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Development and Optimization of SPRI-based Electronic Nose for Highly Selective Detection of Volatile Organic Compounds

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Summary:

The development of an instrument capable of performing at a level comparable to that of the biological nose remains a scientific challenge. In the present work, we have developed and optimized a multiplexed Surface Plasmon Resonance Imaging (SPRI)-based optoelectronic nose coupled to a microarray of novel sensing materials for the sensitive and selective detection of Volatile Organic Compounds (VOCs) in the gas phase. Using pattern recognition algorithms our system is able to discriminate VOCs belonging to different chemical families, as well as VOCs differing by a single carbon.

Keywords: electronic nose, peptide, Surface Plasmon Resonance Imaging, VOCs.

Introduction

The development of an instrument capable of imitating the remarkable capabilities of biological olfaction remains a scientific challenge. However, there is a growing need to reliably detect and monitor volatile organic compounds (VOCs) – the small air-borne molecules responsible for the odor of objects – in various fields, such as quality control for food and cosmetic industries, medical diagnostics and environmental monitoring.

Although sensitive and reliable, classical analytical techniques, such as Gas Chromatography coupled with Mass Spectrometry (GC-MS), require specialized personnel and are incompatible with on-field applications. Alternatively, electronic noses (eNs) refer to a class of multi-sensors designed for the detection of VOCs in the gas phase, drawing inspiration from biological olfaction. These aim to provide rapid, reliable and inexpensive analyses. Although considerable progress has been made, the performance of the biological nose has not yet been achieved by eNs.

In biological olfaction VOCs are detected by olfactory receptors (ORs) in the nose acting in a combinatorial manner, where one VOC can stimulate multiple ORs and vice versa. This allows the recognition of an amount of VOCs various orders of magnitude higher than the number of receptors in the nose.

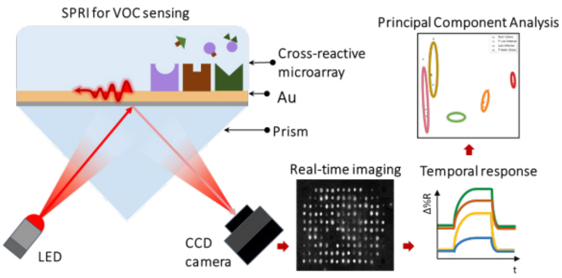

Fig. 1. Working principle of the SPRI-based opto-eN.

Since 2012 our team has been developing an electronic nose based on peptides, coupled with surface plasmon resonance imaging (SPRI), a multiplexed, label-free and real-time transduction technique (Fig. 1) [1]. Herein, a homemade system was designed for the detection in gas phase. Its operating principle, similar to that of the biological nose, consists of an array of cross-reactive peptides whose interactions are imaged by SPRI before using advanced mathematical methods for sample differentiation and identification. Great efforts have been made to optimize multiple optical parameters on the SPR response, resulting in a stable system that can be reused for at least three months with good repeatability.

Materials and Methods

Biochip preparation. The microarray was composed of a gold-coated commercial prism (Edmund Optics, U.S.). Before use, the surface was treated with plasma (Diener electronic, Germany) for 3 minutes to eliminate organic contaminants. All sensing materials were deposited in quadruplicates on the gold surface using a non-contact microspotting robot (Scienion AG, Germany).

Sensing Materials. 19 short peptides were designed to have diverse physicochemical characteristics (positively or negatively charged, hydrophobic, hydrophilic, etc.) to obtain a differential response to VOCs. Additionally, an internal negative control (NC) that is known to not be sensitive to VOCs was added. All sensing materials include a cysteine at one end for their immobilization. For confidentiality reasons, exact sequences are not herein disclosed.

VOC Testing. A homemade fluidic bench was used to perform four-minute injections of VOCs of different chemical families. In each case, 50 µL of VOC were mixed into 1.5 mL of mineral oil (Sigma Aldrich) to promote controlled gradual evaporation and avoid system saturation.

SPRI. The SPRI system is set-up in the Kretschmann configuration, where the whole microarray is irradiated through the prism with a polarized beam. When the incident light is totally reflected, an evanescent wave is created on the ad-layer between the prism and the sensing medium. Surface Plasmon Resonance occurs under certain energy conditions when the evanescent wave resonates with the metal's free electron plasma. Thus, binding events in the sensors result in variations in the reflectivity (Δ%R), which are captured by a CCD camera. These images are then analyzed to obtain kinetic binding curves, called sensorgrams. After each injection, the microarray is regenerated using purified dry air. Afterwards, the average reflectivity of sensing molecules' replicates at the equilibrium is plotted, generating a distinct pattern for each VOC tested. Finally, principal component analysis (PCA) can be performed for VOC classification.

Results

Our system's versatility allows us to analyze many different VOCs. Figure 2 shows the sensorgrams obtained for VOCs of different chemical families, as well as their distinct equilibrium pattern. Additionally, the PCA in Fig. 2 E) clearly shows that our system is able to differentiate VOCs of different chemical families.

Great efforts have been made for the optimization of the system [2], including of the light source's wavelength, prism configuration and the immobilization of sensing biomolecules. Additionally, a passivation step to reduce the drift, poisoning and aging effects, the controlled and reproducible injection of VOCs into the analysis chamber, and the nature of sensing biomolecules for the greater sensitivity and selectivity of the system [3], [4].

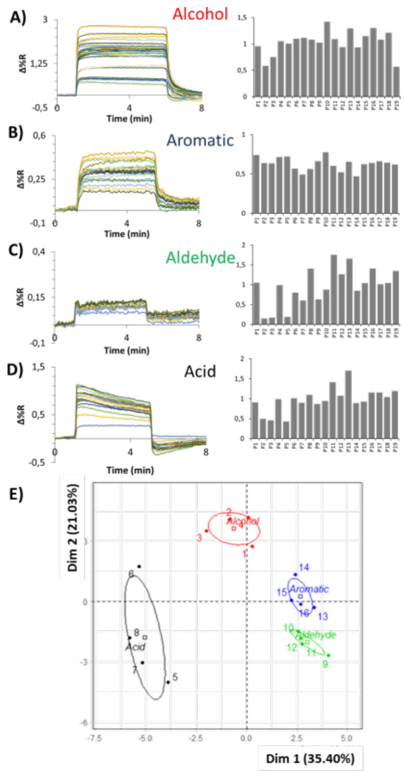

Fig. 2. Sensorgrams (%R versus time) and equilibrium patterns obtained for 50µL of A) 1-Hexanol, B) Toluene, C)Hexanal, D) Hexanoic acid; E) PCA for the four aforementioned VOCs belonging to different chemical families.

Comparing to existing eNs, our system has very good sensitivity, selectivity and stability, with performances getting closer to that of the human nose.

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