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Use of electronic nose to determine defect percentage in oils. Comparison with sensory panel results

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ABSTRACT

An electronic nose based on an array of 6 metal oxide semiconductor sensors was used, jointly with linear discriminant analysis (LDA) and artificial neural network (ANN) method, to classify oils containing the five typical virgin olive oil (VOO) sensory defects (fusty, mouldy, muddy, rancid and winey). For this purpose, these defects, available as single standards of the International Olive Council, were added to refined sunflower oil. According to the LDA models and the ANN method, the defected samples were correctly classified. On the other hand, the electronic nose data was used to predict the defect percentage added to sunflower oil using multiple linear regression models. All the models were able to predict the defect percentage with average prediction errors below 0.90%. Then, the develop is a useful tool to work in parallel to panellists, for realizing a rapid screening of large set of samples with the aim of discriminating defective oils.

1. Introduction

Food industry, especially dairy industry, has been one of the earliest users of sensory analysis, which is an extremely useful tool for flavour researchers [1]. There are two major types of sensory analysis: affective and analytical. Affective sensory tests are based on consumers and their perceptions of acceptability, and are important to the food industry because they explain the role of flavour, texture, and appearance in influencing consumer acceptability. These types of techniques can only measure what untrained consumers think; they tend to suffer from extensive person-to-person variability. Therefore, polling a large number of consumers (>50) is typically done to improve the statistical validity of the information obtained [1]. On the other hand, analytical sensory techniques are based on trained panelists. Discriminatory tests (difference and threshold), as well as descriptive sensory analysis, are perhaps the most powerful sensory tools. Analytical techniques are well suited for both identifying flavours in a product and discriminating sensory properties between products [1].

The most important phase of olive oil sensory analysis is represented by its aroma. Aroma is a very complex sensation, being identified more than 7100 volatile compounds in foods overall [2,3]. Each volatile compound may *potentially* contribute to aroma perception, depending upon their concentrations and sensory thresholds. The definition of sensory threshold was introduced in sensory analysis as a threshold in which any sensation was perceived. Regarding olive oil sensory analysis, the olfactory sensory threshold of a panel with respect to some defects is evaluated to habilitate the panel as official, recognized by the International Olive Council (IOC) or by the Ministry of the different European Countries. On the other hand, the sensory analysis is one of the most important tools useful to classify the virgin olive oils (VOOs) in different commercial categories (extra virgin, virgin and lampante), which is mainly evaluated with the presence of sensory defects [4]. The most frequent off-flavours of VOO are grouped into five main defects: fusty, muddy, mouldy, winey and rancid. Several works in literature have focused the correlation between defects perceived by a trained panel in VOOs and the presence of specific volatile compounds in the head-space of these samples. Morales et al. [5] have studied VOOs differently defected by dynamic headspace high-resolution gas chromatography coupled with mass spectrometry detection and olfactometry, identifying the volatile compounds mainly responsible for the off-flavours. Considering the ratio between the volatile concentration and its odour threshold in oil the mouldy defect resulted strictly related to the presence of some C_8 compounds produced by specific mould enzymes as 1-octen-3-one and 1-octen-3-ol. On the other hand, the winey defect, due to sugar fermentation, was well described by acetic acid and ethyl acetate whereas

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the fusty unpleasant odour was linked with some branched C_5 components as 3-methyl butan-1-ol as a consequence of an anomalous aminoacid degradation; with regard to rancid sensory defect several saturated and unsaturated aldehydes, as nonanal and *E*-2-heptenal respectively, have been detected as characteristic compounds.

The human being is exceptionally sensitive to some volatiles (such as 2-isobutyl-3-methoxypyrazine, which has an odour detection threshold in water of 0.002 ppb [6] and 0.015 ppb in wine [7], and 1-octen-3-ol, with a detection threshold of 1 ppb in oil) [5], but insensitive to many other volatiles (e.g., ethanol has an odour threshold in water and in oil of 100,000 ppb and 30,000 ppb respectively, and a taste threshold of 52,000 ppb in water) [5,6]. A person's ability to detect odours is also influenced by many other factors such as genetic variability, olfactory fatigue, and naturally occurring and unpredictable factors such as temperature and humidity. The complexity of food aromas and sensitivity required, plus the fact that the olfactory system must be able to respond to unknown odorants (it cannot be learned response), make this a most complex phenomenon. For this reason, considerable interest exists in the development of instrumental techniques, non-invasive and non-destructive, in order to make more objective, faster and less expensive the assessments of olive oil sensory quality [8].

Recently, metal oxide semiconductor (MOS) sensors have been applied in VOO aroma control to detect a variety of sensory defects [9–14] and to authenticate VOOs according to varietal or geographical origin of olives [15]. On the other hand, MOS sensors have a low cost and can work on-line without sample pretreatment [16,17]. These sensors do not provide a quali-quantitative analysis of volatile compounds of the samples, but responds to the whole set of volatiles in a unique digital pattern. These patterns are a signature of the particular set of aromatic compounds such as these should determine a specific olfactory perception [18].

Aparicio et al. [9] have used MOS sensors to detect the rancid defect in VOOs, using the information on volatile compounds responsible for rancidity and the sensory evaluation of the samples by assessors for explaining the mathematical selection of sensors. The same studies have been also performed by Garcia-Gonzalez et al. [11] for the detection of vinegary defect. More recently, Cimato et al. [19] have studied 12 monovarietal extra VOOs from Tuscany by means of three different methodological approaches: metal oxide sol–gel thin films based electronic nose and multivariate data analysis (PCA), headspace-solid phase micro-extraction/gas chromatography/mass spectrometry (HS-SPME/GC/MS) and sensory analysis with the aim to discriminate the different samples. Authors evidenced that HS-SPME/GC/MS was possible to obtain the chemical map of the different samples, while with electronic nose samples were separated in clusters.

More recently, Lopez-Feria et al. [20] have developed a fast method based on the direct coupling of HS-MS without chromatographic separation and multivariate tools (SIMCA and PLS) to determine the presence of negative attributes and to classify VOO. Authors analyzed a training set composed by refined olive samples spiked at different levels (from 20 to 100%) with standard defects whereas the prediction set was made up of several unknown samples belonging to different VOO classes. Despite the good results, it should be considered that this type of instrumentation is more complex and expensive than an electronic nose.

The aim of the present study was to develop a non-destructive method, based on MOS sensors, capable of classifying oils containing the typical virgin olive oil defects according to their sensory threshold previously established by trained panellists. For this purpose, linear discriminant analysis (LDA) models and artificial neural network (ANN) method were used. On the other hand, multiple linear regression (MLR) models were also constructed to predict the defect percentage added to sunflower oil.

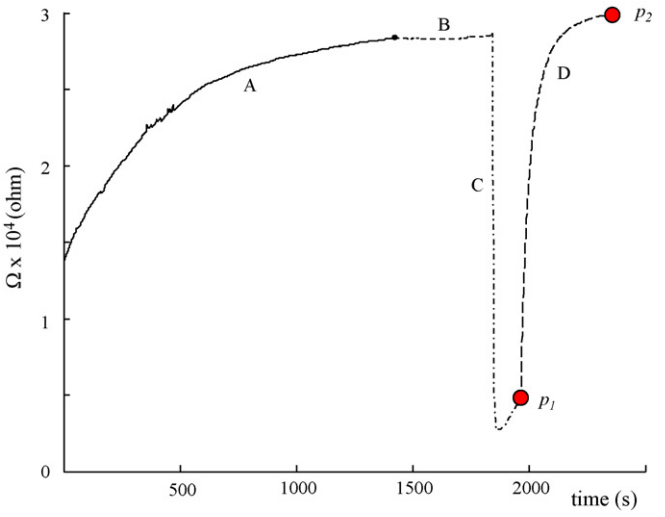

Fig. 1. Plot representing the electric resistance (Ω) of a MOS sensor during oil evaluation: (A) conditioning phase, (B) before injection phase, (C) measurement cycle and (D) recovery phase.

2. Materials and methods

2.1. Instrumentation and working conditions

An electronic olfactory system (EOS 507, Sacmi Imola S.C., Imola, Bologna, Italy) composed of a measuring chamber with 6 metal oxide sensors and a personal computer was used for the acquisition and analysis of the data generated by the EOS 507. The sensors used were: sensor 1 (SnO_2), sensor 2 ($SnO_2 + SiO_2$), sensor 3, 4 and 5 (catalyzed SnO_2 with Au, Ag and PD, respectively) and sensor 6 (WO_3). During the analysis, sensors were maintained at a temperature range of 350–450 °C. The EOS 507 was controlled by an integrated PDA equipped with proprietary software, and was connected to an automatic sampling apparatus (Model HT500H) which had a carousel of 10 sites for loading samples. Samples were kept at controlled temperature (37 °C) and placed in a chamber provided by a system that removes humidity from the surrounding environment.

2.2. MOS sensor array procedure

For each sample, 15 g were placed in 100 mL Pyrex vials equipped with a pierceable silicon/Teflon cap. For each sensor, signal is divided in four parts (see Fig. 1): (A) conditioning phase (25 min period employed to obtain a constant baseline), (B) before injection phase (in which samples were incubated at 37 °C for 7 min before injection), (C) measurement cycle (in which the oil headspace, sampled with an automatic syringe, was then pumped over the sensor surfaces for 2 min during which the sensor signals were recorded; in this phase, sensors were exposed to filtered air at a constant flow rate of 50 sccm (standard cubic cm per min) to obtain the baseline) and (D) recovery phase (another 7 min period applied to restore the original MOS conditions). Ambient air filtered with activated silica and charcoal was used as a reference gas during the recovery phase of the measurement cycle. The previous conditions ensured that the baseline reading had indeed been recovered before the next analysis was performed.

The experimental conditions adapted from Camurati et al. [10] were used, being each sample evaluated in triplicate in different days.