Vapor Measurement System of Essential Oil Based on MOS Gas Sensors Driven with Advanced Temperature Modulation Technique

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Abstract. The aroma/vapor of essential oils is complex compound which depends on the content of the gases and volatiles generated from essential oil. This paper describes a design of quick, simple, and low-cost static measurement system to acquire vapor profile of essential oil. The gases and volatiles are captured in a chamber by means of 9 MOS gas sensors which driven with advance temperature modulation technique. A PSoC CY8C28445-24PVXI based-interface unit is build to generate the modulation signal and acquire all sensor output into computer wirelessly via radio frequency serial communication using Digi International Inc., XBee (IEEE 802.15.4) through developed software under Visual.Net. The system was tested to measure 2 kinds of essential oil (Patchouli and Clove Oils) in 4 temperature modulations (without, 0.25 Hz, 1 Hz, and 4 Hz). A cycle measurement consists of reference and sample measurement sequentially which is set during 2 minutes in every 1 second respectively. It is found that the suitable modulation is 0.25Hz; 75%, and the results of Principle Component Analysis show that the system is able to distinguish clearly between Patchouli Oil and Clove Oil.

1. Introduction
The aroma of essential oils is complex compound; hundreds of components can be present, and most of the components which confer aroma or flavor may be present only at ppm levels [1]. The vapor of essential oils is one of important attributes to indicate the quality of essential oil which depends on the content and amount of the gases and volatiles generated from essential oil. There are 30 volatiles components were identified from patchouli oils of Java, Sumatra and Sulawesi, with 5 main components such as patchouli alcohol, alpha guanine, seychellene, alpha patchouelene and alpha bulnesene [2]. On Bangladesh clove, it was found 38 components in its leaf oil with portion of main components, i.e. eugenol (74.3%), eucalyptol (5.8%), caryophyllene (3.85%) and a-cadinol (2.43%), while from its bud, 31 volatile components were identified and the main components were eugenol (49.7%), caryophyllene (18.9%), benzene,1-ethyl3-nitro (11.1%) and benzoic acid,3-(1-methyl ethyl) (8.9%) [3].

There are a number of causes in which the quality of essential oils can be varied, from the genetic variation and planting conditions to their harvesting, distillation processing, packing, and storage handling [4,5]. As a consumer, farmer or even supplier, it is difficult to assess quality sensuously.

Some analytical methods for qualitative and quantitative analysis of essential oils such as Gas Chromatograph and Mass Spectrometer provide accurate and selective readings. Capillary Gas chromatography-Mass spectrometry (GC-MS) proves to be an efficient and precise method for almost all combinations of components in such mixtures down to minute traces. It commonly used capillary column for the analysis of essential oils is Polyethylene Glycol (PEG). Most of the components of
essential oils are identified using capillary GC with Mass Detector [4,6]. The data can be compared to an established profile or fingerprint for that particular essential oil to finally determine the purity of that oil. However, those instruments are high cost, time-consuming (mostly requires sample preparation), large size, and maintenance cost [7]. Hence, it is difficult for rapid and on-site measurements.

This paper presents a design of quick, simple, and low-cost static measurement system to acquire vapor ‘fingerprint’ of essential oils. Nine MOS gas sensors are employed to capture vapors of essential oils. And, three environment sensors are used to measure temperature and humidity in sensor chamber, and temperature ambient. The MOS gas sensors are operated in dynamic mode by advanced Temperature Modulation technique. A Programmable System-On-Chip (PSoC) based interface system is built to generate the modulation and acquire all sensor data to a personal computer wirelessly through a developed program under Visual Studio. The PSoC is a hybrid (mixed-signal) device, beyond the traditional microcontroller, which has all traditional microcontroller features and reconfigurable analog and digital blocks. It is configured at programming to get specific use digital and analog components, provide flexibility in choices for the benefit and optimum particular systems [8].

2. Materials and methods

2.1. Material and Sample

The materials used to build the vapor measurement system of essential oils are generally divided into 3 units: sensors, interface/acquisition, and samples of essential oils.

1. Sensor material.

Gas and environment sensors used are shown in Table 1. Gas sensors are circuited with simple voltage divider circuit and operated in dynamic mode by technique of Temperature Modulation-Specified Detection Point (TM-SDP) as shown in figure 1. Gas sensors are placed in chamber which made of 5 mm transparent acrylic and formed into square box by size (11x9x7) cm$^3$.

| No | Type     | Main Target                        | Sensing Range     |
|----|----------|------------------------------------|-------------------|
| 1. | TGS2602  | Odorous gases (Ammonia, Ethanol)   | 1-100 ppm         |
| 2. | TGS 2620 | Solvent (organic) vapors           | 50–5,000 ppm      |
| 3. | TGS 2600 | Air Contaminants (H₂, CO)          | 1–30 ppm          |
| 4. | MQ5      | Natural gas, Coal gas              | 200–10,000 ppm    |
| 5. | MQ135    | Air Quality Control                | 10–200 ppm        |
| 6. | MQ138    | Wide volatile compound             | 200–10,000 ppm    |
| 7. | FIS12A   | Methane                            | 300–7,000 ppm     |
| 8. | FIS30SB  | Alcohol                            | 1–100 ppm         |
| 9. | FISAQ1   | Volatile organic compound          | 10–10,000 ppm     |
| 10.| LM35dz   | Temperature                        | 0–100 °C          |
| 11.| HSM30G   | Humidity                           | 10–90 %           |
| 12.| KE-25    | Oxygen                             | 0–100 %           |

Table 1. Gas sensors and environments sensor to capture essential oils profile.

Temperature modulation alters the kinetics of the MOS gas sensor through changes in the operational temperature of device through applying modulated voltage on its heater unit. The operating modulation voltage, also consequently the operating temperature, of the sensor changes periodically either by rectangular or triangular or sine waveform [9].

Principally Temperature Modulation-SDP is similar with general temperature modulation, which besides it modulates the temperature of heater unit, it also modulates the sensing (detector) unit that associated and in same phase with temperature modulation on the heater unit. SDP means the output detection (acquiring) of MOS gas sensor is put at specified point (i.e. at middle of sensing unit modulation) [10]. The signal of TM-SDP is shown in figure 1(c).
2. Interface/Acquisition.
Acquisition materials comprise of i) power supply unit, that provides voltage: -5V, +0.9V, +2.5V, +5V (3 pcs) and +12V, ii) PSoC CY8C28445-24PVXI, iii) Conditioning circuit for sensors, and iv) a pair of XBee (IEEE 802.15.4) with XBee USB Adapter Board 32400.

3. Samples of essential oils.
In this preliminary work, we tested 2 kinds of essential oils (Patchouli Oil and Clove oil). These two oils are potential commodities in Banyumas regency. The samples are taken from a supplier in Banyumas regency.

Figure 1. Sensor Circuitry of (a) TGSs, MQs and (b) FISs, driven in dynamic mode by (c) Temperature Modulation-SDP signal for capturing vapor profile of essential oils.

2.2. Methods

2.2.1. System Diagram. The measurement system of essential oils uses static headspace and static measurement (figure 2), which adopted from [11,10]. Sample Headspace (SH) of essential oils is a 15 ml glass vial with rubber cap. The vapor is delivered to sensor chamber manually using a 1 ml syringe. As Reference is dry air (filtered by silica gel) which pumped constantly to sensor chamber. The Mass Flow Controller (MFC) is set on 0.4 liter per minute (0.67 cm3/s).

A PSoC CY8C28445-24PVXI is employed as the center of interface unit to generate the TM-SDP signal for MOS gas sensors and acquire the outputs of all sensors to a computer wirelessly through Radio Frequency using XBee serial communication (IEEE 802.15.4) Digi International Inc. It has 24 pins GPIO, General Programmable Input Output [8]. We configured 20 GPIOs in PSoC as follow: 14 analog inputs for sensors, 4 digital outputs for TM-SDP signals, and 2 as Tx/Rx for serial communication, to accommodate the system (figure 3). We utilized PSoC Designer 5.4 to build the program into PSoC CY8C28445-24PVXI and Visual Basic.Net 2012 to develop interface software for acquisition in Personal Computer.

Figure 2. Diagram of static measurement for capturing vapor profile of essential oils.
2.2.2. Measurement steps. There are 4 phases in measuring vapor of essential oils with static headspace and measurement, i.e. Idle, Reference capturing (R<sub>o</sub>), Vapor capturing (R<sub>v</sub>) and Purging. The Idle, Ro, and Cleaning phases are the same, i.e. when the sensor does not measure the essential oils. The flow is set from the silica gel container to the purging pump by adjusting The Switch (S), Pump-1 (P1), Pump-2 (P2) are switched on. While the R<sub>v</sub> (measuring the vapor of essential oils) is by injecting the vapor to sensor chamber, the Switch (S), Pump 1 (P1), Pump 2 (P2) are switched off.

As sample preparation, 1 ml of essential oil solution is injected into the SH vial. And the amount of vapor of essential oils from SH vial to be injected into sensor chamber is 3 ml. One cycle measurement of essential oil sample, as shown in figure 4, consists of acquiring R<sub>o</sub> for 1 minute and followed by R<sub>v</sub> for 1 minute. After that the purging of sensor chamber is done in 10 minutes and back to idle phase. Each measurement of essential oil is repeated 5 times.

Response of MOS gas sensors is presented by Sensitivity (S), where R<sub>o</sub> is MOS resistance when measuring the reference (dry air) and R<sub>v</sub> is MOS resistance when measuring the vapor of essential oils.

\[ S = \frac{R_o}{R_v} \]  

3. Result and discussion

3.1. The measurement system of vapor of essential oils

Figure. 4 shows the built-system, program interface, static headspace (SH) vial, and injection process of essential oils vapor. The configurations of PSoC CY8C28445-24PVXI are shown in table 2 and figure 5. We set the pair of wireless serial communication XBee (IEEE 802.15.4) into direct transmission (point to point) using XCTU software, where one is set as coordinator while another act as a router [12]. Both XBees are configured 19200 bps, 8 bit of data, no parity, 1 stop bit and none flow control which accorded with PSoC serial communication.
The TM-SDP signal and output sensors are successfully generated and acquired respectively into personal computer wirelessly using developed software under Visual Basic.Net 2012. The software (figure 4(b)) is connected to Microsoft Excel to store and process data, such as: (a) create file, read and write data, and (b) determine automatically the average value of each sensor for each measurement mode (R_0 and R_V). Our acquisition software makes automatically 3 worksheets to store 2 mode measurement and fractional data at once procedure measurement.

**Table 2.** PSoC CY8C28445-24PVXI configuration for interface unit

| Part          | Important Configured Features                                                                 |
|---------------|---------------------------------------------------------------------------------------------|
| Global Resource | Sysclock=5V;24MHz, V_c1= 2MHz, V_c2=153.846kHz, V_c3= 10kHz, Ref Mux=±Vdd/2, Analog SC On/Ref High. |
| ADC Incremental | Clock=V_c1, 14 bits, Unsigned data format, normal clock phase.                               |
| Dual ADC      | Clock=V_c1, 13 bits, Unsigned data format, normal clock phase.                               |
| Timer8        | Clock=V_c3, Capture=High, Terminal count and compare out= none, Period=9, Interrupt type=Terminal count Invert capture=normal. |
| PGA           | 2 PGAs connected to Dual ADC and 1 PGA to ADC Inc, Ref=Vss                                       |
| UART          | Clock=V_c2→ 19200 kbps, 8 bit, no parity, 1 stop bit and none flow control                   |
| GPIO          | - 14 pins connected to Analog Mux Input, drive as High Z analog.                                |
|               | - 4 pins as Digital Output (StdCPU), drive Strong.                                              |

Figure 5. (a) Vapor measurement system, (b) acquisition program interface, (c) SH vial, and (d) vapor injection process.
3.2. The Temperature Modulation-Specified Detection Point (TM-SDP)

Modulations applied on MOS gas sensor were checked with oscilloscope Tektronix TDS-2024B. For instance as shown in figure 7, for desired TM-SDP 0.25Hz; 75%, the measured frequency of $V_H$ was 0.2510 Hz and the high of $V_C$ is laid in middle 75% of high of $V_H$. The acquiring of all MOS (in array) begins at middle of $V_H$ and takes 0.08s to complete it. The high of $V_H$ of TGS and FIS were measured about 4.98 V and 0.95 V respectively, and the $V_C$ of both TGS and FIS were 4.98 V.

By applying TM-SDP, it may lead to prevent sensor from possible migration of heater materials into the sensing material which could causes long-term drift of sensing material's resistance to higher values. It means that a pulsed-$V_C$ giving less force to drive migration than a constant $V_C$, rendering negligible possibility of migration, particularly when operated under high humidity and temperature [10].

Figure 6. (a) Configuration of PSoc CY8C28445-24PVXI using PoSC designer 5.4.

Figure 7. Captured signal of TM-SDP on MOS gas sensors of 0.25 Hz with duty cycle 25%, 50% and 75%, where: VH (orange) = 2V/div; VC (blue) = 5V/div; SDP (purple) = 5V/div; Time-Div = 1s.
3.3. Response of MOS gas sensors under various TM-SDP for Patchouli Oil and Clove Oil.
We tested the vapor measurement system to Clove Oil and Patchouli Oil for various modulation of TM-SDP, namely without modulation, frequency modulation (0.25 Hz, 1 Hz, and 4 Hz), and duty cycle modulation (25%, 50%, and 75%). During measurement, the condition of temperature environment was at 18.6 °C to 26.4 °C. While the oxygen level was at to 21.3 % to 25.8% (average 23.8%). The oxygen concentration in the chamber was conditioned manually by flowing oxygen gas inside the chamber when its level is below 21%. Typically the MOS gas sensors (such as TGSs) require the presence of minimum 21% (ambient) oxygen in their operating environment in order to work and properly [13].

The presence of minimum required ambient oxygen is essential to the sensor’s operation which means oxygen plays an important role to reducing gases and its concentration effected to detection of combustible which mediated by reaction with adsorbed oxygen on the sensor surface [14,15]. The behavior of steady-state resistance of MOS gas sensor is greatly influenced by the concentration of ambient oxygen and the reduced oxygen pressure will lead the decrement of the resistance of sensor [13].

Firstly, we investigated the responses of each MOS at a particular frequency of TM-SDP (for instance 0.25 Hz) with different duty cycle. We found that at TM-SDP of frequency 0.25 Hz, among duty cycle 25%, 50%, and 75%, the duty cycle 75% provided the most distinguished response to Clove Oil and Patchouli Oil. This result also shown by the TM-SDP of frequency 1 Hz and 4 Hz (figure 8). Secondly, by applying the 75% duty cycle we investigated the different frequency (0.25 Hz, 1 Hz, or 4 Hz). The results show that frequency 0.25 Hz provide most distinguished response (figure 9). Hence it reveals that the suitable TM-SDP which lead most selective response is the frequency 0.25 Hz; duty cycle 75%.

From the figure 8 and 9, it also shows that some MOS gas sensor has of each are a cross-sensitivity response. This is considered as a limitation of MOS gas sensors that potentially caused from temperature variation which changes the baseline of the sensor signal shifts. And the most significant, we found that under TM-SDP 0.25H; 75% the TGS2802 and MQ5 were the two most sensitive and selective to response and strongly discriminate between Clove Oil and Patchouli Oil. While FIS12A was very less sensitive to discriminate Clove Oil and Patchouli Oil. Intrinsically, the FIS12A are designed to sense the methane although it also may sense other gases. In other hand, it can be used only TGS2802 and MQ5 to distinguish between Clove Oil and Patchouli Oil.

3.4. Performance of array MOS gas sensor to distinguish Patchouli Oil and Clove Oil.
We utilized the Principal Component Analysis (PCA) to evaluate the selectivity performance of the system that uses array 9 of MOS gas sensors in identifying the Clove Oil and Patchouli Oil on each modulation. PCA is commonly used as feature extraction part to test distinguish (selectivity) performance and a powerful linear classification technique that is usually employed in correlation with cluster analysis and visualization the difference in similarities or differences among the treatments. The large dimension of interrelated variables is reduced into few important Principal Components (PCs).

We use the function of PCA and Graph Plot in Matlab 7.12.0 (R2011a). The input of PCA is the output (S value) of nine MOS gas sensor that operated under TM-SDP 0.25Hz; duty cycle 75%. And the PCA results show that collectively the two PCs hold 81.2% of data. However, by using those first two PCs, the system has been able to discriminate clearly as shown in figure 10. The first two or three uncorrelated components hold most significant of variation present in all variables and widely used in various application [16].
Figure 8. Responses of individual MOS gas sensor (S) to vapor of Clove Oil and Patchouli Oil under no modulation vs TM-SDP 0.25Hz duty cycle 25%, 50%, and 75% where: A=TGS2600; B=TGS2602; C=TGS2620; D=MQ5; E=MQ135; F=MQ138; G=FISAQ1; H=FISSB30; I=FIS12A.

Figure 9. Responses of individual MOS gas sensor (S) to vapor of Clove Oil and Patchouli Oil under TM-SDP Duty Cycle 75% with different Frequency, where: A=TGS2600; B=TGS2602; C=TGS2620; D=MQ5; E=MQ135; F=MQ138; G=FISAQ1; H=FISSB30; I=FIS12A.
4. Conclusions
In this paper, we present a preliminary work of potential application of MOS gas sensors which operates in a dynamic mode using technique of Temperature Modulation-Specified Detection Point (TM-SDP) to measure vapor of essential oils. Nine MOS gas sensors which designed to sense some volatile compounds were employed. We tested various TM-SDP both frequency and duty cycle to capture the volatile fingerprint of Clove Oil and Patchouli Oil. We found that the suitable TM-SDP which lead most distinctly response to Clove Oil and Patchouli Oil is the frequency 0.25 Hz with duty cycle 75%. PCA result shows that the system is able to distinguish clearly between Patchouli Oil and Clove Oil.

Moreover, it is also found that the TGS2602 and MQ5 are the two most sensitive and selective sensor to distinguish between Patchouli Oil and Clove Oil. Hence it is possible to use only them to distinguish those two essential oils when they operate on dynamic mode under TM-SDP 0.25 Hz; 75%.

Acknowledgements
This research is supported by Public Service Agency (BLU) of Jenderal Soedirman University. Authors also would like thank to Indonesian Directorate General of Higher Education (DIKTI) and additional acknowledgement to PT. Indesso Aroma Purwokerto.

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