RAPID METHOD FOR DETECTION OF ETHANOL CONTENT IN MOUTHWASH USING LOCALLY FABRICATED PORTABLE ELECTRONIC NOSE[1]

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Abstract

The purpose of this study is to check for ethanol (EtOH) content in mouthwash products sold in Malaysia market using portable electronic nose (e-nose). For this study, twenty mouthwashes were tested with nine of the samples contain EtOH as part of its ingredients. The problem with those products is that it does not disclose the concentration of the EtOH as part of its labelling. This is important since long-term use of ethanol-containing mouthwash may result in adverse health effect to the consumer. The process parameters used in this study was optimized using Response Surface Methodology (RSM), with strong relations between actual and predicted sensor response yield correlation of determination, R^2 of 0.9756. Optimum process parameters generated by Design Expert 7.1.5 shown that the optimum volume for EtOH sample was 5.84mL for 1.45 min time of detection. While for screening process, it was found that from the detection of alcohol-free mouthwash using portable e-nose, no alcohol content detected with "alcohol free" was displayed on the LCD screen of the device. However, 9 out of 10 mouthwash samples that have no "alcohol free" label on the products contain more than 10% (v/v) EtOH. Hence, this study had successfully optimized the process parameters and screened the mouthwashes sold in Malaysia market for the presence of EtOH.

Keywords: *ethanol; mouthwash; portable e-nose; optimization*

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1. Introduction

Mouthwashes are considered beneficial in the prevention and treatment of variety of oral or orophryngeal diseases such as gingivitis, periodontitis and other inflammatory conditions. Apart from the various therapeutically active ingredients in the mouthwashes such as essential oils, Chlorhexidine, Fluoride, Potassium Nitrate and Benzydamine, one ingredient that is present generally in every mouthwash is ethanol (EtOH). The concentration of ethanol in mouthwash product is between 0-27% that is high compared to the EtOH in beer (4%) and wine (12%). High concentrations of ethanol in mouthwash may have detrimental oral effects such as epithelial detachment, keratosis, mucosal ulceration, gingivitis, petechiae and oral pain [1]. Moreover, there is a possible connection between the long-term uses of ethanol containing mouthwash with oral cancer [2],[3],[5]. To check for the presence of EtOH in mouthwash, a portable e-nose was designed and fabricated for this purpose.

An E-Nose is basically a device that mimics human olfactory system [4] and it is a useful tool for EtOH detection since its allowed identification and fingerprinting of aroma. The use of E-Nose to detect a large number of chemical compounds is appropriate since the detection is based on the principal of gas chromatography, which allows chemical compounds to elute at different times and then the compounds will be detected by the sensitive sensor.

The portable e-nose used for this study, as shown in Figure 1, was designed to be very compact and small, so it can be carried around for an “on-line” detection of the mouthwash or beverage for EtOH detection. The way the device worked was simple which any layman can operate this portable E-Nose. The gas sensor will detect the presence of EtOH which later the output response will be received by the conditioning electronics. The received data were then analyzed by microcontroller and displayed the concentration of EtOH on the LCD display.

Figure 1 The Prototype of the Fabricated Portable E-Nose Used in this Study

The objectives of this study are to check for EtOH concentration in mouthwash product using the fabricated portable e-nose and to test the accuracy and reliability of the sensor used. Various mouthwash products used as samples and been tested by the E-Nose to detect the presence of EtOH substance in it. This study is important to check whether the concentration of EtOH in mouthwash product contain the specific concentration that is allowed.

2. Materials and Methods

2.1 Materials

Ethanol, 95% (v/v) was purchased from HmBg Chemicals Inc. (Germany). 20 mouthwash samples of different flavours from different brands were bought from a local market in Selangor; with 10 of them have "alcohol free" indication on the products' labelling.

2.2 Methods

2.1.1 Calibration

EtOH dilution of 0.1% (v/v), 1.0% (v/v) and 10.0% (v/v) were prepared for calibration purpose. Later, the result was saved in the e-nose database for further used during screening process. The EtOH sample of certain volume (2mL, 4mL and 6mL) was put inside a bottle

and the portable e-nose will take the reading based on the time set for the parameter, which is 0.5 to 1.5 minute with 30 seconds increment.

2.1.2 Screening Process

For screening process, experiments were conducted after optimum time and sample's volume generated from the optimization part in RSM. Then, twenty mouthwashes were tested with nine of the samples contain EtOH as part of its ingredients. Then, reading was taken after the portable e-nose is ready and the concentration of EtOH is displayed on the LCD screen of the device.

3. Results and Discussion

For calibration part, the result of the response will be in terms of an analogue value of the sensor response. While for optimization, process parameters were optimized using Design Expert 7.1.5 to get the optimum values of time and EtOH solution's volume. Lastly, screening of twenty mouthwashes of different flavours from different brands sold in Malaysia market was done, which the results were successfully displayed on the LCD display of the portable E-Nose.

The portable e-nose used for this study can give rapid detection up to 10s at 20% (v/v) and above, of the EtOH concentration. The analogue value starts to spiked rapidly once the EtOH sample was put near the sensor of the e-nose (less than 1s) but will keep on increasing until it goes constant, which reaches its maximum value. Hence, the time chosen as one of the process parameters was up to 1.5 min.

3.1 Calibration Process

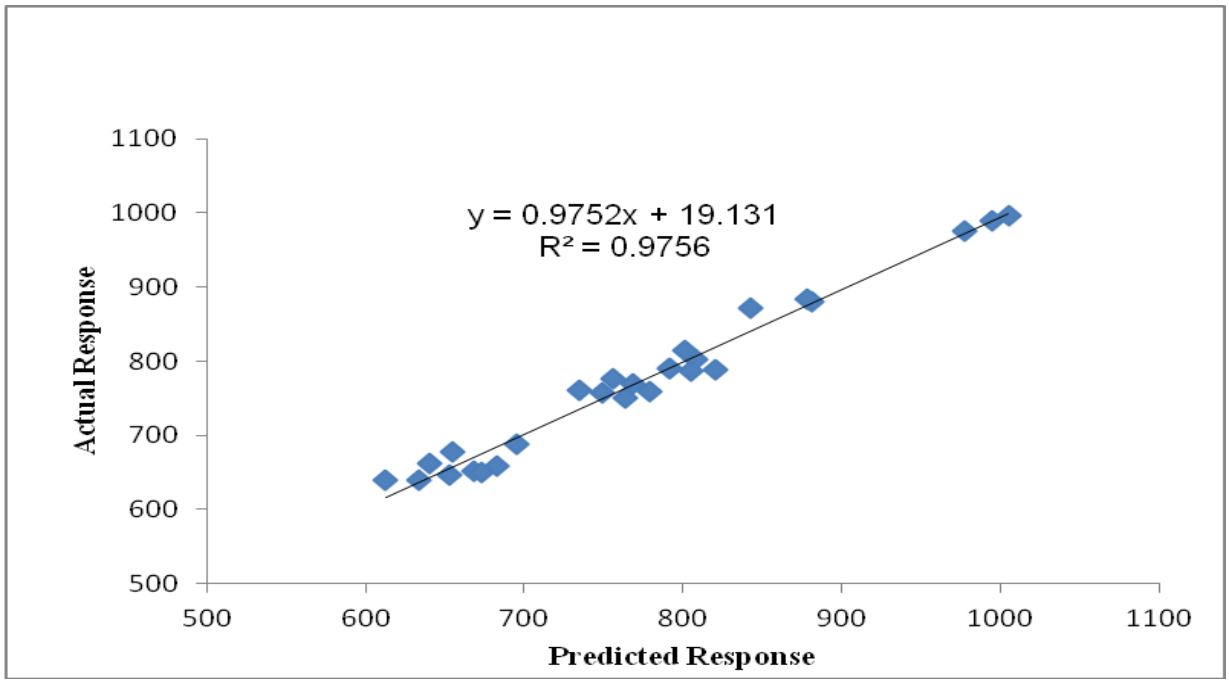
Based on the data in Table 1, it was found that the higher the concentration of the EtOH detected, the higher the analogue value of the sensor response recorded by the portable e-nose. Time of the detection as well as the sample's volume is also plays an important role in increasing the response of the sensor. However, from the observation, the highest concentration had consumed more power for the e-nose, which will result in a shorter amount of time to use the device. This happens because the VOC adsorbed by the sensor was too saturated, which will increase the resistance of the sensor, hence increase the voltage needed for the e-nose to operate. This device has to be used when it is in an optimum condition which the battery is fully charged, or should be around 7v - 9v left, so the results can be taken accurately.

The data shown in Table 1 is also showing two kinds of result which are the actual and predicted sensor response. Actual reading is actually taken from the experimental result, to observe the sensor response while the predicted sensor response was generated from the RSM of the design expert software. From the data, it was found that the results of both responses are not too deviating from each other and this is shown in Figure 2, as most of the responses showed a close relationship between actual and predicted values. From the plotted graph, the R^2 value is 0.9756, which proves that there is a strong relation between both values.

Table 1 Historical Data Design with Experimental and Predicted Values of the Sensor Response.

Run	***Time (min)***	***Sample Volume (mL)***	***EtOH Conc., % (v/v)***	***Actual Sensor Response***	***Predicted Sensor Response***
1	0.5	2	0.1	613	639
2	0.5	4	0.1	633	640
3	0.5	6	0.1	640	662
4	1	2	0.1	653	647
5	1	4	0.1	668	652
6	1	6	0.1	655	678
7	1.5	2	0.1	673	650
8	1.5	4	0.1	683	658
9	1.5	6	0.1	696	688
10	0.5	2	1	763	750
11	0.5	4	1	779	759
12	0.5	6	1	820	788
13	1	2	1	749	758
14	1	4	1	769	770
15	1	6	1	808	803
16	1.5	2	1	735	760
17	1.5	4	1	756	777
18	1.5	6	1	801	814
19	0.5	2	10	805	786
20	0.5	4	10	843	871
21	0.5	6	10	977	976
22	1	2	10	791	791
23	1	4	10	881	880
24	1	6	10	994	989
25	1.5	2	10	791	791
26	1.5	4	10	878	883
27	1.5	6	10	1005	997

Figure 2 The graph of Actual versus Predicted of the Sensor Response.



3.2 Optimization Process

Another objective of this study is to optimize the process parameters using historical data of RSM. For optimization part, time and sample's volume were set "in a range" while sensor response was set as "maximum". These parameters were set with the specific requirement because optimization process for this particular studies is concerning with the highest sensor response can be detected by the portable e-nose. From the results of those parameters, which have been conducted in 27 runs, the highest sensor response of EtOH generated by the software was 1056.81 which was shown in Figure 3 of the contour plot of the optimization graph. While the optimum volume for EtOH sample was 5.84mL for 1.45 min time of detection. In similar case, Figure 4 shows the same result of the optimization graph, only in 3D surface graph. This is important to show the optimum parameters which represented by the 3D graph.

Figure 3 2D Contour Plots of the Optimization Graph.

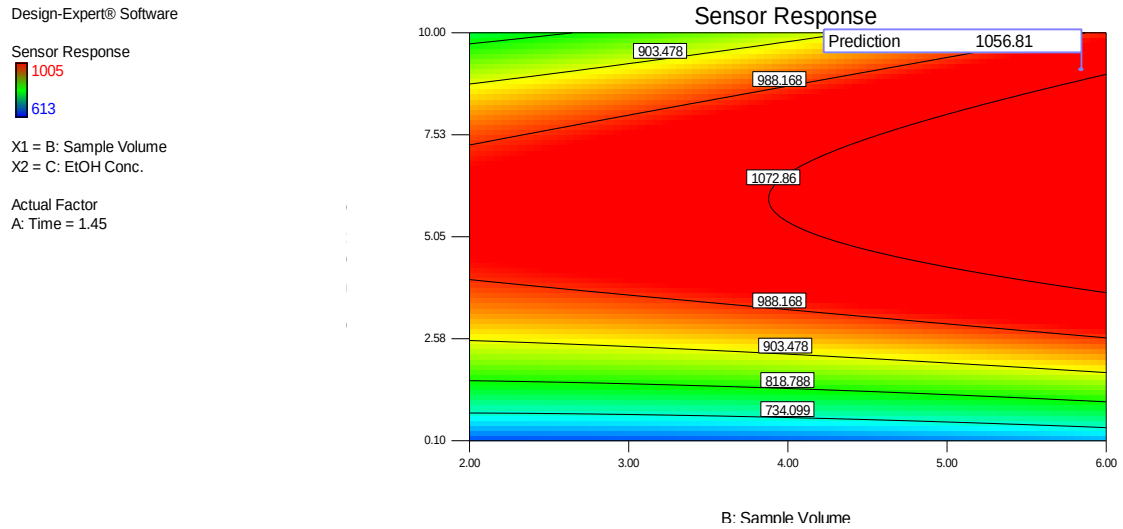
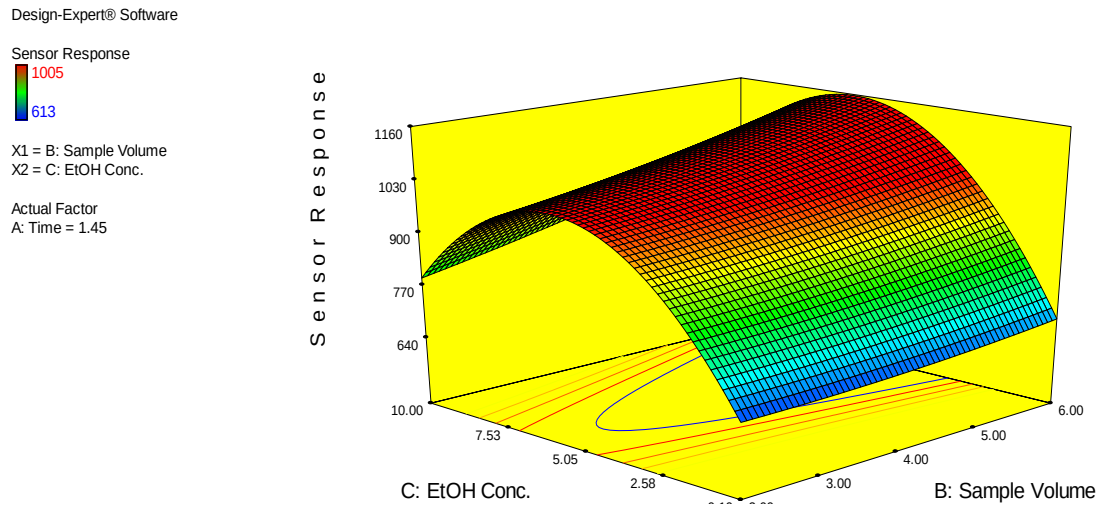


Figure 4 3D Surface Graph of the Optimization Graph



3.3 Screening Process

Detection of ethanol in 20 types of different mouthwash flavours and brands was tested using the portable e-nose prototype for a screening process. Based on the optimum time and EtOH volume from the Design Expert optimization, 5.84mL of mouthwash sample was tested and the result was taken after 1.45 min of the detection. Samples of mouthwash

products were tested, as shown in Table 2 which was from alcohol contained mouthwash and non-alcohol contained mouthwash.

For alcohol free mouthwash, all ten samples have halal logo from JAKIM on the product's label. When testing with the portable e-nose, the device has successfully validated the authenticity of the products, since it has shown "Alcohol Free" on the LCD screen of the device. While for the mouthwashes that has no halal logo, only sample L1 has no EtOH content presence in the sample, while others shown ">10% EtOH" displayed on the LCD screen. The concentration displayed is high that long term usage might give side effect to the consumer's oral health.

Apparently, it was also found that only sample L1 resulted in "Alcohol Free" when testing it using the portable e-nose. This result supported by its labelling since it that has no halal logo on the product and EtOH was nowhere to be found as part of its ingredients, All 20 samples except for sample B1 disclose its ingredients as part of its labelling. Hence, the usage of the portable e-nose is important to check the availability of EtOH in the sample. Based on these findings, in can be concluded that the portable e-nose can be used to check for the presence of EtOH in mouthwash.

Table 2 Screening Process of Different Mouthwashes Sold in Malaysia Market.

Description on the product's label	***Sample***	***Result of EtOH conc.***	***Description on the product's label***	***Sample***	***Result of EtOH conc.***
Alcohol Free	C1	Alcohol Free	*Contain Alcohol*	L1	Alcohol Free
	C2	Alcohol Free		L2	>10%
	C3	Alcohol Free		L3	>10%
	C4	Alcohol Free		L4	>10%
	S1	Alcohol Free		L5	>10%
	S2	Alcohol Free		L6	>10%
	O1	Alcohol Free		G2	>10%
	O2	Alcohol Free		G3	>10%
	G1	Alcohol Free		G4	>10%
	G5	Alcohol Free		B1	>10%

4. Conclusion

This study has successfully calibrated, optimized and screened EtOH content in mouthwash samples bought from Malaysia market using portable e-nose prototype. It was found that all three process parameters; time (min), sample volume (mL) and EtOH concentration % (v/v) can affect the sensor response value, as the higher the parameters was

set, the higher the analogue value displayed by the device. From the calibration process, the lowest concentration of EtOH detected by the portable e-nose was 0.1% (v/v). Apart from that, the strong relations between actual and predicted sensor response yield correlation of determination, R^2 of 0.9756. While for optimization process, optimum time and EtOH sample generated by RSM was 5.84mL for 1.45 min time of detection. In screening process, it was found that from the detection of alcohol-free mouthwash using portable e-nose, the LCD has displayed "Alcohol Free" upon the detection, while 9 out of 10 mouthwash samples of ethanol-containing-mouthwash showed ">10% EtOH" on the LCD screen. Hence, this study had successfully optimized the process parameters and screened the mouthwashes sold in Malaysia market for the presence of EtOH.

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