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Characterisation of fuel volatile compounds using a new ionic microsensor

P. Bonnet
D. Jamois

A. Rachid

Laboratoire d'analyse et de mesures à l'émission
et capteurs (LAME)
Institut national de l'environnement industriel et
des risques (INERIS)
Verneuil en Halatte, BP2 60550

Automatic Systems Laboratory LSA
Jules Verne University of Picardy UPJV
Amiens, Rue du Moulin Neuf 80000

Abstract

This article describes an ionic microsensor capable of characterising the volatile phase of fuels. Ions are generated by the thin film catalytic microsensor developed by LETI and INERIS, associated with a multi-level temperature interrogation technique. A suitably polarised electrode is adapted to this sensor in order to collect the ions. A measurement bench has been developed simultaneously to record the responses of four sensors to mixtures of gases or vapours. Laboratory tests conducted on a wide range of molecules (alkanes, alcohols, ketones, aldehydes, etc.) show that it is possible to differentiate between most of these substances.

Key words: Catalytic microsensor, ionic emission, multilevel interrogation, volatile phase of diesel fuel, diesel pollution

1 Introduction

The "Internal combustion engines" project of the DIVA (Diagnostic Industriel et Véhicules Avancés) [Industrial Diagnostics and Advanced Vehicles] research centre, funded by Région Picardie, aims to develop a real-time system capable of modifying the operating parameters of a diesel engine so as to optimise its pollutant emissions and fuel consumption. In view of the varied compositions of diesel fuels and the effects that composition has on the engine running, there is undoubted technical interest in being able to characterise the fuel in the tank. Existing measurement facilities are too large to be carried on board the vehicle or can't discern variations in diesel fuel composition. This

article describes an ionic microsensor able to provide the engine computer with useable data about the fuel quality. The thermionic emission due to the catalytic combustion of a combustible gas on the surface of a heated platinum filament has been demonstrated in a number of research projects including those M. E. UMSTEAD et al. [1] and W. M. SEARS et al. [2] for example. These authors showed that the total quantity of ions collected during this type of combustion depends on the filament temperature and on the nature of the oxidised molecule [3][4]. The filament in these tests was heated continuously to a given temperature. The filaments used were typically a few centimetres long with a diameter of 0.125 mm.

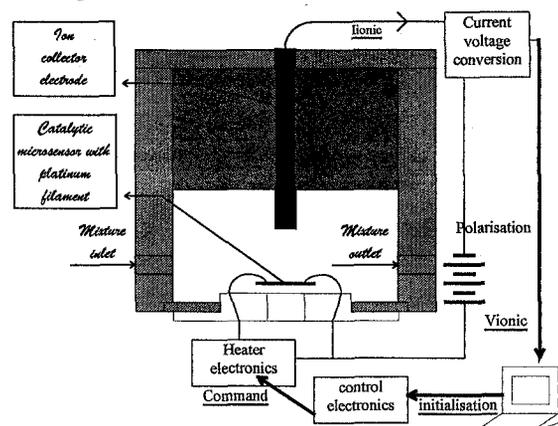


Figure 1: Schematic diagram of the sensor

2 Sensor description

Like PIDs and FIDs, this sensor is composed of two parts (figure 1): the first is based on the catalytic microsensor with platinum filament developed by LETI and INERIS [5], which generates the ions; the second part collects and measures the ions. The

catalytic microsensor used for gas ionisation is a self-supporting platinum thin film (6 μm) measuring 2 mm by 0.3 mm, produced in microelectronics technology (figure 2).

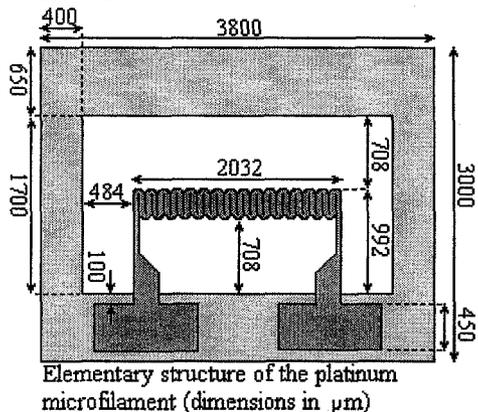


Figure 2: Diagram of platinum filament

The small size of this microfilament offers various advantages. To begin with, filament heating electrical power is low (typically 200 mW). Next, the very low thermal inertia of the filament ensures short response times. Thus it takes only about 10 milliseconds for the filament temperature to stabilise at a given value (between 400 and 1100°C). The electronic system used with the filament is designed to heat it at constant resistance in pulse mode [6] to different temperature plateaux the number, duration and value of which can be controlled by external digital signals. The heating temperature is controlled externally by a digitally controlled potentiometer. The cursor of this potentiometer can be set to 100 different values. Having regard to the practical heating range (from 400°C to 1100°C), the temperature resolution of the electronic system is 7 deg.C. The advantage of using heating cycles (or "interrogations") is twofold. First, the filament wears out more slowly than it does when heated continuously. Secondly the short response time of the filament means that several temperatures can be scanned in a single interrogation. An electronic control card containing the setpoint values corresponding to a given heating cycle (number of temperature plateaux, duration and temperature value of each plateau, and the hold time between two interrogations) is linked to the heating electronics. These values are calculated first from the calibration curve of the platinum

filament which corresponds to the value of its resistance as a function of temperature ($R_{fil} = A \cdot T + R_0$) and, secondly, from the sensor electronics calibration curve which represents the effective heating resistance for a given position of the digitally controlled potentiometer cursor ($R_{heat} = \alpha \cdot Pos^2 + \beta \cdot Pos + \gamma$). To detect ions, a current/voltage converter was adapted to the ion collector electrode. Converter amplification is one volt per nanoampere. The output voltage from the converter is called the "sensor ionic response" (V_{ionic}). The filament heating signals (voltage V_{heat} and current I_{heat}) consist of the different plateaux corresponding to the setpoint values transmitted by the control card. The ionic response of the sensor consists of the different values obtained for each of these plateaux (figure 3).

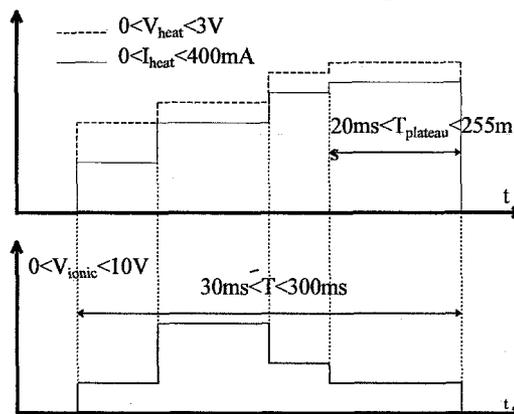


Figure 3: Pattern of the raw responses of the sensor

In fact the actual signals show, at the beginning of each plateau, an unstable portion which represents the time necessary to reach the temperature to be controlled. For the operating temperatures selected, this period of instability never exceeds 10 ms.

3 Test bench

Characterising the sensor responses and investigating the different parameters that might affect these responses involve a very large number of operations. A test bench has been therefore developed to automate as many operations as possible. This test bench can record the simultaneous responses of four sensors to gases or vapours mix-

tures. The vapours are generated using a motorised syringe (figure 4). This type of system can generate all the vapour concentrations needed for the purposes of the test.

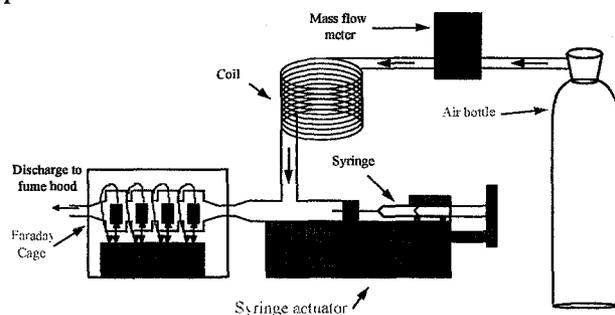


Figure 4: Generating combustible vapours

A data acquisition system simultaneously records the signals from the four sensors: these consist of the ionic responses together with the filament heating voltage and current. Automatic data processing gives the effective temperature of each plateau together with the corresponding ionic response value.

4 Tests carried out

The first task was to study the influence of the operating parameters (electrode-filament distance and bias voltage) and of the ambient measurement conditions (relative humidity and the proportion of oxygen present). The second phase was to investigate the response of the sensor in the presence of combustible molecules. Most of the molecules tested are listed in the following table.

| Name of gas or vapour | Family | Nb of C |
|-----------------------|--------|---------|
| Methane | Alkane | 1 |
| Propane | Alkane | 3 |
| Butane | Alkane | 4 |
| Pentane | Alkane | 5 |
| Cyclohexane | Alkane | 6 |
| 2.2 Dimethyl butane | Alkane | 6 |
| 2.3 Dimethyl butane | Alkane | 6 |
| Methyl pentane | Alkane | 6 |
| N-Hexane | Alkane | 6 |
| Heptane | Alkane | 7 |
| Methyl-cyclo-hexane | Alkane | 7 |
| Octane | Alkane | 8 |

| | | |
|-------------------------|----------|----|
| 2.3.4 triméthyl pentane | Alkane | 8 |
| Nonane | Alkane | 9 |
| Decane | Alkane | 10 |
| Ethanol | Alcohol | 2 |
| Propanol-1 | Alcohol | 3 |
| Propanol-2 | Alcohol | 3 |
| Butanol-1 | Alcohol | 4 |
| Butanol-2 | Alcohol | 4 |
| Hexanol-1 | Alcohol | 6 |
| Acetylene | Alkyne | 2 |
| Butanal | Aldehyde | 4 |
| Hexanal | Aldehyde | 6 |
| Acetone | Kétone | 2 |
| Methyl-ethyl-ketone | Kétone | 4 |
| 2-Methyl-3-butanone | Kétone | 5 |
| Hexanone-2 | Kétone | 6 |
| Methyl isobutyl ketone | Kétone | 6 |
| Benzene | Aromatic | 6 |
| Toluene | Aromatic | 7 |
| Ethyl benzene | Aromatic | 8 |
| Triméthyl 1,2,4 benzene | Aromatic | 9 |
| Triméthyl 1,3,5 benzène | Aromatic | 9 |
| Cumene | Aromatic | 10 |

Table 1: Principal molecules tested.

Some of these molecules were tested at different concentrations using different interrogation cycles (1, 6, 12, 24 or 100 temperature plateaux according to the molecules).

4.1 Reference tests

In order to take into account any variation in the sensor ionic response with time, or response dispersion between sensors, reference tests were conducted periodically. Accordingly the sensors characteristics were recorded in N50 synthetic air, 0.69% butane and 1000 ppm acetone for an electrode-filament distance of 2 mm and a bias voltage of -80 V. There is no sensor ionic response for temperatures below 1100°C in air. The response in butane (6900 ppm) shows a maximum (100 mV or 100 pA) around 900°C. The response to acetone (1000 ppm) shows a maximum (220 mV) around 950°C. Making allowance for the differences between the filaments reactive surface areas, all these results agree with the data from the literature.

4.2 Influence of the operating parameters of the sensor

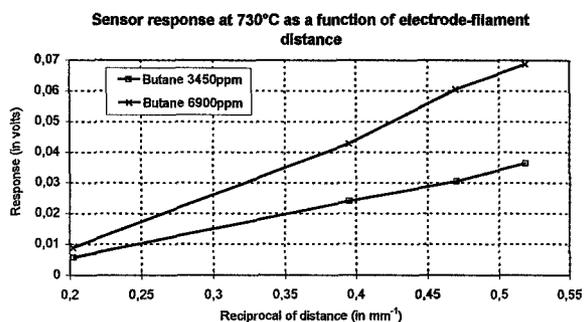


Figure 5

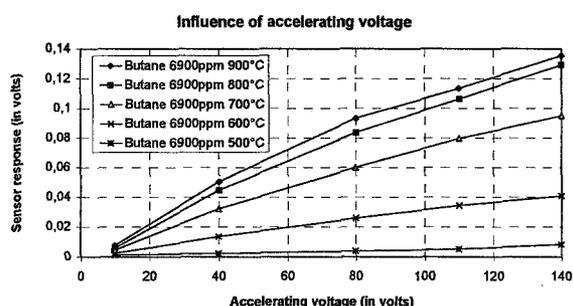


Figure 6

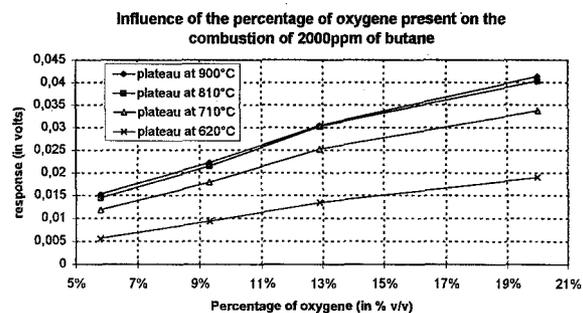


Figure 7

The ions created in combustion reactions desorb from the platinum filament at a velocity v_0 and are then accelerated by the electric field produced by the bias voltage applied to the collecting electrode. The intensity of this acceleration is proportional to the bias voltage applied between the electrode and the filament, and inversely proportional to the electrode-filament distance. It can be seen from the curve in figure 5 that the ionic response is inversely proportional to the electrode-filament distance. The shape of the curves on figure 6 shows that the efficiency of ion collection is dependent of the

applied accelerating field. The moving ions are slowed down and their direction changed essentially by impacts with neutral molecules in the surrounding atmosphere. Accordingly the number of ions collected on the electrode is a function of the accelerating electric field: this is certainly related to the detecting head geometry which was not optimised for maximum collection efficiency. The accelerating voltage (-80 V) and the reference electrode-filament distance (2 mm) were determined from these results for the four sensors.

4.3 Influence of measurement conditions

Quite apart from the nature and quantity of the combustible gas to be detected, other parameters can influence measurements. It was confirmed that variations in flow rates between 50 cm²/min and 2 l/min do not change the ionic response. Figure 7 shows the influence of the oxygen percentage presence (from 20% to 6% by volume) on the sensor ionic responses at different temperatures under the reference conditions. As the oxygen concentration falls, the practically linear ionic response is also seen to fall. Also, it is possible to evaluate the power dissipated by the catalytic combustion reaction by measuring the heating parameters of the microsensor. However no fall in catalytic activity, obtained from microsensor heating parameters measures, is observed as the oxygen concentration declines. It must therefore be concluded that although catalytic activity is necessary for ionic emission [4] during the different combustion stages, at least one specific stage in ion creation process is limited by the oxygen concentration. It can be seen however that for a given oxygen concentration the responses ratios for different temperatures remain the same. Consequently the discrimination potential of the sensor does not appear to be adversely affected by a fall in the oxygen concentration.

4.4 Responses to combustible molecules

Owing to the varied nature and proportions of the fuel components, it was not possible at this stage to conduct systematic tests for each diesel fuel ingredient. This investigation attempts to

determine the main sensor characteristics in the presence of representative molecules. To begin with, it was confirmed that the responses to simple gas mixtures were additive. On that basis it seems reasonable to assume that the separate investigation of the combustible molecules representative of those found in the diesel fuel volatile phase will give a good approach of the sensor ionic response in the presence of a real fuel. Moreover, the ionic response varies in a linear manner versus concentration at all the temperature plateaux. This significant property had already been demonstrated by SEARS [3] for a given heating temperature. The first molecules to be studied were the linear alkanes (from C₃ to C₁₀).

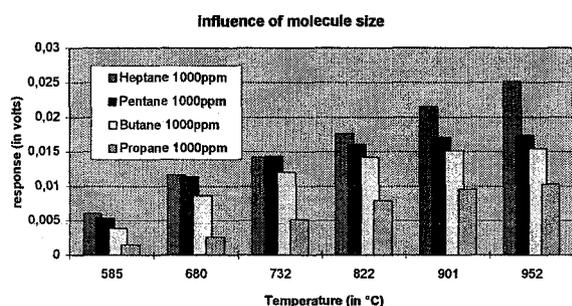


Figure 8

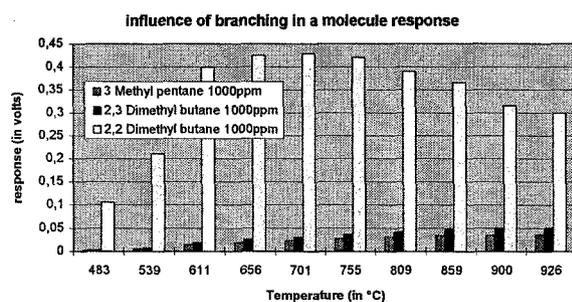


Figure 9.

Figure 8 shows the sensor responses to four linear alkanes (propane, butane, pentane and heptane) between 580°C and 950°C. The increased ionic response for longer carbon chains had already been demonstrated in the literature for a given heating temperature. Here we observe the same phenomenon at all the temperatures even though there are relative variations in ionic response from one temperature to another. Indeed these variations suggest the possibility of discrimination with suitable data processing. Generally speaking, the ionic

response shape varies with the molecular size of the alkane tested but, for high heating temperatures, the ionic response is proportional to the number of carbon atoms in the molecule. In fact this rule applies only to linear alkanes. From the example shown in figure 9 it is possible to compare the molecular geometry influence on the ionic response obtained using alkanes containing 6 carbon atoms. A quaternary carbon atom presence, in other words a carbon atom linked to four other carbon atoms and not to a hydrogen atom, substantially increases the sensor ionic response (in the example, the response is 420 mV at 700°C for 2,2 dimethyl butane compared with 50 mV at 930°C for 2,3 dimethyl butane). Else, the comparison of 2,3 dimethyl butane and 3-methyl pentane tends to show that the more branched a molecule, the higher its response (+ 40% at 930°C). Once again, the shape of the ionic response is seen to vary with the nature of the molecule. These results are in agreement with the literature [1]. Figure 10 illustrates the effect of different functions (acid, alcohol and aldehyde) on the ionic response for non-branched molecules containing four carbon atoms. The presence of the function and its nature can be seen to affect the level and shape of the sensor response. Just as for the alkane series, the function location in a molecule is important. This is very well illustrated by figure 11 which shows that the alcohol function location in propanol can modify the response by a factor of 6 and completely change its shape (maximum around 700°C for propanol-1 and above 960°C for propanol-2). Figure 12 shows the influence of molecular size on the ionic response in the presence of ketones.

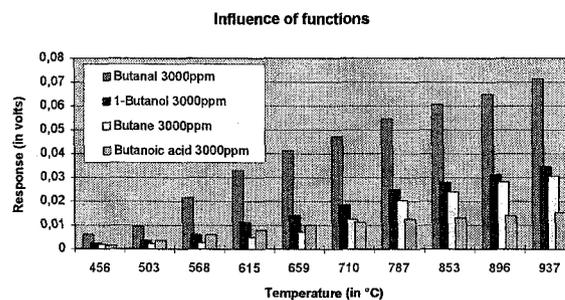


Figure 10

Unlike the alkanes, the ionic response falls as the length of the carbon chains associated with the ketone function increases. Indeed as the size of the molecule increases, the ionic response tends towards that of the alkanes of equivalent molecular weight, as if the function specificity is attenuated by the length of the carbon chains. Accordingly the function has most effect on molecules of small size. Figure 13 shows the responses obtained for a number of saturated and aromatic cycles. In fact these responses are extremely low (frequently below 1 mV). Only the cyclanes and light aromatic compounds are liable to give usable responses.

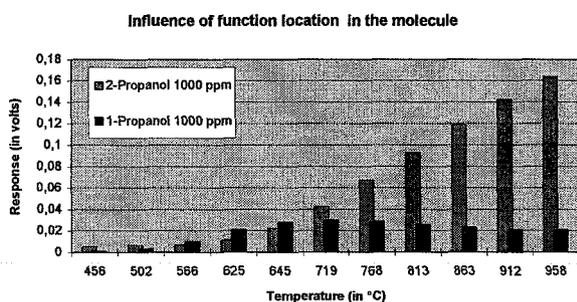


Figure 11

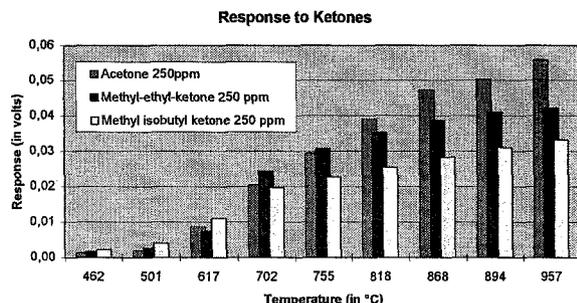


Figure 12

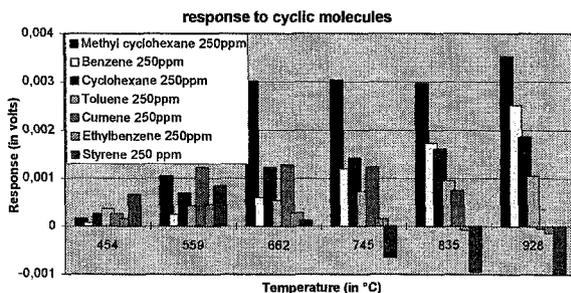


Figure 13

5 Composition of a diesel fuel

Although the compositions of diesel fuels are extremely varied, essentially owing to additives, it is possible to discern major molecular families. Figure 15 shows the average composition of a commercial diesel fuel.

| Type of molecule (size) | Proportions by mass |
|--|---------------------|
| Alcanes (C ₁₀ à C ₂₀) | 30% |
| Cyclanes (>C ₇) | 35% |
| Aromatics (>C ₆) | 20% |
| Ethers (C ₂ à C ₁₁) | 10% |
| Alcohols | <5% |

Table 2: Mass composition of Diesel fuel [7].

On the basis of this typical diesel fuel composition, an attempt can be made to determine what the main composition of its volatile phase will be. Since most of the molecules in diesel fuel have a high molecular weight, the volatile phase consists essentially of the lightest ethers and alcohols, a few cyclanes and aromatics, and other light molecules resulting from imperfections in refining, the nature and quantities of which are not well known. However, it can be seen that the ionic responses to cyclanes and aromatics are low compared with those to ethers and alcohols. On the other hand, the presence of ethers and alcohols gives ionic responses at high levels and with fairly characteristic shapes.

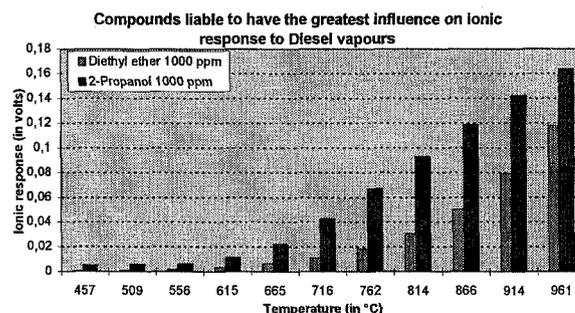


Figure 14

Figure 14 shows the ionic response obtained in the presence of two molecules representative of the two most volatile compounds families (ethers and alcohols). It can therefore be expected that the ionic sensor will be fairly sensitive to ethers and

alcohols concentrations for different diesel fuels, or to change in their composition by the progressive depletion of the most volatile compounds gaseous phase.

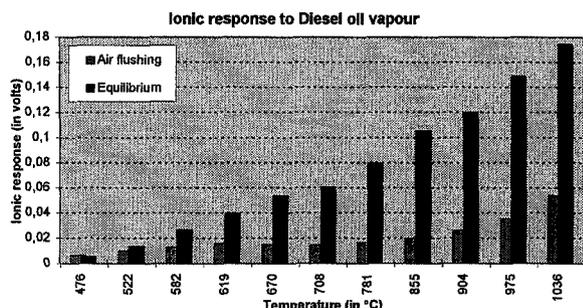


Figure 15

Figure 15 shows typical experimental ionic responses obtained in the presence of diesel fuel vapours once the liquid-vapour equilibrium has been reached, and then in unbalanced conditions (test volume flushed with air and renewed every two minutes), after one hour. In spite of the low saturation diesel fuel vapour pressure [7], a quite satisfactory signal level is obtained. The ionic response obtained for diesel fuel in static air shows a number of inflection points that are characteristic of a mixture of different kind of molecule. The large signal at high heating temperatures recalls the curve shape obtained for ether, with in addition a local maximum around 650°C, which suggests an alcohol-1 response (Figure 11). When the air above the fuel is renewed at a fairly rapid rate, the vapour concentration falls. This explains the fall in the average level of the ionic response observed. Since the fuel quantity used was very low for an extensive liquid-gas exchange surface, it is likely that the relative proportion of highly volatile compounds fell with respect to other components. This could explain a relative fall in the signal attributed to the presence of ethers for high heating temperatures. It is now necessary to make measurements on a number of fuels in rigorous test conditions in order to ensure reproductibility and usability of ionic responses.

6 Conclusion

The ionic sensor described here can detect most volatile organic molecules. The ionic response as a function of temperature varies with the nature and concentration of molecules. The multiple temperature plateaux pulse mode has renewed the interest in such a sensor since the research already undertaken by other teams. This property shows the discrimination capability of such a sensor in circumstances where only a single fuel molecule has to be identified. Since the responses to mixtures are additive, it could possible to combine such a sensor and a suitable data processing system in order to identify the constituents of a gas. The tests conducted on diesel fuel show that it is possible to detect certain molecules constituting its volatile phase. At this stage of the research it seems reasonable to believe that this sensor will differentiate certain variations in diesel fuel composition.

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