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Development of a Gas Sensor for *Eucalyptol* Supervision: A Supporting Tool for Extreme Wildfire Management †

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Abstract: Recent research on volatile organic compounds (VOC) released by the heated vegetation has shown that, under specific conditions (e.g., extreme heat, humidity, wind, and topography), VOC might foster wildfire ignition sources and explain sudden changes in fire behavior, particularly in the most susceptible and flammable forests (eucalypt forests). This work aims to develop an electronic nose (e-nose) based on a sensor's array to monitor the concentration of eucalyptol, the major VOC compound of the *Eucalyptus globulus* tree. The detection of this target compound was achieved by measuring the impedance spectra of layer-by-layer developed thin films based on polyethyleneimine, poly(allylamine hydrochloride), and graphene oxide, by injecting the analyte into a custom-made vacuum chamber system. The obtained results were analyzed by the principal component analysis method. The developed e-nose sensor was able to distinguish different concentrations in a range from 411 to 1095 ppm.

Keywords: wildfires; volatile organic compounds; eucalyptol; electronic nose; impedance spectroscopy

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1. Introduction

Extreme wildfires cause the loss of various human lives and have a significant impact on the biodiversity of ecosystems. These phenomena are, still, not yet fully understood. Recent studies have proposed a new theory, suggesting that flammable gases generated from heated vegetation, in particular, Volatile Organic Compounds (VOC) common in Mediterranean plants may, under some topographic and wind conditions, accumulate in locations where, after the arrival of the ignition source, they rapidly burst into flames as occurs in explosions [1,2]. VOC can exhibit a flammable nature, enabling fire ignition sources and sudden changes in the fire behavior [3].

The electronic nose (e-nose) system, which comprises an array of sensors with partial specificity and an appropriate pattern recognition system, can recognize complex gases. Moreover, e-noses have shown favorable efficiency in monitoring applications, making them a potential tool for the study of VOC [4–6]. Although the e-nose exhibits high sensitivity, forest environments consist of a complex mixture of gases and therefore the used sensors must be able to detect, classify and quantify the target compound. To improve the sensor's sensitivity, different materials can be used as coatings, thus enhancing the chemical and physical properties of the sensor [7–9].

The purpose of this work was the development of a custom-made measuring system attached to an e-nose system to monitor eucalyptol in a range of concentrations, from 411 to 1095 ppm. The concentration range was chosen based on the concentrations found in

Mediterranean vegetation (including the Eucalyptus tree [10]) and a range that was the lower flammability limit for terpenes (<1% (*v*/*v*)) [11], for laboratory safety reasons.

Thus, different layer-by-layer (LbL) thin films were developed in order to attain the best combinations for the monitoring of the target compound. The thin films were produced with polyethyleneimine (PEI), poly(allylamine hydrochloride) (PAH), and graphene oxide (GO), namely (PEI/GO) and (PAH/GO). These films have been already described in [12–14] and, thus, may have an interesting potential to monitor VOC, namely eucalyptol.

2. Materials and Methods

The developed e-nose consists of an array of sensing devices based on ceramic solid supports with deposited gold interdigitated electrodes (IDE), comprising eight "fingers" each, with dimensions of 22.8 × 7.6 × 0.7 mm and each "finger" has 200 µm of width. These solid supports were acquired from DropSens (Oviedo, Asturias, Spain) [15].

The thin films were deposited on the sensors IDE by the layer-by-layer (LbL) technique, which consists of the alternate deposition of polyelectrolytes layers with opposite electrical charges, to obtain several bilayers. The polyelectrolytes used to built-up the thin films layers were polyethyleneimine (PEI), poly(allylamine hydrochloride) (PAH), and graphene oxide (GO), all purchased from Sigma-Aldrich, Steinheim, Germany. The aqueous solutions of the polyelectrolytes were prepared with a 10^{-2} M concentration of each polyelectrolyte. Each of the aqueous solutions were prepared with ultrapure water, obtained in a Milli-Q ultrapure water system (Millipore GmbH, Billerica, MA, USA). This process was carried out by alternated adsorption of the positive PEI or PAH polyelectrolytes and the negatively charged GO molecules.

After each adsorption of the polyelectrolyte layers, the solid support was immersed in water in order to remove any polyelectrolyte molecules that were not completely adsorbed. The immersion time, in which the adsorption of the molecules takes place, was 60 s for each of the polyelectrolytes used and 30 s for the washing process. After the adsorption of each bilayer, the thin film was dried using nitrogen gas stream (99% purity, Air Liquide, Algés, Portugal). Thus, thin films of (PEI/GO) and (PAH/GO), with 5 bilayers each, $(PEI/GO)_5$ and $(PAH/GO)_5$, were produced.

The eucalyptol (99%) used for the experiments was purchased from Sigma-Aldrich, Steinheim, Germany. To test the response of the sensor when exposed to the eucalyptol, a range of concentrations from 411 to 1095 ppm was evaluated.

The measurements of each sensor were performed inside a custom-made vacuum chamber system designed by the author's team, which is depicted in Figure 1.

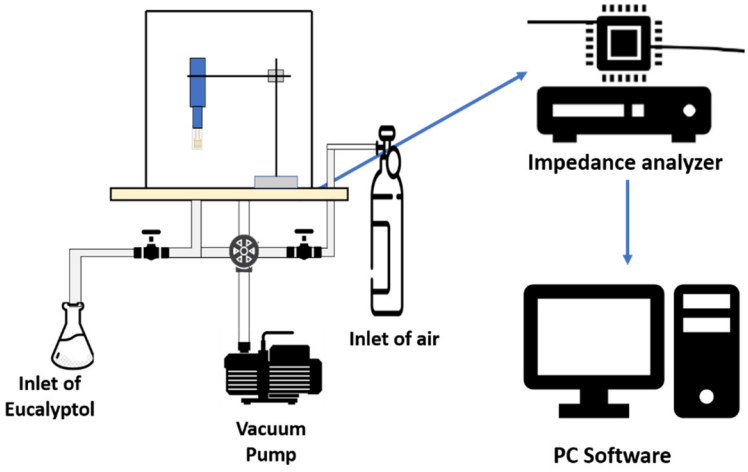

Figure 1. Schematic illustration of the experimental setup, including the custom-made vacuum chamber.

A sample holder containing the sensor was placed inside the chamber which presents an approximate volume of 58 L. A rotatory vacuum pump was also connected so that

primary vacuum could be achieved and maintained inside the chamber during the tests, enabling a "clean" environment for the measurements. The sample holder was connected to a Solartron 1260 Impedance Analyzer (Solartron Analytical, AMETEK scientific instruments, Berwyn, PA, USA), in order to measure the impedance spectra at the IDE terminals. The chamber also has two inputs for the inlet of the eucalyptol and compressed air in the chamber, allowing the interaction between the target compound and the sensor.

In order to start the testing process, the sample holder with the sensor was placed inside the chamber and connected to the Impedance Analyzer. After that, the vacuum pump was switched on to achieve a pressure of 1.3×10^{-3} mbar. Following this, the eucalyptol would be evaporated into the chamber by the opening of a needle valve that connects the chamber with the mixture of eucalyptol. Subsequently, and after the evaporation of the compound and reaching a certain pressure level, the inlet was open to inject the compressed air until the pressure of 1.3×10^{-3} mbar was attained. Afterward, the electrical measurements were conducted in a frequency range of 1 Hz to 1 MHz, and an AC signal voltage of 25 mV. This process was then repeated for each eucalyptol concentration.

The electrical impedance spectra data features were assessed with the Principal Component Analysis (PCA) method to reduce the data size and to obtain a new space of orthogonal components in which different concentration patterns can be observed. The principal component analysis (PCA) plots were obtained by performing the normalization (Z-Score normalization (value-μ)/ϑ, μ and ϑ being the mean value and the standard deviation of the samples, respectively) of the impedance spectroscopy data.

3. Results and Discussion

Figure 2 shows the electric impedance spectra of the sensors, coated with thin films of $(PEI/GO)_5$ and $(PAH/GO)_5$, when in contact with different concentrations of eucalyptol, for different frequencies.

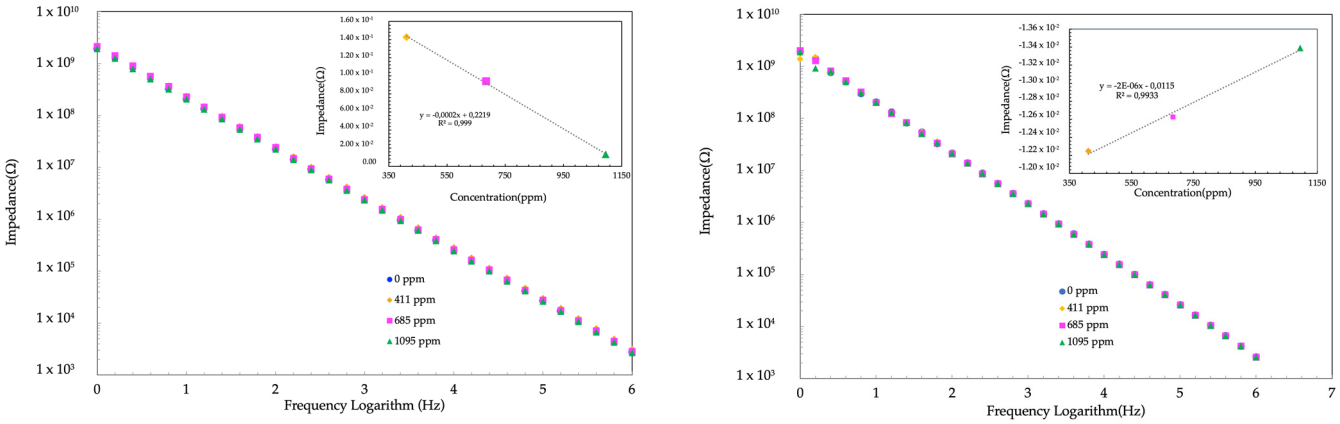

Figure 2. Impedance spectra measured with $(PEI/GO)_5$ (**a**) and $(PAH/GO)_5$ (**b**) LbL films inside of the chamber filled with different eucalyptol concentrations. In the insets are shown the evolution of the impedance at 63 and 10 kHz as a function of concentration, respectively.

In order to have a more thorough analysis, a normalization was performed on the data, using the following equation [12]:

$$\frac{PP(C) - PP(0ppm)}{PP(0ppm)} \quad (1)$$

where $PP(C)$ corresponds to a physical property at a given eucalyptol concentration, and $PP(0ppm)$ to a measure at a reference concentration, in this case when there was 0 ppm of eucalyptol. In each of the cases represented in the insets of Figure 2a,b, the physical property used was the impedance, at a constant frequency, where the effects of the eucalyptol are

better represented. In both cases, it may be observed that an increase in the concentration of eucalyptol results in the decrease in the sensors' impedance values.

Furthermore, a preliminary analysis of the electronic nose concept was performed by the mean of the Principal Component Analysis (PCA). Thus, the data of each one of the sensors, $(PEI/GO)_5$ and $(PAH/GO)_5$, when in the presence of different tested concentrations of eucalyptol were plotted, as shown in Figure 3.

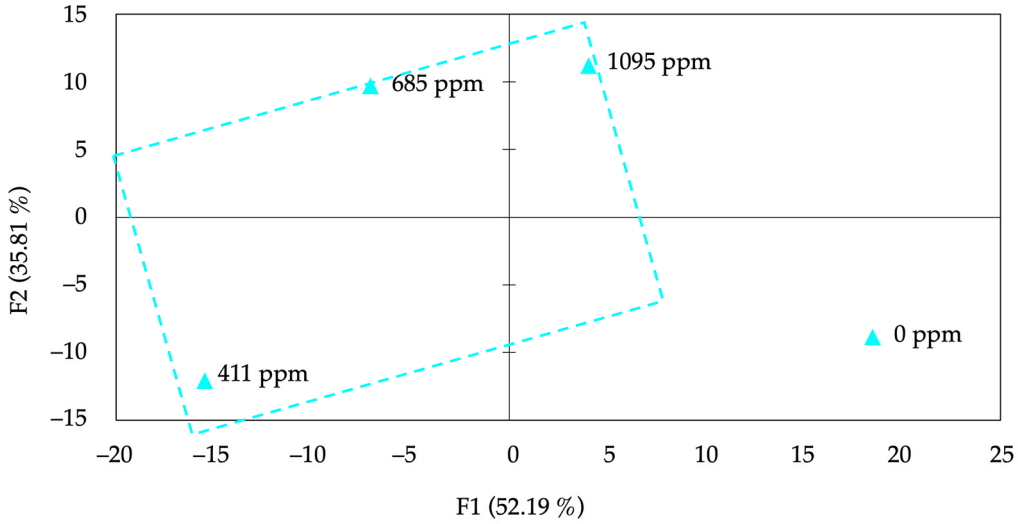

Figure 3. PCA plot for both sensors used with thin films of $(PEI/GO)_5$ and $(PAH/GO)_5$, for a range of eucalyptol from 0 to 1095 ppm.

By the PCA analysis, it can be observed that the e-nose assembled, with two sensors, each one coated with thin films of $(PAH/GO)_5$ and $(PEI/GO)_5$, can distinguish between the blank and the different concentrations of eucalyptol that they interacted with.

In fact, the choice of the GO as the upper layer seems to increase the efficiency and discrimination of the measurements, as the molecules of the thin film may react with the target compound enabling a better adsorption, since it possesses many functional groups.

4. Conclusions

The electronic nose, consisting of an array of two sensors coated with $(PEI/GO)_5$ and $(PAH/GO)_5$ thin films, built-up with the LbL technique, was able to detect eucalyptol and distinguish three different concentrations levels, as the PCA technique has shown. The use of graphene oxide as the thin film bilayer increased the interaction between the custom-made chamber's head space and the thin film coating, and consequently the efficiency of the impedance measurements and capability of the e-nose to distinguish different eucalyptol concentrations.

The present work presents a novel and preliminary study, with an in-deep effort in the build-up of the custom-made chamber. It should be also noted that this project is under development; thus, the build-up of different coatings, e.g., different combination of polyelectrolytes and/or other sensing materials, to improve the e-nose performance, is expected.

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