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MEASUREMENT OF ODOROUS COMPOUNDS WITH A DEVICE BASED ON SPRi TECHNOLOGY

MEDIDA DE COMPUESTOS OLOROSOS CON UN DISPOSITIVO BASADO EN LA TECNOLOGÍA SPRi

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Abstract

A device developed by Aryballe Technologies (Grenoble – France) and based on Surface Plasmon Resonance (SPR) imaging was used to measure odorous compounds. One advantages of such a device is to propose a large number of receptors inside the measurement cell. This aspect allows a distinction capability that cannot be obtained with classical instruments. Presented results show a strong capacity of distinction of compounds even isomers and a detection limit dependent on the family of compounds and the size of the molecule.

Se usó un dispositivo desarrollado por Aryballe Technologies (Grenoble, Francia) y basado en Surface Plasmon Resonance (SPR) imaging para medir compuestos olorosos. Una de las ventajas del dispositivo es proponer un gran número de receptores dentro de la célula de medición. Este aspecto permite una capacidad de distinción que no se puede obtener con instrumentos clásicos. Los resultados presentados muestran una fuerte capacidad de distinción de compuestos incluso isómeros y un límite de detección dependiente de la familia de compuestos y el tamaño de la molécula.

1.Introduction

The technology based on Surface Plasmon Resonance (SPR) imaging was proposed as alternative to classical sensor arrays or e-noses and was tested in a large research and development project called WISE (Wellness & medical dIagnostics olfactory SEnsors).

Like all sensors or e-noses, the device is more designed for air quality monitoring in stable atmospheres and needs developments for environmental applications. But for odour characterization, the number of receptors inside the measurement cell allows a distinction capability that cannot be obtained with classical instruments. This capability is then a real progress for odour discrimination and then identification of sources. For example, it's easy to distinguish two compounds of the same chemical family and in some case cases, make the difference between isomers or even enantiomers. We could also imagine getting an idea of component proportion in simple mixtures of 2 or 3 compounds. So, the device offers a complementary approach of: chemical identification with GC/MS, potential odour with CG/MS-O and odour concentration measurement by olfactometry. With precise fingerprints that are obtained, it might be an efficient tool, in the next future, to detect abnormal air composition (odour change or variation of VOC composition). As all devices with sensors or receptors, the system must be trained for an application or must be used only if odours (odorous compounds) that are monitored are in the database of the equipment.

2.Materials and methods

All measurements were carried out with a portable and universal odor detection device, the Neose instrument (figure 1) from Aryballe Technologies (Grenoble – France) because it was the equipment to be tested in the frame of the WISE project. Baed on digital olfaction platform,, the device detects and identifies odors with O-Cell technology to mimic the human sense of smell. Digitized odours are stored in a reference database, The O-Cell (based on SPRi principle) is the key component for capturing odour signatures based on the volatiles' interactions with a combination of biosensors.

In comparison with Neose and for concentration evaluation of mixtures, a total hydrocarbon analyser HCT (Chromatec – France) was used.

Fig. 1.: Neose device developped by Aryballe with above from left to right, the 3 key steps of the measurement: Binding of VOCs (or odorous compounds) on the biosensors arrayed on SPR prism covered by a gold layer ; interrogating the surface with O-cell based on SPRi ; Data Treatment: image analysis and data transfer

Pure compounds (purity>97%) from different chemical families were selected for experiments as listed in table 1.

Table 1: Tested compounds

Chemical family	Compounds	Supplier	Purity (%)
Alcane	Pentane Hexane Heptane Nonane	Janssen Riede DeHaenag Rectapur Alfa Asar	98 99 98 99
Alcohol	Methanol Ethanol Butanol Octanol Linalol	Fischer VNR Chemi Sigma Aldrich Acros Aldrich	99 >99.5 >99.5 98 97
Fatty acid	Propionic acid Butyric acid Valeric acid	Fluka Acros Fluka	99.5 99 99
Terpene	Limonene (R & S)	Alfa Aesar	97
Aromatic	Xylenes (o & m) Xylene (p)	Acros Carlo Erba	99 99
Cetone	Methyl Iso Butyl Cetone 2-Heptanone Di-isobutyl cetone	Prolabo Fluka Prolabo	>99.5 98 98

All connection (tubing, valve.) were Teflon or PTFE tubes or equivalent polymer that do not interfere with VOCs. Atmospheres created by VOC injection in a sample bag filled with ambient air and made with Nalophan (Micel-France) and PEHD/PP valve (VWR-France) or stainless valve. The figure 2 shows the equipement connected to a bag. A 3 ways valve allows the connection of the equipement with ambiant air (as reference) and sample into the bag.

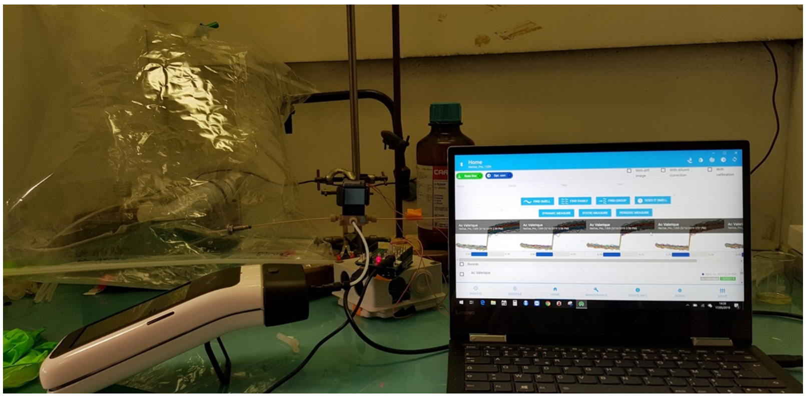

Fig. 2.: Equipement (NeOse) at the left, sample bag at top left and laptop on the right for data collection.

3.Results and discussion

Three main series of experiments are presented in this section. It concerns:

- Capability to distinguish and compare compounds
- Influence of molecular size for recognition in a mixture
- Influence of molecular size for sensitivity

For the first criteria, different compounds were tested and as shown in figure 3, clusters of response are well defined for different pure compounds or mixture like orange juice (JO) or grapefruit juice (JR). The capability to identify different structure is a first goal, but the objective is to be more precise as possible. So, when focusing on results for fruit juices or for isomers (figure 4), the potentiality to distinguish compounds/odours is then well shown. 2 clusters for fruit juices are obtained even if the global matrix of these juices are very close and it was the result obtained without specific development of the device for this application. For isomers ans specifically enantiomers that cannot be distinguished by techniques like GC/MS, the results of figure 4 illustrate a high potentiality of the method to analyse such compounds. It is crucial for odour application because enantiomers of limonene do not present typically the same odour (like very often for enantiomers). The R-limonene leads typically to orange-like odour when the S-limonene is more related to turpenine-like odour as a lemon note.

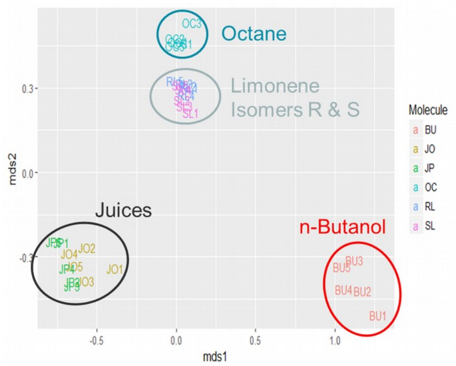

Fig. 3.: Distinction of compounds on principal component analysis for 5 repetition of samples.

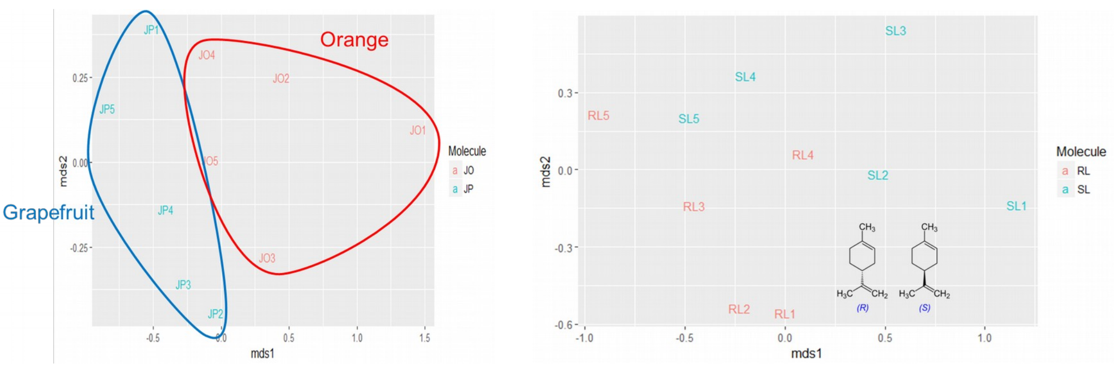

Fig. 4.: Distinction of fruit juices (left) and strong tendency to distinguish isomers (right).

If the equipment shows a capacity for compounds disctinction, it is interesting to understand how this distinction can be carried out. Of course the number of sensors is essential but the size of compound is also an important (major) criteria to orientate discrimination for mixtures. When we consider mixture (50/50 in liquid) of 2 compounds with for example Octane associated to Ethanol or octane associated with n-Butanol , in all repetitions, the mixture of both compounds (or even 3 compounds with a liquid proportion of 1/3 each) is identified as Octane. So, the biggest compound has an important impact on the fingerprint.
The size is also an important factor for detection limits. This aspect is shown on Table 2 for different chemical families.

Table 2: Sensitivity for selected compounds of four chemical families

Alcohols	**Méthanol**	**Ethanol**	**Octanol**	**Linalol**	
Detec. limit	>400 mg/m^3	>400 mg/m^3	11 mg/m^3	**6,5 mg/m^3**	
Alcanes	**Pentane**	**Hexane**	**Heptane**	**Octane**	**Nonane**
Detec. limit	>400 mg/m^3	284 mg/m^3	24 mg/m^3	12 mg/m^3	**11 mg/m^3**
Carboxylic acids	**Propionic acid**	**Butyric acid**		**Valeric acid**	
Detec. limit	23 mg/m^3	156 mg/m^3		**1,6 mg/m^3**	
Ketones	**2-Heptanone**	**Methyl IsoButyl ketone**		**Diisobutylketone**	
Detec. limit	40 mg/m3	>400 mg/m3		10 mg/m3	

4.Conclusions

The SPRi technology applied for air analysis gives a high potentiality for recognition of compounds/odours with the large number of sensors used on the cell. It is typically the main progress given by this technology for instrumental odour measurement. The optical measurement is not the classical method for e-noses or equivalent measurement devices competitively to electrical sensors and shows without wavelength optimization detection limits in the same range than some metal oxide sensors. Presented results can be considered as a first step for this new technique that can be applied easily with an autonomous and portable device.