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Differentiation of Philippine Aromatic Rice Varieties Using Electronic Nose

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Abstract: Aromatic rice varieties are often more preferred by consumers because of their distinctive aroma, taste, and flavor. Accordingly, these varieties command higher market price than ordinary rice, and become direct targets for adulteration and mislabeling. Currently, aromatic rice quality are differentiated through techniques having lengthy processing time, and relatively high operational cost. This study explored the utilization of an electronic nose system to differentiate Philippine aromatic rices. The sensor responses were assessed by principal component analysis (PCA), and hierarchical clustering analysis (HCA). Visual patterns from the PCA precisely classified (≈95 %) the samples into different varieties. On the other hand, HCA generated three separate clusters putting all traditional varieties in one group. The result demonstrated that the electronic nose can be used as an alternative tool to differentiate the quality of Philippine aromatic rice varieties based on the generated volatile compounds from the samples.

Keywords: Rice, Aroma, Electronic nose, Headspace, Principal Component Analysis.

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1. Introduction

Aromatic rice has long been very popular among South and Southeast Asians, and in recent years, it has gained wider acceptance in Europe and the United States. Consequently, the demand for aromatic rice varieties worldwide has increased and their popularity directed high prices in markets. Because of its quality traits, aromatic rice commands a price much higher than non-aromatic rice [1]. This high economic value has motivated fraudulent practices such as the adulteration of aromatic rice with look-alike low quality varieties [2].

The authentication of aromatic rice has become a key concern for consumers, retailers, and regulatory agencies. Because each variety is characterized by unique grain appearance, texture, aroma, cooking properties, sensory characteristics, nutritional values and processing attributes, differentiation has been conducted based on morphological characteristics [3-5], physicochemical properties [6, 7], and chemical components of rice [8-10], both cooked and raw. Nonetheless, molecular technique such as DNA analysis has also been explored [11-13].

Grain appearance, texture and aroma can be assessed through descriptive sensory analysis by consumer panelists [14]. But, since the sensory properties of rice are imperceptible, cooked rice, rather than grains, have been used in a number of studies which emphasized texture and cooking quality [15-17] instead of flavor [18]. Although panelists in sensory evaluations are usually trained, the objectivity of the tool has always been doubted.

The scent of aromatic rice has been recognized to provide a basis for a non-destructive technique for rice differentiation [19]. It is due to the vapor generated by its volatile constituents. More than 200 volatile compounds in rice have been identified with the most prominent being 2-acetyl-1-pyrroline [20].

Gas chromatography has been applied in the identification of rice volatiles [21-23]. Moreover, volatile fractions released from rice cultivars have been investigated via GC-mass spectrometry to identify discriminatory compounds, and indices of aroma quality, or to compare between varieties [24-27]. However, this method is expensive, complex, time-consuming, and needs technical skills to set-up, and operate.

Electronic noses have been explored for simple, rapid and non-destructive identification and classification of rice varieties through their volatiles [28-33]. A sensor-based electronic nose mimics the sense of smell. It is made up of gas sensors, acting as the odor receptors that provide detection which is not fully selective and are treated with a variety of odor-sensitive biological or chemical materials. Thus, the identity of the sample will be obtained through signals of several sensors, or sensor array, from odorous, and even from odorless VOCs to produce a pattern known as smellprint [34]. Like the spectrum produced by spectrophotometers, electronic nose data needs to be transformed into a useful setusing chemometrics.

This study explored the differentiation of aromatic rice varieties through a commercially-available electronic nose that is based on metal oxide semiconductors. Several aromatic rice varieties are cultivated and marketed in the Philippines, including traditional varieties such as Dinorado, Milagrosa and Ifugao and new cultivars classified under the *Mabango* (fragrant) series [35-37]. These varieties are not well studied; hence, little of their quality traits is known.

2. Methods

2.1. Rice Samples

Seven aromatic rice varieties were included in the study: three traditional Philippine aromatic rice cultivars (Dinorado (N), Milagrosa (F) and Ifugao (A)) and four in-bred varieties of the *Mabango* series (NSIC Rc148 (L), NSIC Rc218 (W), NSIC Rc342 (C) and NSIC Rc344 (K)). The traditional rice cultivars were purchased from retailers while the *Mabango* varieties were obtained as hulls from the Philippine Rice Research Institute (PhilRice) and International Rice Research Institute (IRRI). Relevant information on the rice samples are given in Table 1.

All samples, (2.00 ± 0.01) grams each, were pre-weighed in 2-mL cryogenic vials, and stored at -30 °C freezer prior to analysis.

Table 1. Description of aromatic rice samples in this study [35-39].

Variety	Type	Registration Number	Owner or Breeder
Dinorado	Tropical Japonica	IRGC 96107	Traditional
Milagrosa	Indica	IRGC 5159	Traditional
Ifugao	Tropical Japonica	IRGC 8156	Traditional
Mabango 2	In-bred	NSIC Rc148	IRRI
Mabango 3	In-bred	NSIC Rc218	PhilRice
Mabango 4	In-bred	NSIC Rc342	PhilRice
Mabango 5	In-bred	NSIC Rc344	IRRI

2.2. Electronic Nose

A Fox-4000 from AlphaMOS (Toulouse, France) was used as the electronic nose system. It consists of sample delivery, detection, and computing systems. The sample is heated, and agitated in the sample delivery system wherein a fraction of the generated headspace is sent to the detecting system of the instrument. The detection system houses an array of 18 metal oxide sensors with different polarities, which change electrical properties when in contact to the produced volatile compounds. Responses of each sensor are recorded by an electronic interface which then transforms the signal into a digital value.

The sample headspace was generated from 2.00 g of rice in a sample vial kept in a heating block at 60 °C and agitated at 500 rpm for 1800 s. A sampling needle kept at 65 °C withdrew 2500 µL of the headspace vapor and injected it into the detection system. The vapor was delivered to the sensor by an air carrier gas with a flow rate of 150 mL min^{-1}. The sensor response was recorded twice every second for 120 s. The next sample injection was made after 1800 s.

2.3. Chemometric Analysis

The resulting electronic nose responses were subjected to Principal Components Analysis (PCA), and Agglomerative Hierarchical Cluster Analysis (HCA) using the XLSTAT software package (Addinsoft, USA).

The PCA transforms the generated data into components, and eliminates redundancies without losing important information. Each component is a linear combination of interrelated variables, and is graphically illustrated through PCA score and loading plots. A score plot provides information on data clustering while a loading plot is used to explore the contribution from each sensor.

The HCA separates data into specific groups by considering a Euclidian distance and generates a dendogram plot. The technique sequentially proceeds from less inclusive clusters to larger clusters and continues to cluster until all variables are clustered in a single group. Bar graph and radar plots were generated using Microsoft Excel (Washington, USA).

3. Results and Discussion

The eighteen MOx sensors in the e-nose generated varied responses to the headspace vapor of the rice samples. Fig. 1 presents a bar graph of the results of the sensors to the aromatic rice samples. The sensor responses exhibited good repeatability and reversibility. The relative standard deviation obtained for the sensor response ranged from 0.11 to 22.15. The sensors have different sensitivities towards various volatile organic compounds such as alcohols, amines, short-chain alkanes and oxidizing gases.

Correlation analysis and PCA loading plots showed that the number of sensors for the differentiation of the rice samples can be reduced to eight. The eight sensors that can highlight the variation among the rice samples, in ellipses, are: LY2/gCT, LY2/AA, LY2/gCTL, LY2/LG, TA/2, P40/1, T40/2 and P30/2. The LY sensors are based on chromium-titanium oxides and tungsten oxide, while the T and P sensors are based on tin dioxide but have different geometries. The response of the other ten sensors exhibited high correlations with one of the eight sensors and; therefore, would provide redundant information.

Fig. 2 shows the generated loading biplot using the eight sensors described above. It further illustrates that LY2 sensors mostly accounted to the differentiation of in-bred varieties. These sensors are basically sensitive to short alkanes, alcohols, oxidizing gases and sulfides. While the sensors P40/1, T40/2 and P30/2, discriminated the traditional varieties Dinorado and Milagrosa from the group.

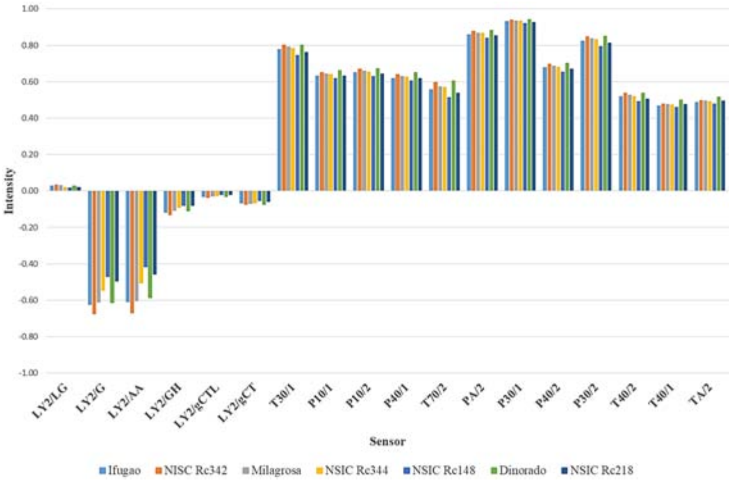

Fig. 1. Response of the 18 sensors in the electronic nose to the aromatic rice samples.

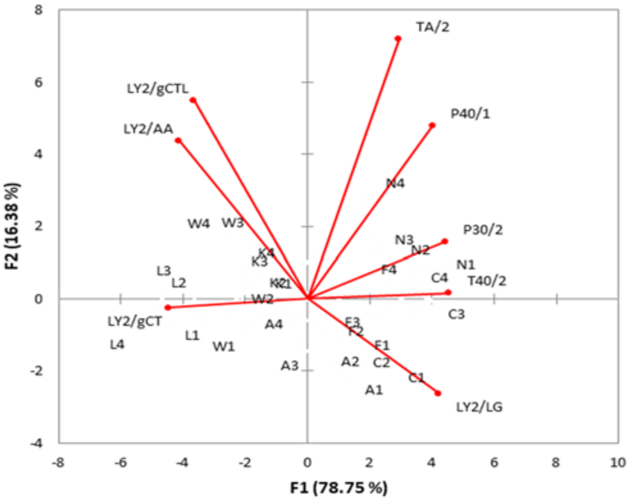

Fig. 2. Loading biplots of F1 and F2 for the responses of the 8 MOx sensors to aromatic rice samples.

The responses of the eight sensors to the rice samples varied greatly as shown in Fig. 3. The magnitude of the sensor responses are determined by the concentration of the volatile compounds in the headspace of the rice samples. It was observed that LY2/AA and P30/2 sensors consistently gave the highest negative and positive responses, respectively, for all the rice samples. It is interesting to note that both of these sensors are sensitive to alcoholic components of the volatiles. Among the rice samples, Dinorado demonstrated the highest response from most of the sensors except LY2/AA while NSIC Rc148 generated the lowest response from all the sensors.

A visual comparison of the sensor responses for each rice sample can be better achieved through a radar plot. A similarity in the pattern can be observed in the radar plots of the different rice samples (Fig. 4). The variations depicted in the signal intensities could be due to the differences in the aroma concentration in the rice samples. Rice have been documented to generate similar patterns from volatile components in studies using different sensing materials and rice varieties [28, 30]. It can be easily discerned from the plots that the greatest variation in the responses occurred from sensor LY2/AA.

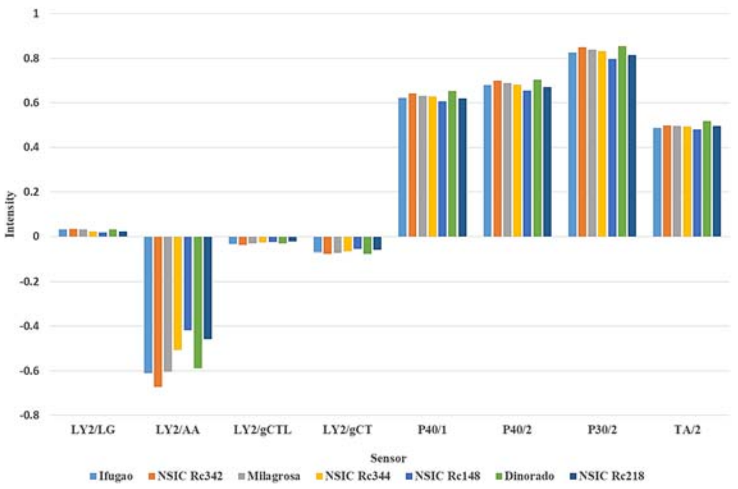

Fig. 3. Response magnitude of the eight MOx sensors to aromatic rices.

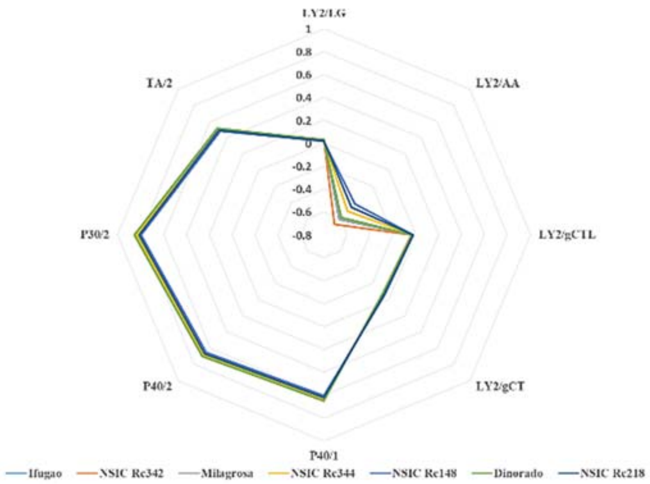

Fig. 4. Radar plot of the response values of the sensors to aromatic rices.

The variations in a multivariate dataset can be quantified and highlighted through Principal Component Analysis (PCA). The analysis is the most consistently used data reduction technique in electronic noses due to its simplicity and intuitive procedure. It has been usually employed to provide visual solution to multi-dimensional problems. A comprehensive view of the PCA score plot for a dataset obtained from the eight sensors is illustrated in Fig. 5. The first two principal components were used to plot the observations since the total accumulation of these two components is more than 95 % of the total variance information. Most of the traditional rice were on the right side of the first principal component (F1) plane. The F1 accounts for 78.75 % of the total variance of 95.14 %. The second principal component (F2) explains 16.38 % of the variation. These values indicate contribution rates to pattern separation, which means that majority of the contribution to the pattern separation is contributed by F1. Other studies suggested that F1 represents aroma richness generated from the samples subjected to electronic nose analysis [40, 41].

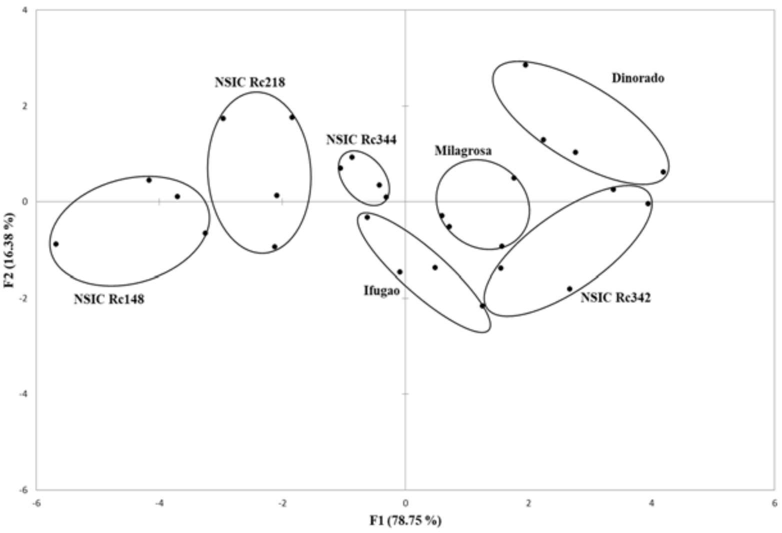

Fig. 5. PCA score plot of Philippines aromatic rice varieties.

To identify the natural groupings of the rice samples based on their characteristic similarities based on Euclidean distance, agglomerative hierarchical clustering analysis (HCA) was performed. The resulting dendogram (Fig. 6) features three clusters: Cluster 1 Traditional varieties.

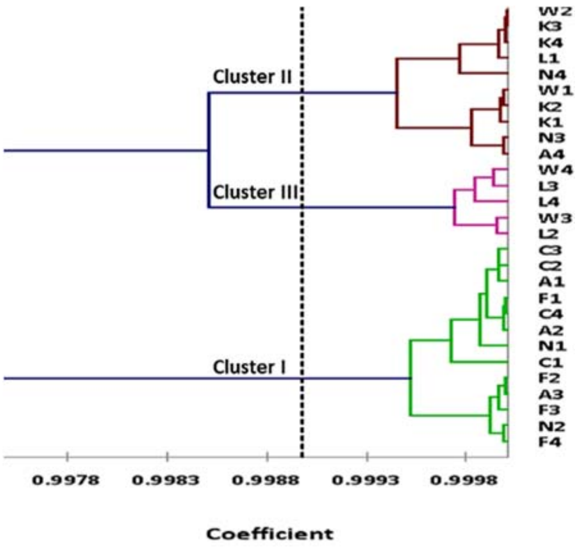

Fig. 6. Dendogram showing similarities among traditional and in-bred aromatic rice varieties.

Dinorado, Ifugao, Milagrosa and NSIC Rc342; Cluster 2 NSIC Rc344 *Mabango 5* and Cluster 3 NSIC Rc148 *Mabango 2*.

NSIC Rc342 or *Mabango 4* could have clustered with the traditional varieties because one of its parent line comes from Jasmine which is highly considered as a traditional variety in Thailand. Furthermore, NSIC Rc218 or *Mabango* 3 may have characteristics that are similar to both *Mabango* 2 and *Mabango* 5 that is why it was present in Clusters 2 and 3.

4. Conclusions

The electronic nose demonstrated its success in differentiating Philippine aromatic rice varieties based on the volatile organic components generated from the samples. The most prominent sensor types that generated high magnitude response were those that are particularly sensitive to alcohols. Clusters presented by the PCA were more defined and showed visually observable differentiation among samples.

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