5. AIP 2023_Characteristics of array MOS gas sensors in detection of adulteration on patchouli oil with candlenut oil

by Arief Sudarmaji

Characteristics of array MOS gas sensors in detection of adulteration on patchouli oil with candlenut oil

Cite as: AIP Conference Proceedings **2586**, 070016 (2023); https://doi.org/10.1063/5.0106394
Published Online: 24 January 2023

Arief Sudarmaji, Agus Margiwiyatno and Susanto Budi Sulistyo

Characteristics of Array MOS Gas Sensors in Detection of Adulteration on Patchouli Oil with Candlenut Oil

Arief Sudarmaji[1, a)], Agus Margiwiyatno[1, b)], and Susanto Budi Sulistyo[1, c)]

[1] Department of Agricultural Engineering, Faculty of Agriculture, Jenderal Soedirman University, Jl. Dr. Soeparno, Karangwangkal, Purwokerto 53132 Indonesia

[a)] Corresponding author: arief.sudarmaji@unsoed.ac.id
[b)] agus.margiwiyatno@unsoed.ac.id
[c)] susanto.sulistyo@unsoed.ac.id

Abstract. The high price of essential oils, especially Patchouli Oil, leads to adulteration by mixing with cheaper oils. The similar color and viscosity make it difficult to be recognized or distinguished by human sensing. In general, a technique for measuring essential oils is to use capillary Gas Chromatography/Mass Spectrometry (GC/MS). However, GC/MS is high cost, time-consuming (requires sample preparation), and requires adequate skill. This study aims to determine the characteristics of gas sensors made from Metal Oxide Semiconductor (MOS) which is used to detect adulteration of patchouli oil with candlenut oil. The measurement uses 9 MOS to capture gas/aroma from samples in a chamber. The output of MOS is acquired in a PC. The sample tested is pure Patchouli Oil, pure Candlenut Oil, 1% mixture, 5% mixture, 10% mixture, 15% mixture, and 20% mixture. The mixture is Patchouli Oil with Candlenut Oil. The individual response characteristics and the MOS series were analyzed using box plot graphs and Principal Component Analysis (PCA) respectively. It is found that modulation on MOS led the sensors more sensitive and PCA results showed that the system is adequate to distinguish mixing of in Patchouli Oil.

INTRODUCTION

Patchouli Oil is one of Indonesian potential export products which has high price in the international market. Indonesia holds up to 85% world market share of Patchouli Oil [1], and is the three larger of International supplier of Patchouli Oil [2][3]. 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 [4].

Patchouli Oil is mostly resulted by Small and Medium Enterprises (SMEs) from steam distillation of patchouli plant (*Pogostemon cablin Benth*) 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. Many Patchouli Oil made by SMEs has not met the quality requirement to be exported.

The high economic value and high demand of Patchouli Oil, lead to its adulteration 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. Candlenut Oil is one of cheaper oils and has same color which can disguise its presence in Patchouli Oil. 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 [1]. Thus, it is needed an instrumental technique to assure the authenticity of Patchouli Oil by indicating the presence of sufficient accuracy for the level of SME.

The determination of Patchouli Oil contents accurately and widely applied using the Gas Chromatography-Mass Spectrometry method. GC and HPLC physical-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

The Third International Symposium on Food and Agrobiodiversity (ISFA 2021)
AIP Conf. Proc. 2586, 070016-1–070016-7; https://doi.org/10.1063/5.0106394
Published by AIP Publishing. 978-0-7354-4231-3/$30.00

[5][6]. However, this method may not be used by SMEs because of the complexity of use and the price of the equipment is very expensive, cannot be done by 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 [7] distinguished essential oils from sweet oranges, chamomile flowers, and jasmine flowers, and [8] 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 [9][10][11][12]. This technique was further developed by [13] known as Temperature Modulation with Specified Detection Point (Temperature Modulation-SDP). The use of MOS in detection of Patchouli Oil has been also done by [14] that successfully distinguished between Patchouli Oil and Clove Oil clearly. However, there are no studies yet that test the modulations on MOS gas sensors to detect the Patchouli Oil adulteration (such as with Candlenut Oil). Since the applied modulation leads unique response to a particular substance, it is believed that the modulations will change according to the adulterant of Patchouli Oil. Therefore, this paper presents the characterization of array MOS gas sensors that driven in Temperature Modulation to indicate the adulteration substance (i.e., Candlenut Oil) in Patchouli Oil.

MATERIAL AND METHODS

The measurement materials include MOS gas sensors, sensor chamber, sample headspace, reference headspace, bottle vial, syringe/vapor injector, mini air pump, acquisition unit, and computer unit with acquisition interface software. The solution samples consist of pure Patchouli Oil, pure Candlenut Oil, and mixture of Patchouli Oil and Candlenut (i.e. 5%, 10%, 15%, and 20%). Thus, we examined 6 categories of solution samples. While the content of Patchoulol (patchouli alcohol) of Patchouli Oil were tested using the Gas Chromatography-Mass Spectrometry (GC-MS) method.

The measurement setup and apparatus of measurement are shown in Fig. 1 and Fig. 2 respectively. The nine MOS gas sensors (Table 1), which aimed to sense several odorous gases and volatiles, were used to capture the vapor of Patchouli Oil. All sensors were put inside a sensor chamber made of 5 mm acrylic and formed into 693 cm^3 square box (11x9x7) cm. MOS gas sensors are operated in dynamic mode with temperature modulation-SDP technique. We tested 3 modulations: without modulation, 0.25 Hz modulation, and 1 Hz modulation. The outputs are acquired to a computer through PSoC CY8C28445-24PVXI based interface unit and xBee wireless communication. The excel file is created to store the output data.

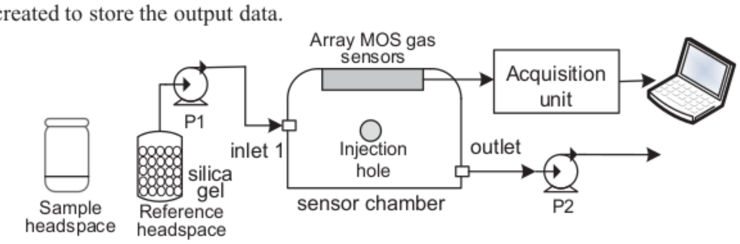
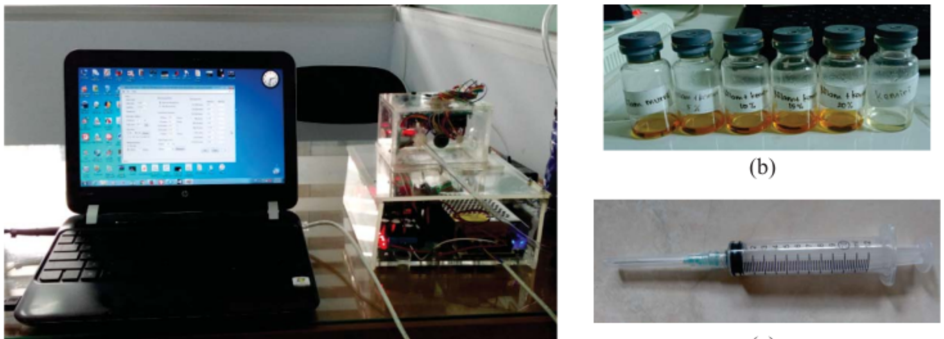


FIGURE 1. Measurement diagram for capturing vapor of Patchouli Oil sample

TABLE 1. MOS gas sensor for capturing gases and volatiles of Patchouli Oil

No	Type	Main Gas/Vapor 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



(b)

(c)

(a)

FIGURE 2. (a) Measurement apparatus, (b) sample of Patchouli Oil in a 15 ml vial headspace, (c) 10 ml syringe for transporting gas and vapor of Patchouli Oil to sensor chamber

The samples used to be detected were as follow: (1) Pure (100%) Patchouli Oil, (2) Pure (100%) Candlenut oil, (3) Mixture of 5% of Candlenut oil in Patchouli Oil, (4) Mixture of 10% of Candlenut oil in Patchouli Oil, (5) Mixture of 15% of Candlenut oil in Patchouli Oil, and (6) Mixture of 20% of Candlenut oil in Patchouli Oil. We tested three Modulations to drive the MOS gas sensors: (1) Without Modulation, (2) 0.25 Hz Modulation, and (3) 1 Hz Modulation. Each measurement of sample was five times repeated. Thus, we got 90 measurements.

Vapor Measurement Steps

The solution sample is prepared as follow: An aliquot (1 mL) of sample solution was put inside the static headspace vial to generate its vapor. A 15 mL glass bottle with rubber cap was used as a static headspace vial. The vapor of Patchouli Oil was manually delivered to the sensor chamber using a 10 mL syringe when measuring step. One cycle measurement consists of two steps: Patchouli Oil vapor measurement (Rg), and purging phase as shown in Fig. 3.

The pumps (P1 and p2) were switched on when warming up and purging phase and 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 when warming up and purging process. 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.

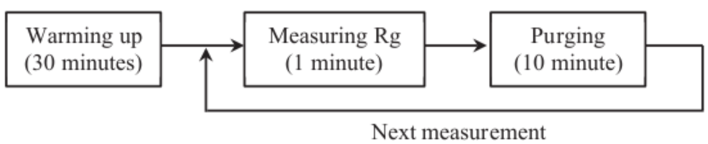


FIGURE 3. Measurement steps of Patchouli Oil.

Characterization and Analysis

We applied three ways to analysis the characteristic of MOS gas sensors in discriminating the type of samples for indicator the adulteration. They are: (1) The individual response characteristics using box plot method, (2) The significance of each MOS gas sensors to outputs in sensing samples using Loading plot of Principle Component Analysis (PCA), and (3) Classification Performance using score plot of Principle Component Analysis (PCA). PCA was performed by means of Minitab 16 Statistical Software.

RESULT AND DISCUSSION

Individual response of MOS gas sensors on various Patchouli Oil adulterations

One measurement (Rg) was acquired as many 30 data/sample, resulted from each 2 second in 1 minute measurement. We used box plot analysis to show the ability of MOS to sense and distinguish the five kinds of patchouli oil adulteration.

We found that the MOS sensors can sense vapor of patchouli oil with different adulterations. However, almost the responses of MOS gas sensors in each modulation driven were highly overlap, as exemplified in Figure 4. Therefore, there is no single MOS gas sensor used (i.e., general gases and volatiles sensor) that able to distinguish among the type of samples, especially discriminating the non-adulterated and adulterated Patchouli Oil.

The compound complexity of Patchouli Oil vapor might cause the overlapping response. [15] 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 [16] and to have poor selectivity (cross-sensitivity) to other gases [17,18]. MOS sensor could be selective to a certain gas but its cross-sensitivity to other gases was not negligible [19]. Table 2 shows detected peaks using GC-MS when measuring the 2 samples of Patchouli Oil.

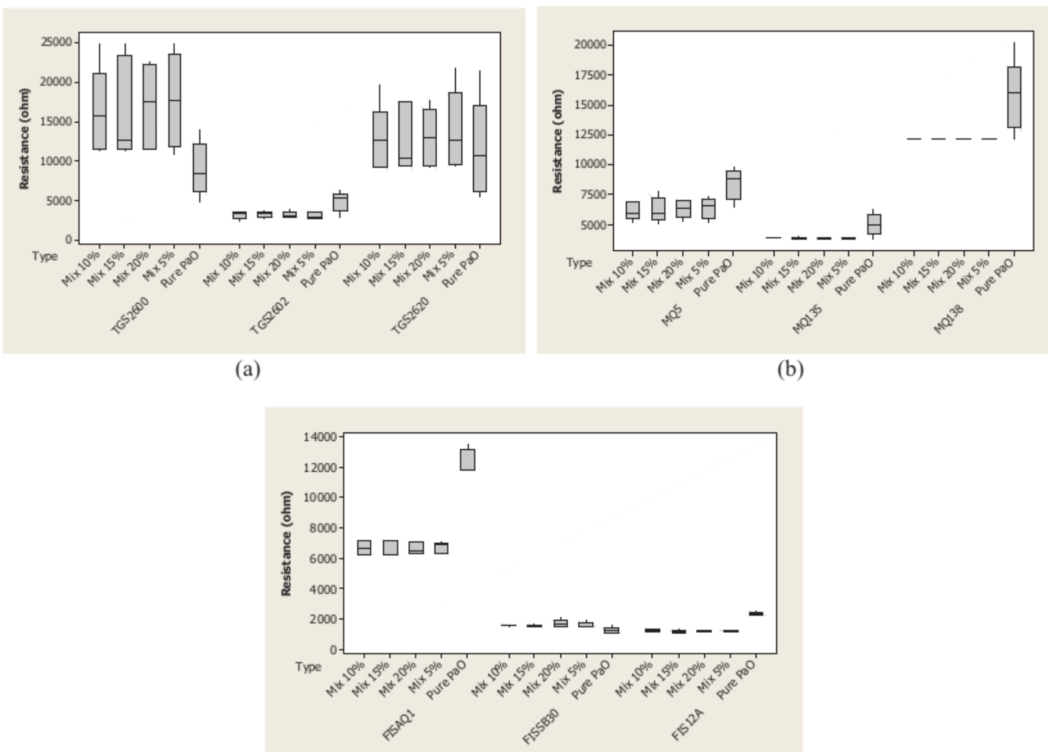


FIGURE 4. Box plot of (a) TGS series, (b) MQ series, and (c) FIS series on 0.25 Hz Modulation.

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

Identification of Patchouli Oil adulterations

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 Patchouli Oil performed by 9 MOS gas sensors used to each Modulation. It can be seen that Modulation on 0.25 Hz leads the sensors to give clear selective response to discriminate between pure and mixture of Patchouli Oil.

PCA result also reveals that the first two principal components were holding 76% 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 applications [20].

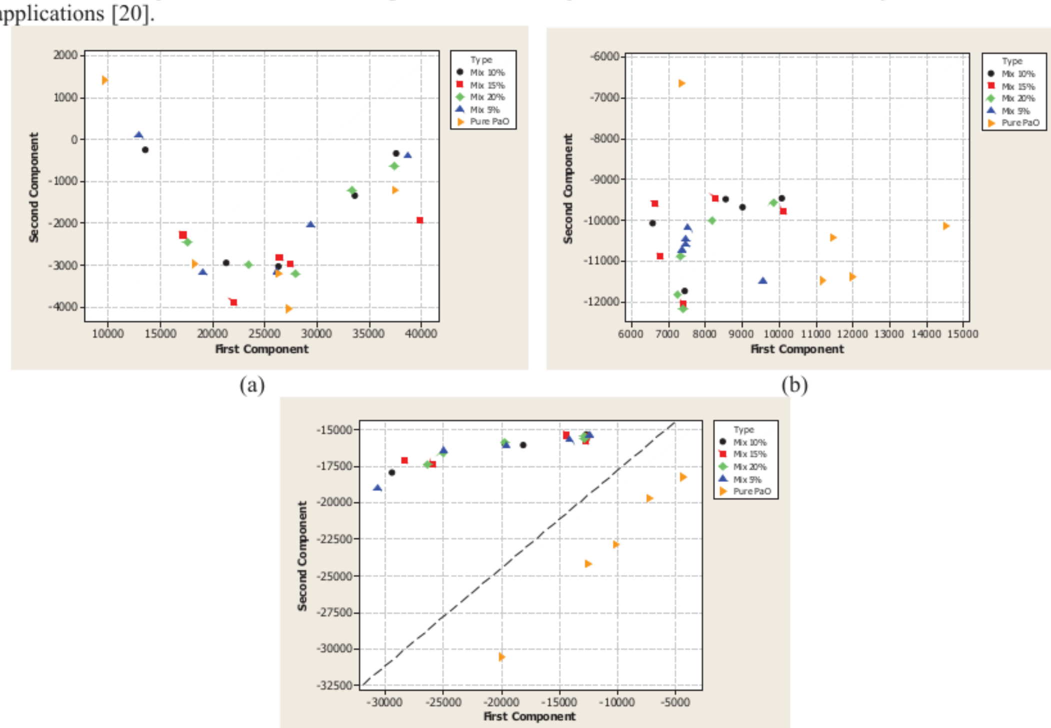


FIGURE 5. Score plots of each MOS gas sensor on (a) without modulation, (b) 1 Hz modulation, and (c) 0.25 Hz modulation

Then, 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 adulterations. As shown in Figure 6, the length of loading plots of all MOS gas sensors were not similar. Therefore, we chose only 6 MOS gas sensors that give high significance to evaluate their performance for indicating the presence of adulterant substance in patchouli oil. The 6 MOS gas sensors are TGS-2600, TGS-2602, TGS-2620, MQ-5, MQ-138, and FIS-AQ1.

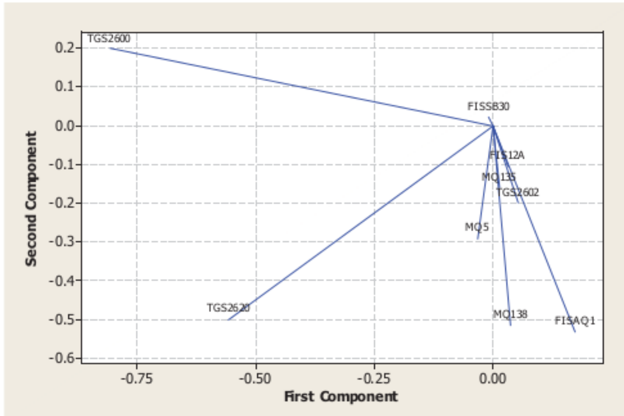
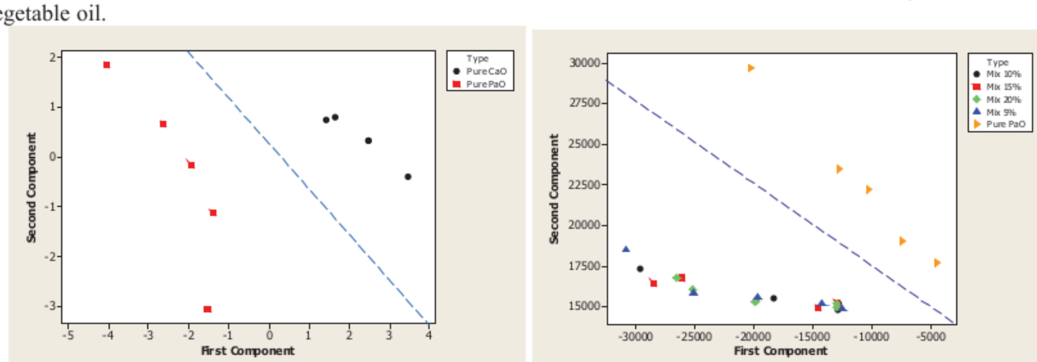


FIGURE 6. The loading plot on MOS gas sensor on 0.25 Hz Modulation

The performance of the 6 chosen MOS gas sensor to distinguish 6 samples of adulteration is shown in Fig. 7. It can be seen that using the 6 Selected MOS gas sensors, the selectivity performance of MOS to distinguish between pure Patchouli Oil and Mixed with candle Oil is similar to all MOS. It means the eliminated MOS gas sensors really less significance, yet the system still have same performance. However, it also reveals that there are many miss-clustering among groups of Patchouli Oil with adulteration to discriminate the level of composition/percentage. It seems that there is similar substance between Patchouli Oil and Mixed with candle Oil since they are made from vegetable oil.



(a) (b)

FIGURE 7. The performance of selected 6 MOS gas sensor to discriminate: (a) between pure Patchouli Oil and Candlenut Oil, and (b) between Pure Patchouli Oil and adulterated Patchouli Oil.

CONCLUSION

The research 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 vapor of Patchouli Oil in mixture Candlenut Oil by 5%, 10%, and 15%. It is found that the 6 most significant MOS gas sensors to discriminate between pure Patchouli Oil and mixture Patchouli Oil are TGS-2600, TGS-2602, TGS-2620, MQ-5, MQ-138, and FIS-AQ1) By PCA classification, the system which applied modulation of 0.25 Hz on MOS gas sensors is proper to distinguish clearly between pure Patchouli Oil and adulterated Patchouli Oil (mixed with Candlenut oil). However, it has not been able to determine the classification of the mixture level of the adulterated Patchouli Oil.

ACKNOWLEDGMENTS

Authors thank to Universitas Jenderal Soedirman and DIKTI for providing fund for this research through scheme of Riset Unggulan 2021.

REFERENCES

1. W. Haryono, Export News Indonesia: patchouli oil. Jakarta, Indonesia: 2015.
2. E. Schmidt. "Production of Essential Oils", In: Bas,er KHC, Buchbauer G, editors. Handb. Essent. Oils Sci. Technol. (Appl., Boca Raton, FL, CRC Press, Taylor & Francis Group, 2016), pp. 1116.
3. A. Hapsari. Indonesia Pensuplai Utama Tiga Komoditi Minyak Atsiri. Suara Merdeka News 2018.
4. Jandico. Aroma Atsiri: Price List August 2020. 2020.
5. E. Schmidt and J. "Wanner, Adulteration of Essential Oils", In: Bas,er KHC, Buchbauer G, editors. Handb. Essent. Oils Sci. Technol. (Appl., Boca Raton, FL: CRC Press Taylor & Francis Group, 2016), pp. 1116.
6. F. Swastawati., A. Ambariyanto., B. Cahyono., I. Wijayanti., D. Chilmawati., H. Hadiyanto, and A. N. Al-Baarri, Physicochemical changes and sensory quality of liquid smoked milkfish nuggets, African Journal of Food, Agriculture, Nutrition and Development 21, 18261–18278 (2021).
7. S. Kim, H. Kim, I. C. Lee, K. Cheong, and M. Lim, The quantitative analysis of aroma gas with gas sensors, Kor J. Aesthet Cosmetol 11, 1163–1179 (2013).
8. A. M. Gorji-chakespari., F. Nikbakht., M. Sefidkon., Ghasemi-varnamkhasti, and E. L. Valero, Classification of essential oil composition in Rosa damascena Mill. genotypes using an electronic nose, J Dermatol Sci 4, 27–34 (2016).
9. S. Ortega., A. Marco., T. Perera., Šundic., A. Pardo, and J. Samitier, an intelligent detector based on temperature modulation of a gas sensor with a digital signal processor, Sensors Actuators, B Chem 78, 32–9 (2001).
10. Y. Sun, X. Huang, F. Meng, J. Liu, Study of influencing factors of dynamic measurements based on SnO2 gas sensor, Sensors 4, 95–104 (2004).
11. X. Huang, F. Meng, Z. Pi, W. Xu, and J. Liu, Gas sensing behavior of a single tin dioxide sensor under dynamic temperature modulation, Sensors Actuators, B Chem 99, 444–50 (2004).
12. J. Liu, X. Huang, and F. Meng, The Dynamic Measurements of SnO2 Gas Sensors and Their Applications. (Nova Science Publishers, New York, NY, USA, 2007), pp. 177–214.
13. A. Sudarmaji and Kitagawa, Sensors and transducers temperature modulation with specified detection point on metal oxide semiconductor gas sensors for e-nose application, Sensors and Transducers 186, 93–103 (2015).
14. A. Sudarmaji, A. Margiwiyatno, R. Ediati, and A. Mustofa, "Vapor measurement system of essential oil based on mos gas sensors driven with advanced temperature modulation technique", in IOP Conf Ser Earth Environ Sci, edited by. (IOP Publishing, Bogor, 2018), pp. 1–10.
15. T. A. V. Beek and D. Joulain, The essential oil of patchouli, Pogostemon cablin: A review. Flavour Fragr J 33, 6–51 (2017).
16. A. Hierlemann and R. Gutierrez-Osuna, Higher-order chemical sensing, Chem Rev 108, 563–613 (2008).
17. A. Bermak, S. B. Belhouari, M. Shi, and D. Martinez. Pattern Recognition Techniques for Odor Discrimination in Gas Sensor Array, Encycl Sensors 10, 1–17 (2005).
18. S. Di Carlo and M. Falasconi, "Drift Correction Methods for Gas Chemical Sensors in Artificial Olfaction Systems: Techniques and Challenges" in Advances Chemical Sensor, (InTech, London, 2012) pp. 305–26.
19. A. Wilson and M. Baietto, Applications and advances in electronic-nose technologies, Sensors. 9, 99–148 (2009).
20. Z. Haddi, M. Bougrini, K. Tahri, Y. Braham, M. Souiri, N. El Bari., A. Maaref., A. Othmane., N. Jaffrezic-Renault, and B. Bouchikhi. A hybrid system based on an electronic nose coupled with an electronic tongue for the characterization of moroccan waters, Sensors & Transducers 27, 190–197 (2014).

5. AIP 2023_Characteristics of array MOS gas sensors in detection of adulteration on patchouli oil with candlenut oil

ORIGINALITY REPORT

10%	5%	9%	0%
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

MATCH ALL SOURCES (ONLY SELECTED SOURCE PRINTED)

9%

★ A Sudarmaji, A Margiwiyatno, R Ediati, A Mustofa. "Vapor Measurement System of Essential Oil Based on MOS Gas Sensors Driven with Advanced Temperature Modulation Technique", IOP Conference Series: Earth and Environmental Science, 2018

Publication

Exclude quotes	Off	Exclude matches	< 2%
Exclude bibliography	On		