Design of Microcontroller-Based Potentiostat for Determination of Ethanol Integrated with Smartphone through Internet of Things

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Abstract. Ethanol is the most alcohol used in daily life. Ethanol can be found in drinks, cosmetics, medicines, flavorings, and many more. Each product requires a different concentration of ethanol. Ethanol concentration can be measured using conventional alcohol meter, but requires a large number of samples and mistaken from reading the measurement can occur. This study aims to make a potentiostat based on the microcontroller to determine ethanol concentration that is easy and accurate. Potentiostat consists of several components of resistors, capacitors, operational amplifiers, and Arduino Mega 2560. Measurements were carried out using the electrochemical analysis fixed potential amperometry which the fixed potential was determined by linear sweep voltammetry. Carbon (C) is used on the working electrode and counter electrode which act as the sensor. From the test results obtained a negative relationship between the increasing concentration against current with a correlation coefficient 0.9998. The level of precision and accuracy of the device that has been made shows good results. The level of precision represented by the mean relative standard deviation (MRSD) obtained a result of 95.18%. While the accuracy value represented by the root mean square error (RMSE) results of 97.08%.

1. Introduction

Ethanol (also called ethyl alcohol, pure alcohol, or simply alcohol). Ethanol is included in a single chain alcohol, with the chemical formula C2H5OH and empirical formula C2H6O [1]. Ethanol is a volatile, flammable, colourless, and the most commonly used alcohol in everyday life. Ethanol can be found in beverages, cosmetics, antiseptics, as fuel for vehicles (bioethanol), medicines, flavourings and food colouring, and as a synthesis material to produce other chemicals such as acetic acid (CH3COOH).

Ethanol sold on the market usually has concentrations of 70%, 96%, and 99%. But in its use, ethanol concentration has to be adjusted to the needs. For example, in beer the alcohol content is used 2-6%. 30-40% perfume, 70% antiseptic, 99-100% bioethanol, and much more. To meet the required concentration the easiest way is by dilution. After doing the dilution it is necessary to measure the ethanol level whether it is appropriate or not because sometimes between practice and theory is not appropriate.

Ethanol concentrations can be measured conventionally using a hydrometer or alcohol meter which based on Archimedes' Law principle. In measuring ethanol concentrations with alcohol meters it...
requires at least 270 mL test samples, and because ethanol is a colourless liquid, the reading results in alcohol meters will be difficult because the values below the liquid can still be read so that it can make the eyes fooled that can make mistakes in reading the measurement results.

In addition to conventional methods, accurate measurement of ethanol levels can be done through methods such as capillary electrophoresis, high-performance liquid chromatography, gas chromatography-mass spectrometry, gas chromatography, NMR spectroscopy, and Raman spectrometry [2]. This method takes a lot of days and must be done in a laboratory that requires a lot of costs.

Research conducted by Adnyana et al. [3] has made a device to detect alcoholic (ethanol) levels digitally based on the ATmega328 microcontroller using the MQ-3 gas sensor. The use of gas sensors, alcohol in the form of liquid must be preheated so as to produce steam then detected by the MQ-3 sensor which this course is not practical.

Reza et al. [4] reported having succeeded in making a portable device to detect the ethanol content of alcoholic drinks without having to be heated into steam. The device made is a unit of the sensor in the form of Nickel (Ni) as a working electrode, and Platina (Pt) as a comparative electrode, microcontroller, and transimpedance op-amp. The electrochemical analysis technique used is cyclic voltammetry. On the results of measurements made there is a negative relationship between voltage and alcohol content. From the linear equation, this device can only measure alcohol up to 83.71%.

The purpose of this study was to design and make a microcontroller-based potentiostat. Potentiostats are simple devices that rely on operational amplifiers to keep a desired potential difference between two electrodes (working and reference electrodes) immersed in a solution while recording the electrical current that flows between them. Normally a third electrode (counter electrode) is added to the system in order to isolate the electrode used as a potential reference from the charge transfer reaction [5]. A basic potentiostat can be assembled using a handful of simple electronic components consisting of some operational amplifiers, resistors, and amplifiers [6]. Determine the characteristics of carbon electrodes (C) as sensors, and determine the precision and accuracy of the device. It is expected that this device can be a solution in measuring ethanol concentration that are easy (portable), cheap, accurate, and integrated with smartphone through Internet of Things.

2. Methodology

The working principle of the device utilizes electrochemical analysis techniques. This technique analyses the behaviour of chemical compounds using electrical energy. There are two important components in this technique, those are electrodes and potentiostat. In this study, Carbon (C) will be used as a working electrode as well as auxiliary electrodes because it has a wide response range [7]. The potentiostat will control the voltage between the two electrodes. When the state is open circuit, the ions are idle. The voltage will be flowed from the working electrode (anode) to the auxiliary electrode. The cation around the working electrode will carry electrons to the auxiliary electrode and will be known as a change in current. This change in flow will be reprocessed by a potentiostat. In this study, the analysis technique to be used is a derivative of amperometry, called fixed potential amperometry, where linear sweep potential analysis techniques are used to determine the fixed potential to be used.
Figure 1 shows the design of the device that has been made, consisting of Arduino Mega 2560, MCP4725 Digital to Analog Converter (DAC), Operational Amplifier TL074 which is applied as a summing amplifier (Figure. 1A.), the most used of the op-amp circuits is the summing amplifier circuit[8], and transimpedance amplifier (Figure. 1C.), electrode as sensor (Figure. 1B.), and Analog to Digital Converter (ADC) ADS1015.

Because the Arduino Mega 2560 does not have a true digital to analog converter (DAC) but only pulse-width modulation (PWM) and for electrochemical analysis, the ramp signal should be applied to the potential controller, then the MCP4725 external DAC is used to generate a ramp signal.

\[ V_{out1} = -R_3 \left( \frac{V_{in1}}{R_1} + \frac{V_{in2}}{R_2} \right) \]  

Table 1. Truth table for the summing amplifier, showing its voltage output as a function of the DAC voltage/PWM level

| Input (digital level/voltage) | Output (V) |
|------------------------------|------------|
| 0 / 0V                       | +5         |
| 2048 / +2.5V                 | 0          |
| 4095 / +5V                   | -5         |

MCP4725 can only provide potentials from +0 to +5V, whereas in linear sweep voltammetry analysis requires a negative and positive potential, therefore an op-amp is applied as a summing amplifier is needed to provide the potential needed -5 to +5V. To achieve this, the values of R1, R2, and R3 need to be determined through (1) and the truth table in Table 1, where V_in2 has been set at -5V. The results are R1, R2, and R3 are 510k ohms, 1k ohms, and 1k ohms respectively.

\[ V_{out2} = -R_3 \left( I_{in} + \frac{V_{in}}{R_4} \right) \]
Table 2. Truth table for the transimpedance amplifier

| Input ($I_{in}$/µA) | Output ($V_{out}$/V) | ADC level |
|---------------------|----------------------|-----------|
| -200                | +5                   | 1700      |
| 0                   | +2.5                 | 850       |
| 200                 | +0                   | 0         |

The response from the sensor is in the form of current, while the Arduino Mega 2560 can only process voltage values with ADC. So, a current converter circuit is needed to become a voltage with a transimpedance amplifier. In this design, the current that can be handled is limited to -200 to 200 µA. To achieve this, the values of $R_4$ and $R_5$ need to be determined through (2) with the provisions in Table 2. The results are $R_4$ and $R_5$ is 24k ohms and 12k ohms. From the table it also can be seen that when the output voltage at +5V the digital level read by ADC is 1700, it is because the potential range input ADC is from -6.144V to +6.144V, so from 2048 to 4095 is for from -6.144V to -0V.

In measuring ethanol concentrations, a sample of 27 mL is placed in acrylic cuvette. The electrode will be placed on the cuvette lid, the distance between the electrodes is 4 mm according to the diameter of the electrode, the distance of the electrode interacting with the solution is 15 mm Figure 2. shows the design of the cuvette and sensor design.

After designing and fabricating the device, the next step is to do a preliminary test to assess the capabilities of the device that have been made and to verify the device if it was working as expected, a resistor 1 and 10k ohms is used. The resistor was connected between the working electrode and the counter and auxiliary electrode (which were short-circuited together). The potential for sweep from -2 to +2V then measures the current value.

Sensor characterization was carried out to find out the relationships between ethanol concentration and current, the amperometric linear sweep method will be used to test samples of ethanol solutions at a level of 3% and 84% while determining the fixed potential to be used fixed potential amperometry to measure ethanol levels. The potential in the sweep is from -3.33 to + 5V, then the current is recorded.

The next step is validation and analysis, carried out using the fixed potential amperometry analysis technique in several samples of ethanol content variations ranging from 0 (aquadest) to 84%. These ethanol variations have been validated using pycnometer and would be compared to the reading of the device. Each ethanol level is recorded as many as five times. One time recording data is taken every 10 ms for 1000 ms. Next is the analysis that aims to determine the performance of the device. The performance testing process uses two measurement methods, namely precision and accuracy. The term
precision is used to express the random measurement error. The level of precision is said to be high if in some experiments the measurement produces the same or not much different results. Accuracy calculates how close the measurement results are to the actual value. The level of accuracy is said to be high if the difference between the measurement results and the actual value is close to zero. Performance testing is carried out by measuring various variations of ethanol.

Figure 3. Internet of Things Infrastructure

Figure 3. shows the Internet of Things Infrastructure. The device connected to internet through Wi-Fi connection to send the result of measurement that will be stored at Blynk database. Blynk is a hardware-agnostic IoT platform with white-label mobile apps, and private clouds. User can view the result through smartphone.

3. Results

Figure 4. The results of device fabrication
Figure 4. shows the results of device fabrication, to take measurements, 27 mL of the ethanol is put into cuvette. To initiate measurements, press the push button on the rotary encoder, then after processing the results will be presented on an OLED screen. The OLED screen is a user interface (UI) that has a 128 x 32 pixels resolution, the screen will show the display at idle, perform the measurement process, and display the measurement results.

![Figure 4](image)

Figure 5. Polarization curves for (A) 1kΩ resistor, (B1) 10 kΩ resistor, and (B2) 5kΩ parallel resistor association.

Based on the results of the preliminary tests that have been done, it can be seen from the polarization curve of the resistor in Fig. 4. The potential increase is proportional to the increase in current passing through the resistor. The red and blue lines are linear lines of the curve with a very good correlation coefficient \((R^2)\) which is 0.99998; 0.99999; and 0.99999 for 1k, 5k and 10k ohm resistors respectively. This indicates that the device is working properly, and is ready for use in electrochemical analysis. The resistor value can be known through the inverse value of the slope of the line, the resistor value is 999.73 ± 2.7 ohm; 9958.04 ± 115.8 ohm; 4996.548 ± 61.01 ohm.

![Figure 5](image)

Figure 6. Sensor characterization using linear sweep voltammetry

The following is the result of sensor characterization that has been done which is presented in Fig. 5. It can be seen that at the potential of -3.33V the current is negative, meaning that cation diffuses into the cathode because it has a small ionization tendency than the anode. Conversely, when the current is positively diffused anion to the anode because the ionization slope changes to be greater than the cathode. These ions carry an electric charge which is flowed by the electrode. The lower the level, the
more the number of ions will occur because ions are present in water molecules and more electricity can be carried.

A case example when the potential is given is -3.33V, seen in the graph that the current at 3% ethanol concentration is -219.72 µA, at 84% ethanol concentration of -71.95 µA. However, when the potential is given at + 3.33V the current at 3% ethanol concentration is only 127.68 µA, at 84% ethanol concentration of 41.14 µA. This means more current flows when negative potential is given. It is also seen in the graph that the two ethanol variations in the sweep from -3.33 to + 5V have not seen a decrease in the current in the positive region and the increase in the current in the negative or anode peak potential and the cathode peak potential. This means that the potential width range needs to be widened to obtain the anode and cathode peak potential so that it can be used as a parameter for the fixed potential determination of the fixed potential amperometry analysis technique. However, this research can use potential in the negative and positive regional boundaries. This study chose potential in positive areas that have a range of +0 to + 5V. Potential + 2.5V is chosen because of the middle point. If it is too high the stability will be low, while if it is too low the accuracy will decrease.

After getting a fixed potential value obtained from sensor characterization. Then the fixed potential amperometry analysis technique uses potential + 2.5V. Data collection was carried out on variations in ethanol levels ranging from 0% to 84%. Each ethanol level is recorded five times, one time recording data is taken every 10 ms for 1000 ms.

![Figure 7. (A) Graphic of current respond against ethanol concentration (B) selected data](image)

Current values are plotted against concentration, then analysed by linear regression methods resulting in the linear lines shown in Fig. 7A. A good correlation coefficient is obtained, namely $R^2 = 0.9989$ with a linear equation $y = -98.10246x + 129.0151$. From this equation, one of the best data from each concentration will be found so that the most linear results are obtained. After getting the least error data, then the data is plotted again and analysed again by linear regression. The results are shown in Fig. 7B. better correlation coefficient value obtained is $R^2 = 0.9998$ with linear equation $y = -97.79124x + 128.7264$. Through this equation, it will be used to determine the ethanol content of the current value.

| Concentration (%) | Experiments (%) | Average (%) | Standard Deviation | RSD |
|-------------------|----------------|-------------|--------------------|-----|
| 84                | 83.78          | 83.78       | 84.03              | 83.78 | 0.16 | 0.19 |
| 75                | 74.73          | 74.98       | 74.48              | 75.23 | 74.73 | 0.26 | 0.34 |
From the data that has been obtained, it is then analysed to determine the performance of the device with two measurement methods, namely the precision test and the accuracy test. Precision values are represented by the percentage of mean relative standard deviation (MRSD) of repeatability. The smaller the coefficient of variation after repetition, the better the precision. In testing the level of precision, the measurement results at the concentration of 0% (aquadest) are not involved, because it makes the results irrelevant. Can be shown at Table 3 that there is a slump the lower the ethanol concentration, the higher the RSD value. RSD value on 84% ethanol concentration measurement; 75%; 60%; and 55% sequentially 0.19%; 0.34%; 0.77%; and 1.31%; looks increasingly up but down on the measurement of 41% ethanol concentration of 0.91%; then back up to 32%; 22%; 13%; and 3% sequentially 2.60%; 4.28%; 6.85%; and 26.11%. Overall, the average standard deviation obtained is 0.64 and the average deviation relative deviation is 4.82% or in other words the level of precision is 95.18%. These results indicate that this device has a good level of precision.

Table 4. The result of accuracy performance test

| Concentration (%) | Experiments | Result (%) | Error (%) | Absolute Error (%) | RMSE (%) |
|-------------------|-------------|------------|-----------|---------------------|----------|
| 84                | 1           | 83.78      | -0.22     | 0.22                | 0.0484   |
| 84                | 2           | 83.78      | -0.22     | 0.22                | 0.0484   |
| 84                | 3           | 84.03      | 0.03      | 0.03                | 0.0009   |
| 84                | 4           | 83.78      | -0.22     | 0.22                | 0.0484   |
| 84                | 5           | 83.53      | -0.47     | 0.47                | 0.2209   |
| 75                | 1           | 74.73      | -0.27     | 0.27                | 0.0729   |
| 75                | 2           | 74.98      | -0.02     | 0.02                | 0.0004   |
| 75                | 3           | 74.48      | -0.52     | 0.52                | 0.2704   |
| 75                | 4           | 75.23      | 0.23      | 0.23                | 0.0529   |
| 75                | 5           | 74.73      | -0.27     | 0.27                | 0.0729   |
| 60                | 1           | 60.65      | 0.65      | 0.65                | 0.4225   |
| 60                | 2           | 60.65      | 0.65      | 0.65                | 0.4225   |
| 60                | 3           | 59.39      | -0.61     | 0.61                | 0.3721   |
| 60                | 4           | 60.15      | 0.15      | 0.15                | 0.0225   |
| 60                | 5           | 60.15      | 0.15      | 0.15                | 0.0225   |
| 55                | 1           | 54.11      | -0.89     | 0.89                | 0.7921   |
Table 4. The result of accuracy performance test

| Concentration (%) | Experiments | Result (%) | Error (%) | Absolute Error (%) | RMSE (%) |
|-------------------|-------------|------------|-----------|---------------------|----------|
| 55                | 2           | 54,62      | -0,38     | 0,38                | 0,1444   |
| 55                | 3           | 53,61      | -1,39     | 1,39                | 1,9321   |
| 55                | 4           | 55,62      | 0,62      | 0,62                | 0,3844   |
| 55                | 5           | 53,86      | -1,14     | 1,14                | 1,2996   |
| 40                | 1           | 40,79      | 0,79      | 0,79                | 0,6241   |
| 40                | 2           | 41,79      | 1,79      | 1,79                | 3,2041   |
| 40                | 3           | 41,29      | 1,29      | 1,29                | 1,6641   |
| 40                | 4           | 41,29      | 1,29      | 1,29                | 1,6641   |
| 40                | 5           | 40,79      | 0,79      | 0,79                | 0,6241   |
| 32                | 1           | 31,23      | -0,77     | 0,77                | 0,5929   |
| 32                | 2           | 31,74      | -0,26     | 0,26                | 0,0676   |
| 32                | 3           | 31,23      | -0,77     | 0,77                | 0,5929   |
| 32                | 4           | 32,74      | 0,74      | 0,74                | 0,5476   |
| 32                | 5           | 30,23      | -1,77     | 1,77                | 3,1329   |
| 22                | 1           | 21,43      | -0,57     | 0,57                | 0,3249   |
| 22                | 2           | 22,94      | 0,94      | 0,94                | 0,8836   |
| 22                | 3           | 21,18      | -0,82     | 0,82                | 0,6724   |
| 22                | 4           | 22,94      | 0,94      | 0,94                | 0,8836   |
| 22                | 5           | 20,67      | -1,33     | 1,33                | 1,7689   |
| 13                | 1           | 12,88      | -0,12     | 0,12                | 0,0144   |
| 13                | 2           | 11,62      | -1,38     | 1,38                | 1,9044   |
| 13                | 3           | 12,88      | -0,12     | 0,12                | 0,0144   |
| 13                | 4           | 10,87      | -2,13     | 2,13                | 4,5369   |
| 13                | 5           | 11,37      | -1,63     | 1,63                | 2,6569   |
| 3                 | 1           | 1,82       | -1,18     | 1,18                | 1,3924   |
| 3                 | 2           | 3,58       | 0,58      | 0,58                | 0,3364   |
| 3                 | 3           | 4,58       | 1,58      | 1,58                | 2,4964   |
| 3                 | 4           | 3,58       | 0,58      | 0,58                | 0,3364   |
| 3                 | 5           | 3,83       | 0,83      | 0,83                | 0,6889   |

Accuracy level is represented by root mean square error (RMSE). The smaller the RMSE value, the better the level of accuracy. From this result it can be seen that each measurement must have an error even though the value is small (less than 1.5%). This device has accuracy of approximately 0.25%; the round value is only found at 59%; 60%; and 61%. Possibly this could happen because at the time of sample validation of ethanol concentrations for data collection using Pycnometer data which has an accuracy of only 1%, it could be that the ethanol concentration tested for example is 10.20% but in the Pycnometer data the value is closest to 10% so the data should 10.20% is considered only 10%. Overall, the RMSE value is 0.9223 or in other words the accuracy rate is 99.08%. These results indicate that this device has a good level of accuracy.
Figure 8. Result displayed in smartphone

Figure 8. shows Bylnk application on smartphone that shows the result of measurements.

4. Conclusion
It has been successfully demonstrated that the fabrication and design of microcontroller-based potentiostat that is capable to determinate ethanol concentration in a solution using simple and readily available electronic components. The carbon that used as sensor can drain more current when negative potential is given. There is negative relationship between the increasing concentration against current with correlation coefficient $R^2 = 0.9998$ and the linear equation $y = -97.79124x + 128.7264$. The level of precision and accuracy of the device that has been made shows good results. The level of precision represented by the mean relative standard deviation (MRSD) obtained a result of 95.18%. While the accuracy value represented by the root mean square error (RMSE) results of 97.08%.

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