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Measurement of Patchouli oil vapor using array of MOS gas sensors in various adulteration substances and concentrations

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Abstract

Indonesia is one of the main suppliers of Patchouli oil in the world market. It has high economical value. Indonesian Patchouli oil is mostly produced by SMEs using the distillation technique. However, the high demand and price of Patchouli oil led to the fraud of adulteration. SMEs intentionally mixed Patchouli oil with cheaper oils. This paper presented the vapor measurement of Patchouli oil by using an array of metal oxide semiconductor gas sensors (MOS) which may apply to indicate the presence of adulteration substance in Patchouli oil. A total of nine MOS gas sensors were tested. All MOS are driven with temperature modulation technique. We built an acquisition unit based on the PSoC device to acquire the MOS outputs to a computer. We tested two adulteration substances (palm oil and biodiesel oil), and two compositions (1:3 and 1:5) on two levels of Patchouli oil. Individual response of MOS was examined. The Principle Component Analysis (PCA) method was used to show the classification performance to distinguish the adulteration types in Patchouli oil. We found that there was no single MOS that able to distinguish the adulteration individually, and there were many overlapping responses to adulteration substances and compositions. The PCA results showed that on each level of Patchouli oil, nine MOS gas sensors can distinguish clearly between the with and without adulteration substances (palm oil and biodiesel oil).

1. Introduction

Patchouli oil is a leading export commodity in Indonesia. Indonesia is the three larger suppliers to the world market of Patchouli oil (Hapsari, 2018; Schmidt, 2016). Among the various essential oils in Indonesia, Patchouli oil has good prospect and price in the international market. The quality of Indonesia's Patchouli oil is known to be the best and holds a world market share of up to 85%. (Haryono, 2015). Patchouli oil has a high priced value in the oil industry. The price of Indonesia's Patchouli oil in August 2020 was 52.30 USD to 62.10 USD per kg for a minimum order quantity of 1000 kgs (Jandico, 2020).

In Indonesia, Patchouli oil is mostly resulted by SMEs from steam distillation of leaves, stems and branches of patchouli plant (*Pogostemon cablin Benth*). The Patchouli oil has a fresh and distinctive aroma of the plant which cannot be substituted by synthetic material. Patchouli oil is obtained through a distillation process which is taken from a separator tank. In general, the separation is done by waiting for the oil to cool in order to avoid the water particles move to Patchouli oil. Oil contaminated with water will reduce shelf life that leads to lower price. However, the quality of Patchouli oil produced by many SMEs has not been met the requirement.

Due to the high economic value and high demand of Patchouli oil, the Patchouli oil is subjected to be adulterated with other cheap oils to get economical profit. SMEs intentionally added Patchouli oil with cheaper oils to increase the weight. The practice of adulteration becomes an issue for consumers, producers, and regulatory bodies. The lack of knowledge and the availability of tools to detect the presence of impurities in Patchouli oil cause local collector/SME to experience a lot of economic losses when selling their products to exporter or industries (Haryono, 2015). Thus, it is needed an instrumental technique to assure the authenticity of Patchouli oil by indicating the presence of

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sufficient accuracy for the level of SME.

Currently, the determination of Patchouli oil contents accurately and widely applied is using the Gas Chromatography-Mass Spectrometry method. GC and HPLC physico-chemical analysis are the most advanced methods among them. Some adulterations can be detected simply by GC-MS tests with technology such as GC-IRMS and SNIF-NMR (Schmidt and Wanner, 2016). However, this method may not be used by SMEs because of the complexity of use and the price of the equipment is very expensive, beyond the ability of SMEs.

The gases and volatiles of essential oils can be captured using an array of Metal Oxide Semiconductor (MOS) gas sensors. The MOS gas sensor is small and compact, and are multi-series to detect a wide variety of compounds. Several studies that have utilized the MOS sensor gas line, including Kim *et al*. (2013) distinguished essential oils from sweet oranges, chamomile flowers, and jasmine flowers, and Gorji-Chakespari *et al*. (2016) detected and classified the variety of Rosa Damascena oil into three categories. And one technique that has been studied for a long time and succeeded in increasing the sensitivity and selectivity of MOS is temperature modulation (Ortega *et al*., 2001; Sun *et al.*, 2004; Huang *et al*., 2004; Liu *et al.*, 2007). This technique was further developed by Sudarmaji and Kitagawa (2015) known as Temperature Modulation with Specified Detection Point (Temperature Modulation-SDP). Sudarmaji *et al.* (2018) used this technique to measure volatility and were able to clearly distinguish between Patchouli oil and clove oil. This paper presents the vapor measurement of Patchouli oil by using an array of MOS gas sensors operated in Temperature Modulation that may indicate the presence of adulteration substance in Patchouli oil as adulterated or unadulterated Patchouli oil.

2. Materials and methods

2.1 Sample of Patchouli oil

The samples of pure Patchouli oil are from SMEs in Banyumas regency, Central Java, Indonesia. The samples have tested the level of Patchouli oil using the Gas Chromatography-Mass Spectrometry method. We chose two levels of Patchouli oil (26.94%, and 29.52%). Patchouli oil content is defined from the content of Patchoulol (patchouli alcohol). And, we used palm oil and biodiesel oil as the impurities of Patchouli oil. We tested two portions of the impurity oil to Patchouli oil, namely 1:3 and 1:5. Thus, we had 5 categories of each level of Patchouli oil, i.e. without adulteration (pure), Patchouli oil + palm oil (1:3), Patchouli oil + palm oil (1:5), Patchouli oil + biodiesel oil (1:3), and Patchouli oil + biodiesel oil (1:5). Each measurement of the sample was five times repeated.

2.2 Measurement and experiment setup

The measurement diagram of Patchouli oil using static headspace and static measurement can be seen in Figure 1. The nine MOS gas sensors (Table 1), which pointed to sense several odorous gases and volatiles, were employed to capture the vapor of Patchouli oil. All MOS have operated in dynamic mode with temperature modulation-SDP technique. The temperature Modulation -SDP used was square modulation on 0.25 Hz. All sensors were put inside a sensor chamber made of 5 mm acrylic and formed into 693 cm^3 square box (11x9x7) cm. The outputs are acquired to a computer through PSoC CY8C28445-24PVXI based interface unit.

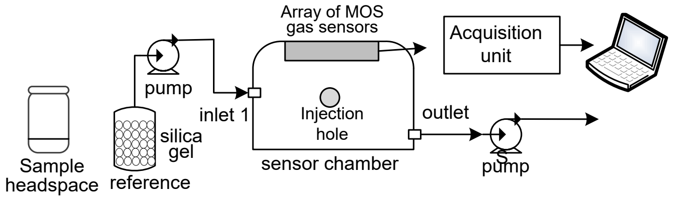

Figure 1. Diagram of static measurement for capturing vapor of Patchouli oil

A 15 mL glass bottle with rubber cap was used as a static headspace vial. An aliquot (1 mL) of Patchouli oil solution was put inside the static headspace vial. The sample was heated to the boiling point of Patchouli oil (280°C) for 5 mins. The vapor of Patchouli oil was manually delivered to the sensor chamber using a 3 mL syringe. One cycle measurement consists of three steps: heating the sample, Patchouli oil vapor measurement

Table 1. MOS gas sensor for capturing gases and volatiles of Patchouli oil

No	Type	Gas Target	Range
1	TGS-2602	Odorous gases (Ammonia, Ethanol)	1-100 ppm
2	TGS-2620	Solvent (organic) vapors	50 – 5,000 ppm
3	TGS-2600	Air Contaminants (H_2, CO)	1-30 ppm
4	MQ-5	Natural gas, Coal gas	200-10,000 ppm
5	MQ-135	Air Quality Control	10-200 ppm
6	MQ-138	Wide volatile compound	200-10,000 ppm
7	FIS-12A	Methane	300-7,000 ppm
8	FIS-30SB	Alcohol	1-100 ppm
9	FIS-AQ1	Volatile organic compound	10-10,000 ppm

(Rg), and purging phase as shown in Figure 2. The pumps were switched on when measuring the R_o and purging phase, while the pumps were stopped when measuring the R_g. The output was defined as R_g where R_g is resistance when measuring vapor of Patchouli oil. Dry air (filtered by silica gel) was constantly pumped to the sensor chamber and was used as a reference. An acquisition software was developed under Visual Studio 2019 to set the temperature modulation and to show and store the MOS outputs into an MS Excel file.

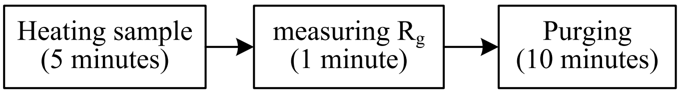

Figure 2. Measurement steps of Patchouli oil.

3. Results and discussion

3.1 Measurement system of Patchouli oil

Figure 3 shows the measurement apparatus, software interface, sample of Patchouli oil inside the static headspace vial, and injection step. The interface unit, PSoC CY8C28445-24PVXI, was programmed to generate the temperature modulation signal and acquired the output of MOS gas sensors. We configured the pair of XBee (IEEE 802.15.4) into direct transmission (point to point) using XCTU software, as coordinator and as a router (Digi, 2008). Both XBees were configured on 19200 bps, 8 bit, no parity, 1 stop bit and none flow control which accorded with PSoC serial communication. Sudarmaji *et al*. (2018) applied these configurations to measure the Clove Oil and Patchouli oil, and the use of 0.25 Hz temperature modulation led to distinguish between Clove Oil and Patchouli oil clearly.

The Temperature Modulation signals are settable and the output sensors are acquired respectively into personal computer wirelessly using developed software under Visual Basic.Net 2019. The software creates a file (Excel) to store data and determine automatically the average value of each sensor for each measurement. The acquisition software creates automatically 3 worksheets to store the values of R_o, R_g, and their ratio.

3.2 Individual response of MOS gas sensors on various Patchouli oil adulterations

We investigated the response of each MOS gas sensor on 5 kinds of adulteration Patchouli oils, namely: pure Patchouli oil, 1:3 Patchouli oil with palm oil, 1:5 Patchouli oil with palm oil, 1:3 Patchouli oil with biodiesel oil, and 1:5 Patchouli oil with biodiesel oil. The measurements were acquired 150 data/sample of Patchouli oil (30 data and repeated 5 times). For the individual response of MOS gas sensor, we used box plot analysis to show the ability of MOS to sense and distinguish the five kinds of Patchouli oil adulteration.

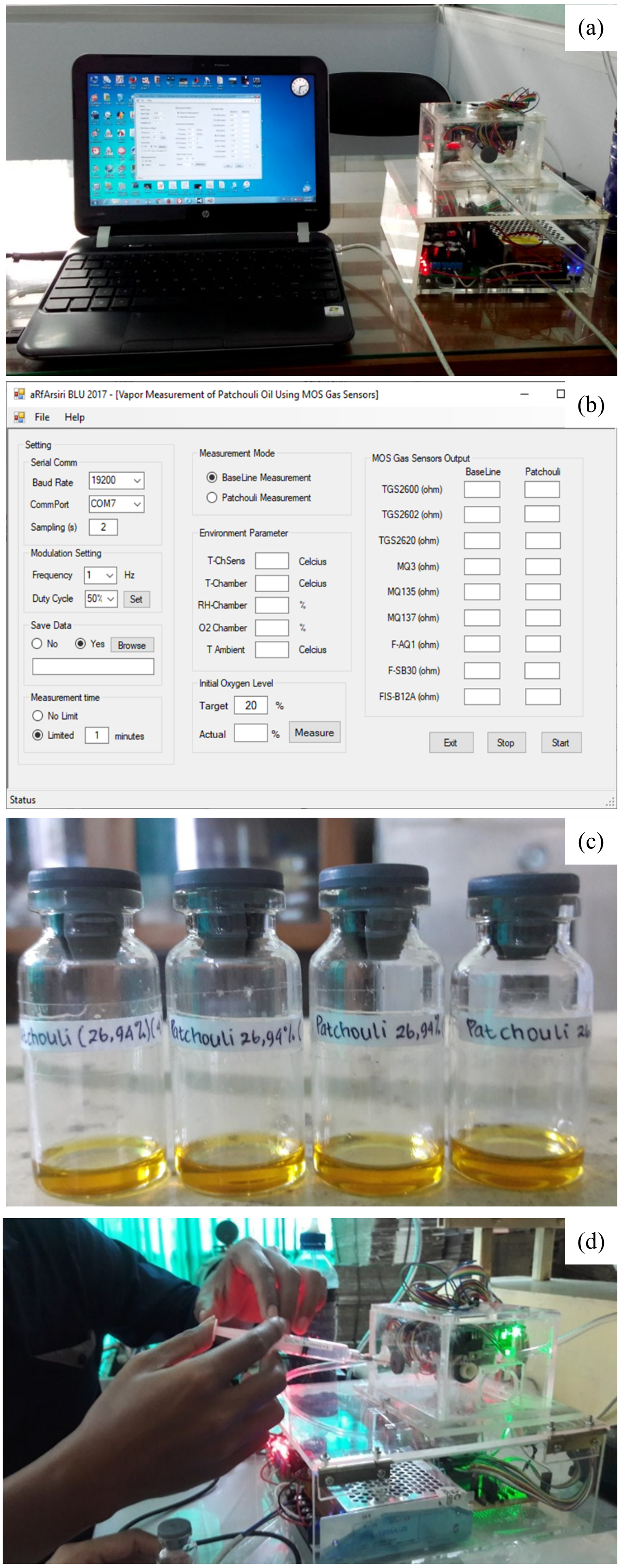

Figure 3. (a) measurement apparatus, (b) software interface, (c) static headspace vial, and (d) vapor injection process.

For example, the box plot graphs of resistances of each MOS gas sensor to sense the 5 adulterations on Patchouli oil of 26.94% are shown in Figure 4, 5, and 6. It can be seen that the MOS sensors can sense vapor of

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Patchouli oil with different adulterations. We found that among the MOS tested, the TGS and MQ series tended to have a lower resistance value when sensing Patchouli oil without adulteration than when sensing Patchouli oil with adulteration. Meanwhile, the FIS series tended to give the opposite response. And, Figure 5 also reveal that MQ5 was the least sensitive to the various adulteration types which its box plots show almost at the same range of resistance for the 5 treatment of adulteration.

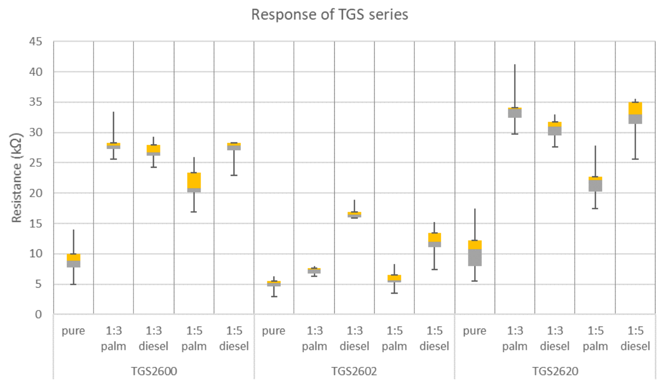

Figure 4. Response of individual TGS Series on 5 adulterations of 26.94% Patchouli oil

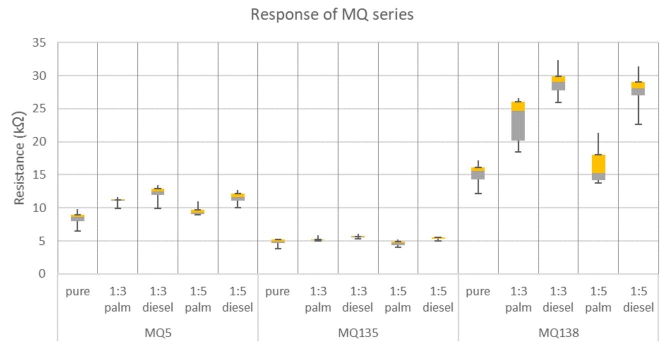

Figure 5. Response of individual MQ series on 5 adulterations of 26.94% Patchouli oil

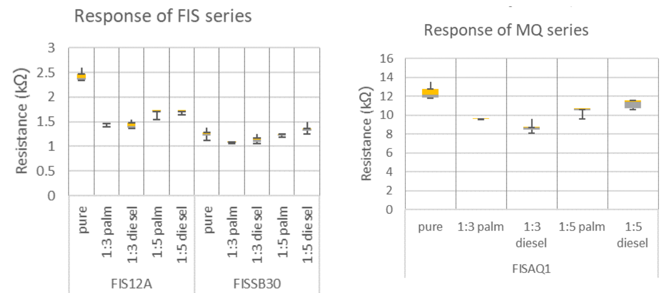

Figure 6. Response of individual FIS series on 5 adulterations of 26.94% Patchouli oil

However, it also clearly seen that almost all MOS gas sensor has high overlap response among 5 kinds of adulteration. So that there is no single MOS gas sensor used (i.e. general gases and volatiles sensor) that able to distinguish them. It might be caused by the compound complexity of Patchouli oil vapor. Table 2 shows detected peaks using GC-MS when measuring the 2 samples of Patchouli oil. Van Beek and Joulain (2017) reported that it is found 32 detected peaks and their odor descriptions of Patchouli oil using GC-MS analysis. Besides, the MOS sensors tended to drift (Hierlemann and Gutierrez-Osuna, 2008) and to have poor selectivity (cross-sensitivity) to other gases (Bermak *et al*., 2005; Di Carlo and Falasconi, 2012). MOS sensor could be selective to a certain gas but its cross-sensitivity to other gases was not negligible (Wilson and Baietto, 2009).

Table 2. Peaks detected by means of GC-MS method of Patchouli oil

Sample	Patchoulol level	GC-MS Peak detected
Patchouli oil 1	26.94%	80
Patchouli oil 2	29.52%	100

3.3 Identification of Patchouli oil adulterations

We used the loading plot of Principal Component Analysis (PCA) to know the effect or significance of each MOS gas sensor to the resistance in sensing the 5 samples of adulteration. As shown in Figure 7, the length of loading plots of all MOS gas sensors was closely similar, either on 26.94% Patchouli oil or 29.52% Patchouli oil. Therefore, we applied the 9 MOS gas sensors to evaluate their performance for indicating the presence of adulterant substance in Patchouli oil.

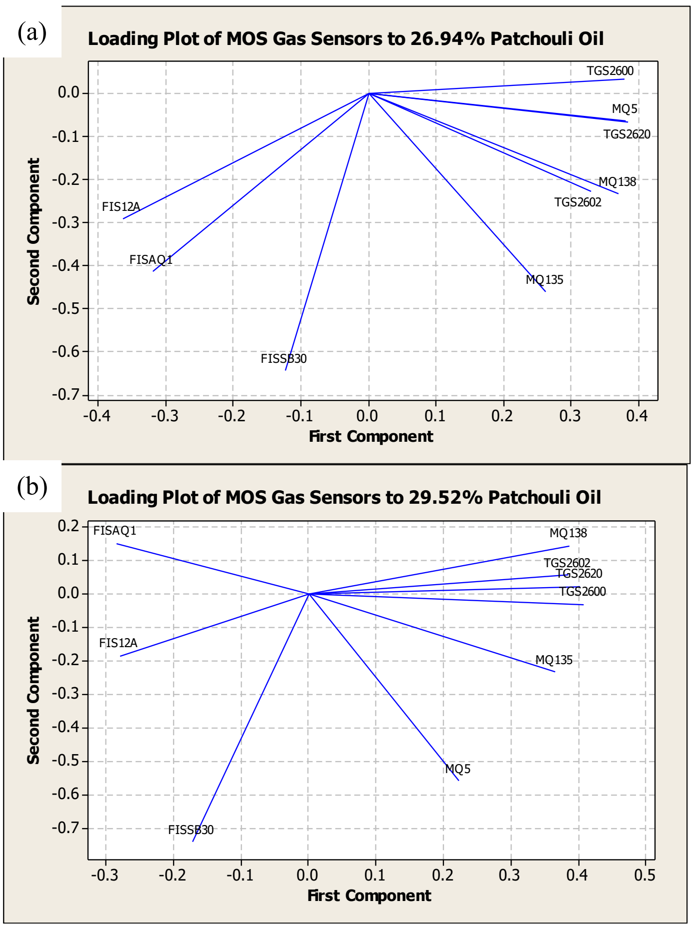

Figure 7. Loading plot of MOS gas sensors to (a) 26.94% Patchouli oil and (b) 29.52% Patchouli oil

We utilized the Principal Component Analysis (PCA) to evaluate the selectivity performance in discriminating among the 5 adulteration treatments.

Figure 8 shows the PCA plot of discrimination of five categories on 26.94% Patchouli oil and 29.52% Patchouli oil. The first two principal components were holding 75.4% of the data. PCA is commonly used as a feature extraction part to test selectivity performance and as a linear classification technique. It is usually utilized in correlation with cluster analysis and visualization of the differences among the treatments. The large dimension of interrelated variables is reduced into few important principal components. The first two or three uncorrelated components hold the most significant variation present in all variables and widely used in the various application (Haddi *et al*., 2014).

Figure 8 depicts that by using the first two principal components, the nine MOS gas sensors able to discriminate clearly the Patchouli oil with adulteration or Patchouli oil without adulteration (separated by a linear dash line). However, it also reveals that there are some miss-clustering among groups of Patchouli oil with adulteration to discriminate the kind of substance and composition. It seems that there is similar substance between palm oil and biodiesel oil since the biodiesel is made from vegetable oil. Recent Indonesian biodiesel is a mix of 20% palm oil-based biodiesel with 80% fossil fuel (called B20) (Silalahi *et al*., 2020).

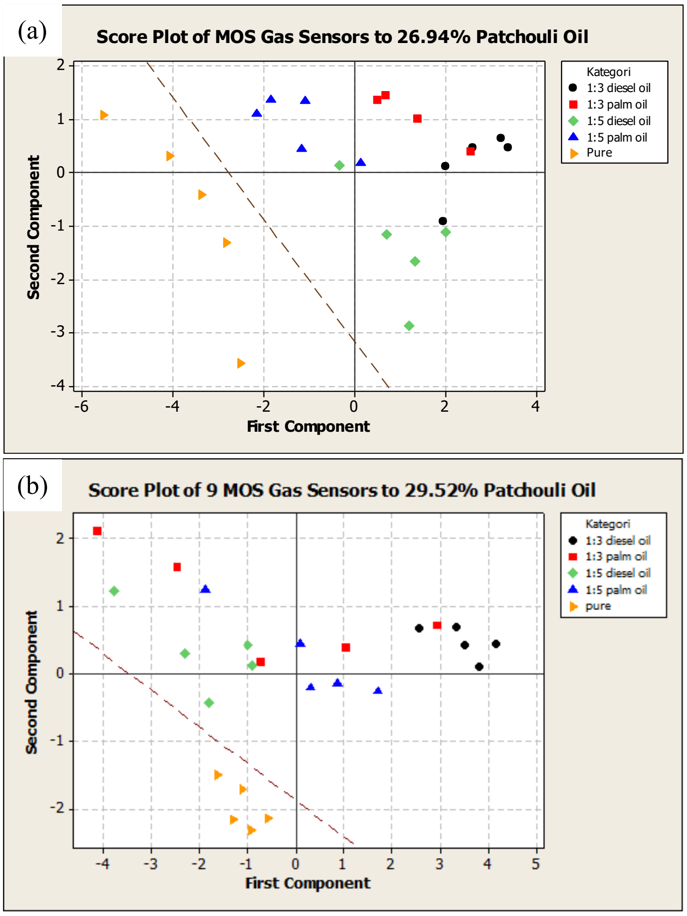

Figure 8. PCA discrimination plot of (a) 26.94% Patchouli oil and (b) 29.52% Patchouli oil

4. Conclusion

This paper presents a test of MOS gas sensors (TGS-2600, TGS-2602, TGS-2620, MQ-5, MQ-135, MQ-138, FIS-AQ1, FIS-SB30, and FIS-12A) for measuring Patchouli oil in various impurities and concentrations. Those MOS gas sensors, which basically designed to sense odorous gases, volatile compound, and organic solvent, had a good response for indicating the presence of impurity substances (palm oil and biodiesel oil) in Patchouli oil as adulteration. The impurity compositions for Patchouli oil were 1:3 and 1:5. By using the PCA tool, the MOS gas sensors had a strong performance to discriminate the Patchouli oil with adulteration or Patchouli oil without adulteration.

Conflict of interest

The authors declare no conflict of interest.

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References

Beek, T.A.V. and Joulain, D. (2017). The essential oil of patchouli, Pogostemon cablin: A review. *Flavour and Fragrance Journal*, 33(1), 6-51. https://doi.org/ https://doi.org/10.1002/ffj.3418

Bermak, A., Belhouari, S.B., Shi, M. and Martinez, D. (2005). Pattern Recognition Techniques for Odor Discrimination in Gas Sensor Array. *The Encyclopedia of Sensors*, *X*, 1–17.

Di Carlo, S. and Falasconi, M. (2012). Drift Correction Methods for Gas Chemical Sensors in Artificial Olfaction Systems: Techniques and Challenges. In Wang, W. (Ed.). Advances in Chemical Sensors. InTech Open E-Book. https://doi.org/10.5772/33411

Digi. (2008). X-CTU Configuration and Test Utility Software: User's Guide. Retrieved from Digi website: https://www.digi.com/resources/documentation/digidocs/PDFs/90001458-13.pdf

Gorji-Chakespari, A., Nikbakht, A.M., Sefidkon, F., Ghasemi-Varnamkhasti, M. and Valero, E.L. (2016). Classification of essential oil composition in Rosa damascena Mill. genotypes using an electronic nose. *Journal of Applied Research on Medicinal and Aromatic Plants,* 4, 27-34. https://doi.org/10.1016/j.jarmap.2016.07.004

Haddi, Z., Bougrini, M., Tahri, K., Braham, Y., Souiri, M., Bari, N. El, Maaref, A., Othmane, A., Jaffrezic-Renault, N. and Bouchikhi, B. (2014). A hybrid

eISSN: 2550-2166

system based on an electronic nose coupled with an electronic tongue for the characterization of moroccan waters. *Sensors and Transducers*, 27 (May), 190–197.

Hapsari, A. (2018, April). Indonesia Pensuplai Utama Tiga Komoditi Minyak Atsiri. Suara Merdeka News. [In Bahasa Indonesia].

Haryono, W. (2015). Export News Indonesia: Patchouli oil. Indonesia: Directorate General of National Export Development, Ministry of Trade of The Republic of Indonesia.

Hierlemann, A. and Gutierrez-Osuna, R. (2008). Higher-order chemical sensing. *Chemical Reviews*, 108, 563–613. https://doi.org/10.1021/cr068116m

Huang, X., Meng, F., Pi, Z., Xu, W. and Liu, J. (2004). Gas sensing behavior of a single tin dioxide sensor under dynamic temperature modulation. *Sensors and Actuators, B: Chemical*, 99(2–3), 444–450. https://doi.org/10.1016/j.snb.2003.12.013

Jandico. (2020). Price List August 2020. Retrieved from Jandico website: http://jandico.co.uk/wp-content/uploads/2020/08/Atsiri_August_2020.pdf

Kim, S.T., Kim H.S., Lee, I.C., Cheong, K.J. and Lim, M.H. (2013). The Quantitative Analysis of Aroma Gas with Gas Sensors. *Korean Journal of Aesthetics and Cosmetology*, 11(6), 1163–1169.

Liu, J., Huang, X. and Meng, F. (2007). The Dynamic Measurements of SnO2 Gas sensors and their Applications. In Aswal, D.K. and Gupta, S.K. (Eds.). Science and Technology of Chemiresistor Gas Sensors, p. 177–214. New York, USA: Nova Science Publishers.

Ortega, A., Marco, S., Perera, A., Šundic, T., Pardo, A. and Samitier, J. (2001). An intelligent detector based on temperature modulation of a gas sensor with a digital signal processor. *Sensors and Actuators, B: Chemical*, 78(1–3), 32–39. https://doi.org/10.1016/S0925-4005(01)00788-2

Schmidt, E. (2016). Production of Essential Oils. In Baser, K.H.C. and Buchbauer, G. (Eds.), Handbook of Essential Oils: Science, Technology and Applications. 2nd ed., p. 1116. Boca Raton, USA: CRC Press.

Schmidt, E. and Wanner, J. (2016). Adulteration of Essential Oils. In Baser, K.H.C. and Buchbauer, G. (Eds.), Handbook of Essential Oils: Science, Technology and Applications. 2nd ed., p. 1116. Boca Raton, USA: CRC Press.

Silalahi, F.T.R., Simatupang, T.M. and Siallagan, M.P. (2020). Biodiesel produced from palm oil in Indonesia: Current status and opportunities. *AIMS Energy*, 8(1), 81–101.

Sudarmaji, A. and Kitagawa, A. (2015). Sensors and Transducers Temperature Modulation with Specified Detection Point on Metal Oxide Semiconductor Gas Sensors for E-Nose Application. *Sensors and Transducers*, 186(3), 93–103.

Sudarmaji, A., Margiwiyatno, A., Ediati, R. and Mustofa, A. (2018). Vapor Measurement System of Essential Oil Based on MOS Gas Sensors Driven with Advanced Temperature Modulation Technique. *IOP Conference Series: Earth and Environmental Science*, 147, 012046. https://doi.org/10.1088/1755-1315/147/1/012046

Sun, Y., Huang, X., Meng, F. and Liu, J. (2004). Study of Influencing Factors of Dynamic Measurements Based on SnO2 Gas Sensor. *Sensors*, 4(6), 95–104. https://doi.org/10.3390/s40670095

Wilson, A.D. and Baietto, M. (2009). Applications and advances in electronic-nose technologies. *Sensors*, 9 (7), 5099–5148. https://doi.org/10.3390/s90705099

