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Design of System Batch Injection Analysis (BIA) for Monitoring the Production of Alcohol (II)

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Abstract - *The main purpose of this work is to report the development of batch injection analysis (BIA) for monitoring the production of Alcohol. The activities focus on the concepts BIA and design of syringe pump and stepper pump. Both pumps were adjusted flow-rate and controlled by computer with microcontroller Arduino Uno R module using software Labview 2013 . The results showed that both pump have a good performance. This was marked by relation coefficient 0,99 and a little variance < 5%.*

Key word *: BIA, syringe pump, stepper pump, microcontroller, Labview, Alcohol.*

INTRODUCTION

Automated syringe pumps are used throughout research institutions, medical facilities, and industry for infusion and withdrawal of a wide variety of fluids at flow rates ranging from nL/hr to mL/sec, a range of more than nine orders of magnitude. A variety of automated syringe pumps

have been developed. Traditional approaches to automated syringe pump design have focused on reduction or elimination of dynamic behavior. Specially, dynamic behavior in the syringe is either designed out by using high stiffness materials (e.g. glass, stainless steel), or by operating syringes in steady-state configurations only (e.g. as in medical applications for drug delivery).

The most important aspect of a flow analysis system is the fluid propulsion process, which is usually performed using a peristaltic pump.(Prados-Rosales , 2002) Other fluid propelling devices, such as solenoid mini-pumps (Rodrigues , *at all*., 2012) and multisyringes, 35,36 have also been employed. While the peristaltic pump and solenoid mini-pump propel solutions forward, syringe pump operation comprises two alternating steps, one for solution loading and another for solution delivery. This working pattern has a potential limiting factor, but may be overcome by including solenoid valves in the manifold (Chaparro, *at. all*, 2015) .Syringe pumps have a relatively simple design that enables their construction without the need for sophisticated machining of components, thus making them cost-effective fluid propelling devices that can be constructed in a typical laboratory workshop.

Flow analysis, particularly flow-injection analysis, has received increasing attention in recent years because of its versatility in solution handling, simple instrumentation, richness of information, easy operation, high-sampling throughput, and low consumption of reagent and sample. Even though its potential for process analysis or industrial routine analysis is generally recognized and some practical applications have been reported , the number of practical applications is quite small compared with the large amount of research articles published. Although there are many reasons for this, such as the relatively later introduction of FIA compared with other instrumental methods, lack of reliable instruments and accurate methods for major components are two important factors.

In some flow analysis systems, syringe pumps rather than peristaltic pumps are used to transport liquids through tubing and simultaneously mix the solutions. Approaches include sequential injection analysis (SIA) (Ruzicka, 1990), lab-on-valve (LOV), hybrid flow analyzer (HFA) (Amornthammarong , 2006) , and multi-syringe flow (Cerda , 1999). In such systems mixing coils can be added to the flow path in order to improve mixing efficiency. In most situations the mixing achieved is not significantly different than in similarly arranged systems that use peristaltic pumps. In some cases, SIA and LOV in particular, it has proven difficult to attain the same levels of mixing efficiency. In an analytical system using a syringe pump the syringe itself can act as a primary mixing chamber but nonetheless an additional mixing coil is needed to enhance mixing (Sakamoto, 1996) . The advantage of using the syringe as a mixing chamber is its larger cross-section therefore higher Reynolds number.

The development of instrumentation for monitoring the production of alcohol in the bioreactor has changed very admirable. Various methods and sensors used to improve system performance in monitoring alcohol production. That methods include biocalorimetry (Türker, 2004), SIA techniques with biosensor (Lapa, 2003), Application of ATR infrared spectroscopy (Wolf, 1999). mid-IR spectroscopy (Schenk, 2007) and Near infrared spectroscopy in combination with chemometrics (Jin, 2013). Various sensors or transducers as support in monitoring also has such various types: potentiometric, amperometric, conductimetric, lmpedimetric, Optical, Calorimetric, Acoustic, Mechanical, and Molecular electronic.

However, in this study monitoring production of alcohol has used transducer of conductance made metal oxides.

The aim of this work is to design a syringe pumps for liquid propelling, sample/reagent introduction and component commutation, ensuring an effective and precise control of the sampled volume, either on a time-based or on a pulse counting-based strategy, and of its transportation towards the detector. In this sense, it would be then possible to modify the sampled volume at will, which could be exploited, for instance, to widen the linear working range of a determination. Moreover, the syringe pumps could be used also as mono-commuting devices that are operated individually for the selective introduction of reagents, assuring a versatile manipulation of the reagents addition process. The approach combines the favourable characteristics of the discontinuous flow (Cardwell, *at. All*, 1990), the multisyringe (Albertus , 1999), the tandem-injection (Israel, 1989) and the earlier multicommuted (Malcolme-Lawes, 1988) systems.

METHODS

A. Instrumentation

The oxide metal, MQ3, was used to sense cord the presence of ethanol in beverages. Data from the sensor was acquired every tenth of a second as an analogue voltage in the range 0–5V using a Arduino module. A homemade syringe pump was used in the BIA system, and the switching on and off and the direction of the pump were controlled using 5V TTL was controlled using the 0–5V analogue voltage output from Arduino module. 1.5mm i.d. pump tubing was obtained fromUpchurch Scientific® PEEK™ Tubing, IDEX Health & Science. Teflon tubing for the holding coil and detector coil was purchased from http://www.globalfia.com/store(USA). Software for the control of the pump and switching valve and for the data acquisition was written using the graphical programming language LabVIEW™ 2013(National Instruments). The BIA system used is as shown in Fig. 1 with the peristaltic pump and homemade syringe pump being attached to a a controller which is connected to the batch system.

B. Reagents

Alcohol (95–97%) was purchased from Merck (Darmstadt, Germany). Deionised water was produced using a Milli-Q with being characterized in terms of resistivity (typically 18.2 MΩ·cm at 25 °C). The 1% solutions of all alcoholic samples were prepared in order for their ethanol concentrations to be in the analytical range of the detection system.

C. Design of BIA System

Determination of ethanol in this study used BIA system. In this BIA system, the sample solution is passed into a batch using a syringe pump and diluted by flowing water into the batch, then the the alcohol content was detected by the alcohol sensor. Design of BIA system for analysis of ethanol content using oxide semiconductor sensor shown in figure 1.

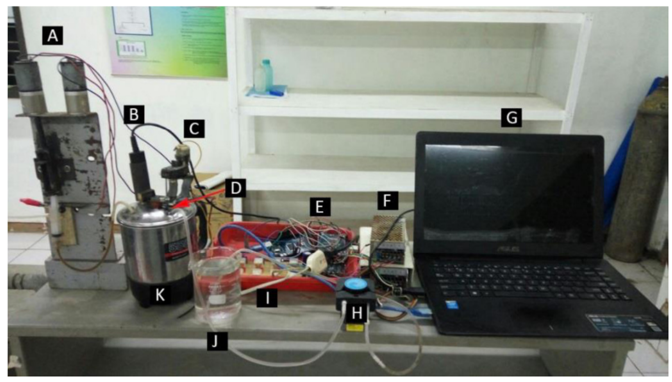

Figure 1. Design of BIA system Syringe pump B. Temperature sensor C. Stirring motor D. Alcohol Sensor E. Arduino module F. Power Supply G. Computer H. Stepper Pump I. Tube J. Vessel K. Batch

The picture shown in Figure 3.1 is a set of device which actually used in this research, whereas in Figure 3.2 BIA system is a scheme based on the actual instrument design.

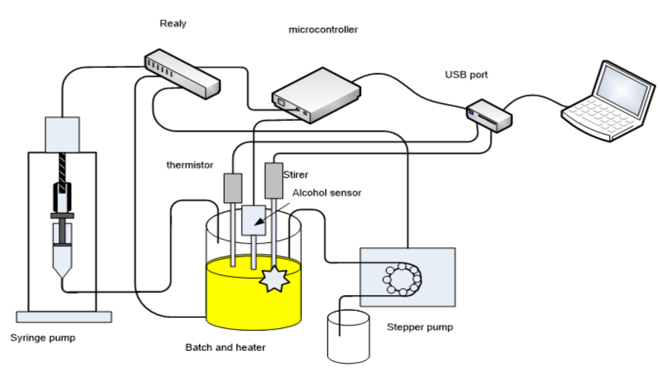

Figure 2. Schematic of analysis system

The schematic system shown in Figure 2. consists of a syringe pump with tube 7 cm long and diameter 2.4 mm that serves to drain the ethanol into a batch, while the stepper pump with a tube length of 10 cm and a diameter of 3.8 mm is used to drain water that serves as ethanol or water from the container into the batch. The temperature sensor read as a temperature change in solution in batch, while the mixer acts as a stirrer in order to make a homogeneous solution. When the temperature in the batch reaches the desired value, it will automatically detect the sensor ethanol in the ethanol vapor in batches to measure levels of ethanol. Data measured by the sensor is stored and processed by computer. All components contained in the BIA system connected by computer via microcontroller Arduino. This microcontroller work as a in the BIA system which is controlled by computer. Relay work as a switch that is controlled by an electric magnet.

D. Procedure in monitoring production of alcohol in bioreactor.

Electronic valve in the bioreactor is opened in quick time with electronic control, liquid containing alcohol in bioreactor flows out towards a particular container. Fluid is then aspired by precise syringe pump and fed to the BIA system with a certain volume before the BIA system has been filled with water as the solvent. Temperature condition is set at a temperature 40 °C and stirred continuously. Once the temperature has reached 40 °C, the alcohol sensor responds and the amount of alcohol content is recorded, calculated, processed and displayed on the monitor screen with software.

RESULTS AND DISCUSSION

Analysis of alcohol was conducted using BIA (Batch Injection Analysis) using metal oxide semiconductor sensor. Before it is used to measure the concentration of ethanol, adjusting the flow rate syringe pump and pump stepper in the BIA system and determine the effect of temperature on the analysis of ethanol using metal oxide semiconductor detectors. The sample used in this study is the beer and wine ginseng.

A. Determination of flow rate

Determination of the flow rate of the ethanol sample is done by using syringe pump with a tube length of 7 cm and a diameter of 2.4 mm tube. Determination flow rate was used to obtain a linear equation so that the flow rate of ethanol was set into a computer program. Furthermore, the amount of alcohol that flowed is determined according to the number of iterations program. The varied number of iterations is 500; 1000; 1500; 2000; 2500; 3000; 3500; and 4000.

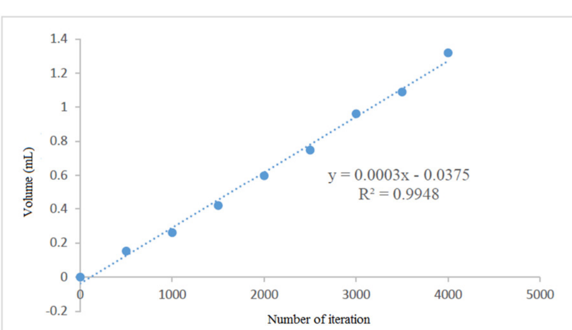

Figure 3. the relationship of the volume of water in the syringe pump to the number of iterations in the program.

The graph shown in Figure 3. shows the relationship of the volume of liquid to the number of iterations set by the program. Equation obtained from the graph can be used to determine the amount of a specific desired volume. The number of the desired volume can be defined by entering a volume value (y) in the equation shown in Figure 4.3 so that the number of iterations (x) can be calculated. The value of x is the number of iterations that entered into the program Labview.

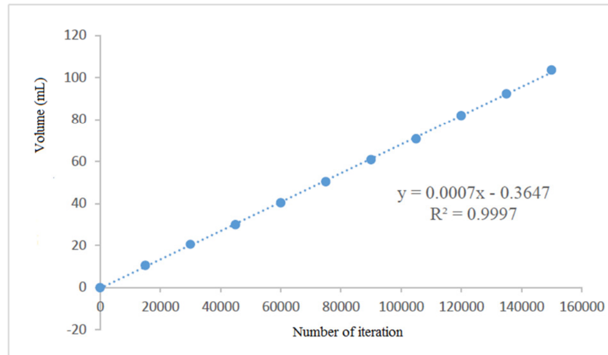

Figure 4. the relationship of the volume of water propelled by the stepper pump to the number of iterations in the program

The graph shown in Figure 3.4 shows the very close relationship between volumes toward the number of iterations set by the program. This is pointed out in coefficient value in linier regression, 0999. Equation obtained from the graph can be used to determining a number of specific desired volumes. This one is applied to dilute the alcohol in the bath so that it gets to the point of desired volumes.

B. Calibration curve

A calibration curve was made using ethanol 98.5%, with variations in concentration of 0.2%; 0.4%; 0.6%; 0.8%; and 1% v/v. Sensor ethanol used is following equation $R_S \cong K\, C^{\pm n}$, which are measured by the sensor is V out (output voltage). Then of V out is converted into Rs by following the following equation:

$$R_s = R_L\left(\frac{V_s}{V_{out}} - 1\right)$$

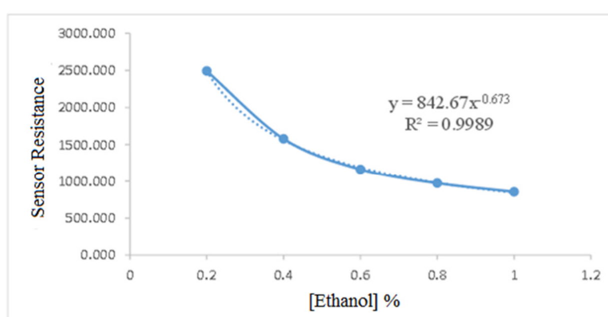

Figure 5. graph of the calibration curve ofthe concentration of ethanol to resistance of sensor R_S

Power equation shown in Figure 4 is a relationship of ethanol concentration to sensor resistance. Based on the above equation, sensor resistance decreases with increasing concentrations of ethanol.

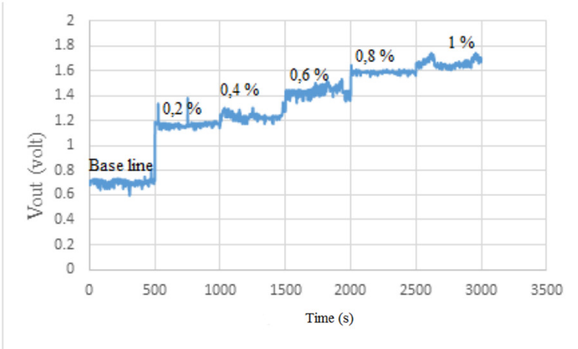

Figure 6 is the response of the sensor (Voutput) with respect to time at various concentrations

Figure 6 shows a graph of ethanol gas sensor response in form `V out to time. The initial signal is base line followed by successive ethanol at a concentration of 0.2% -1%. Initial Signal is the base line followed by the signal from the sensor response to ethanol with a concentration of 0.2% -1%. Any increase in concentration, then V out also increased. Data in the form of V out eventually to be converted into a R_s so that it can be calculated concentration of ethanol contained in the ethanol solution.

C. Temperature optimization in the BIA system

Temperature variation was performed to determine the effect of temperature on the measurement results of ethanol by the ethanol sensor with the BIA system. That is room temperature, the temperature of 28ºC, 40ºC, 50ºC and 60ºC.

Table 1 Value of correlation (r) at various temperatures

Suhu (°C)	Value of correlation
28	0,9689
40	0,9989
50	0,9597
60	0,9598

Based on table 1, the temperature 40 ° C gives the correlation value (R) the best of the other temperature variations. These results indicate a correlation value of the most powerful in the detection of ethanol in the BIA system in this experiment produced on measurements at 40 ° C.

D. The characteristic of measurement

1. Limit of Detection

Limit of detection is the lowest concentration of an analyte that can be detected and give a significant response by means of a method of measurement (Harmita, 2004). The smaller concentration of ethanol that can be detected the better performance of a method such measurements. Based on the calculation of the detection limit of the calibration curve obtained value is 0.031%. It showed that the lowest concentration limits can be detected by sensors ethanol (MQ3) to detect levels of ethanol in system BIA being 0.031%. If the ethanol concentration is lower than that value, instrument can't give the significant response.

2. Sensitivity

The sensitivity of the tool or method is the ability of a tool or method to give a different response each change in concentration (Skoog, 2007). Great value sensitivity shows that changing small concentration of the analyte can provide a significant response. Sensitivity obtained from the slope of the calibration curve with a concentration range of 0.2-1% in Figure 3.5. The equation obtained from calibration curve is y = 842.67 x-0673. Based on these equations obtained sensitivity value is $-567.112x^{-1,673}$.

3. Reproducibility

Reproducibility is a method of precision measurement results. Expected results pengukiuran give 95% each of the repetitions or more different. Reproducibility is expressed with value kv (coefficient of variations) that indicates the level of measurement error due to repetition. Reproducibility kv said to be good when the value is less than 5%.

Based on Table 2, it shows that the lowest Kv value of calibration measurements is 1.918% v/v ethanol at a concentration of 0.6% while the greatest value reached 5.456% at a concentration of 0.2%. Of the five concentrations are calculated the coefficient of variation, only at concentrations of 0.2 Kv values obtained are exceeded 5%, in addition Kv values below 5%. So, average value of Kv is overall still below 5%. These results indicate that the repeatability of the gas sensor to detect ethanol is good enough.

4. Accuracy

Determining the accuracy of a quantitative method by analyzing synthetic samples, samples of known composition or use samples that have been determined by other methods, was made as a comparison (Khopkar, 1990). Accuracy value obtained from the sample beers Star is 91.063%, while for ginseng wine obtained 117%. This is because the value measured by sensor exceeds the value stated on the label. Values measured by the sensor by 17.2%, while the value stated on the label of 14.7%. This could be due to error or contained matrix in the levels in such products that exceed the levels indicated on the label.

5. Sample Analysis

Samples of ethanol used in the present study is the star beer and wine kolasom which has a concentration of

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ethanol by 4.7% and 14.7%. From the analysis of the ethanol content using metal oxide semiconductor sensor obtained concentration of 4.4% for beer samples star and 17.2% for ginseng wine samples that can be seen in Table 2.

Table 2 Results of measurement of samples

Sample	Rs (ohm)			Average Rs (Ohm)	Measured Result (% v/v)	Labelled Result (% v/v)
	1	**2**	**3**			
Beer	2522.46	2461.07	2746.21	2576.578	4.4	4.7
ginseng wine	1394.9	1446.85	1362.62	1401.454	17.2	14,7

CONCLUSIONS

Batch injection analysis offers interesting properties in connection with various techniques for analytical applications. Here it has been demonstrated that the main components of BIA i.e. syringe pump and stepper pump having a good performance. This is shown very good relation of volume to a number of iterations. Both pumps have correlation coefficient 0,99. BIA system have good performance. This is indicated by the value of accuracy and precision.

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