Identification of Organically Grown Shallot Based on Electronic Nose System

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Abstract

The method of electronic nose to evaluate quality of shallot was developed. The response signals of sensor array to shallot odor were measured. Six plots of shallot were cultivated with different chemical substances. The patterns of sensor responses to shallot odor of each plot were clustered by two-dimensional principal component analysis (PCA). The result shown that six shallot plots were clearly classified into 2 groups. The same observation was also seen in the PCA scores based on the optimized set of sensors without any significant performance changes. These results suggest that the shallot cultivated by additional nutrient can be possibly evaluated in the simple and fast way using low-cost electronic nose system.

1. Introduction

Shallot (Allium cepa L. var. aggregatum) is known since ancient times. It has been cultivated as vegetables and for its medicinal properties. Recently, shallot has been reported to show antioxidative, antibacterial, and free radical scavenging abilities, since it has high concentration of quercetin [1-4]. Since the economically important part of shallot is bulb, many chemical substances, such as plant nutrient and nutrient, are used in order to accelerate the growth of shallot bulb [5, 6].

Recently, the increasing of demand for organic products including shallot has resulted in the use of organic substances instead of chemical substances in plant cultivate. Therefore, we can find shallot bulb, which labeled as organic product in the market. However, verification of organic products by consumer is not an easy task. Although, chemical composition of shallot odor can be analyzed using high performance liquid chromatography [7] or gas chromatography-mass spectrometry [8]. However, these methods are complicated, require specialized skills, and also time consuming. Therefore, a simple method for qualitification of shallot is needed to confirm its organic certification.

An electronic nose system is the simple and fast method, which has been successfully used to evaluate the odor of Allium [9]. It uses a group of non-specific gas sensors to detect and discriminate among complex odors. The identification of odor is based on a response pattern from all sensors rather than that from a particular one [10]. Recently, the ready-to-use gas sensor modules, especially metal oxide semiconductor type, are commercially available and have been widely used to form sensor array for odor measurement [11]. Moreover, the odor measurement system with portable size can also be simply developed at a low cost.

In this study, we applied the method of electronic nose to classify shallot harvested from 6 plots, which were cultivated with different chemical substances. The performance of this devloped electronic nose system in classifying the shallot cultivated by additional nutrients was confirmed in the experiment.

2. Electronic nose system

The electronic nose system was developed in order to measure and classify the shallot odor. Eight commercially available gas sensors were used. The sensing materials of all sensors were semiconductors of metal oxide. Their commercial product codes and selectivity's were shown in Table 1. The sensor array was arranged at the lid of the 2.4 L chamber. These all sensors were connected to the measurement circuits as shown in Fig. 1. A 5 V power supply was used for both heater voltage (V_H) and circuit voltage (V_C) of all sensors. The sensor response was obtained from the voltage across a load resistor R_L (V_{RL}) as Eq. (1), which is connected in series with the sensor resistance (R_S).

Table 1. Selectivity of sensors

Sensor	Code	Selectivity
S1	MQ-2	H_2, LPG, Methane, CO, Alcohol, Propane
S2	MQ-135	CO_2, Ammonia, NO_x, Alcohol, Benzene
S3	TGS822	Acetone, Ethanol, Benzene, Carbon monoxide
S4	TGS826	Ammonia
S5	TGS2600	Hydrogen, Carbon monoxide
S6	TGS2602	Hydrogen sulphide, Ammonia
S7	TGS2611	Methane, Iso-butane, Hydrogen, Ethanol
S8	TGS2620	Ethanol, Hydrogen, Iso-butane, CO, Methane

$$V_{R_L} = \frac{R_L V_C}{R_L + R_S} \qquad (1)$$

The output voltage responses of the sensor array were digitized by A/D transfer device (USB6009, National Instrument inc., USA) with 14 bits resolution and then were sent to PC for later signal processing. After finishing each measurement process, the odor inside the measurement chamber were purged using the pump and solenoid valves, so that the sensor baselines were generated.

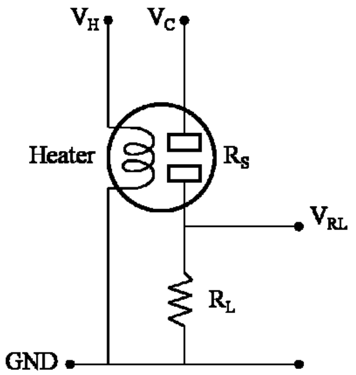

Fig. 1. Circuit diagram of a semiconductor gas sensor.

3. Experiment

3.1. Shallot sample

In this work, six shallot plots were cultivated with different conditions in the area of Ubon Ratchathani University, Thailand. Chemical fertilizer, insecticide, plant growth nutrient and root growth nutrient were applied to each shallot plot as shown in Table 2. Plot#1 was a controlled plot without any additional chemical substances. Three formulae of Nitrogen-Phosphorous-Potassium (NPK) fertilizer were used. Ammonium sulfate 21-0-0 fertilizer was applied after day 14th of cultivation, 15-15-15 fertilizer was applied after day 35th of cultivation, and 13-13-21 fertilizer was applied when shallot bulbs formed. Plant growth nutrient, which composed of Potassium, Calcium, Magnesium, Sulfur, Manganese, Zinc and Iron was applied every 2 weeks. Bulb induced nutrient, contained mainly Phosphorous, Potassium, Calcium, and Boron, was applied every 2 weeks after day 35th of cultivation.

Table 2. Chemical substances for each shallot sample plot (✓ means applied when growing)

Sample plot	Chemical fertilizer	Insecticide	Plant growth nutrient	Bulb induced nutrient
1	-	-	-	-
2	✓	-	-	-
3	✓	✓	-	-
4	✓	✓	✓	-
5	✓	✓	-	✓
6	✓	✓	✓	✓

3.2. Odor measurement

In the experiment, a fresh shallot bulb was cut and placed on petri dish and kept inside the chamber at room temperature. The volatile odor from the cut shallot sample was statically measured by the sensor array for 600 s. The measurement data from the sensors array were collected for every second. This measurement process was automatically manipulated by our developed program using LabView (National Instrument inc., USA). Each shallot plot was repeatedly prepared and measured for 5 times. After that, obtained sensor responses were used as the input data for principal component analysis (PCA) in order to investigate the pattern separation among the shallot plots.

4. Results and Discussion

The obtained output voltage of each sensor was subtracted by its baseline voltage and then used as the response signal for simplicity. The response signals at 600 s after measurement start were used as the representative data for shallot qualification. In order to disregard the effect of circumstance, the response signals of all sensors were compared relatively.

Since each sensor in the sensor array has low selectivity and not all shallot plots can be clearly classified, PCA was applied to improve the classification capability. The normalized output responses of 8 sensors were mapped on the two-dimensional PCA feature space as shown in Fig. 2. The obtained PC1 and PC2 were 76.41% and 15.21% of the variance in the input variables, respectively. Based on PCA, classifying the mapped output responses according to sample plot in Table 2 seems not possible. The response of organic shallot sample of Plot#1 is not distinguishable from other plots. Moreover, the effect of insecticide could not be observed in the PCA result. However, it was found that 6 plots of shallot samples could be classified into 2 major groups; a group of shallot plots that were not applied any plant nutrients (G1) and a group of shallot plots, which plant growth nutrient or bulb induced nutrient was applied (G2). Plot#1, #2 and #3 were categorized into G1 group, while plot#4, #5, and #6 were in G2 group as indicated by the circles in Fig. 2.

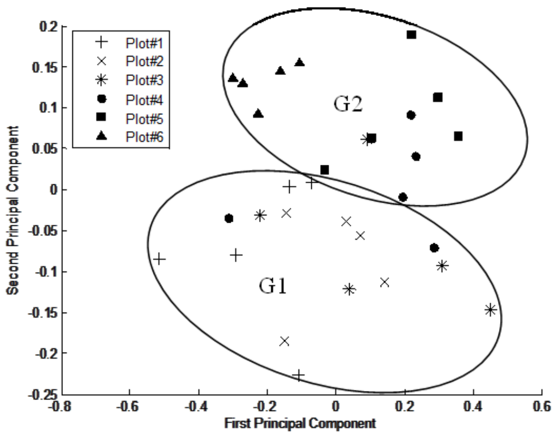

Fig. 2. Two-dimensional PCA plot for the responses of all eight sensors.

In order to investigate the different feature between the responses obtained from G1 group and G2 group, the baseline subtracted response signals of 8 sensors at the last second of measurement were shown by the radar graph in Fig. 3. The thick line and dash line are the average response obtained from shallot samples in G1 group and G2 group, respectively.

As shown in Fig. 3, S3 sensor had the highest sensitivity while small difference in the response levels of S5, S7 and S8 sensors among shallot plots were observed. Although S1 and S2 sensors also have high sensitivity to several gases, but both of them have overlapping response due to their low selectivity. By comparison, the differences among the response levels obtained from 3 sensors (S3, S4 and S6) to each shallot group were noticable.

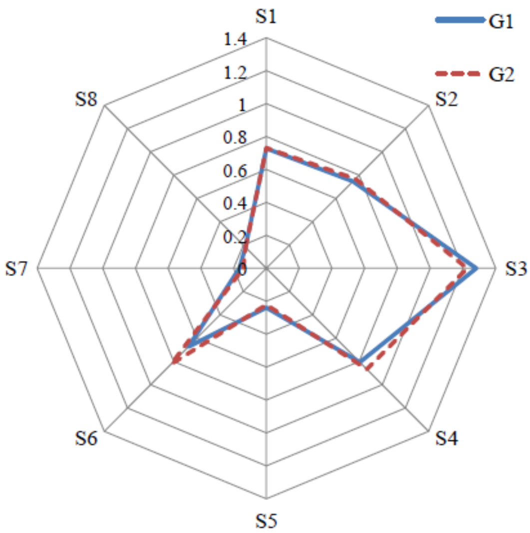

Fig. 3. Average of baseline subtracted responses of 8 gas sensors to the odor of shallot samples

Then, the set of sensor array used in this system was empirically optimized so that redundant information could be reduced. The S1 and S2 sensors were excluded from the sensor array due to their relatively low selectivities. The S5, S7, and S8 sensors were also excluded due to their low sensitivities. Fig. 4 shows the two-dimensional PCA scores of the measured shallot samples based on the optimized set of sensor array. The obtained PC1 and PC2 were 76.99% and 18.58% respectively, which over 99% of the total variance. The same observation in Fig. 2 was also seen in Fig. 4. Thus, the number of sensors used in this developed electronic nose system could be minimized to only 3 sensors (S3, S4 and S6) without any significant performance changes.

In order to confirm the classified result, nine shallot samples of each group were selected and measured by the developed electronic nose system. Fig. 5 shows the two-dimensional PCA scores of the measured shallot samples based on the optimized set of sensor array. The obtained PC1 and PC2 were 84.39% and 14.33% respectively. Although, a few samples has scored differed from the major group, the same observation in Fig. 4 was also seen in Fig. 5. The dash line was drawn as a border line.

In the experiment, it was not possible to differentiate the effect of each chemical substance using obtained sensor responses. However, the effect of additional nutrients, which resulting in the induction of growth and development, could be classified. In bulb vegetables, the major odor compounds are thiosulfinate [6, 7], which readily oxidized into several volatile compounds, including hydrogen sulphide (H_2S) [12], therefore the amount of hydrogen sulphide is possibly considered as a cause of the response of S6 sensor. Thus, it could be considered that applying nutrients related to the amount of thiosulfinates in shallot bulb. However, the further experiment is required to evaluate the chemical compositions inside shallot bulb.

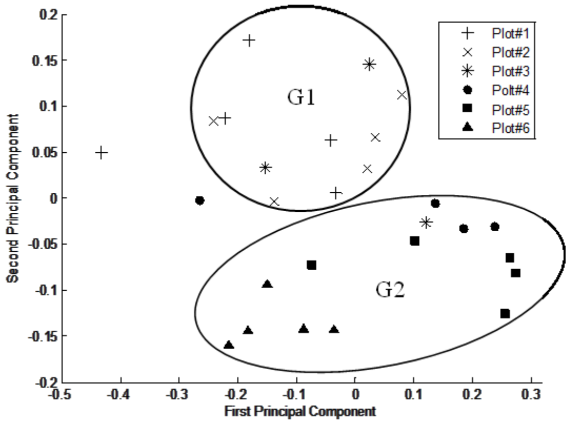

Fig. 4. Two-dimensional PCA plot for the responses of the optimized sensor set.

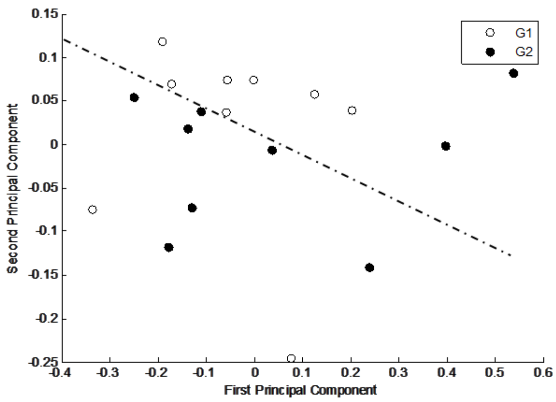

Fig. 5. Two dimensional PCA plot for the responses of the three sensors chosen to verify the system.

5. Conclusions

We have developed the method to evaluate odor of shallot cultivated by different chemical substances using electronic nose system. The odors of each shallot plots were measured using optimized sensor set and were categorized into the two major groups using PCA. In the experiment, it was found that applying additional nutrients related to the difference in amount of volatile compound, resulted in the effective distinguishing between shallot groups. It was confirmed the possibility of using the electronic nose system for shallot odor evaluation. In future work, the chemical analysis will be performed for confirmation.

6.Acknowledgements

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7. References

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