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Electronic Nose Based on Piezoelectric Quartz Crystal for Mango Fruit Quality Assessment

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An electronic nose based on piezoelectric quartz crystal was developed for monitoring the maturation of carabao mango. This device detects the volatile organic compounds present in the headspace of the mango fruit. The crystals were coated with different organic polymers that interact with the volatile organic compounds, and this interaction was monitored through a self-assembled instrumentation and recorded by a computer in terms of frequency change. The quartz sensors gave stable response to the mango fruit sample, exhibited good repeatability (r.s.d. = 3.3 to 5.1% , n = 3) and good reproducibility (r.s.d. = 1.9 to 6.1%, n = 5). Different signals were observed at different stages of the maturation of carabao mango fruit. The application of principal component analysis (PCA) enabled the discrimination of the responses of the electronic nose to mango fruits at different stages of maturation.

***Keywords*:** electronic nose, piezoelectric quartz crystal, mango fruit maturity, principal component analysis

INTRODUCTION

Mango fruit, *Mangifera indica L.*, is a commercially and economically important fruit crop in the Philippines. Three popular mango varieties are grown in the country, namely, *carabao* mango, *pico* mango, and the *katchamita* mango [1]. The most recognized Philippine mango variety in the world is the *carabao* mango. It makes the country competitive in the world market for mangoes and therefore its quality should be established.

In order to ensure optimum quality of the mango fruit, it should be harvested at the hard green stage, when it has reached physiological maturity [2]. Premature harvesting leads to a poor quality, since the fruit fails to develop a full flavor and aroma. Harvesting after physiological maturity allows the carbohydrate content to increase, resulting in a better fruit quality.

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The assessment of the maturity of the fruit is therefore essential for quality control.

The most common method for the evaluation of the maturity of mango fruits is based on the assessment of physical attributes, such as firmness, gloss, color, flavor, etc. However, this method has been found to often yield misleading results [3, 4]. The determination of biochemical or physiological parameters, such as titratable acids, soluble sugar and starch content, provide reliable maturity indicators, but these methods involve the destruction of the fruit, laborious laboratory techniques, skilled personnel, and expensive instrumentation [5].

Nondestructive techniques have been recognized to present several advantages for the measurement of the quality attributes of fruits. A particularly promising method is aroma sensing which is based on the detection of the volatile organic compounds produced by the fruit. These compounds result from the biochemical changes that occur during the ripening of mango; they consist of terpene alcohols, nor-isoprenoid derivatives and aromatic alcohols [6]. Monoterpene and sesquiterpene hydrocarbons are the major volatile components representing 70 to 90 % of total volatiles in all mango cultivars [7].

A recent technological development that has found use in fruit aroma sensing is the electronic nose [8-11]. An electronic nose system consists of an array of chemical sensors which generate a set of signals in response to the volatile organic compounds. These signals are processed to provide a signal pattern that can be used to characterize the sample. The various types of sensors commonly employed in electronic noses are surface acoustic wave (SAW) device, metal oxide semiconductor sensors (MOS), conducting polymer (CP) sensor, and bulk acoustic wave (BAW) devices.

In this work, piezoelectric quartz crystals are exploited as sensors in an electronic nose system for the assessment of the maturity of mango fruits. Several piezoelectric sensors are employed to sense the volatile organic compounds in the headspace of a mango fruit, and the signals are analyzed through a pattern recognition technique to enable the discrimination of different stages of maturity of the carabao mango fruit.

METHODOLOGY

Materials

All reagents were prepared from analytical reagent grade chemicals. AT-cut quartz crystals (10 MHz, Silver electrode area, 5 mm diameter, and 1 μm thickness) purchased from Republic Crystal Laboratory, Manila, Philippines was used throughout the experiment.

Fully mature hard green mango fruit (*Mangifera indica L.*) cultivar *carabao* mango were obtained from the orchard of Nueva Vizcaya State University in Bayom-bong Nueva Vizcaya, Philippines during the August 2006 fruiting season. A total of 12 fruits were selected and the lot was randomly divided into four (4) groups with three (3) mangoes each. Samples were stored at room temperature ripening (25 – 28 °C). One group was kept as a control, while the remaining three groups were subjected to the following analysis: total sugar content and pH analysis after headspace analysis using the electronic nose sensor system.

Chemical analysis

The mango fruit samples were analyzed for sugar content following the Clegg-anthrone method [12], and for pH using a pH meter (691 pH meter, Metrohm).

Instrumentation

A schematic diagram of the instrumentation employed in this study is shown in Figure 1. It consisted of a sample chamber, a sensor chamber, an oscillator circuit and a frequency counter. The sample chamber was fabricated from a PVC pipe (9 cm diameter, 17 cm height) sealed at both ends with PVC screw caps. A hole was bored at the center of the screw-caps to accommodate a tube through which N_2 gas will flow into and out of the chamber. The nitrogen gas flushed the volatile organic compounds in the headspace of the mango fruit sample into the sensor chamber.

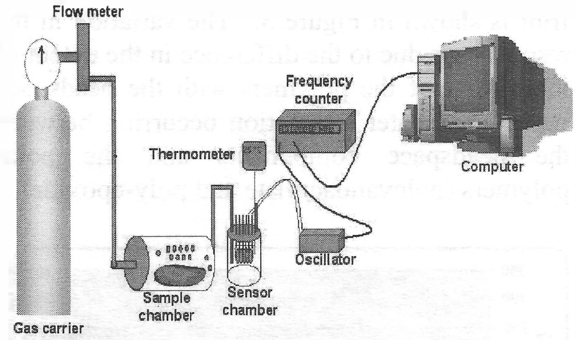

Fig. 1. *Schematic diagram of the electronic nose system*

The sensor chamber was actually a cylindrical glass vessel (40 ml beaker, 4 cm diameter, 4.5 cm height) provided with a rubber stopper on which five piezoelectric quartz sensing crystals were set. The wire terminals of the piezoelectric quartz crystals were passed through the rubber cover and connected to the oscillator circuit through clip connectors. A thermocouple was also set on the cover to record the temperature during the measurement process. An outlet tube was also set on the cover for the release of the measurand gas stream.

A home-made oscillator circuit based on a Pierce CMOS IC was employed to cause the quartz crystal to oscillate [13]. It involved a 10 MΩ resistor which provided a negative DC feedback circuit to the inverter, and capacitors connected parallel to the piezoelectric quartz crystal which controlled the phase change in the circuit. A portable DC adaptor connected to the mains supplied a voltage of 5 V, and a universal frequency counter (Thurlby Thandar) displayed the oscillation frequency of the crystal. A computer was interfaced to the frequency counter for data acquisition and recording.

Preparation of the quartz crystal sensors

Five (5) AT-cut quartz crystals were each coated with one of the following polymers: polystyrene, polyvinyl chloride, poly(dimethyl)siloxane, polycyanoacrylate, and polyepoxide. The polymers were dissolved in a solvent to give a concentration ratio of 2:1 (w/v): polystyrene, poly(dimethyl)siloxane and silicone oil in toluene, and polyvinylchloride, polycyano-acrylate and polyepoxide in tetrathydrofuran. A mechanical shaker and ultrasonic bath was used for 15 minutes to homogenize the coating mixtures. Ultrasonic homogenization was repeated after every hour for 3 hours to completely homogenize the solutions. After mixing, the coating solution was used immediately to prepare the sensing layer.

The crystals were initially washed with acetone and air dried. Five microliters (5 μL) of the polymer solution was applied in the center of the silver electrode on both sides of the quartz plate by means of a micropipette. The solvent was allowed to dry for 30 minutes, after which the coated crystal was set in the sensing chamber. High-purity nitrogen gas (CIGI, Philippines) was passed through the chamber at a constant flow rate (15 mL/minute) for 4 hours to completely dry the sensing materials.

Measurement procedure

The fruit sample was placed in the sample chamber, which was then closed and left to equilibrate for 1 hour. At the end of this period, nitrogen was passed through the sample chamber to flush the headspace gas to the sensor chamber containing the coated piezoelectric quartz crystals. During the measurement, the oscillation frequency of piezoelectric quartz crystals decreased gradually until a stable signal was obtained. The difference between the frequency of a measurement and the frequency of purging ΔF (Hz) was measured. Measurement for unripe fruit was replicated three times using three mango fruit from the first group. The second group was ripened with an interval of five days from that of unripe stage before measurement was done and another interval of five days from ripe stage was also applied to the third group prior headspace analysis. The fourth group was kept as a control.

RESULTS AND DISCUSSION

Sensor response

An essential component of a chemical sensor is the sensing reagent. It acts as the molecular recognition element providing an interface between the sample and the transducer. In this work, several polymers of varying polarity were employed as the sensing reagent, and were deposited on the surface of a quartz crystal. The reagent interacts with and binds the substances present in the headspace of the mango fruit, causing an increase in the mass on the surface of the sensing crystal and a consequent decrease in the oscillation frequency.

A typical response of the coated crystal to the headspace vapor of mango fruit is shown in Figure 2.

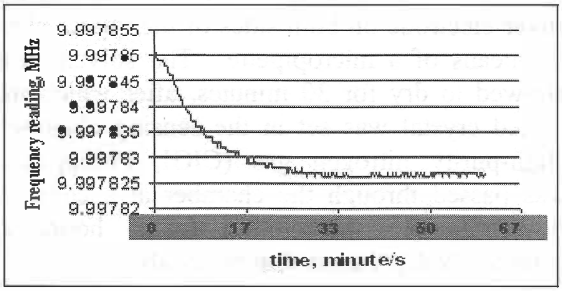

Fig. 2. *Typical response time of a poly(dimethyl)siloxane-coated PQC sensor towards unripe mango fruit. Nitrogen gas flow rate = 15 mL/min*

The measured oscillation frequency decreased exponentially, and attained a steady state after a certain period. The response time exhibited by the coated crystals ranged from 17 to 43 minutes. The variation in the response time can be related to the rate of mass transfer of the components in the flowing gas stream to the reagent phase in the sensor.

Table 1. Repeatability and reproducibility, expressed as relative standard deviation, of the responses of the different polymer-coated piezoelectric quartz crystals towards unripe mango.

Polymer-coated piezoelectric quartz sensor	*Repeatability (n = 3)*	*Reproducibility (n = 5)*
Polycyanoacrylate	1.20	1.91
Polyvinyl chloride	2.25	3.39
Polyepoxide	3.29	4.75
Poly(dimethylsiloxane)	4.48	5.13

The various sensing polymers responded in different ways to the headspace components of the mango fruit. The results obtained for the measurement carried out on the unripe mango fruit is shown in Figure 3. The variation in the responses is due to the difference in the extent of interaction of the polymers with the headspace vapors, a greater interaction occurring between the headspace components and the polar polymers (polcyanoacrylate and poly-epoxide).

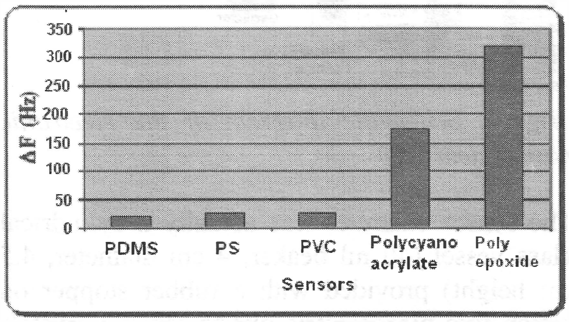

Fig. 3. *Response of the coated crystal towards unripe mango. Nitrogen gas flow rate = 15 mL/min*

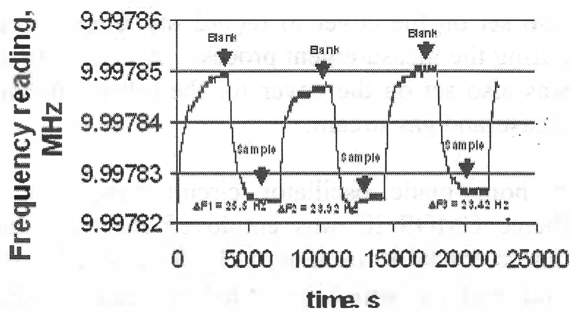

Fig. 4. *Reversibility and repeatability of the response of poly(dimethyl)siloxane-coated quartz crystal sensor to unripe mango. R.S.D = 1.09%; flow rate = 15mL/min.*

The response of the coated quartz crystal sensors was reversible and repeatable, typified by the response of the poly(dimethyl)siloxane-coated crystal sensor shown in Figure 4. The sensor response returned to the original frequency reading when purged with nitrogen gas after being exposed to a gas stream containing the volatile compounds in the headspace of the mango sample. The repeatability of the response of the various sensors involved a relative standard deviation ranging from 1.1 to 5.3% (n = 3). The sensor showed very satisfactory reproducibility, with the responses over 5 days, with a standard deviation of less than 10%, as shown in Table 1.

Parameters affecting sensor response

The response of the sensor was found to vary with several parameters involved in the measurement. The flow rate of the nitrogen gas stream used in the measurement affected the sensor response. The optimum flow rate found to be 15 mL / minute. At flow rates higher or lower than this optimum, the sensors exhibited poor stability and repeatability.

The volume of the sensor chamber was found to influence the response of the sensor. The diameter of the chamber had to be chosen such that it will accommodate the five sensors used in the study. A chamber volume 40 mL was observed to yield the optimum sensor response. When a larger chamber volume (50 mL) was used, the sensor response exhibited a slightly lower response and a much lower re-producibility.

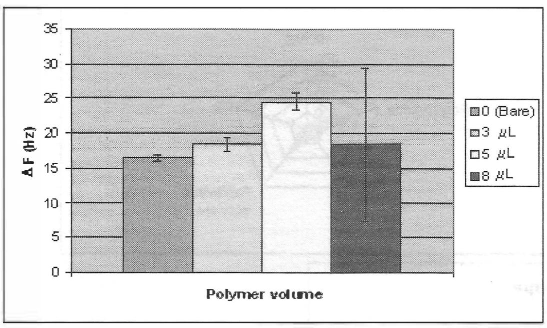

Fig. 5. *Response of the polystyrene-coated crystal sensor towards VOC's of unripe mango fruit at varying polymer volume. (n= 3; flow rate = 15mL/min.)*

The amount of the polymer solution applied to the crystal during sensor fabrication had an effect on the sensor response, as shown in Fig. 5. The response increased as the volume of the polymer solution was increased until a volume of 5 μL. This behavior is expected, since there will be a greater capacity for the reagent phase to bind with the analyte gases. However, it was observed that if the applied volume exceeded 5 μL, the response decreased and the repeatability became lower. This could be caused by the limited area of the crystal surface able to contain this volume of liquid. The results indicated that the sensor prepared using 5 μL polymer solutions exhibited the highest response and a good R.S.D value of 5.10 %.

Sensor response to mango fruit at different maturity

The response of the different sensors investigated varied with the maturity of the mango fruit. Three stages were studied: (1) unripe, green stage, (2) ripe yellow stage, and (3) over-ripe yellow stage. Each of these stages was characterized through the pH and the sugar content of the fruit as in Figure 6. As the fruit matured, the acidity decreased and the sugar content increased.

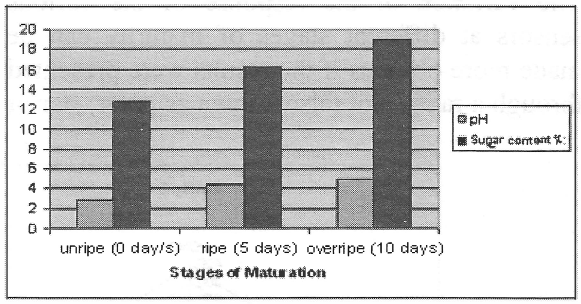

Fig. 6. *pH and Sugar content of mango fruit at different stages of maturation.*

Figure 7 shows the average response of each sensor with respect to different maturation stage of carabao mango fruit. For most of the sensors, except for the poly-epoxide-coated crystal sensor, the response peaked at the ripe stage. For the poly-epoxide-coated sensor, the response was lowest for the ripe fruit. The variation of the sensor response can be associated with the change in the composition of the headspace vapors of the fruit at different stages of maturity. The headspace of the ripe fruit contains more non-polar components, as indicated by the increase in the response exhibited by the sensors coated with non-polar polymers and the decrease in the response of the sensor coated with poly-epoxide, a polar polymer. The dominant volatiles in ripe mango cultivars are the non-polar monoterpene and sesquiterpene hydro-carbons [7].

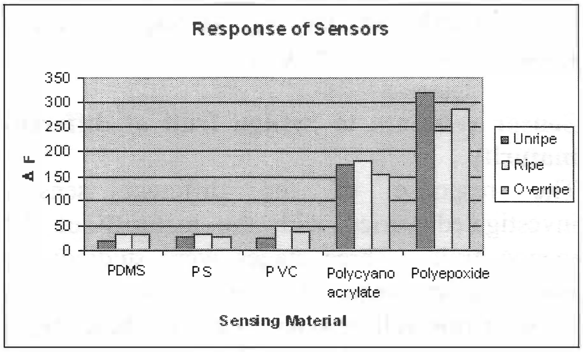

Fig. 7. *Average response of different polymer coated PQC sensors towards mango fruit at different stages of maturation*

The variation of the response of the various sensors at different stages of maturity can be made more obvious if the results were presented through a radar plot (also known as polar, star or spider plot). The response of each sensor is depicted in an axis drawn from certain radius which is separated by a certain angular distance. This graphical plot profile provides a fingerprint of the headspace for the fruit different maturation stage, presenting a distinct characteristic shape at a glance. Figure 8 shows the radar plot of the response of sensors with respect to stages of maturation. The figure shows that at three stages of maturation, it projects distinct pattern/profile and can be useful to discriminate the three stages of maturation of carabao mango fruit.

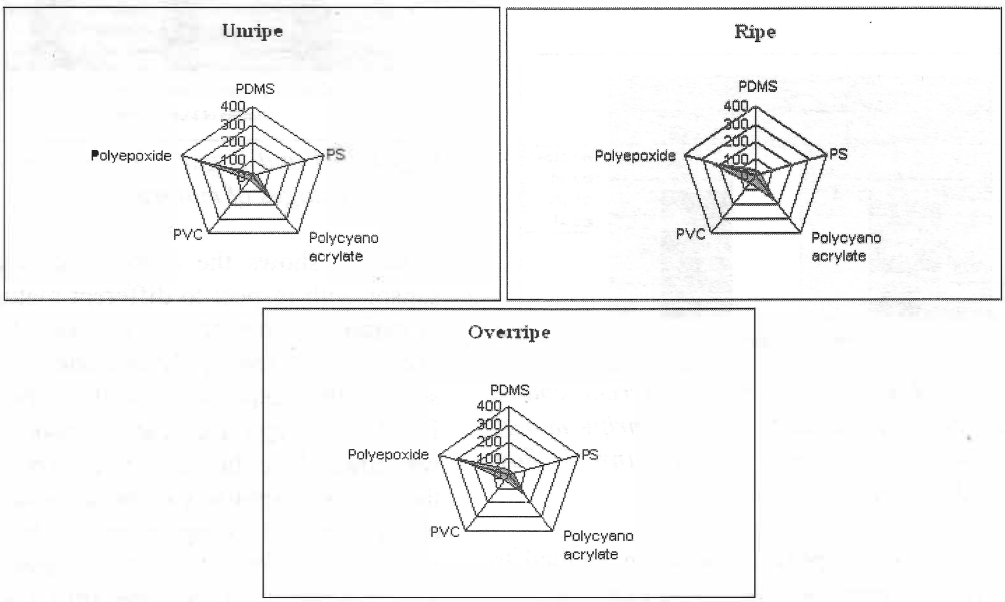

Fig. 8. *Radar plots of the response of sensors with respect to stages of maturation*

Discrimination of the sensor responses to mango fruit at different maturity stage was achieved through the chemometric technique of principal component analysis (PCA). PCA is a useful statistical technique for finding patterns in data of high dimension [14]. It is a chemometric linear, unsupervised pattern recognition technique used for analyzing, classifying and reducing the dimensionality of numerical data sets in a multivariate problem. It yielded a clear discrimination among the various clusters representing the *carabao* mango fruit ripeness state, i.e., unripe, ripe and overripe, as shown in Figure 9. The plot of the eigenvectors Prin 1 and Prin 2 resulted in a model that described 97.12 % of the total variance in data. This percentage is very high and sufficient enough to define as best qualitative representation.

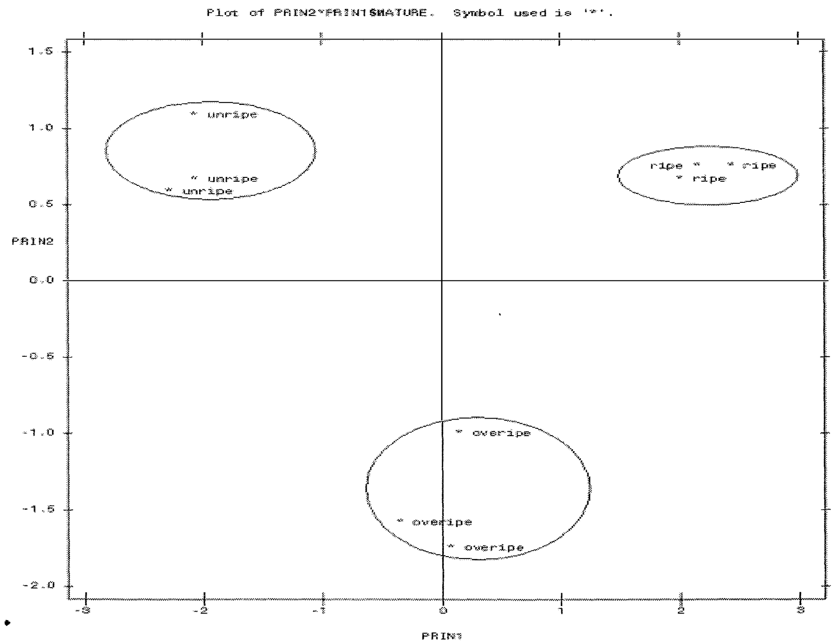

Fig. 9. *PCA Score plot of the responses exhibited by the five sensors to mango fruit at different maturity levels*

CONCLUSION

An electronic nose system for the monitoring of the maturation of mango fruit was assembled based on piezoelectric quartz crystal sensors coated with different polymers. The capacity of this sensor system to discriminate the stages of maturation of mango fruit was demonstrated. Discrimination of the headspace profile of the mango fruit at different maturation stage was better achieved using principal component analysis (PCA) than the radar graphical profile.

The developed system presents a practical and promising approach in assessing the quality of mango. The use of polymer coated piezoelectric quartz crystal sensor arrays as the key element for analytical sensor systems is a very promising technique for fruit quality assessment. In general, the experimental scheme provided an excellent possibility that this approach can be used as an alternative method in evaluating mango quality.

ACKNOWLEDGMENT

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