

Array of sensors based on conducting polymers for the quality control of the aroma of the virgin olive oil

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Abstract

In this paper, a sensor array based on thin films of conducting polymers aiming to discriminate among different virgin olive oils is described. The array has been constructed using eight polymeric sensors. They were deposited electrochemically by using different electrodeposition conditions, different monomers (3-methylthiophene, pyrrole and aniline) and doping agents. Olive oil samples with well-defined organoleptic characteristics have been selected by a panel of experts. They included virgin olive oils of different qualities (extra virgin, virgin and lampante) as well as a refined olive oil. Four types of olive oil samples with well-defined “off odours”, that is with unpleasant aromatic notes, named musty, rancid, fusty and muddy, have also been included in the study. The sensors are stable and show good reproducibility and reversibility when exposed to the headspace of the virgin olive oils. The array of sensors combined with a Principal Component Analysis (PCA) allows the discrimination of different types of olive oils. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Sensor arrays coupled with a pattern recognition technique (the so-called electronic noses) have shown to be useful in the discrimination of the aromas of certain foods and beverages [1–3]. Nevertheless, it is clear now that the development of systems specific for a particular application may prove more successful than attempts to develop a single system suitable for all applications [4,5].

Polymers have been used in the development of a wide range of sensors. In general, they are excellent transducing materials since their physical properties (e.g. conductivity) respond to various chemical and/or physical stimuli. Since these materials, which include polypyrrole (PPy), polyaniline (PAN) and poly-3-methylthiophene (P3MT) are easily synthesised electrochemically, they can be deposited directly onto microelectrode substrates [6,7].

There are several examples in the literature that demonstrate the success of using polymeric array of sensors for the detection of food and beverage odours [8–11].

Our group is currently developing a sensor array specific for the detection of olive oil aroma [12]. This sensor array is formed by conducting polymers that are able to produce a measurable change in their conductivity when exposed to the headspace of the olive oil.

An average olive oil contains more than 100 volatile components that can be grouped in families such as acids, alcohols, esters or carbonyls and their presence is modified by some aspects of the production [13,14]. According to their organoleptic characteristics, the virgin olive oils can be classified in extra virgin olive oils (high quality), ordinary or semifine quality olive oils (medium quality) and the so-called lampante olive oil (lower quality) [15]. In extra-virgin olive oils, only a maximum acidity of 1 g per 100 g is permitted, but in the ordinary or the lampante olive oils of lower quality, a higher acidity is usually found. Moreover, this last type shows unpleasant aromatic notes, which make it unsuitable for the human consumption, and has to be refined by chemical methods. In turn,

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the unpleasant notes can be classified as “fusty”, “muddy”, “musty”, “rancid” and “winey”, following the classification of the International Olive Oil Council [16].

One of the main problems when testing or training such an array of sensors is the need to have available well characterised samples. This implies a degree of difficulty since the samples have to be carefully selected and evaluated by a panel test. Moreover, once selected, the samples must be stored under strict conditions (i.e. avoiding the light) since an inappropriate storage may modify the organoleptic characteristics of the sample under study.

With conducting polymer-coated microelectrode sensors, a number of electrochemical options are available which allow the rapid and simple modification of the response of the sensors. In this work, a series of sensors based on PPy, PAN and P3MT have been prepared using different experimental conditions.

The response of individual sensors towards a selection of volatile components (VOCs) present in the headspace of the olive oil has been evaluated. For this purpose, and in order to take into account the effects of the matrix in the odour release of individual chemical components, an odourless olive oil called “flat oil” has been used as a matrix where the selected VOCs were solved.

An array has been constructed using sensors that showed a certain degree of selectivity towards the VOCs usually present in the headspace of the olive oil and that also presented good characteristics of stability, reproducibility and reversibility.

The array has been exposed to the headspace of different classes of virgin olive oils with well-defined organoleptic characteristics (including “off” odours). In order to evaluate the capabilities of discrimination of the array of sensors, the Principal Component Analysis (PCA) has been conducted.

2. Experimental

2.1. Samples

According to the literature, a series of pure VOCs belonging to the main groups of odourant molecules responsible of the olive oil aroma with well-defined organoleptic properties were selected. They included one alcohol (hexanol) one aldehyde (hexanal) one ester (*n*-butyl acetate) and one acid (acetic acid). All the reagents were purchased from Aldrich.

In order to take into account the effects of the matrix on the odour release behaviour of individual odourant components, the pure VOCs were solved in an olive oil matrix ($0.2 \text{ mol} \cdot \text{l}^{-1}$) which consisted in an odourless olive oil called “flat oil”. The method of preparation of this matrix consists in the extraction of the volatile components of a sample of virgin olive oil by heating the sample at 230°C

under a water vapour flow which was used to carry away the extracted volatile components.

A series of virgin olive oils with different organoleptic properties were characterised by chromatography and a panel of experts from the Instituto de la Grasa from Sevilla (Spain). The different scores awarded by the panel test following the instructions of the International Olive Oil Council [16] allowed the classification of the samples.

The olive oils under study included two types of extra virgin olive oils (highest quality) labelled I and II; one type of virgin olive oil lampante (lower quality) and one type of refined olive oil (a virgin olive oil which has suffered a chemical treatment and that cannot be considered a virgin olive oil). For comparison purposes, a sunflower oil was also included in the study.

In addition, four classes of virgin olive oils with well-defined “off” odours were selected and classified by the panel test as “fusty”, “muddy”, “musty” and “rancid”.

The olive oil samples were stored at -4°C under dark and unfrozen just before use.

2.2. Preparation of the polymeric sensors

Eight different polymeric gas sensors were prepared by electrodeposition.

The P3MT and PAN films were grown electrochemically onto glass substrates covered with ITO electrodes (electrode spacing of $75 \mu\text{m}$). Alumina substrates with gold electrodes (electrode spacing $50 \mu\text{m}$) were used for the fabrication of the PPy sensors. Prior to polymer deposition, the substrates were cleaned with acetone, and rinsed with ultrapure water.

The electropolymerization and the electrochemical measurements were performed in a conventional three electrode cell using an EG&G PARC Potentiostat/Galvanostat (Mod. 263). An electrochemical cell with a thermostatic jacket (Metrohm) and with a temperature controlled liquid system (Neslab) was used. All the polymeric films were grown at a constant temperature (25°C). The solutions were deoxygenated by bubbling nitrogen for 10 min prior to use.

A Ag/AgNO₃ electrode was used as reference electrode for the experiments carried out in non-aqueous media. When water was used as solvent, a Ag/AgCl electrode was used as reference electrode. All potentials quoted are relative to the corresponding reference. The counter electrode was a large surface area platinum gauze, which was flamed prior to use.

The P3MT sensors were obtained from an electrolytic solution of 3-methylthiophene ($0.1 \text{ mol} \cdot \text{l}^{-1}$, purchased from Sigma), in acetonitrile (Sigma–Aldrich, HPLC grade). The effect of the doping anion was tested by using several electrolytes ($0.1 \text{ mol} \cdot \text{l}^{-1}$) including lithium perchlorate anhydrous (LiClO₄) (Fluka), lithium trifluoromethane sulfonate (LiCF₃SO₃) (Fluka), tetrabutylammonium perchlorate (TBAP) (Sigma) and tetrabutylammonium tetrafluoroborate (TBABF₄) (Fluka).

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