Use of array of conducting polymers for differentiation of coconut oil products

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A B S T R A C T

An array of chemiresistors based on conducting polymers was assembled for the differentiation of co-conut oil products. The chemiresistor sensors were fabricated through the potentiostatic electro-deposition of polyaniline (PANi), polypyrrole (PPy) and poly(3-methylthiophene) (P-3MTp) on the gap separating two planar gold electrodes set on a Teflon substrate. The change in electrical resistance of the sensors was measured and observed after exposing the array to the headspace of oil samples. The sensor response was found rapid, reversible and reproducible. Different signals were obtained for each coconut oil sample and pattern recognition techniques were employed for the analysis of the data. The developed system was able to distinguish virgin coconut oil (VCO) from refined, bleached & deodorised coconut oil (RBDCO), flavoured VCO, homemade VCO, and rancid VCO.

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1. Introduction

Coconut oil is a common edible vegetable oil in various tropical countries and because of its attractive features; it has been used in different food commodities and processed products. One of the most popular coconut oil products is virgin coconut oil (VCO). It becomes popular in recent years due to its beneficial claims for human such as antigenotoxicity, antimicrobial, antiviral effects and prevents cardiovascular diseases [1,2]. The increasing demand for these products and high market value could lead to the emergence of fraudulent and adulterated products, which can endanger the health of the consumers. The authenticity and quality of these commodities have to be monitored in order to protect consumers' health and to sustain market confidence.

The analysis of VCO commonly involves measuring physico-chemical characteristics of oil, such as free-fatty acid, moisture, colour and peroxide value (PV) [3,4]. However, these properties of VCO do not differ much from refined, bleached and deodorised (RBD) oil [5,6]. Descriptive sensorial analysis has been shown to discriminate VCO and RBD oil samples [2]. Instrumental methods, such as gas chromatography-mass spectrometry and high-pres-sure liquid chromatography [3,4], NMR spectroscopy [7], Fourier-

transform mid-IR spectroscopy [8] and differential scanning ca-lorimetry [9] have been applied for the detection and quantifica-tion of adulteration of VCO.

Headspace analysis presents an alternative method for the as-sessment of the quality of VCO and its discrimination from RBD oil. The headspace contains volatile compounds present in a material and used as a sample in the analysis of the material. Headspace solid-phase micro-extraction/gas chromatography mass spectro-metry (SPME-GC–MS) was applied on VCO; however, it was not able to differentiate VCO and RBD oil [10]. Headspace analysis using an ultra-fast gas chromatography with a SAW device de-tector allowed the detection of the adulteration of VCO [11].

Chemical sensors that are sensitive to gases provide a rapid and simple method for headspace measurement. A number of sensing principles have been exploited for vapour sensing, among which are conductimetric sensors [12], piezoelectric sensors [13] and optical sensors [14]. Most of these sensors have low selectivity, but combining several sensors into an array yields a very useful system known as electronic nose [15]. Electronic noses have been applied for the evaluation of olive oil [16–19] and other vegetable oils [20–23], but not for virgin coconut oil.

Conducting polymers are utilised as sensing material for elec-tronic nose system. These polymers are easily prepared through chemical or electrochemical processes, and their molecular chain structure can be modified conveniently by copolymerisation or structural derivations [24]. In comparison to metal-oxides, con-ducting polymers have many improved characteristics these

includes sensitivity, short response time and operates at room temperature [24–26]. Furthermore, conducting polymers have good mechanical properties, which allow a facile fabrication of sensors [25,26].

In this paper, an array of chemiresistors coated with conducting polymers, such as polyaniline, polypyrrole and poly (3-methyl-thiophene) were utilised to differentiate VCO from other coconut oil products. These polymers generate responses when exposed to the headspace vapour of the oil sample. Chemometric techniques based on pattern recognition were used to assess the capability of the chemiresistor array to differentiate VCO from other coconut oil products.

2. Experimental section

2.1. Materials

Reagent grades aniline and 3-methylthiophene were obtained from Sigma Chemicals Company (USA). Pyrrole (reagent grade) was purchased from Aldrich Chemical Company (USA). The three monomers were purified by simple distillation and stored in amber bottles. Each monomer was purged with nitrogen gas (CIGI, 99.99%) to provide an environment that will prevent auto-oxidation. The monomers were stored in the refrigerator (4 ± 2 °C). All purchased chemicals and organic solvents were directly used. Triple distilled water was utilised during the entire experiment.

Samples of unflavoured and flavoured (banana essence) cold-pressed VCO, refined bleached and deodorised coconut oil (RBDCO) were purchased from the supermarket. Rancid VCO samples were obtained by heating the coconut oil at high temperature, 180 °C for several minutes until it releases an acidic odour and changes its colour. Homemade VCO was prepared by modified kitchen method [27]. The samples with different manufacturing date, packaging type and size, were gathered within the same period. To preserve the quality of the oil samples, a portion was placed in a clean dry amber bottle, and the remaining samples were kept in a cool and dark cabinet. Triplicate portions of 5.0 mL oil samples were obtained and transferred to a 20 mL amber bottle.

2.2. Sensor fabrication

The sensors were prepared through the electrodeposition of the polymers on the space between two gold circular electrodes (diameter=0.62 mm; distance=200 μm) mounted on a Teflon substrate (area=40 mm^2; thickness=0.4 cm). The polymers were formed by means of potentiostatic electropolymerization in a three-electrode single compartment cell using a LC-3E Petit Ampere potentiostat (Bioanalytical Systems, Inc., USA). A silver/silver chloride electrode (Metrohm^{TM}) was used as the reference electrode, and platinum wire was the counter electrode. The Ag/AgCl electrode and the Pt electrode were totally immersed in the solution, while the gold electrode was dipped in such a manner that the electrodes touched the surface of the solution. The polymers were grown at a constant temperature of 25 °C. The solutions were deoxygenated by sonicating for 5 min and purging with nitrogen gas (CIGI, 99.99%) for 10 min.

Polymers such as polypyrrole (PPy), polyaniline (PANi) and poly-3-methylthiophene (P3MTp) were prepared by potentiostatic polymerisation with different doping agents at certain mole ratio. A constant potential was applied until a polymer film bridge the Au electrodes.

The electrodeposited polymeric sensing films were conditioned by immersing in 5 mL of a fresh solution of the dopant and applying conditioning potentials ranging from −1.0 V to 1.0 V for
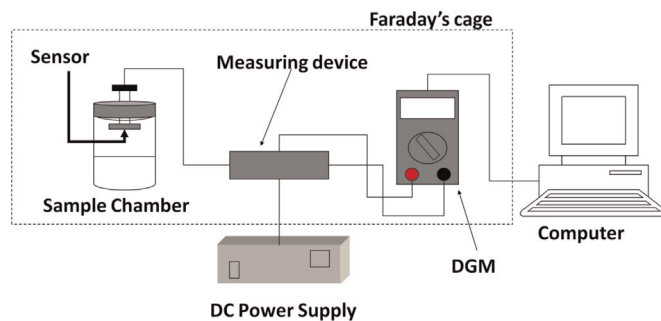

Fig. 1. Schematic diagram of the instrumentation system used in the measurement.

Table 1
The polymerisation parameters that were applied for this study.

Sensor #	Type (polymer/dopant)	E_p (V)	mol ratio	Bridging time (s) ($n=3$)	Sensor resistance (Ω) ($n=3$)
S1	PPy/LiClO$_4$	1.0	1:1	840	2519
S2	PPy/p-TSA	1.0	1:1	600	2190
S3	PPy/SDS	1.0	1:1	360	1533
S4	PANi/HCl	0.9	1:2	180	211
S5	PPy/DBSA	1.0	1:1	420	4612
S6	PANi/H$_2$SO$_4$	0.9	1:1	120	329
S7	P-3MTp/LiClO$_4$	1.6	1:1	180	2565

60 s. The conditioned polymer films were washed with distilled water and flushed with N$_2$ gas.

2.3. Measurement set-up

Fig. 1 shows the instrumentation used in this study. It consisted of a sample chamber, bridge circuit, a DC power source, a high impedance digital multimeter (DMM) and a personal computer. The sensor was connected to a bridge circuit that was powered by a DC power supply of 8.0 V. The sensor chamber, bridge circuit and DMM were enclosed in a faraday cage and it was interfaced to a personal computer for easy data processing. The sensor response was calculated from Eq. (1).

$$\frac{\Delta V}{V} = \frac{(V_S - V_B)}{V_B} \times 100 \tag{1}$$

where V_S is the output voltage after exposure to the oil sample and V_B initial voltage output of the sensor [28].

2.4. Measurement procedure

The oil samples were subjected to static headspace analysis. The sensor electrode was set at a fixed distance from the surface of the oil sample such that it would not touch the oil sample. The oil samples were measured at 32 (± 2 °C). To ensure that the temperature of the oil sample would be maintained during the analysis, the oil sample bottles were placed in a thermal box.

Before the sample was introduced into the measurement system, the system was flushed with nitrogen gas to remove any volatile organic compounds adsorbed on the sensing material and to stabilise the output voltage baseline. After 10 min, the sample was introduced and the stable output voltage reading with the sample was recorded before the sample was removed. The sensors were cleaned with 2.0% (v/v) n-butanol (J.T. Baker, analytical grade) saturation vapour for 30 s and purged for 10 min with nitrogen gas. The measurement was done in triplicate.