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Electronic nose system based on polyaniline films sensor array with different dopants for discrimination of artificial aromas

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ABSTRACT

The aroma quality analysis in terms of sensory properties is important to the food industry. Chemical sensors based on polyaniline (PANI) films were produced and used in a sensors array (electronic nose) to distinguish three artificial aromas: strawberry, grape and apple. The sensors were produced by *in situ* PANI polymerization on interdigitated graphite electrodes and doped with different acids (hydrochloric acid - HCl, camphor sulfonic acid - CSA and dodecylbenzenesulfonic acid – DBSA). Morphological characterizations by field emission scanning electron microscope (FE-SEM) revealed the best superficial regularity with smaller and better distribution of particles to the HCl-doped PANI film, which exhibited highest and fastest response and best sensitivity. It was also demonstrated by principal component analysis (PCA) that the sensor array was highly efficient to distinguish artificial aromas, thereby being a promising tool for aroma quality analysis in various food industry sectors.

1. Introduction

Food quality involves nutritional and organoleptic characteristics that are important for consumers such as freshness, appearance, odor, taste and texture. Food aromas, as well as taste, are extremely important for the food industry, as the sensorial perception of a specific food stimulates its consumption that is intimately connected to the consumers' food acceptance. Thus, aroma analysis can be an indication of acceptance and quality of food products. Aroma release profile evaluation on formulated products is a real challenge for the food industry, since any change that may occur during formulation must be evaluated, for it can affect the aroma's volatile release impairing its perception and global sensorial quality.

Current methods for the detection of volatile aromas include headspace gas chromatography and sensory evaluation using trained sensory panels (Procida, Giomo, Cichelli, & Conte, 2005). Chromatography analysis can detect smoothly the volatile aromas present in the gas phase, employing, however, a pre-treatment for the volatiles' isolation and enrichment is required (Wardencki, Chmiel, & Dymerski, 2013). On the other hand, sensory analyses require highly specialized and trained sensory panels (Peris & Escuder-Gilabert, 2009) that may undergo both incoherence and unpredictability due to individual variability, sensibility decrease due to prolonged exposure, fatigue and variable mental state, as well as the techniques' limited to non-toxic compounds. Furthermore, such techniques employ expensive methods and long times.

Electronic nose systems have emerged as promising alternatives for aromas recognition and discrimination, since aroma provides relevant information regarding quality, freshness, and safety of foods (Pennazza et al., 2013; Peris & Escuder-Gilabert, 2009). The application in the food industry is adequate due to its portability, small size, and short recording and analysis time, as well as odorant non-destructive sampling (Wilson & Baietto, 2009).

Electronic noses are usually composed of a non-specific sensors array that must respond differently to a specific odor and a recognition pattern used on results analyses, categorizing odors. Sensors with conductive polymers stand out among the different sensors used on electronic noses. Intrinsically conducting polymers, such as polyaniline (PANI) are good sensitive layer to be use in gas sensors. PANI presents in its chemical architecture a π-conjugated electronic system, which has single and double bonds alternating along the polymer chain. Resulting in the electron delocalization along polymer chain, increasing the charge mobility (Heeger, 2001). Furthermore, the addition of dopants (for instance protonic acid) improves PANI conductive properties (Brugnollo et al., 2008). The acidic PANI doping also increases its crystallinity, and leads to higher sensitivity towards analytes (Manzoli et al., 2011). Hence, PANI doping with organic acid, such as HCl, CSA and DBSA tends to create more ordered films, readily soluble,

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chemically stable, and electrically conductive.

In the present study, we report the use of an electronic nose system based on a gas sensors array with sensing PANI units made with different dopants: (hydrochloric acid - HCl, camphor sulfonic acid - CSA and dodecylbenzenesulfonic acid – DBSA). The PANI films were deposited onto interdigitated graphite electrodes with tracing papers as substrate. The E-nose system combined with principal component analysis (PCA) statistical method was evaluated on the discrimination of different artificial aromas concentrations (apple, strawberry, and grape). The gas sensors with PANI films have been characterized in terms of morphology, sensitivity, reversibility and response time.

2. Material and methods

2.1. Interdigitated electrodes

The low-cost interdigitated graphite electrodes with a rectangular area of 16 mm by 14 mm were obtained by the Line Patterning Technique (LPT) on tracing paper substrate (weight of 63 g/m^2), which was purchased from local stations. The interdigitated part of these electrodes consisted in 11 parallel pairs, 0.25 mm wide, separated by 0.5 mm gaps (Manzoli et al., 2011; C. Steffens, Franceschi, Corazza, Herrmann, & Oliveira, 2010; Venancio, Mattoso, Herrmann Júnior, & MacDiarmid, 2008). The LPT process use the Paintbrush *software* (Microsoft™) to draw the mask of interdigitated electrodes and a conventional Laser Jet printer (NASHUA XF - 20) to print the negative image of the mask on the substrate. An aqueous graphite solution (Aquadag E, Acheson Colloids Company) was deposited onto the interdigitated electrode printed regions. After solvent evaporation, the printed regions were removed with acetone (Sigma – Aldrich) using an ultra-sonic bath (Transsonic 310 - Elma) where only the covered pattern remained. The printed graphite interdigitated electrodes were stored in a vacuum desiccator at room temperature.

The fabrication scheme of interdigitated electrodes in 11 pairs and electrodes and of whole system (computer, chamber and electronic circuit) images have been published in previous works (Manzoli et al., 2011; Steffens et al., 2010).

2.2. In situ polymerization of PANI

All directions for obtaining the PANI film in the emeraldine oxidation state by *in situ* polymerization have been published elsewhere (Steffens et al., 2010). *In situ* polymerization on the interdigitated electrodes consisted of immersing the electrode interdigitated area in an aniline (Sigma-Aldrich 99.5%) plus HCl 1 M (Vetec) solution. In order to start the PANI-HCl synthesis, ammonium persulfate (Sigma-Aldrich, 98%) with HCl 1 M (Vetec) solution was slowly added to aniline solution described above. The reaction was maintained at 0 °C for 100 min with magnetic stirring (Fisatom 752A). After synthesis completion, each sensor with thin PANI-HCl film was washed with 5 mL of HCl solution (1 M, pH 3) and dried under dynamic vacuum. Then, the PANI-HCl sensors were stored in a vacuum desiccator.

2.3. Gas sensor doping

The complete doping procedure has been described in our previous publications (Manzoli et al., 2011). The gas sensor with PANI-HCl obtained by the *in situ* polymerization were dedoped by immersion in 0.1 M NH_4OH solution for 30 s (to form PANI-emeraldine base) and then redoped for 90 s with a 0.1 M solution of the DBSA or CSA.

2.4. Morphological characterization by scanning electronic microscopy for field emission (FE-SEM)

The PANI films doped with different acids (HCl, DBSA and CSA) morphology deposited on the gas sensors was examined with a Zeiss Supra 35 field emission scanning electron microscope (FE-SEM). The gas sensors were coated with a 2 nm gold layer.

2.5. Voltage measurement in electronic nose for each aroma

The PANI sensors were connected to an electronic nose system with five channels connected to a computer. The electronic system consisted of five independent two-terminal voltmeters working in parallel, with the gain set manually to allow optimization of the analog-digital conversion range. A pulsed constant current was supplied to each sensor through a pulse-width modulated current source (operational amplifier feedback network) of frequency 1.0 kHz, adjusted to set each PANI sensor baseline (doped with HCl, DBSA and CSA) to the same value of 400 mV, as previously described on Manzoli et al. (2011).

The artificial fruits aromas (oil base) evaluate were grape, strawberry and apple, which were obtained from the supplier Duas Rodas (Duas Rodas Industrial Ltda). After obtaining baseline in laboratory air for 10 min, the PANI sensor response to volatile compounds of different aromas (apple, strawberry, and grape) was evaluated in voltage. The different aromas were inserted in the measuring chamber with a syringe in a liquid form, which was used for obtaining the voltage values, collected every 1 s for 10 min. In this study, the aroma concentration has been used taking into account a 0.2% percentage in aroma weight used in a candy industry corresponding to 44.44 ppm. Temperature and humidity inside the chamber were measured by a Thermo-hygrometer (MINIPA MT-241).

Multivariate analysis was carried out by PCA, a statistical method to reduce dimensionality in a way that retains as much as possible of the data set variation. The first principal component, PC 1, has the largest possible variance, PC 2 the second largest and so on (Santonico et al., 2008). The PCA was performed with software Statsoft Statistica Version 5.0. The PCA plot was constructed using the maximum voltage values obtained for each of the sensors (PANI-HCl, PANI-DBSA and PANI-CSA) when exposed to different artificial aromas volatiles (grape, strawberry and apple).

2.6. Sensors sensitivity to different aromas

The array of sensors doped with different acids (HCl, DBSA and CSA) were first exposed to ambient conditions (acclimatized room) without the presence of aroma, recording voltage values at each 30 s during 10 min to obtain the baseline. Then, the sensors were exposed to aroma volatiles (strawberry, grape and apple) at desired concentration of each aroma for 10 min, recording the voltage values every second, and finally the sensors were again exposed to ambient conditions during 10 min. This procedure was performed in triplicate with the same sensor. The sensitivity of the gas sensors to each aroma was evaluated from Eq. (1) (Feng & MacDiarmid, 1999).

$$\Delta S = \frac{(V - V_0)}{V_0} x \ 100 \quad (1)$$

where V_0 is the initial voltage of the sensor in ambient conditions and V is the voltage after exposure to an aroma.

2.7. Sensors response time to different aromas

The response time is determined as the time it takes for the system to reach 63.2% of its final value (Cui et al., 2012; Rinaudo, Paya-Zaforteza, Calderón, & Sales, 2016). The response time was calculated considering 63.2% the difference between the final voltage signal (steady state) and the initial voltage signal of the gas sensors doped with different acids (HCl, DBSA and CSA).