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Low-cost gas sensors with polyaniline film for aroma detection

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ABSTRACT

A low-cost gas placement has been designed to detect different artificial fruit aromas (apple, grape and strawberry). The sensors have been developed through polyaniline deposition using *in situ* polymerization technique on the inter-digitated area of the graphite electrode, which was accomplished using the line-patterning technique over tracing paper substrate. The sensitivity, reversibility, response time, hysteresis and electronic nose system detection limit have all been evaluated using different fruit aromas (apple, grape and strawberry), under controlled temperature and humidity conditions. The sensitivity decreased gradually as the storage period increased. It was possible to notice that the gas sensors presented high sensitivity and reversibility during the three analyzed cycles on apple, grape and strawberry aromas as well as the detection limit that was lower than 0.62 ppm. Therefore, it demonstrated the potential electronic nose systems have using low-cost gas sensors with polyaniline film in the evaluation of commercially prospected aromas.

1. Introduction

Flavorings are complex mixtures of substances that provide aroma to food products. Through odor analysis it is possible to obtain and to provide valuable information about food quality (Dymerski et al., 2011). The sensory analysis of food aroma during the product development is typically performed with organoleptic analysis using a panel of trained judges (Aumatell, 2011).

The use of panelists for aroma analysis is a great tool to perform consumer preference tests. However, it is an expensive and lengthy approach limited only to the use of non-toxic compounds. Incoherency and unpredictability influenced by human factors such as; individual variability, decrease on sensitivity after prolonged exposure, tiredness and mental state variations can occur. That calls for the use of more objective and faster methods.

The sensory analysis of aroma attributes could be substituted by analytical and instrumental methods such as gas chromatography coupled with odorimetry and mass spectrometry for quantification of volatile aroma compounds. However, these analytical methods are usually complex and expensive. In addition to that, some volatile compounds are not efficiently separated by gas chromatography as they are recognized by the human olfactory system (Santonico et al., 2008).

Many studies have been conducted in order to develop new methods to analyze food aromas in a more objective and faster manner. One area of particular interest (Aishima, 1991; Hossain et al., 2012) among these approaches, is the attaining of fingerprints by the use of chemical sensors placements. Electronic gas sensors systems, for instance, began to be used in the Food, Cosmetic and Packaging Industries due to their simplicity, rapid response and objectivity (Steffens et al., 2012).

The detection principle of electronic noses is based on changes in the electrical properties of a sensitive layer (metal oxide or conducting polymers) as per its contact with volatile substances (Cao et al., 2013). The particle size control of the layer is a key aspect for the achievement on devices with high degrees of both sensitivity and reproducibility. The techniques most commonly used on layers manufacturing with well-controlled particle sizes include; spin-coating, casting, self-assembly, Langmuir–Blodgett films and *in situ* polymerization (Bai and Shi, 2007). Conducting polymers present special advantages as sensitive layers over inorganic semiconductors, particularly due to their high sensitivity at low temperatures, inexpensive synthesis and wide detection range of

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volatiles. Polyaniline has been the most studied conducting polymer owing to its simple synthesis, high chemical stability and disposable features (Adhikari and Majumdar, 2004; Manzoli et al., 2011; Steffens et al., 2013). Polyaniline can also be used to coat various substrates such as tracing papers. Thereby justifying variations in its physical and chemical properties.

There have been very few studies dedicated to elucidate the relationship between artificial flavoring addition and food matrix composition. This is a major problem in the Food Industry where artificial flavorings are used to improve acceptability, particularly in the development of new products. Thereby, electronic noses have appeared as important tools on aroma quantification, supporting the evaluation of foods attributes, uniformity and consistency, as well as monitoring all the industrial processing stages (Wilson and Baietto, 2009). In this way, the main objective of this study was to use low-cost gas sensors based on polyaniline-coated tracing papers to detect different artificial fruit aromas used in the Food Industry. Apple, grape and strawberry fruit flavorings have been used to evaluate the gas sensors performance by means of resistance measurements.

2. Material and methods

2.1. Inter-digitated electrodes

The inter-digitated graphite electrodes were obtained using Line Patterning Technique (LPT), as described by (Steffens et al., 2010). The process has been designed using main stream *computer software* (PaintBrush, Microsoft™) and used a conventional Laser Jet printer (NASHUA XF - 20) to print the negative image of the mask on the substrate (tracing paper - thickness 63 g/m^2). An aqueous solution of graphite (E Aquadag, Acheson Colloids Company) was deposited onto the inter-digitated electrode and its printed regions were removed using the ultra-sonication process with acetone (Sigma–Aldrich). The dimension of the inter-digitated electrode in 11 pairs had been described in a previous paper (Manzoli et al., 2011).

2.2. Deposition of polyaniline in situ

The methodology described by (Steffens et al., 2010; Venancio et al., 2008) has been used for the polyaniline film deposition by *in situ* polymerization in the emeraldine oxidation state. Briefly, the procedure consisted of immersing the inter-digitated area of the graphite electrode in a glass beaker containing solution A (aniline + chloridric acid). Afterwards, a solution B (ammonium persulfate + chloridric acid) was slowly added to solution A. This reaction occurred at 0 °C for 100 min using magnetic stirring. After synthesis completion each gas sensor with polyaniline-HCl thin film was washed with 5 ml of a pH 3 HCl solution and then dried under dynamic vacuum until reaching a constant resistance. After that, the gas sensors were stored in a vacuum desiccator.

2.3. Aroma tested

Compounds of artificial fruit aroma (important for further applications on foods) have been chosen to be evaluated in this study. The tested aromas from apples, grapes and strawberries were supplied by Duas Rodas (Duas Rodas Industrial Ltd.).

2.4. Gas sensors responses at different aromas

The gas sensors responses at different aromas (apple, grape and strawberry) were evaluated in relation to their sensitivity (S) and reversibility (η) by Eqs. (1) and (2) respectively (Feng and MacDiarmid, 1999).

$$S = \frac{(R - R_O)}{R_O} 100 \quad (1)$$

$$\eta_{\%} = \frac{\left(R - R_f\right)}{(R - R_O)} 100 \quad (2)$$

Where R_0 is the initial resistance of the sensor in air, R is the resistance after exposure to an aroma and R_f is the minimum resistance in laboratory air after the aroma exposure.

The sensibility and reversibility evaluate, respectively, the percentage of absorbed analyte on the sensory layer and the ability of the sensors over various cycles, to change under the action of aroma and then return to its initial state when the aroma ceased.

The experiment has been made by exposing the sensors. First, under environment conditions (laboratory air) with the electrical resistance data measured by a multimeter (FLUKA77I) for 15 min at 60 s intervals. Later, the sensors were inserted into the gas chamber (2.5 L) and exposed to the specific fruit aroma for 15 min. The aroma in the liquid form was inserted using a syringe to obtain the desired concentration (200 ppm). The data acquisitions of resistance were accomplished each second and finally had the sensors removed out of the chamber to achieve the response without aroma (clean air) returning back to the initial value, for further 15 min. After this cycle, the experiment was repeated several times. These experiments were done in triplicate, thereby allowing the repeatability of the system to be observed. Both temperature and relative humidity were monitored inside the chamber with a commercial thermo-hygrometer sensor (IMIMIPA MT -241). This procedure has been done individually on each experiment. The sensors responses (in a function of storage time) for periods of 0, 7, 14, 21, 35 and 42 days, were evaluated by means of measuring the gas sensor resistance in the presence of diverse fruit aromas as a function of time (from 0 to 15 min). The sensors were stored in a vacuum desiccator during that length of time.

The detection limit and sensitivity to various concentrations of aromas (0–200 ppm) were also evaluated. A baseline was initially obtained for three (3) minutes. Afterwards, the aroma was introduced into the chamber and the sensor response was observed for over a 10 min period. In order to remove this aroma concentration, the chamber was purged with 0.1 L/min flow of dry nitrogen gas (with analog flow mass controllers). This experimental sequence was repeated for all evaluated concentrations. The measurements were performed at a constant humidity level (55 ± 2.0%) inside the chamber and were monitored using a commercial sensor (Sensirium TM). After each aroma measurement, the materials that had been in contact with the vapors (the chamber and tubes) were cleaned and rinsed using acetone, isopropyl alcohol and distilled water.

2.5. Atomic force microscope (AFM)

The characterization of the polyaniline film on tracing paper substrate was performed with the Dimension V (Veeco) AFM, using a pyramidal silicon nitride tip attached to a cantilever with a spring constant of 42 N m^{-1}, in tapping mode at a scan rate of 1 Hz. The images were processed and the polyaniline thickness and tracing paper interface were calculated with Gwydion 2.1 data analysis *computersoftware* (Version 2.18, November 2008).

3. Results and discussion

The gas sensors responses were assessed through continuous