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Polymer-Coated Piezoelectric Quartz Crystal Sensors for the Authentication of Virgin Coconut Oil

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Abstract: The authentication of virgin coconut oil is important in view of its increasing popularity and great potential in the international market. In this study, a novel approach that could elucidate the distinct quality characteristics of virgin coconut oil was developed. An electronic nose based on polymer coated piezoelectric quartz crystal was assembled to discriminate different quality of coconut oils such as virgin coconut oil (VCO), flavored VCO, rancid VCO and refined, bleached and deodorized (RDB) coconut oil. It consisted of four polymeric sensors, an oscillator and a digital frequency counter. The sensors gave a stable response (response time = 5 to 8 minutes) and good reproducibility (r.s.d. = 6.48, 3.83, 6.45, 7.52; n=7) and repeatability (n=3). A unique quality profile of authentic VCO was observed against flavored and rancid VCO and RBD coconut oil using radar plot. The image formed is a chemical signature of an odor for a well-defined quality of VCO. The inherent structure of data was also analyzed using Principal Component Analysis (PCA). This technique decides which among all possible projections is the best for representing the clusters of data. The results have converged in suggesting that even two sensors are appropriate in distinguishing patterns or relationships in variables.

Keywords: Piezoelectric quartz sensors, Virgin coconut oil, Authentication, Principal component analysis.

1. Introduction

Virgin coconut oil (VCO) has become a high-value product. It is an in-demand commodity in the health and wellness market due to numerous claimed health promoting effects, ranging from cardioprotection to stress reduction and immune boosting [1]. It is an ingredient in the manufacture of popular snack food, food supplement, personal care and cosmetics products [2]. As a specialty oil produced in limited amount, VCO commands a premium price, costing about fifty times more than the common refined bleached and deodorized (RBD) coconut oil. This high cost has made VCO a target for unscrupulous traders to market low quality, mislabeled or adulterated products in order gain higher economic profits.

The authenticity of VOC supplies has emerged as a major issue to protect the interest of consumers and importing countries. The need to differentiate VCO and fraudulent products has motivated the development of authentication methods. A sensory evaluation technique employed quality criteria for appearance, aroma and taste to authenticate VCO [3]. Phosphorus-31 nuclear magnetic resonance (^{31}P-NMR) discriminated VCO and RBD coconut oil through free fatty acid and diglyceride levels [4].

Fourier-transform infrared spectroscopy (FTIR) detected and quantified adulteration through changes in the absorption spectra of VCO caused by adulterant vegetable oils [5-7]. Differential scanning calorimetry (DSC) monitored VCO adulteration with plant oils or animal fat through the decrease in the crystallization and melting enthalpies [8, 9]. Gas chromatography (GC) determined the presence of animal fat adulterants in VCO through the measurement of cholesterol in the oil sample [10].

Sensor technology has provided simple and rapid methods for the authentication of VCO. These methods are non-destructive, generating an electrical response when exposed to the headspace of the sample. A commercial electronic nose discriminated pure and adulterated VCO samples through chromatographic separation and surface acoustic wave detection of the components of the headspace vapor [11]. An array of chemiresistors differentiated VCO from other coconut oil products through the electrical resistance of conducting polymer sensing elements [12]. An assembly of metal oxide gas sensors detected rancidity of VCO samples through the profile of the electrical resistance of the component sensors [13].

This paper presents a sensor system based on an array of polymer-modified piezoelectric quartz crystals for the authentication of VCO samples. It is based on the measurement of the change in the resonance frequency of modified quartz crystals when placed in the headspace of a VCO sample. The headspace components are adsorbed by the polymer coating of the sensor, causing a change in the surface mass and consequently in the resonance frequency of the piezoelectric sensor.

2. Experimental

2.1. Materials

The following polymers were purchased and employed in the fabrication of the sensors: polystyrene (PS, average MW 280,000, Aldrich Chemical Company Ltd., U.S.A.), polyethylene glycol (PEG, average MW6000 from Ajax Finechem, Australia) and cyanoacrylate (CA, commercial grade, Cord Chemicals Inc., Philippines). Pyrrole monomer (Py, Sigma Chemicals Company, U.S.A.) was purified by distillation and stored in amber bottles in a refrigerator (4±2)ºC. Dodecylbenzene sulfonic acid (DBSA, Sigma, Chemicals Company) was used without purification.

AT cut quartz crystals (International Crystal Manufacturing Co., U.S.A.) were used in the experiments. The piezoelectric crystal consisted of a thin circular wafer (0.15 mm thickness, 8 mm diameter) coated on both sides with circular polished gold (4 mm diameter, 1 µm thickness) and had a resonant frequency of 9 MHz were used.

The oil samples consisted of four different classifications of coconut oil with corresponding representative brand names: virgin coconut oil (7 samples), flavored VCO (1 sample), RBD coconut oil (3 samples) and rancid VCO (3 samples). The different brands of VCO products had a Philippine Standard (PS) mark, ensuring that the product complies with the product specifications. The RBD and flavored VCO were selected based on the leading commercial brands and manufactured by highly recognized companies in the Philippines.

2.2. Instrumentation

The instrumentation consisted of a sample chamber, a sensor chamber, a nitrogen gas supply with a flow controller, an oscillator circuit and a digital frequency counter. The schematic representation is shown in Fig. 1. Nitrogen gas flowed into the sample chamber to facilitate the generation of headspace vapor and its transfer to the sensor chamber where the vapor came in contact with the quartz crystal sensor. The quartz crystal sensor was driven to oscillate by an oscillator circuit, and its resonant frequency that was measured by a frequency counter.

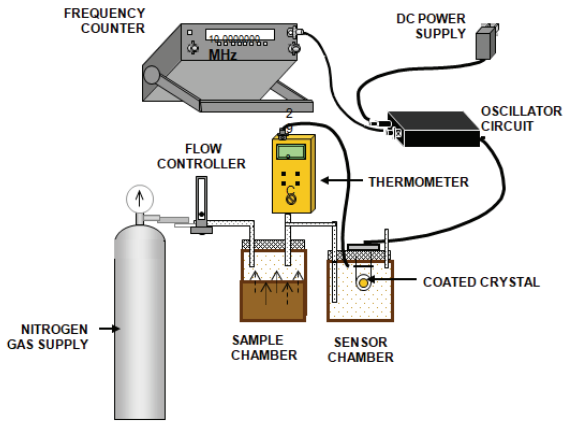

Fig. 1. Schematic diagram of the instrumentation.

2.3. Sensor Fabrication

The sensors were fabricated by coating the surface of the quartz crystal with a polymer layer. Two deposition techniques were employed: spin coating and electrodeposition. Spin coating was used to modify the quartz surface with a film of polystyrene, polyethylene glycol and cyanoacrylate, and electrodeposition was used to prepare polypyrrole-modified quartz crystals.

For the spin-coating method, solutions of the polymers were prepared in different solvents with a concentration ratio of 2:1 (w/v): PEG in chloroform; PS in toluene, and CA in tetrahydrofuran. An aliquot was dropped on the surface of the crystal and allowed to rotate for 5 minutes using an improvised spin coater (1800 rpm). The optimum volume of the aliquot was 10 µL for PEG and CA, and 20 µL for PS. The crystal was air dried for a few minutes then gentle flow of nitrogen gas was introduced to completely dry the

crystal. The coated crystal was kept for a day before using to attain enough curing time.

For the electrodeposition method, galvanostatic electropolymerization was carried out using an electrochemical cell with a carbon black rod as cathode and the quartz crystal electrode as anode. The electrodes were immersed in an aqueous solution containing the Py monomer (0.10 M) and DBSA (0.05 M). A current limiting device (National Semiconductor IC LM 334) was connected in series with the voltage source (<30 V), the current meter and the cell. The optimum electropolymerization conditions involved a current of 2 mA passed through 5 mL of solution for a period of 1 min. At the end of the polymerization period, the coated quartz crystal was washed with distilled water, allowed to dry at room temperature for few minutes and subjected with nitrogen gas for complete drying.

2.4. Measurement Procedure

The oil sample (20 mL) was kept in a sealed amber bottle overnight and pre-conditioned at (30±1) ºC for an hour before sampling for headspace measurement. Nitrogen gas was first allowed to flow through the sensor chamber until the resonant frequency reached a steady baseline value (F_1). Then, the headspace gas sample was introduced into the sensor through the nitrogen carrier gas at a flowrate of 9 mL/min with a temperature reading of (29±1) ºC. The resonant frequency (F_2) was recorded until a stable response was attained. Subsequently, the sensor was purged with nitrogen gas and the frequency reading was also recorded to monitor the recovery of the sensor response of the blank solution, indicating the complete removal of the adsorbed analyte on the quartz crystal. The sensor response was expressed in terms of the frequency shift (ΔF) which was calculated as follows: $\Delta F = F_1 - F_2$.

2.5. Statistical Data Treatment Analysis

The raw responses gathered using four polymeric sensors were integrated and evaluated using different statistical techniques. Graphical representation such as bar chart and radar plot was used for the rapid visualization of the differences of typical response patterns. Multivariate methods such as principal component analysis (PCA) and hierarchal cluster analysis (HCA) were employed to highlight the variations and relationships in the data. PCA and HCA were performed on the data using the XLSTAT software package (Addinsoft, USA)

3. Results and Discussion

3.1. VCO Samples

The authenticity of the VCO samples employed in the study was verified through the measurement of essential quality factors such as the peroxide value (PV), moisture and volatile content (MVC), free fatty acid (FFA) and fatty acid composition. Table 1 shows the chemical characteristics of VCO samples, together with the maximum allowable value specified by the Philippine National Standard for virgin Coconut Oil - PNS/BAFPS 22:2007 [14].

Table 1. Quality parameters of the VCO samples.

Parameter	Acceptable values [14]	VCO sample						
		1	2	3	4	5	6	7
Peroxide value (meq/kg of oil)	< 3.0	0	0	0.16	0	0	1.3	0
% (w/w) moisture and volatile content	< 0.2	0.12	0.18	0.13	0.10	0.12	0.11	0.12
% free fatty acid (as lauric acid)	< 0.2	0.17	0.1	0.12	005	0.18	0.03	0.04
C 6:0	0.1-0.7	0.30	***0.76***	***0.84***	0.30	0.29	0.47	0.51
C 8:0	4.0-10	5.10	5.80	6.07	4.96	5.76	6.21	7.03
C 10:0	4.0-8.0	5.10	4.18	4.18	5.08	5.13	5.28	6.06
C 12:0	45.1-56.0	51.3	55.2	54.0	49.4	52.3	48.4	52.2
C 14:0	16.0-21.0	17.5	17.3	17.8	17.6	17.8	17.6	15.0
C 16:0	7.5-10.2	8.40	7.98	7.57	9.44	8.37	9.15	7.72
C 18:0	2.0-5.0	2.65	***1.54***	***1.74***	3.77	2.13	2.80	3.10
C 18:1	5.0-10.0	8.28	6.01	6.40	8.43	7.19	8.89	7.40
C 18:2	1.0-2.5	1.40	1.24	1.46	***0.98***	1.07	1.14	1.00

The values of the PV, MVC, and FFA of all the VCO samples are within the acceptable values. However, for the fatty acid composition, Sample 2 and Sample 3 had caproic acid (C6:0) and stearic acid (C:18) content lower than the allowable range, and Sample 4 have lower linolenic acid than allowed. In

spite of this deficiency, samples 2, 3 and 4 can be considered as of good quality and authentic VCO, since their lauric acid levels which are within the allowable limits. Lauric acid has been associated with health-promoting effects of VCO [1].

3.2. Sensor Response

Seven sensors were initially fabricated based on polymers of varying polarities: polystyrene, polyethylene glycol, polyvinyl chloride, polyyrrole, polyaniline, poly(cyanoacrylate) and silicone. However, only the following four polymers exhibited a response when exposed to the headspace of a VCO sample: polypyrrole (Ppy), polystyrene (PS), poltethylene glycol (PEG) and cyanoacrylate (CA).

These four sensors responded immediately to the presence of the headspace vapor. A typical behavior of the sensor response is depicted for the polystyrene-modified quartz crystal sensor in Fig. 2. The oscillation frequency of the sensor decreased exponentially until a steady state value was achieved. The constant value was attained within 2 to 3 min. The decrease in the oscillation frequency indicates an increase in surface mass of the quartz crystal due to the absorption of the vapor by the polymer layer.

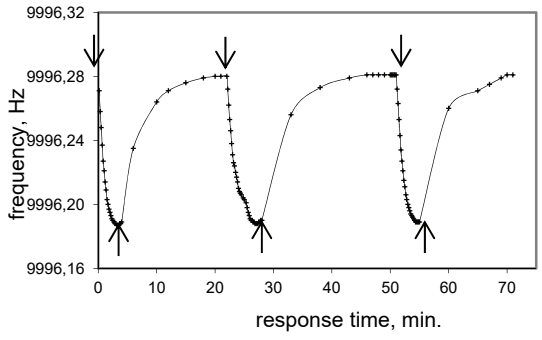

Fig. 2. Sensor response to repeated exposure to VCO.

The sensor responses were reversible, recovering their original oscillation frequency when exposed to a stream of the nitrogen carrier gas. This behavior indicates the removal of the retained headspace vapor from the polymer layer. Fig. 2 illustrates a typical sensor response to a series of alternating exposure to the headspace vapor and to the nitrogen carrier gas. The repeatability of the sensor response was very good, with a relative standard deviation ranging from 3.8 to 8.0 %. The response of the sensors displayed a very good long-term precision over a period of 10 days (relative standard deviation = 3.5 to 6.8; n = 10).

The sensor response was dependent on the thickness of the polymer film. In drop casting (for PS, PEG and CA), the thickness of the film was determined by the amount of polymer solution applied on the quartz crystal, and in electropolymerization (for polypyrrole), the polymerization time was the critical factor. The response increased as the thickness of the polymer film increased until an optimum value is reached. Beyond this, the film became physically unstable and caused damping in the oscillation of the piezoelectric crystal. For the spin-coated crystals, the optimum thickness of the sensing film was achieved when a volume of 10 μL of the coating solution was used. For the electropolymerization, a polymerization time of 1 min produced the optimum thickness.

The sensor response was affected by the flow rate of the carrier gas, increasing as the flow rate was increased. A critical flow rate value was observed, beyond which the response became unstable. The optimum flow rate was found to be 15 mL min^{-1}.

3.3. Sensor Responses Toward Oil Samples

Distinct profiles could be discerned in the sensor bar graph of the responses obtained from the different types of coconut oil samples (Fig. 3). The response of all the sensors was highest for the flavored VCO sample, indicating the greatest concentration of volatile constituents released by the sample, particularly by the flavorant mixed with the VCO.

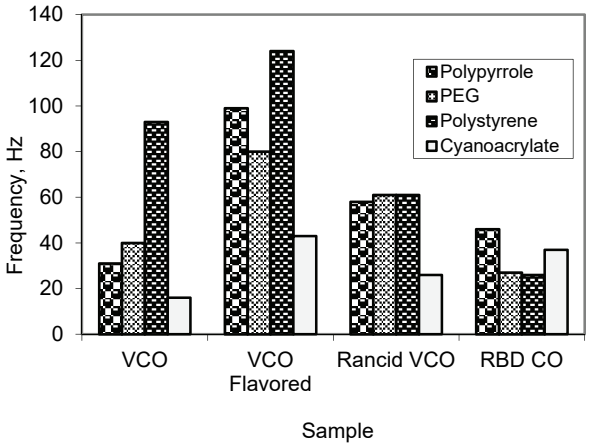

Fig. 3. Bar graph profile of the response of the VCOs to the sensor array.

Discrimination between the coconut oil samples could be easily performed if the responses for each sample were plotted in a radar plot (Fig. 4). These plots exhibited distinctive patterns which can be associated with each type of coconut samples. The patterns can serve as a unique fingerprint which can be easily recognized visually to differentiate VCO from low quality or rancid VCO and RBD coconut oil.

3.4. Principal Component Analysis

Principal component analysis (PCA) was performed on to highlight the similarities and the

variations in the response of the sensor array to the different types of coconut oil samples. It reduced the dimensionality of the multivariate data set to allow the display of the information in a two dimensional plot (Fig. 5). The scatter plot of the first two principal components (PC1 and PC2) derived from the response array yielded a cumulative variance of 94.6 %. PC1 accounted for 54.8 % of the variation, clearly differentiating quality VCO from low-quality rancid VCO (RCD) and flavored VCO (VCO8). PC2 contributed 39.8 % to the variation, discriminating well RBD coconut oil from the VCO samples.

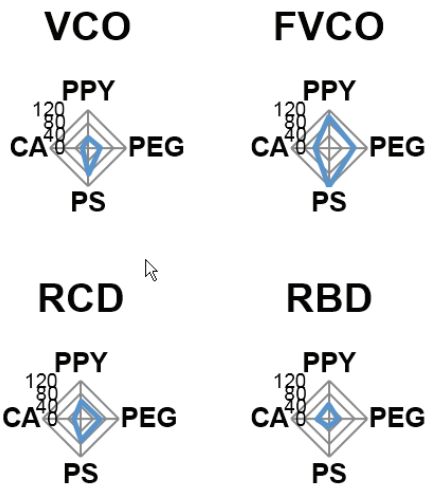

Fig. 4. Radar plot of the responses of the sensors towards individual oil sample.

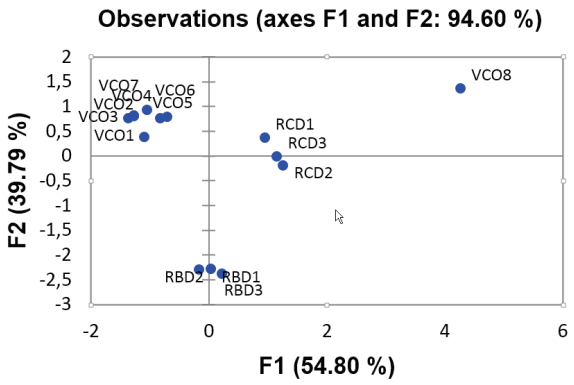

Fig. 5. Score plot of the principal components of the responses of the sensor array towards oil samples.

3.5. Hierarchical Cluster Analysis

A Hierarchical Cluster Analysis (HCA) of a multivariate dataset groups the data points based on Euclidean distances. Application of HCA to the sensor responses to the different coconut oil samples CA yielded a dendrogram (Fig. 6), where dissimilarity relationships between the oil samples are visible. The results of HCA complement those of PCA demonstrate that VCO can be differentiated from RBD coconut oil and rancid VCO through headspace analysis using a chemiresistor array.

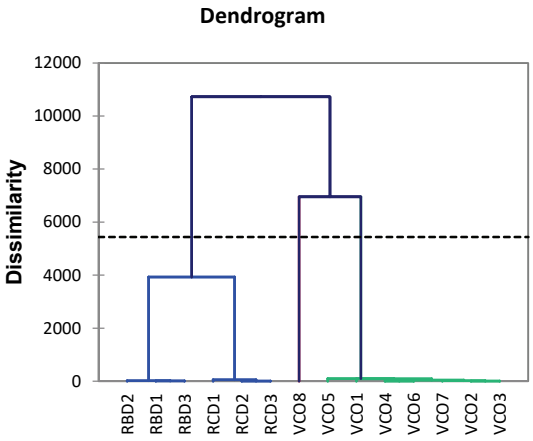

Fig. 6. Dendrogram of the responses of the sensor array towards oil samples.

4. Conclusion

VCO was differentiated from RBD coconut oil, rancid coconut oil and flavored coconut oil through an array of polymer-coated piezoelectric quartz crystals. The polymer coatings interacted with the volatile components of the coconut oil samples generated in the headspace causing a decrease in the oscillation frequency of the piezoelectric sensors. The sensing polymers used in the study (polypyrrole, polystyrene, polyethylene glycol and poly(cyanoacrylate)), had different polarities and interacted with the headspace constituents to different extent. Multivariate analysis of the sensor responses highlighted the difference in the responses, giving rise to clusters in principal component analysis and groups in hierarchical cluster analysis.

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