Classification of banana fruit maturity using zNose

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Abstract: A study was undertaken to classify the banana fruits based on their ripening/maturity by using zNose flavour detection technique. The quality parameters of banana fruits viz., respiratory quotient (RQ), total soluble solids (TSS), moisture content and firmness at each ripening/maturity stages were determined and the results were correlated with zNose flavour data. The principal component analysis (PCA) was used to identify the ripening/maturity stages of banana fruits and also to test the variability of the observed data. By using multiple linear regressions (MLR), models were established to predict the fruit quality parameters. The coefficient of determination (r2) corresponding to the predicted respiratory quotient, total soluble solids, moisture content and firmness were found to be 0.93, 0.94, 0.96 and 0.95, respectively, signifying better prediction of the banana fruits into different ripening/maturity stages.

Keywords: E-Nose/Z-Nose, banana fruits, maturity, ripening, PCA, MLR

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1 Introduction

Optimum ripening/maturity stage for banana bunches/fruits is one of the important factors that determine the quality, price and consumer satisfaction. The quality parameters are influenced by various pre and post harvest operations, which include correct stages of harvesting, ripening, storage and transportation. The fruit ripening and maturity standards are territory specific and vary from land to land, depending upon the expected green life required by the fruit before ripening takes place. The quality attributes of a fruit are categorized as sensory, hidden and quantitative. The sensory attributes are color, glossiness, size, shape, defects, flavour, texture (firmness, crispiness and toughness) and taste. The hidden attributes are nutritive values, presence of dangerous contaminants and poisonous materials (Elmasry et al., 2007).

The quantitative parameters are those which contribute to the overall food quality. Various methods have been used to determine the maturity stages of banana, but the techniques adopted are destructive involving pulp to peel ratio and firmness of the fruit (Ramma et al., 1999). It is expected that any technology that can classify the fruits based on colour, texture, taste, flavour and nutritive value would assure more fruit quality and consumer acceptance (Lu and Ariana, 2002).

Generally, fruits are sorted mainly manually or mechanically based on the external quality features. But the internal quality attributes such as moisture content, total soluble solids and firmness are also increasingly important in the growing market. Most of the instrumental methods and manual work employed to measure these properties are destructive to the fruit. It has become the cardinal quintessence to arrive at a non-destructive method to measure the internal quality of the fruit for the benefit of consumers and industry.

Flavour detection using nondestructive methods are becoming popular, since flavour has a combination of both aroma and taste of the product (Lammertyn et al.,

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2002). Flavour analysis of food products using analytical and quantifiable methods such as gas chromatography (GC) with headspace sampling, HPLC and GC-MS with solid phase extraction are common methods (Moreira et al., 2002). Similar to GC, the flavor measurement using electronic nose (E-nose) is one of the developing techniques, which can be used to detect the flavour components of food products (Booth and Arnold, 2002).

E-noses have been used to evaluate the quality of modified atmosphere packaged poultry meat (Rajamani et al., 2006), identification of the deteriorated beef (Panigrahi et al., 2006), fish quality (Olafsdottir et al., 2004), milk flavor quality (Laberche et al., 2005), olive oil quality (Brezmes et al., 2005) and discrimination of red wines based on flavor from the same variety of grapes (Garcıa et al., 2005). The E-noses technology have also been used for the quality discrimination of fruits, such as mandarins (Gomez et al., 2006), oranges (Di Natale et al., 2001), melons (Oshita et al., 2000), blueberries (Molto et al., 1999), ripening of pears (Brezmes et al., 2000), tomato maturity stage (Gomez et al., 2006) and post harvest quality of orange and apples (Di Natale et al., 2001).

The E-nose technique has been used to detect flavour as a non-destructive and at-line analysis. But the E-nose analysis has not always been successful due to its high sensitivity to drift (Lammertyn et al., 2004). The latest non-destructive technique in the E-nose series is the zNose^{TM} (7100 Fast GC Analyzer, Electronic Sensor Technology, New Bury Park, CA, USA) which has been introduced and commercially available for flavour detection (Lammertyn et al., 2004). The zNose^{TM} is a fast gas chromatograph (GC) with a surface acoustic wave (SAW) sensor. It has separating compounds with a GC column and can detect the amount of compound through the SAW sensor. Thereby the instrument can give a fingerprint of flavour information in terms of retention time and peak area. Using zNose, flavors of apple and wine (Li et al., 2006), honey (Lammertyn et al., 2004), and vegetable oil (Gan et al., 2005), have been detected and classified. With a specialized GC column (DB-5), zNose^{TM} can collect and detect chemicals having 5-22 carbon atoms (C5-C22). Therefore, a study was undertaken to classify the maturity stages of banana fruits using zNose flavour detection technique. Also this technique has also been used to predict the banana fruit quality parameters *viz*., RQ, TSS, moisture and firmness..

2 Materials and methods

Matured banana fruits without any visible damages were selected and stored at the temperature of 20^{o}C with 70% relative humidity for the experimental purposes. Two hundred and seventy fruits were selected for the experiment and they were divided into six groups (each group 15 bananas) for representing different maturity/ripening stages from one to six. The experiment was replicated thrice. The group was selected randomly for zNose analysis and subsequently checked for quality on a daily basis.

The tested fruits in each maturity stage were randomly divided into two sub groups. Sub group 1 considered as a training set and it consisted of 10 fruits and the sub group 2 consisted of five fruits considered as a validation of training models.

2.1 zNose^{TM} flavour measurements

The flavour of the banana fruits at different stages were measured by using zNose^{TM} (7100 Fast GC Analyzer, Electronic Sensor Technology, New Bury Park, CA, USA). The zNose^{TM} is a miniature, high-speed gas chromatograph (GC), containing a detector, a short separation column, and support electronics. The detector of the zNose is an uncoated, high quality piezo-electric quartz crystal with a sensitivity of parts per billion. The detector crystal operates by maintaining high frequency acoustic waves on its surface, and the measured compound lands and sticks on the detector and changes its frequency. The crystal is in contact with a thermoelectric element, which controls the temperature for cooling and heating during vapour adsorption and cleaning of the crystal, respectively. The change in frequency (Counts) is measured by a microcontroller and processed by software, allowing the compound to be identified and quantified. The flavour compounds are separated by a short column, which contains an internal coating of a bonded liquid phase before they reach the detector, volatile compounds are separated in this liquid phase. As they leave the column at different times, the separation is further enhanced by heating the column using a programmable temperature profile. The time during which one compound retained in the column was recorded as its retention time (RT), which is supposed to be unique for each specific component. The area of each peak was considered as qualitative measurement of a volatile amount present in the sample. The zNose™ employs headspace or bubbler technique for its sampling mode. The instrument has a side Luer needle for sample odor injection and a spark needle for the bubbler generator. A rotating valve was used to turn the machine in sampling position and inject position, a trap was used as pre-concentrator to collect and hold volatile samples. High grade helium was used as a carrier gas for the flavour analysis.

This problem of drifting in the zNose was corrected by preheating for 2 h to achieve stabilization of the instrument before starting the measurement. Also, n-Alkanes standard solution (widely used in GC analysis) was used to calibrate the system for every 1 h to convert the retention time to Kovat index.

The banana fruit was allowed to evolve flavour for two hours in a sealed glass container having silicone septum on the lid. All the fruits in a group were tested for the flavour analysis in the following operation mode: sampling through side Luer needle for 10 s, separating different compounds in column for 14 s, acquiring data at every 0.02 s for 20 s, and finally baking sensor for 30 s. The sensor detection temperature was set to 60℃, column temperature was ramped from 40℃ to 180℃ at a rate of 10 ℃/s, sensor baking temperature was 150℃, carrier gas flowing rate was 3.0 cm^3/s. Between the measurements, one air blank measurement was conducted to clean the systems and to have a stable baseline signal peak under 200 counts.

2.2 Banana quality parameters

The quality parameters of banana fruit *viz.*, respiratory quotient, total soluble solids, moisture content and firmness were measured and they were used for the prediction model with zNose data. The banana fruit samples were kept in the glass bottles and sealed for 30 min to measure the respiration. The head space gas composition inside the bottles was analyzed using a Gas Chromatograph (SRI Instruments Inc., California, USA; Model-8610A) equipped with a thermal conductivity detector. The respiration of banana fruits in terms of respiratory quotient (RQ) was calculated as following Equation (1) and Equation (2):

$$\text{Respiratory Quotient} = \frac{\text{Respiration rate } (RR_{CO_2})}{\text{Respiration rate } (RR_{O_2})} \tag{1}$$

$$\text{Free volume, ml} = \left[\text{Container volume, ml} - \left(\frac{\text{Fruit mass, kg}}{\text{Fruit density, kg/m}^3}\right)\right] \tag{2}$$

The total soluble solids (TSS) were determined using a refractometer with a range of 0-32 Brix (Model no. ATC-1090, Atago Co., Ltd., Japan). The TSS (Brix) of the banana pulp was measured by dividing the fruit into three equal parts (length wise). From each part, ten gram sample was pulped using pestle and mortar. Then the pulped samples were used to find the TSS and reported as a mean of three replications. The moisture content was determined by drying the samples at 70°C to constant weight using a hot air oven.

The firmness of banana fruits was measured using Universal testing machine (Instron Corp., USA; Model – 4500). The fruit was cut into 5 cm length and the firmness was measured with a cylindrical Teflon probe of 0.5 cm diameter at a crosshead speed of 10 mm/min. The firmness value was recorded in terms of Newton and reported as a mean of three observed readings.

2.3 zNose flavour Data analysis

The data obtained from the zNose analysis was grouped into 15 retention time segments based on the peaks. Under each retention time, the amount of volatiles corresponding to the peaks at each ripening/maturity stage was selected for the analysis.

Principle component analysis (PCA) was conducted using MATLAB program platform (MATLAB 7.0, The Mathworks, Inc., MA, USA) to classify the banana fruits into different ripening/maturity stages based on the zNose flavour values. Then the zNose values were used to predict the quality parameters *viz*., respiratory quotient, total soluble solids, moisture content and firmness based on multiple linear regression (MLR) analysis (MATLAB program platform (MATLAB 7.0, The Mathworks, Inc., MA, USA).

3 Results and Discussion

3.1 zNose data analysis using PCA

The zNose data was grouped into 15 segments based on the retention time of each peak. Since, each peak represents different compounds responsible for the flavour evolution, the area of each peak represents the amount of that particular flavour compound. After grouping, the zNose flavour data was tested for its ability to classify the banana ripening/maturity stages using the principle component analysis (PCA) as shown in Figure 1.

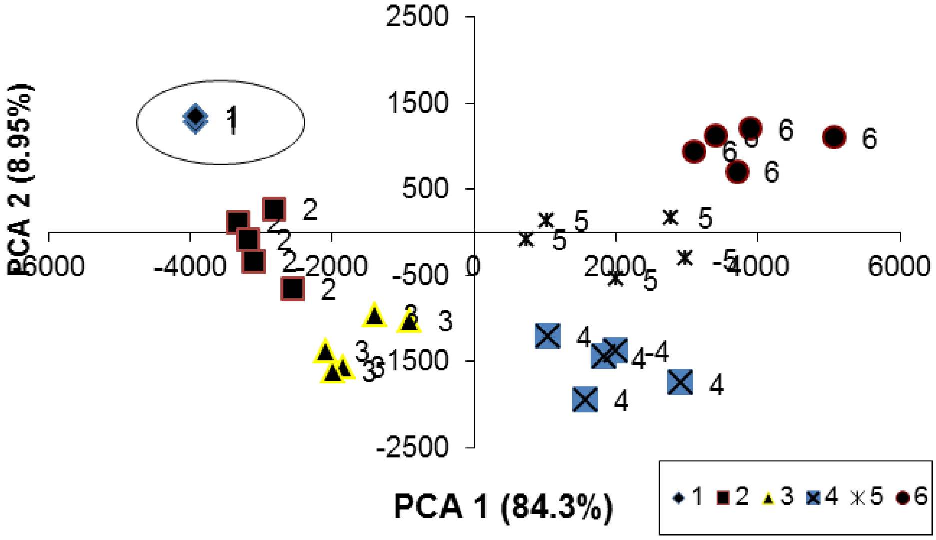

Figure 1 Principal component analysis of the banana maturity stages (1-6) using Znose flavour retention time

The PCA analysis on the retention time resulted in a better classification of the fruits into 6 stages with PC1 and PC2 explaining 93% of the total variance. From the figure, it is clear that all the six stages of fruit ripening were clearly distinguished based on the flavor retention time and the peak area formed. The group 1, had significantly lower flavour and formed an isolated group from the rest of the banana stages. The second and third stages of the banana fruits were also clearly separated. The fourth and fifth stages of the banana fruits were also separated along the PC2 axis. During the last stage (stage 6), the flavour of the banana fruits were clearly distinguished from the rest of the stages. The overall PCA results showed that the banana fruits could be clearly distinguished into categories with different ripening stages into different ripening/maturity stages using zNose according to the intensity of the flavour developed during the ripening process. Similarly, Gomez et al. (2006) classified the tomato fruits according to their maturity stages by conducting PCA analysis of the electronic nose data. Also, Lammertyn et al. (2004) and Li et al. (2006) classified The flavor of honey, apples and Lavandula species based on on zNose data using PCA.

The zNose flavour data in terms of retention time for each peak was used to predict the observed quality parameters such as respiratory quotient, total soluble solids, moisture content and firmness using multiple linear regressions.

3.2 Total soluble solids content

The predicted TSS based on zNose values and observed TSS based on experiment are shown in Figure 2. The values were analyzed using MLR. From the figure, it is observed that the TSS prediction is within the 15 groups of the flavour retention time selected using zNose. The MLR model indicated that the prediction with 15 retention times were appropriate. The coefficient of determination r^2 was found to be 0.94, signifying good prediction of TSS using zNose values for the classification of banana fruits into different ripening/maturity stages. The TSS of the banana fruit started increasing from the stage one to five and in the last stage; it was decreased due to the starch breakdown. Subedi and Walsh (2011) also reported that the TSS content decreased at the breakdown stage of banana fruits. To predict the changes in TSS of the banana fruits at different/maturity stages, the following linear relationship Equation (3) was obtained:

$$TSS = 0.944x + 1.0042 \quad R^2 = 0.944 \quad (3)$$

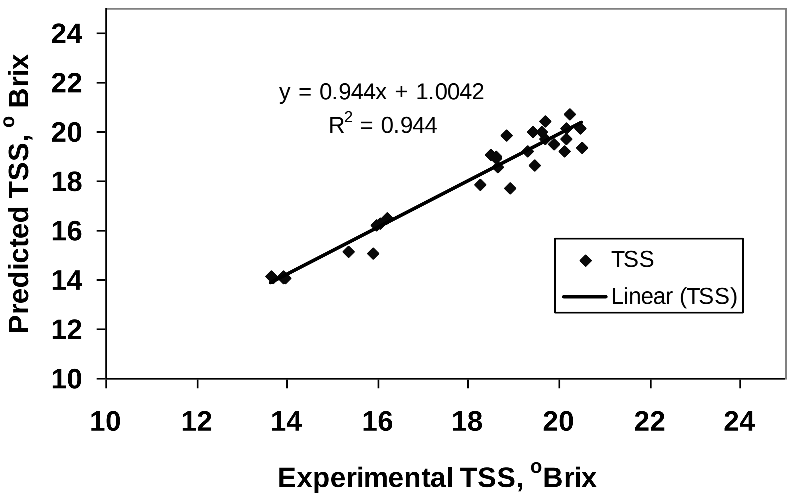

Figure 2 Experimental and predicted total soluble solids (TSS) of the banana fruits using MLR

The quality parameters of the banana fruits at different maturity stages are presented in Table 1.

Table 1 Quality parameters of the banana fruits at different maturity stages

Banana fruits	Stage1	Stage2	Stage3	Stage4	Stage5	Stage6
Firmness	9.95 ±0.44a	6.33 ±0.66b	5.89 ±0.49c	5.78 ±0.56d	4.33 ±0.34e	1.14 ±0.32f
TSS	13.92 ±0.13a	18.42 ±0.44b	18.55 ±0.52c	20.3 ±0.63cd	19.92 ±0.29e	15.77 ±0.32f
Moisture	74.87 ±0.73a	76.82 ±0.36b	78.93 ±0.81c	79.70 ±0.75d	79.97 ±0.72d	85.28 ±0.48e
RQ	0.91 ±0.02a	1.01 ±0.01b	1.05 ±0.02c	1.04 ±0.01c	1.15 ±0.02d	1.09 ±0.05e

From the Table 1, the experimental data showed that the TSS was significantly different at each stage.

3.3 Moisture content

The MLR prediction model for the moisture content of banana fruit is shown in Figure 3. The coefficient of determination was found to be 0.96, which indicates a better correlation between observed and predicted moisture values based on zNose flavour retention time. The statistical analysis of the measured moisture content (Table 1) showed that there was a significant difference in the moisture content representing the maturity stages from one to three. But at the fourth and fifth stages, the moisture content of the fruits were on par with each other and at the sixth stage, the fruits had significantly higher amount of moisture in the pulp due to the degradation of fruit and osmotic movement of moisture from peel to pulp. The following linear relationship Equation (4) was obtained to determine the moisture content of the banana fruits at different/maturity stages.

$$M.C = 0.9647x + 2.8025 \quad R^2 = 0.9647 \quad (4)$$

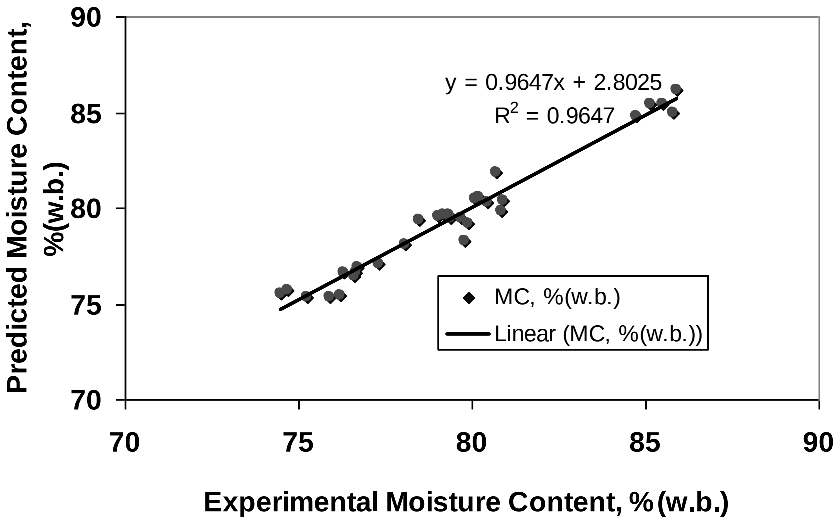

Figure 3 Experimental and predicted Moisture content of the banana fruits using MLR

3.4 Firmness

The coefficient of determination for the whole data set was found to be 0.95 as shown in Figure 4. The results showed that the selected 15 zNose flavour retention times were required to predict the fruit firmness for classifying the fruits into different ripening / maturity stages. The measured firmness values (Table 1) showed that there was a significant difference in firmness of banana fruits in each stage of ripening/maturity. Also, the results showed that the firmness values were significantly decreased with increase in ripening process. The decrease in the firmness of banana fruits is similar to the results reported by Kojima et al. (1992) for banana during ripening process. The prediction of firmness is an important textural property of banana, which directly influences the shelf life and consumer acceptance. The changes in firmness of the banana fruits at different ripening/maturity stages were found with the following linear relationship Equation (5):

$$Firmness = 0.956x + 0.2541 \quad R^2 = 0.956 \quad (5)$$

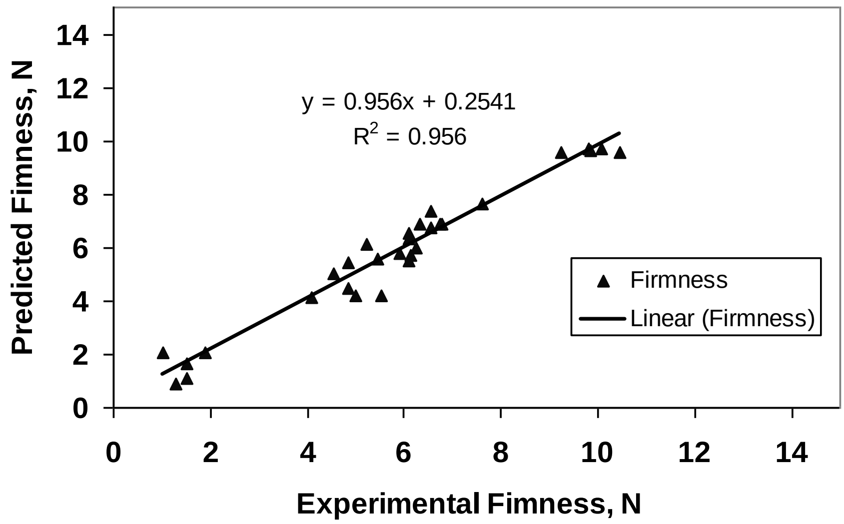

Figure 4 Experimental and predicted firmness of the banana fruits using MLR

4 Conclusions

The retention time and peak values of the zNose data were successfully used as the important parameters for the classification of banana fruits into different ripening/maturity stages. The multiple linear regression analysis using zNose data, predicted the quality parameters of banana fruits such as respiratory quotient, total soluble solids, moisture content and firmness with the corresponding coefficient of determination (r^2) value of 0.93, 0.94, 0.96 and 0.95, respectively. Therefore, the zNose flavour detection data can be used effectively as a non-destructive measurement technique for the classification and quality prediction of banana fruits into different ripening/maturity stages.

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