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Development of a New Instrumental Measurement of Odorous VOCs Based On Precise Fingerprints Obtained by a Multitude of Biosensors

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Research regarding qualification and quantification of air contaminants such as odorous compounds has increased in the recent years. This paper deals with the results obtained with a new device and shows the potentialities of the instrument monitoring method concerning odorous volatile compounds. This new instrument called NeOse is developed by a French company (Aryballe Technologies, Grenoble - France) and the improvements are being performed in an innovative research project named "**W**ellness & Medical D**I**agnostics Olfactory **SE**nsors" (**WISE**). This project is based on the combination of a skill multitude in many domains (nanotechnologies, environmental engineering, analytical chemistry, data processing…) and is thrown by diverse scientific partners and financiers. This new analytical tool can be used to identify, classify, compare, and also to visualize the odorants that are generally odorous **V**olatile **O**rganic **C**ompounds (**VOCs**).This visualization is obtained by a precise fingerprint for each odor or odorant mixture obtained by a multitude of Biosensors.
The technology of this device is based on **S**urface **P**lasmon **R**esonance **I**maging (**SPRi**) and is usually used for liquid samples. However, with this new approach that consists to use another matrix based on gas samples (gas or mixture of gases) analyzed in head-space, various applications could be targeted (non-exhaustive list):

- Medicine (diseases detection),
- Food industry (product quality),
- Daily for anosmic person (safety alarms or knowledge of their gaseous environment),
- And others fields.

Odor measurement can be helpful for products characterization; quality control and traceability in many domains. Actually, this device may recognize at least 300 odors and each fingerprint can be used like a visual representation of each odorous compound (each odorant).

1. Introduction

Usually, the odor qualification for various products is known with human nose training (human panel) and physico-chemical analysis (Gas chromatography coupled with mass spectroscopy) can complete the characterization by identification of compounds (odorants) in the global mixture. New electronic noses might be able to mimic the phenomenon of qualification (after learning and training). The basis of electronic noses is sensor array where odorous VOCs interact on the sensor surface. Despite the fact that sensors are not very specific, electronic noses having a fingerprint response for each odorous VOCs and pattern recognition software lead to identification and discrimination.
Nowadays, several studies showed an increasing interest about improvement of electronic noses and their sensors. Many sensors types can be used in electronic noses.
The most known are conductivity sensors such as metal-oxide semiconductors and piezoelectric sensors like surface acoustic wave. These sensors technologies present advantages and drawbacks.

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Many scientific researchers have proposed interesting works on electronic nose technology and this tool can be already used in various scientific research field such as in medicine, aromatherapy, environmental monitoring. Electronic noses with arrays up to 20 sensors have often been used in different studies. Bai et Zhou (2014) described a study to qualify and quantify H_2, CO and NO_2 with 6 sensors; Cui et al. (2015) used 18 sensors to qualify and quantify aroma compound characteristics of ginseng at different ages; Westenbrink et al. (2015) used 13 sensors for the detection of colorectal cancer; Sun et al. (2017) used 9 sensors for identification of ginsengs; Chen et al. (2018) used 14 sensors to evaluate the freshness of fresh-cut green bell pepper; Saidi et al. (2018) used 6 sensors for a study on non-invasive diagnosis of diseases as diabete; and Guner et al. (2017) highlighted the possibility to introduce a smartphone into the system. Others studies showed the interest to use instruments as artificial olfactory systems to detect, visualize, characterize and quantify an odor or a substance with a large number of arrays and biometric approach. e.g., LaFratta et al. (2008) proved the contribution of very high density sensing arrays and listed them. In addition, Di Natale et al. (2008) and Marco et al. (2014) tried to build artificial olfaction system based on neural structure in mammals. Another approach can be cited: Rakow et Suslick (2000) used colorimetric system to visualize an odor. The instrument used in this study (NeOse) has at least 50 sensors which can allow detecting, visualizing and characterizing several odorous VOCs at the same time. Another study described this device (Guillot et Lafhal Sakiou (2018)).
Concerning sample delivery and capturing/detection system of the new prototype described in this study, the odorous sample is pumped into the NeOse and induces a reversible physico-chemical change in the surface of sensing material, which causes another change in optical properties.
It was set up to develop a new generation of bio-sensors which allow the visualization of odorous compounds or mixtures. The odorous mixtures can be classified and compared for their discrimination and quantification. The system can be connected to a smartphone, laptop or tablet via a wireless or Bluetooth network.
In this project, each partner is in charge of development of a part of the equipment (electronic system, prism, data treatment, test of efficiency and test of the impact of humidity or temperature …). At IMT *Mines Ales*, experiments are carried out on odorous compounds.

2. Material and Methods

The NeOse was developed for the detection of "odorous compounds and mixtures". The core part is composed biochemical sensors and uses the principle of SPRi. SPRi is based on the **S**urface **P**lasmon **R**esonance (SPR) (Madeira et al., 2009). It is an optical sensing mode that occurs when a polarized light reaches a prism covered by a thin layer of metal (gold in this study case). A visualization of all the sensors (biochip) is obtained via a video camera and each active site (spot) provides SPR information. The system can be connected to a smartphone as shown in the figure 1 via a wireless or Bluetooth network. The way of connection is easy to use and create conditions of communication between the user and the monitoring device. Since manufacturing of the device, three prototypes were built with three acquisition methods: in the laboratory, on land (e.g. in industry) or in the house (helpful for persons without smell sensation). The improvement has been in the addition of the smartphone interface as well as on miniaturization of the system.

Figure 1: NeOse connected to a smartphone

The device is easy to handle. The global device is illustrated by Figure 2: The first step is odorous air pumping (1); followed by the transport of the compounds in the chamber (2); then there is an interaction of the compounds with chemical sensors on a prism with a thin layer of gold (3). The prism is later illuminated with a lamp (4) and the signals are recovered with the camera (5) and stored for analysis (6).

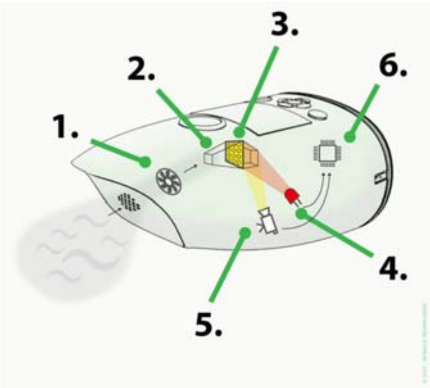

Figure 2: General principle of NeOse: 1- Pumping of air and odorous molecules; 2- Transport of compounds to the chamber; 3- Interaction of compounds with chemical sensors arrayed on a prism; 4-Lighting the prism with LED lamp; 5- Recording optical signal transduction with a camera; 6- Storage (database) and analysis results

As shown in the Figure 3, at least 50 sensors (68 exactly) on the surface (array) of prism allow a high capacity to distinguish odors. The number can be extended to 100 allowing a higher measurement precision. It is a great improvement compared to e-noses in the past works.

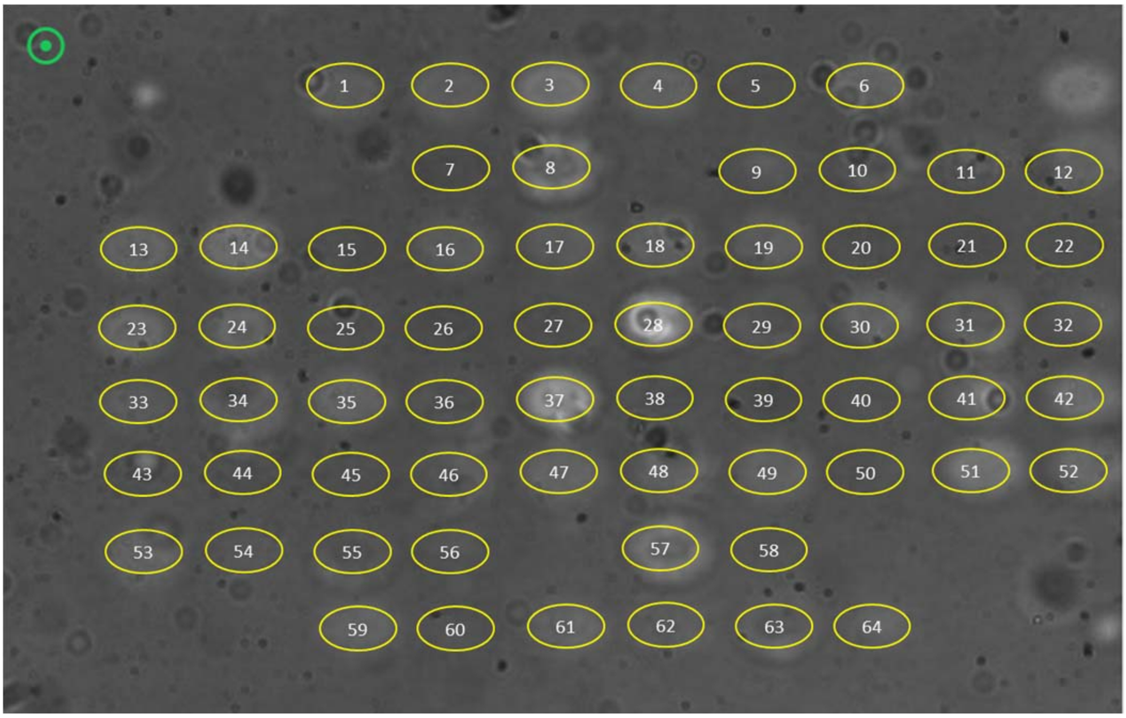

Figure 3: Representation of spotfile with sensors

Pure standard substances butanol, 3,7-dimethyl-3-octanol, octane and 1-octen-3-ol were purchased from Sigma Aldrich, Aldrich Chemistry, Aldrich and Merck respectively and their chemical purities are greater than 99%. Head-space of the bottle (60 mL) allows the introduction of sample in the device by aspiration. A blank with air (and humidity) is registered previously to analysis and the sample must be collected with a constant flow to warranty the same interaction equilibrium between compounds and biosensors.
Raw data can be visualized with a radar plot (fingerprint) but comparison needs more data treatment. Therefore, data analysis is performed by a **M**ulti**D**imensional **S**caling (**MDS**) and a **P**rincipal **C**omponent **A**nalysis (**PCA**) which are exploratory methods. These methods allow the reconstruction of a map from a matrix based on the similarities/dissimilarities concerning distances between samples. It is a methodology to reduce multivariate data to a few important axes.

This procedure allows to give an interpretation of patterns with recognition and discrimination between samples. And **L**inear **D**iscriminant **A**nalysis (**LDA**) allows classifying samples.
During the data processing, the normalization pretreatment technique was used.

3. Results and Discussion

Results as radar charts illustrate that this new measurement device gives a more informative fingerprint than classical sensor array described in the literature. The four samples (butanol, 3,7-dimethyl-3-octanol, octane and 1-octen-3-ol) were analyzed ten times. As shown in the figures 4 and 5, the NeOse allows having precise fingerprints as radar chart for these compounds. The intensity which is related to the concentration decreases slightly and remains stable over time for the octane and the butanol. This strongest information offers a warranty in term of quality and recognition of odors.

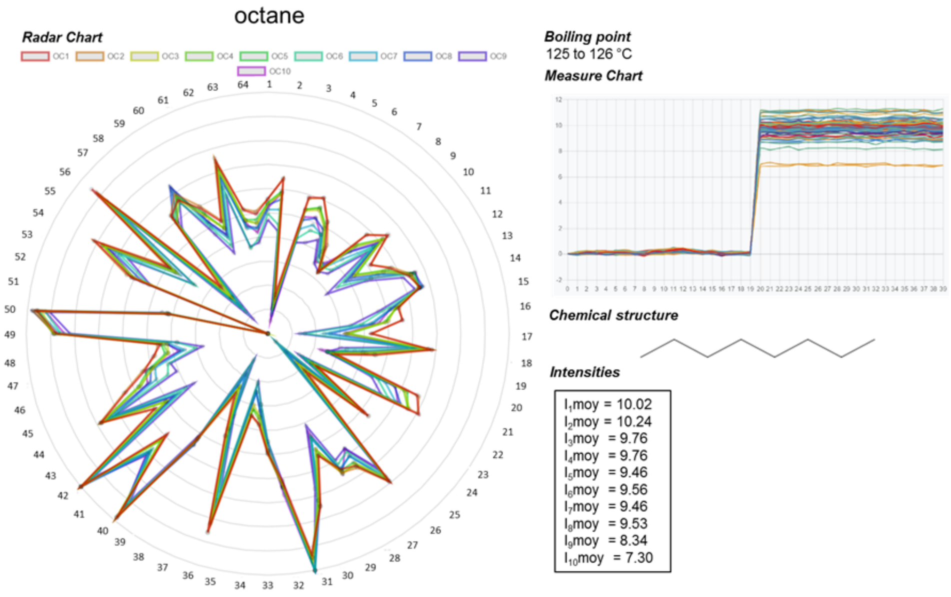

Figure 4: Octane fingerprints

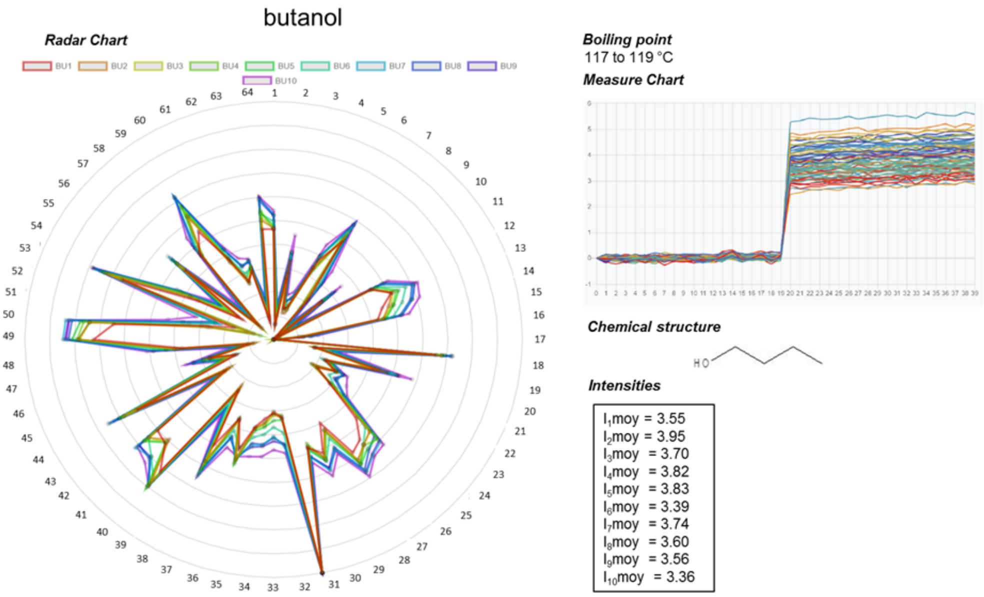

Figure 5: Butanol fingerprints

The results are identical for the other compounds. *As shown in the figure 6,* MDS *and PCA* with the four odorous compounds *can give good representations of the discrimination between the four compounds*. PCA1 and PCA2 represent 90.8% and 5.8% of the variance. There is a very good discrimination between the four compounds presenting similarities (C-8 linear carbon chain, alcohol function…). The NeOse is able to distinguish these compounds (odorous or weakly odorous). And LDA gives very good results with 100% of good classification.

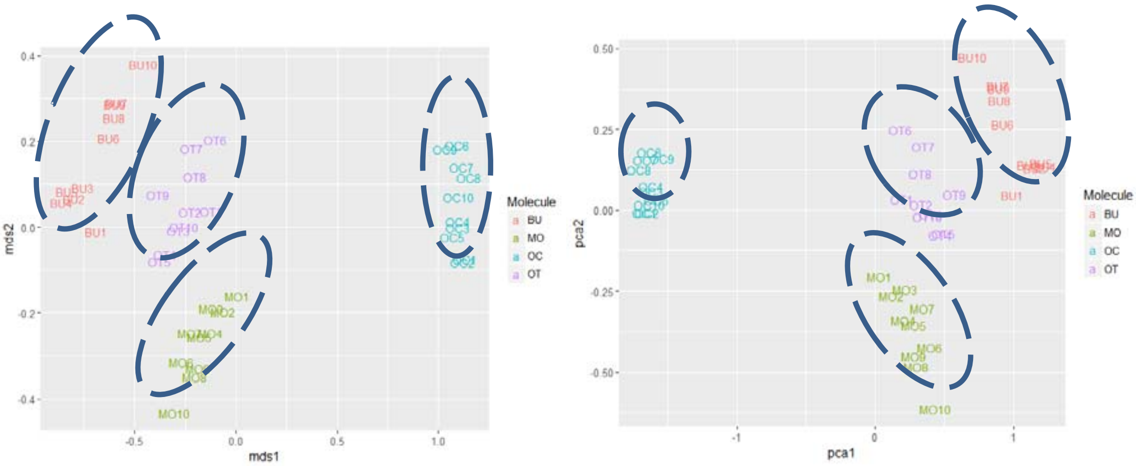

Figure 6: MDS and PCA with four compounds results obtained by NeOse

4. Conclusions

The new device NeOse is clearly an analytical tool for odorous compound/mixture measurement thanks to a multitude of information collected. This instrument can be used to complete other techniques such as GC/MS, GC/MS-O and odor concentration measurement by olfactometry. The association of the NeOse with an appropriate classification tool such as MDS could be successfully used in identification and discrimination of odorous VOCs. This device presents many advantages in relation to odor identification (after training step), possibility to quantify (after calibration), their potential of miniaturization and portability, and to propose a continuous measurement which remains the main advantage.

In addition, this instrument can be used easily due to its simplicity. A lot of applications are described in the literature and this prototype can be helpful for various fields. This device could lead to a more aware decision making process in various fields. However, further studies are required to improve the predictive model.

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