DETERMINATION OF ETHANOL IN ENVIRONMENTAL WATER

By

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FINAL PROJECT REPORT

Submitted to the Chemical Engineering Programme
in Partial Fulfillment of the Requirements
for the Degree
Bachelor of Engineering (Hons)
(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Approved:

_____

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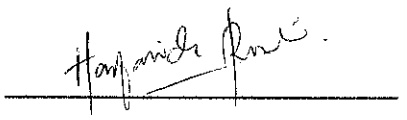
Project Supervisor

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK

January 2005

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.



Hasfanida Rusli

ABSTRACT

The main objective of this research project is to determine the performance of Gas Chromatography using Flame Ionized Detector (GC/FID) and Ultra Violet visible (UV-Vis) for the analysis and quantification of ethanol. This research project is based on the development of analytical methods for environmental studies. Ethanol in environment might be present in air, soil, and water. Ethanol is a known contaminant in environmental waters. Even though the concentration of ethanol is normally low in the environment, analytical methods in determining the concentration of ethanol in water need to be developed due to its effect on tumor growth hence human health in general. Once it is identified and detected, the contaminants can be removed or separate from the environmental waters. The scope of study for this project are to find the best method in terms of accuracy and precision for the analysis of ethanol in water and to use the best method identified to determine the ethanol content in environmental samples. From the experimental results, GC/FID has higher accuracy and precision. GC/FID is a good method in determining the lower concentration of ethanol in water.

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GC/FID – Gas Chromatography using Flame Ionized Detector

UV-Vis – Ultra Violet Spectroscopy

CHAPTER 1
INTRODUCTION

1.1 Background of Study

Water is the major constituent of living matter. Water contaminated with alcohols is one of the problems occurred that gives problem to environment and this may also affect human health. Alcohol is chemically hazardous to human being if inhaled or swallowed it into the body.

There are many causes that contribute to water contaminated with alcohol. Oil spill and gas storage leakage are the examples that contributed to this problem. When ethanol combined with water, its structure is easily breakdown and it become soluble in the water. Besides, in environmental case, ethanol in lake or ocean will easily evaporate to air. For this unique characteristic of ethanol, it becomes hard for scientist to determine ethanol content.

Researcher has to know the concentration of ethanol in the water to avoid problems with human health. By knowing the concentration of ethanol content in the water, will facilitate scientist to find out the best methods or ways to treat the ethanol in water. Researchers are continuously developing and improving methods to find the most suitable for the analysis of these alcohols in water.

In this research, two methods will be used to analyze ethanol in environmental water. Ethanol content or concentration will be determined. The methods used are Gas Chromatography (GC) using Flame Ionized Detector (FID) and Ultra Violet Visible (UV-Vis). Experiments have been conducted on both equipments in order to find the best method to determine the contents of alcohols in water.

1.2 Problem Statement

Researches have lead to a model that may explain how alcohols stimulate tumor growth. Study shows that alcohol content in human's body will increase the risk of cancers of the stomach, liver, breast and brain. Ethanol, in particular has shown to increase the production of signaling protein in blood vessel growth in tumors.

This alcohol is of interest to investigation on surface groundwater at sites where paints, solvents, adhesives are stored. These compounds too are a priority in investigation of gasoline storage tank leakage as they are occasionally used as oxygenate.

The analysis of ethanol in water is difficult. Ethanol is a small, polar molecule. Ethanol associates (hydrogen bond) with water are difficult to measure in low concentration in the environmental water. From study, few researches have been done to determine ethanol in water, since ethanol is not included in several comprehensives references of groundwater contaminants. In addition, because the human body tolerates percent quantities of ethanol that are present in alcoholic beverages, human consumption of trace quantities of ethanol, which might contaminate food and drinking water, have not been of great concern.

For this research project, gas Chromatograph using Flame Ionized Detector (GC/FID) and Ultra Violet Visible (UV-Vis) have been chosen as the methods to determine ethanol content in environmental water. The results of the study will be used to determine the ability of these instruments to detect and quantify ethanol in environmental waters. The performance of these instruments will be compared for further development of the analytical methods.

1.3 Objective and Scope of Study

Two main objectives have been identified to focus on the deliverables within the given time frame. The main objective of this research project is to determine the performance of Gas Chromatograph using Flame Ionized Detector (GC/FID) and

Ultra Violet visible (UV-Vis) for the analysis and quantification of ethanol. The relevance of the project is to develop and improved methods available for future studies on ethanol content in the environmental waters.

The scopes of study for this project are as follows:

i. To find the suitable method in terms of accuracy and precision for the analysis of ethanol in water.
ii. To use the suitable method identified to determine the ethanol content in environmental samples.

CHAPTER 2
LITERATURE REVIEW AND THEORY

Few papers have been published describing the analysis of ethanol in environmental samples. From the researches, it has been found that some methods to determine the ethanol content have been developed. Besides, there are some researches that use the GC/FID and UV-Vis equipment to determine other components in solution.

2.1 Determination of alcohol using different methods.

From research, there has been an increased interest in use of ethanol and other alcohol fuels as alternative energy sources. Most countries have established programs for the development of alternative energy sources with the purpose of reducing their dependence on petroleum. The use of ethanol-fueled vehicles popularly leads to a high level of atmospheric acetaldehyde since the combustion of ethanol in spark-ignition engines results in the increased emissions of primary acetaldehyde. A study has reported the results of the atmospheric alcohol and aldehyde concentrations in Japan, where alcohol-fueled vehicles have not been introduced, and in Brazil, where ethanol-fueled light duty vehicles are in high use. The atmospheric methanol, ethanol and isopropanol concentrations have been measured from May to December 1997, in Osaka, Japan, and from 3 to 9 February 1998 in Sao Paulo, Brazil. The alcohols were determined by the alkyl nitrite formation reaction using gas chromatography (GC/ECD) analysis [1].

Previous research has been done in analyzing alcohol content in denatured fuel grade ethanol by GC/FID. The overall purity of denatured fuel ethanol must be measured by gas chromatograph (GC) to meet the American Society for Testing and Materials D5501 (ASTM) specifications and to determine the amount of methanol impurity present in the material. The research developed method of determining alcohol concentration has been made by using two short columns of different selectivity. The

two-dimensional gas chromatography application provides high qualitative and quantitative precision for this measurement. Besides, by this method, complete separation of the polar alcohol from the nonpolar hydrocarbons can be made in much less time than is needed with a single, long column. The columns that have been used are HP-1 column, 0.25μm film, 15m x 0.25 mm id as the primary column and INNOWax column, 0.25μm film, 15m x 0.25 mm id as the secondary column [2].

Besides, ethanol has been analyzed previously by food and biomedical industries. The method used was an oxygen-electrode sensor (5-10 ppm) that has a large dynamic range. From the journal, it stated that recent methods cited used headspace gas injection or direct injection of the biological fluid coupled with gas chromatography combined with flame ionization detection (GC/FID). Through this research, it is found that GC/FID is more analyze specific than many of the electrochemical methods used in the alcoholic beverage industry. Because of their good detection limit, GC/FID methods are potentially applicable for ethanol determination in environmental samples [3].

Researchers at the University of Nebraska have developed a solid-phase microextraction (SPME) method coupled with GC/MS for the determination of ethanol in water. The SPME method uses a small fiber (~1 cm in length by ~0.3 mm in diameter), which is coated with 85μm of a carbon/polydimethylsiloxane polymer to extract ethanol in water. After it has been soaked in the sample, the fiber that containing ethanol is removed from the sample and directly injected to GC-MS so that the amount of ethanol that has been collected can be measured [3].

In the research, it has been found that the determination of ethanol in the blood of drivers suspected of driving while intoxicated is probably the single greatest application of static headspace (SHS) GC. This means that the GC and headspace conditions are given for determination of ethanol in water with n-propanol internal standard. Optimum GC and headspace conditions for ethanol in water are identical to those used in the determination of ethanol in blood and urine; therefore, aqueous solutions are normally used during method development [4].

2.2 The used of equipment Ultraviolet visible spectroscopy for other components.

From the previous research, a new method for protein analysis was developed. The method used was ultraviolet/visible spectroscopy. In the research, it shows that some waste biomass is becoming more useful in biomass to ethanol conversion. The protein analysis has been done in order to have better understanding in the process that converts biomass into ethanol. The Biofuels Ethanol Program wants to be able to monitor protein content in biomass and track it through ethanol conversion process. Corn stover, a waste biomass, is used in this analysis. Lignin is one of the substances that give corn stover its structure and it is toxic to all the organisms currently used to ferment sugars to ethanol. Lignin and amino acids, the base of protein were being measured by UV/visible spectroscopy [12].

2.3 Theories and methods of the equipments.

2.3.1 Gas Chromatograph using Flame Ionized Detector (GC/FID)

Chromatography is a separation technique in which substances are separated by mobility differences by the distribution difference between stationary phase and mobile phase. In gas chromatography (GC), the sample is vaporized and injected onto the head of chromatographic column. Elution is brought about by the flow of an inert gaseous mobile phase. For gas chromatography (GC), the mobile phase is a gas which does not chemically interact with the substances being separated, and the stationary phase distributions enable the separation [9]. The analysis is done at high temperature, usually 5-10^{o}C higher than the highest boiling point in the mixture.

The Flame Ionized Detector (FID) is the most common ionization detector. This detector has a very wide dynamic range, has a high sensitivity and, with the exception of about half dozen small molecular weight compounds, will detect all substances that contain carbon [7].

The FID is an extension of the flame thermocouple detector and is physically very similar, the fundamentally important difference being that the ions produced in the flame are measured as opposed to the heat generated.

$$\text{Ionization reaction: } CH + O \rightarrow CHO^{+} + e^{-}$$

Hydrogen is mixed with the column eluent and burned at small jet. Surrounding the flame is a cylindrical electrode and a relatively high voltage is applied between the jet and the electrode to collect the ions that are formed in the flame. Changes in current within the flame are measured and sent to the computer to be seen as peaks on the chromatogram. FID detector requires three separate gas supplies together with their precision flow regulators. The gases normally used are hydrogen for combustion, helium or nitrogen for the carrier gas and oxygen or air as the combustion agent [8]. FID is a good general detector for organic compounds, and is able to detect at the nanogram level.

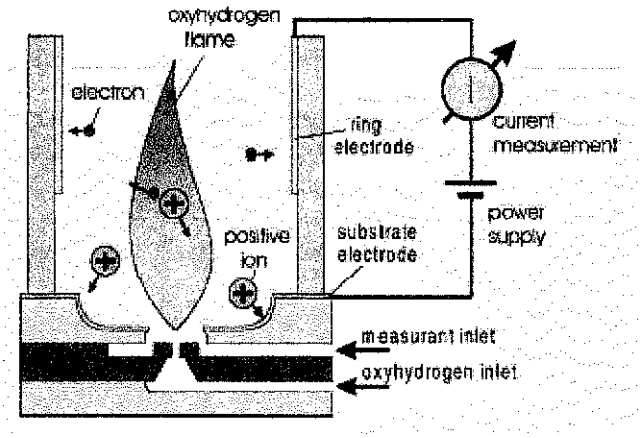

Figure 1 Measuring Principle of GC/FID

2.3.2 Ultra Violet Visible (UV-Vis)

The basic principle of UV-Vis is a beam of UV light passes through the nonabsorbing eluent and impinges on a photomultiplier. When susceptible solute enters the light

path, energy is adsorbed and the photomultiplier senses a decrease in light intensity. The UV detector is less sensitive to temperature [6].

Ultraviolet and visible spectroscopy (UV-VIS) is a common analytical technique for quantitative and qualitative analysis of solid, liquid, or gas samples including conjugated unsaturated, carbonyl, nitro, bromine, and/or iodine containing organic compounds and transition metal complexes. The methods are based on the absorption of energy of a compound in the wavelength range 200-800 nm. The light absorbed by a sample can be calculated and provides a very sensitive and reproducible means for determining the concentration of absorbing species.

A UV-vis spectrum was collected from 190 nm to 350 nm, using a Hewlett Packard UV-Visible spectrophotometer with a diode array detector. The spectroscopic data was converted to spreadsheet form, which made it easy to view the spectrum graphically and to perform calculations from the absorbance data. Water was used as a background reference. Wavelength of maximum absorbance for ethanol has been set up as 254.5 nm. The wavelength of ethanol is determined by analyzing pure ethanol using UV-Visible Spectrophotometer.

2.4 Ethanol structure and its characteristics

Ethanol is one member of a family of substances called alcohols which have a C-OH functional group in their structure. Ethanol is one of the organic compounds and the structure is given as: CH_3CH_2OH.

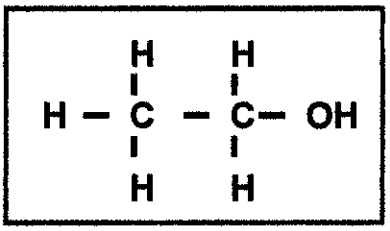

Figure 2 Ethanol Structure

Ethanol is a substance which is also known as alcohol. It is a clear, colourless liquid that is flammable and can be produced from the fermentation of renewable biomass

such as sugar. Ethanol is a low-molecular-weight alcohol. Ethanol is soluble in water in all portions. Their ability to participate in intermolecular hydrogen bonding not only affects the boiling points of alcohols, but also enhances their water solubility. The attractive force between –OH groups in alcohols is called hydrogen bonding. Hydrogen bonding between the hydroxyl group (OH) and water molecules makes the water solubility of alcohols greater than that of hydrocarbons. Hydrogen –bonded networks, in which alcohol and water molecules associates with one another, replace the alcohol-alcohol and water-water hydrogen-bonded networks present in the pure substances. Because of the structure, ethanol is volatile and easily evaporates to the air. Thus, in environmental water, it is hard to determine the content of ethanol as it is very soluble in water and easily evaporates to the air.

2.5 Ethanol effects to human health.

Ethanol, the active ingredient of alcoholic beverages, has been part of the human diet and the human environment for thousands of years. It is produced by fermentation by fungi and other microorganisms, and is found at low levels in the blood and breath of persons who do not drink alcohol. Ethanol is present in pharmaceuticals, mouthwash products, alcoholic beverages, cleaning products, solvents, dyes, and explosives. However, at sufficiently high doses, ethanol can cause toxic effects in humans, increases the risks for several forms of human cancer.

The occupational standard for ethanol in air is 1000 ppm (1900 mg/m3) on an eight-hour basis. For higher concentrations, ethanol vapor causes eye and upper respiratory tract irritation, fatigue, headache, and sleepiness [13].

For persistence of ethanol in water, in a December 1999, there is a report to the California Environmental Policy Council that under aerobic conditions, the reported half-lives of ethanol in surface waters are short. Half-lives span 6.5 to 26 hours for ethanol [13]. Anaerobic biodegradation in oxygen-limited environments is also expected to proceed at rapid rates. Reported half-lives for ethanol biodegradation under anaerobic conditions ranges from 1 to 4.3 days. From the report, it shows that ethanol is not expected to persist in groundwater because it biodegrades easily. Thus, ethanol itself does not appear to pose as great a danger to groundwater supplies.

Taste thresholds [for ethanol] range from approximately 6 ppm to 42 ppm. The draft health-protective concentration for oral exposures to drinking water for ethanol is 1,100,000 mg/l [13]. However, it is highly unlikely that the public will be exposed to large quantities of ethanol from drinking water contamination.

The concentration of alcohols in breath and urine in human body mirrors the concentration of alcohols in blood. This means that alcohol in breath can be detected, measured, and used to calculate a person's Blood Alcohol Concentration (BAC) [5]. From this research, it shows that, concentration of alcohols in human body also can be determined by analytical method.

CHAPTER 3
METHODOLOGY / PROJECT WORK

3.1 Preparation procedures for calibration curve.

i. Standard solution is prepared (volume %) in 100 ml volumetric flasks solutions ranging from 10% to 100% solutions of ethanol, using water to dilute the solutions.

ii. All the solutions have been run through the GC/FID and UV-Vis equipments.

iii. Beginning with the 10% solutions:

iv. For GC/FID: 0.2µL of solution has been injected into the injector port. Wait a few minutes and a peak should form.

v. For UV-Vis: 2ml of solution has been dropped into a small tube and has been put in the UV-Vis equipment. Observe the absorbance value for the solution.

vi. Steps (ii) were repeated using the rest of the solutions. The experiment was performed in triplicate.

vii. Data collected for three readings and three series of solutions will be used to construct calibration curve. Limit of detection (LOD) will be determined using both methods.

viii. Prepare a standard curve (calibration curve) using Peak Area vs. Concentration for GC/FID. For UV-Vis is Absorbance vs. Concentration.

3.2 To test the unknown sample.

i. Spiked water sample analysis has been conducted by using the same method as above (in triplicate) to determined percentage of recovery, reproducibility / precision and accuracy.

ii. To determine the concentration, calibration curve of ethanol has been referred.

3.3 The equipments, glassware and chemicals required.

Table 1 Major equipments for this research.

No	Equipment	Specifications	Purpose
1.	GC/FID	Phase: BP20, 0.25µm film. Column: 30m x 0.25mm ID Column temperature = 25^0 C Equilibration Time = 3 minutes Column Max Temperature = 260^0 C Initial Temperature = 45^0 C Final Temperature = 80^0 C/min Rate = 3^0 C/ min Injector = 0.2µL Retention time = 2.4 min	To determine ethanol concentration in water
2.	UV-Vis	Ethanol wavelength = 254.5 nm	To determine ethanol concentration in water

Table 2 Glassware and chemicals required for this research.

No	Glassware/Chemical	Quantity
1.	Volumetric flask, 100 ml	8
2.	Beaker, 100 ml	3
3.	Measurement cylinder, 50 ml	3
4.	Micropipette, 1 ml – 5 ml	1

Table 3 List of chemicals required for this research.

No.	Chemicals	Quantity
1.	Ethanol, (C_2H_5OH)	As required
2.	Distilled water	As required

3.4 Experiment Flow Chart

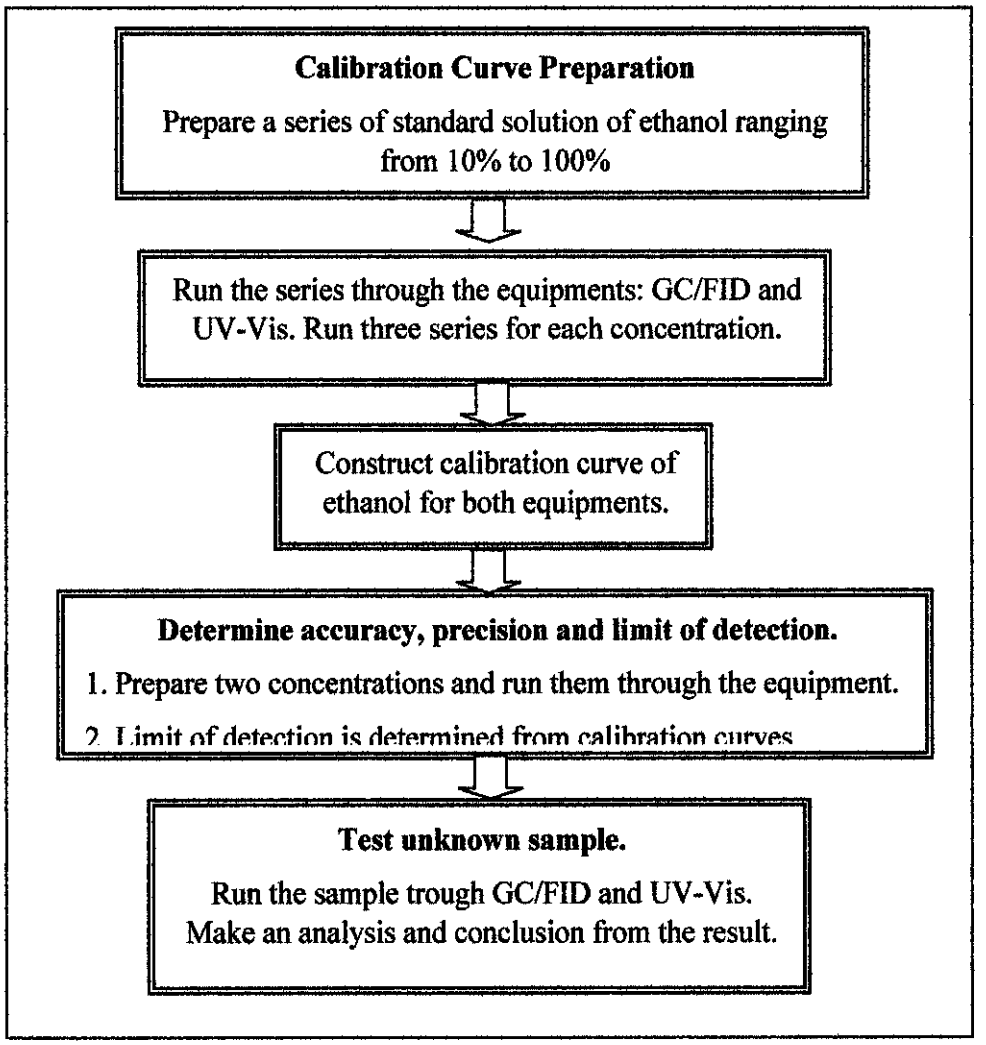

Figure 3 Process flow Diagram for method analysis of determination ethanol in water.

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Calibration curves of ethanol for GC/FID and UV-Vis.

The first step in this research is the preparation of calibration curve of ethanol for GC/FID and UV-Vis. A calibration curve is a graphical display of the functional relationship between the expected value of the observed signal (the instrument or detector response) to the analyte amount. In analytical chemistry, a calibration curve is a standard reference for determining the concentration of any given compound or element. The analysis of the standard solutions using both methods produces a series of readings.

To construct a calibration curve, a series of standard ethanol solution need to be prepared. The series ranging from 10% - 100% concentration has been prepared in the 100 ml volumetric flasks. The pure concentration of ethanol provided in the chemical lab is 17.15M. The standard solutions have been prepared by diluting the ethanol in water according to the percentage volume calculated. Three series of standard solution are run through GC/FID and UV-Vis. Different series of similar concentration solutions are tested for accuracy and precision. In order to construct a good calibration curve, at least seven points of data is required.

In this experiment, both equipments work on different principle in determining the concentration of a given solution. For GC/FID, the signal is computed to peak area. The peak area relates to the quantity of each material, and the retention time is used to identify the ethanol compound in water. The data of average mean area of peak are tabulated in Table 4. The plots of calibration curve for GC/FID is shown in Figure 4.

Table 4 Data for calibration curves using GC/FID.

No	Concentration		Mean area of peak for different series			Average mean area of peak
	(%)	(ppm)	1st series	2nd series	3rd series	
1	0	0.0000	51.05	46.27	59.03	52.12
2	10	0.0325	2055078	1808471	1495061	1786203.33
3	30	0.0975	6246617	5826032	5818940	5963863.00
4	40	0.1300	7345238	7623561	7737197	7568665.33
5	50	0.1625	10410357	10332746	10094000	10279034.33
6	60	0.1955	11886003	12482711	12191258	12186657.33
7	80	0.2610	15800623	15800623	15656883	15752709.67
8	100	0.3260	19339908	19007889	18579035	18975610.67

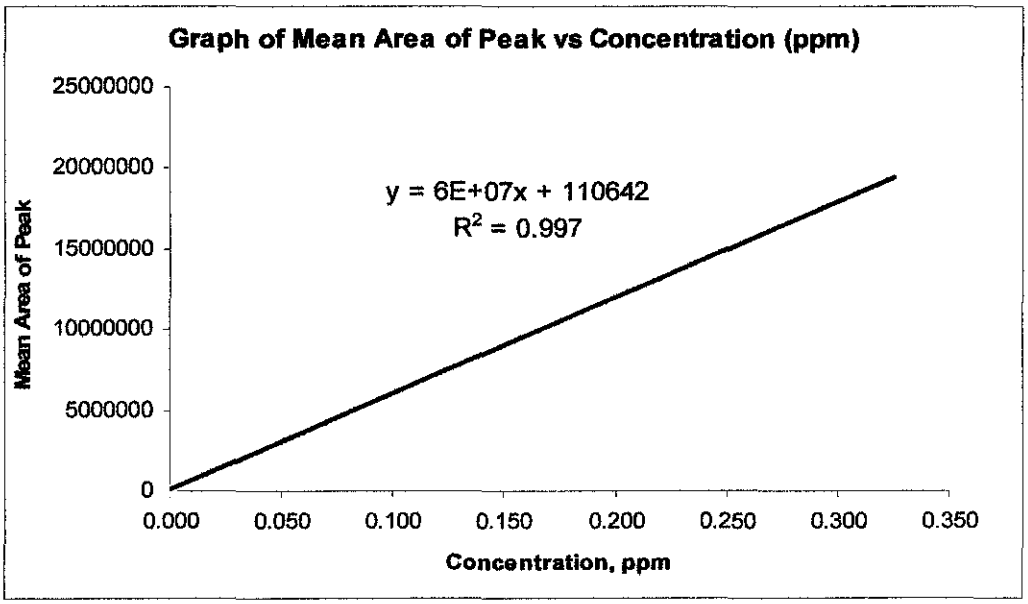

Figure 4 Calibration Curve for Ethanol by Using GC/FID.

In UV-Vis, the instrument scans the ethanol wavelength and the absorbance at that wavelength is then calculated. The absorbance value and the ethanol concentration give a linear relationship. The data of average values of absorbance are tabulated in Table 5. The plot of the calibration curve for UV-Vis is shown in Figure 5.

Table 5 Data for calibration curve using UV-Vis.

No	Concentration		Absorbent reading for different series			Average absorbent reading
	(%)	(ppm)	1st series	2nd series	3rd series	
1	0	0.00	0.060	0.060	0.050	0.057
2	10	3.25	0.060	0.089	0.087	0.079
3	30	9.75	0.094	0.094	0.092	0.093
4	40	13.00	0.112	0.081	0.110	0.101
5	50	16.25	0.139	0.143	0.129	0.137
6	60	19.55	0.170	0.165	0.173	0.169
7	80	26.05	0.225	0.229	0.227	0.227
8	100	32.60	0.275	0.288	0.280	0.281

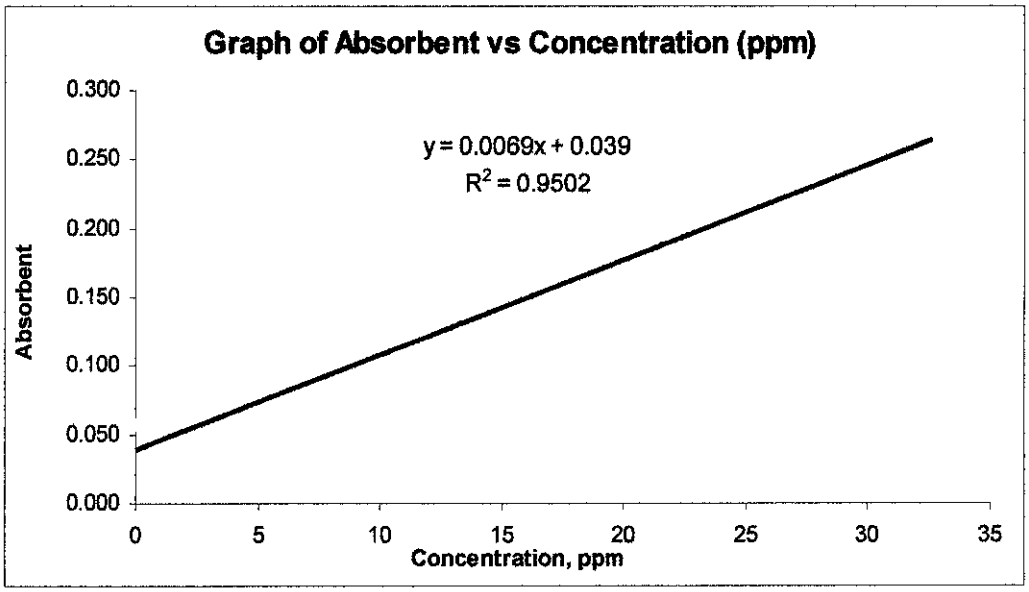

Figure 5 Calibration Curve for Ethanol by Using UV-Vis.

A calibration curve constructed from the mean area of peak versus the ethanol concentration in Figure 4 produced a linear response. The equation for the line was y = 6E7 x + 110642, where y is the mean area of peak produced and x is the concentration of ethanol in ppm (mg/L). The range of ethanol concentration is from 0 to 0.35 ppm. The linear regression value, R^2 for the calibration curve is 0.997. From the graph, the intercept-y value referred to the noise value of the equipment. The noise value for GC/FID is 110642.

A calibration curve for UV-Vis constructed from the absorbance versus the ethanol concentration in Figure 5 produced a linear response. The equation for the line was $y = 0.0068x + 0.039$, where y is the absorbance value and x is the concentration of ethanol in ppm (mg/L). The range of ethanol concentration is from 0 to 35 ppm. The value of R^2 is 0.952. The noise value for UV-Vis equipment is 0.039.

The different range of ethanol concentration among the two instruments is because of the different volume used for the analysis. Higher volume has been tested in UV-VIs. From the experiment, it shows that, GC/FID is equipment that can detect lower concentration compared to UV-Vis.

To determine the best data line for calibration reading, linear regression, R^2 need to be determined. As R^2 value reaches 1, the values of readings obtained is more precise and more accurate. From the regression value of two calibration curves, GC/FID gives a good calibration curve as its R^2 closer to 1.

The noise values are obtained from the disturbance in the equipment itself. The disturbance in the equipment could be air that contained some concentration of ethanol. The values of noise are used in determining the limit of detection (LOD) and the Limit of quantitation (LOQ).

4.2 Limit of detection (LOD) and Limit of Quantitation (LOQ).

The limit of detection (LOD) and the limit of quantitation (LOQ) were calculated from the signal-to-noise ratio [11]. LOD is defined as the lowest concentration that can be detected by the equipment. This concentration is recommended to be three standard deviations above the measured average difference between the sample and blank signals. Thus, LOD was defined as 3 times S/N ratios. LOD is important in trace analysis, to decide whether the contaminant is present below or above the legal limit. Ideally, the LOD of the method selected should be at least one-tenth of the concentration to be measured.

LOQ needs to be considered to detect the presence of analyte and to determine the amount present with a reasonable statistical certainty. LOQ is typically used to define the lower limit of the useful range of the measurement technology in use. Samples that do not bear residues at or above the LOQ are often referred to as "nonquantifiable." The corresponding sample/blank difference is recommended to be 10 standard deviations above the blank. Thus, the LOQ was defined as 10 times the S/N ratios respectively [11].

The values of LOD and LOQ for both equipments are tabulated in the Table 6 below. From the table, it shows that GC/FID can detect lower concentration of ethanol in water compared to UV-Vis. This is because of the smaller amount of solution that has been tested in the GC/FID equipment.

Table 6 LOD and LOQ values for GC/FID and UV/Vis

Equipments	LOD (ppm)	LOQ (ppm)
GC/FID	0.00368	0.0165
UV/Vis	11.3	50.87

4.3 Analysis of real sample of environmental water.

One sample of environmental water has been tested through the equipments. The sample has been taken from the laboratory waste water that contains most of chemicals. The sample has been run for both equipments for triple times. The results are shown in the Table 7 below.

Table 7 Real sample test results through GC/FID and UV/Vis.

Equipments	Unknown sample reading (ppm)
GC/FID	Cannot be detected
UV/Vis	11.8

The results show that the concentration of ethanol in the sample is 11.8 ppm by UV/Vis and the concentration of ethanol cannot be detected by GC/FID. The GC/FID cannot detect the ethanol concentration in the environmental sample although the sample has been run through the equipments for more than triple times. From the results, UV/Vis reading is above the LOD of the equipment. So, the concentration of ethanol in the sample can be detected by this equipment. For GC/FID, the sample should be detected because it is above the LOD reading, but GC/FID cannot detect the ethanol concentration for some reasons.

There are some reasons that contribute to the results. Higher volume of samples, 2ml is used for analysis through UV-Vis compared to GC/FID that injected only 0.2μL into its column. This difference in volume tested affected the results obtained. Besides, as ethanol is very volatile in the air, it is hard to detect the amount of ethanol in a smaller volume in the column of GC/FID. Other factor that may affect to the uncertainty result is the interference of air in the GC/FID equipment sample injection. In addition, the content of ethanol in environmental water is very low since it is very soluble in water.

The results obtained so far show the capability if this method to detect the presence of low concentration ethanol in environmental water samples but further work is required on real samples to confirm the concentrations determined.

4.4 Method Validation

In analytical method research, precision, accuracy and limit of detection are the important criteria that evaluate the performance of the equipment. The American Food and Drug Administration (FDA) has adopted certain guidelines for bioanalytical methods validation to ensure accuracy and precision, sensitivity, selectivity, recovery and stability. AS per FDA guidelines [11], the calibration point should consist at least six points in triplicates. The accuracy of each calibration point should be 85 – 115 %.

4.4.1 Accuracy

Accuracy is the closeness of the agreement between the result of a measurement and the true value. In other words accuracy is a measure of position. For accuracy of the data for both methods, two samples of different concentrations ethanol in water have been prepared and determined by the analysis of at least triplicate. The mean calculated concentration should be within 15% of the intended concentration value. The percent accuracy is calculated as follows: (Cm/Ci) x 100 (Eqn.1), where Cm is the mean of the calculated concentrations and Ci is the intended concentration [11].

4.4.2 Precision

Precision is the closeness of a series of replicate measurements to each other. Precision provides a measure of the random error of an analysis. There are some characteristics that expressed in numerical terms that are called figures of merit. The figures of merit for precision include absolute *standard deviation, s* and *relative standard deviation, RSD.* Precision is often calculated as: (SD/Cm) x 100 (Eqn. 2), where SD is the standard deviation and Cm is the mean of the measured concentration [11]. The lower the value of SD, the more precise the data is. The results of the accuracy and precision test are listed in Table 8 and Table 9.

Table 8 The accuracy and precision of the GC/FID method.

Intended Conc, Ci		Mean Conc, Cm	SD	Accuracy	Precision
(%)	(ppm)	(ppm)		(Cm/Ci)x100	(SD/Cm)*100
20	0.065	0.062	0.0021	95.38	3.42
55	0.18	0.179	0.0007	99.44	0.40

Table 9 The accuracy and precision of the UV-Vis method.

Intended Conc, Ci		Mean Conc, Cm	SD	Accuracy	Precision
(%)	(ppm)	(ppm)		(Cm/Ci)x100	(SD/Cm)*100
20	6.5	5.45	0.742	83.85	11.42
55	18	17.05	0.672	94.72	3.73

From the value of accuracy, the results show that GC/FID method gives higher accuracy compared to UV-Vis method. Besides that, in precision, GC/FID also is more precise than UV-Vis. So, in this research, it has been found that, GC/FID has higher accuracy and precision in determining the concentration of ethanol.

4.5 Error analysis

There are some errors contributed to inaccuracy and imprecision in the results of experiment. Human error occurred while conducting the experiment. Glassware used may content previous concentration of ethanol that contributes to imprecise concentration of standard solution. Parallax error occurred during reading have been taken for chemicals. In this condition, to avoid errors in next experiments, glassware cleanliness and purity need to be considered by cleaning and drying it before using it for another solution.

In conducting the equipment, the tube and the column used may content previous concentration of ethanol. This gives errors in data values in determining the concentration. Thus, to avoid this, the apparatus should be in clean condition by running it with solvent prior any analysis with ethanol solutions.

CHAPTER 5
CONCLUSION AND RECOMMENDATION

Ethanol has been chosen to be the experimental compound in determining the suitable method to study its content in environmental water. In environmental water, ethanol is hard to be determined as it is very volatile and very soluble in water. From studies done, research to determine ethanol content in environmental water is less frequently done than determine it in other medium such as petroleum and blood.

In this research, GC/FID and UV-Vis are the methods used in determining the concentration of ethanol in environmental water. The performance of each method has been evaluated. Due to expected human and instrumental errors, unknown sample cannot be detected on GC/FID. However, as shown in the experimental conducted on the three series of standard solutions and supported by previous research works, GC/FID can detect ethanol at lower concentration. This means that GC/FID is a good equipment in determining lower concentration of ethanol in environmental waters. .

In this research, the equipments used are hard to compare to each other since the methods require different volume of sample to be tested on the equipment. UV-Vis method tests a higher volume of environmental water samples. Further experiment needs to be conducted on comparing sample of similar concentration for a more reliable result.

Both of the equipments have their strength and weakness. GC/FID is easily used because it automatically separates the compound from other components. But on the other hand, GC/FID is destroying the sample. For UV-Vis, the sample must be diluted before being tested. The solution also must be transparent in order to avoid other wavelength of component interrupted the wavelength detected by the absorbance.

Besides that, separation process is needed before using UV-Vis as the environmental water content many substances.

There are recommendations for further studies in order to improve the methods used in determining the concentration of ethanol in environmental water. As the ethanol is very volatile and soluble in environment, GC/FID would be very sensitive in detecting derivatized ethanol. By derivatization, other compound that has bigger molecule is used to hold the volatile compound. Thus, by that method, the new compound is less volatile and easy to be detected.

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APPENDICES

APPENDIX A

EQUIPMENT USED

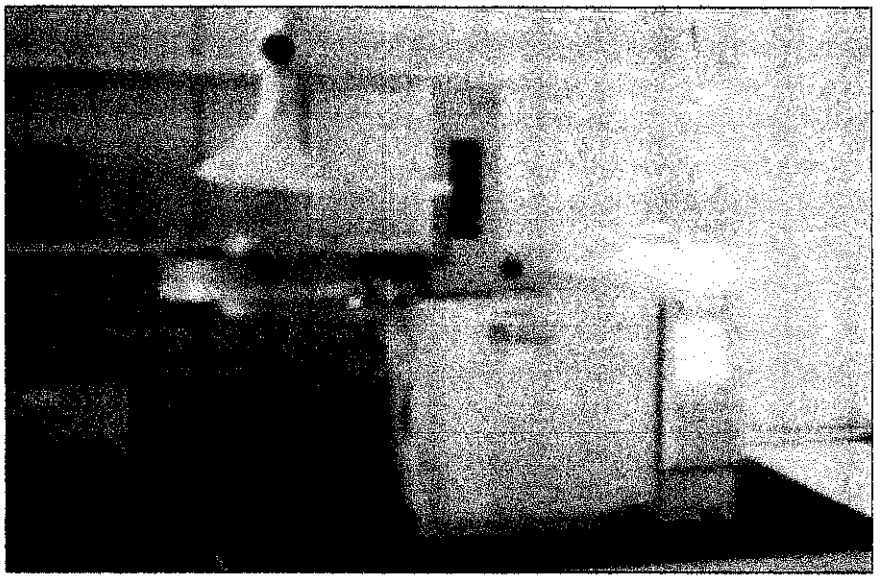
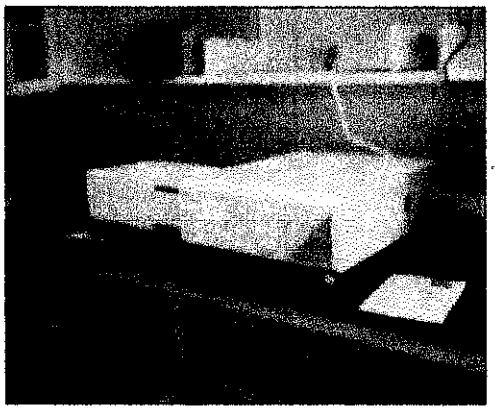


Figure 6 Gas Chromatography – Flame Ionized Detector



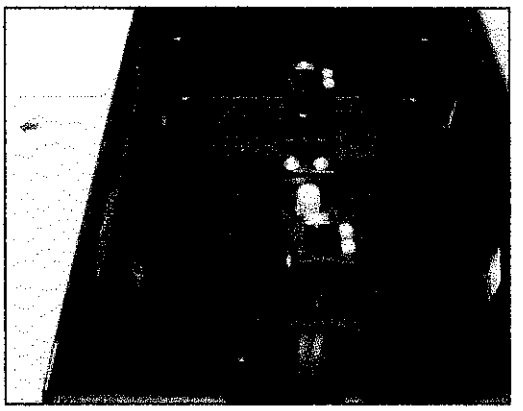


Figure 7 Ultra Violet Spectroscopy