to study the composition of fuels (Kim et al., 2000). Using porous silicon as active layer they studied the dielectric response for methanol-water and ethanol-water. In both systems, increasing the alcohol concentration led to the elevation of the capacitance.

Li et al. (Li et al., 2007) using as active layer nanoporous silicon between interdigitated electrodes observed a non-linear increase of the capacitance when the concentration of ethanol in air was increased. This interesting result is shown in Fig. 8. Other important features mentioned in this work are long-term stability, high sensitivity and fast response time.

Wiziack et al. (Wiziack et al., 2009) used an array of eight capacitive polymeric sensors to discriminate gasoline, diesel, ethanol and some common fuel adulterants as toluene, hexane and water. These results depend on the polymeric material used as active layer and their interaction with organic volatile compounds. Since it is not possible to represent all the experimental data generated by eight sensors in a two dimensional plot, the authors used principal component analysis (PCA) projecting the original data in two main dimensions as represented in Fig. 9.

Fig. 9. Biplot of principal components obtained from capacitance measurements (Reproduced from Wiziack et al., 2007, with permission of Elsevier ©)
As can be seen, this multi sensor system can discriminate efficiently different fuel adulterants. The capacitive sensors presented good reliability for the measurements of fuel components. A drawback is that the equipment setup is expensive.

2.3 Fuel sensors based on refractive index measurements

Among the different existing gas sensors, optical sensors based on the change in the refractive index are important in the study of different analytes, such as arterial blood (Soller, 1994; Leiner, 1995), organic solvents (Abdelghani et al., 1997; Albert et al., 2001), combustion gas (Brown et al., 2008) and fuel (Falate et al., 2005). Sensors based on refractive index are usually constituted of optical fibers (OFs) coated with sensing materials such as polymers, porous silica, and fluorescent indicators. In the experimental setup other components as, for instance, light sources and detectors are also necessary. The operation principle is based on the optical changes exhibited in response to the exposure to different volatile chemical compounds.

Optical fibers began to be used in commercial communication systems in the 1970s and the transmission is based on a dielectric optical waveguide. The light is confined to the core of the waveguide by total reflection inside the structure. Thus, OFs need a high refractive index material in the core (n₀) compared to that of the cladding layer (n₁) and it is possible to define a critical angle (θₑ) (Bass et al., 1995; Yin, Ruffin & Yu, 2008) as:

$$\Theta_e = \arcsin\left(\frac{n_0}{n_1}\right)$$ (7)

For the total reflection to occur it is necessary that the light that enters the fiber forms an angle greater than the critical angle. The transmission in these OF sensors is based on different physical processes such as fluorescence, chemiluminescence, bioluminescence, surface plasmon resonance (SPR) and absorption, being the latter the most useful for fuel analysis. In such experiments the light energy is absorbed by atoms and molecules of the sensitive layer (cladding) or the core, and is described mathematically by the Lambert-Beer law:

$$I = I_0 \exp(-\alpha C \Delta x)$$ (10)

Where I₀ is the intensity of the incident light, α is the absorption coefficient of the absorbing agent, C is the concentration of the analyte and Δx is the thickness of the sensitive layer.

Another method to determine the interaction of volatile substances is the study of the reflectivity of the active sensitive layer to the analyte which depends on the difference between the refractive index of the analyte and that of the sensitive layer. The reflectivity (R) is given by:

$$R = \left(\frac{n_A-n_F}{n_A+n_F}\right)^2$$ (11)

in which nₐ the refractive index of the analyte and n₁ of the sensitive layer.

Using the methodology described above, sensors based on refractive index have been studied by several research groups in different countries for the determination of fuel composition. For instance, in India where adulteration of fuel is a major problem, Roy (Roy, 1999) studied the adulteration of diesel and petrol by addition of kerosene. The increase of kerosene concentration in the mixture diesel-kerosene decreases the refractive index. On the other hand, it increases as the kerosene concentration becomes higher in petrol-kerosene blends. These results are shown in Fig. 10.
As described in section 1.2, Brazil also suffers from fuel adulteration practice and studies focused on determining fuel composition by refractive index changes in optical fibers have been published. Thus, Falate et al. (Falate et al., 2005) studied the vapour of hydrocarbons and possible adulterants in gasoline. In their work they used fiber optics connected to long-period gratings (LPG) to measure changes in attenuation peak wavelength for ethanol-gasoline mixtures in different proportions, and adulteration by addition of other solvents such as naphta, turpentine and paint thinner in Brazilian commercial gasoline. It was possible to observe changes in the position of the maximum peak in the electromagnetic spectra and consequently also in the refractive index values (Fig. 11).
alcohol or mixtures of both of any composition (gasohol), (b) the increasingly strict laws for emissions of pollutants from motor vehicles and (c) illegal practices as, for instance, mislabeling or physical adulteration of fuels by adding lower-price components, with no regard for health and safety considerations; the need for novel in situ, low-cost and reliable sensors for monitoring fuel composition and, hence, its quality has become a high priority. Recent progress achieved in the field of chemoresistive, chemocapacitive and chemooptical sensors, briefly described in this chapter, will certainly play an important role to accomplish these tasks.

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5. References


In the last few years the automobile design process is required to become more responsible and responsibly related to environmental needs. Basing the automotive design not only on the appearance, the visual appearance of the vehicle needs to be thought together and deeply integrated with the power developed by the engine. The purpose of this book is to try to present the new technologies development scenario, and not to give any indication about the direction that should be given to the research in this complex and multi-disciplinary challenging field.

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