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CHARACTERIZATION OF ETHANOL CONCENTRATIONS AT ULTRAVIOLET WAVELENGTH REGION

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ABSTRACT

This paper presents the measurement of optical absorption spectrum for different concentrations of ethanol at ultraviolet wavelength. Ethanol absorption spectrum was measured using portable spectroscopy setup from Avantes. It consists of Balanced Deuterium Halogen light source and spectrometer. The light source can deliver a continuous broad spectrum ranging from 0.2 to 2.5 µm and the spectrometer has the detection range of 0.2-1.1 µm. Several mixtures of ethanol in de-ionized water were prepared with various concentrations of 0%, 0.1%, 0.5%, 1.0%, 2.5%, 5%, 10%, 15%, 25%, 50% and 100 vol%. The baseline of the absorption spectrum was being analyzed and corrected using MATLAB software. From the results, the spectroscopy setup was successfully detecting ethanol concentration from 2.5-100vol%. However, only concentration range from 2.5-50vol% has shown 99% of fulfilment towards the Beer's Lambert Law.

Keywords: ultraviolet wavelength; spectroscopy; optical absorption; ethanol concentration; absorption spectrum baseline; Beer's Lambert law.

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1. INTRODUCTION

Nowadays, spectroscopy techniques has received much attentions in investigating the ethanol compound at Ultraviolet (UV) [1-2], Near-infrared [3-4] and Mid-Infrared (MIR) wavelength regions [5-7]. Spectroscopy offers repeatable and reliable results and has simple sample as compared to fiber optic sensors which is fragile and tedious to be fabricated [8-9]. Most of the spectroscopy technique concerns for high concentration of ethanol like in manufacturing of alcohol industry [2-3, 10-11], but none reported work done in qualifying and quantifying the percentage of low ethanol concentrations. This research is important for Muslim in halal practice. For that reason, this analytical method was chosen to characterize the presence of ethanol.

With the advanced of technology, the portable version of spectroscopy setup also available in the market. Spectroscopy is one of the analytical techniques used in sensing technology when dealing with chemical substances or materials. The basic principle is that each compound absorbs or transmits light over a certain range of wavelength. The amount of light being absorbed represents the concentration of the ethanol compound. Spectroscopy technique is proposed as a method for providing real-time information of ethanol concentrations in different concentration of ethanol-water mixture. Spectrometer quantitatively compares the fraction of light that passes through a reference solution and a test solution. When a beam of light passes through a substance or a solution, some of the light may be absorbed and the remainder transmitted through the sample. Fig. 1 shows the illustration of light passes through the sample [12].

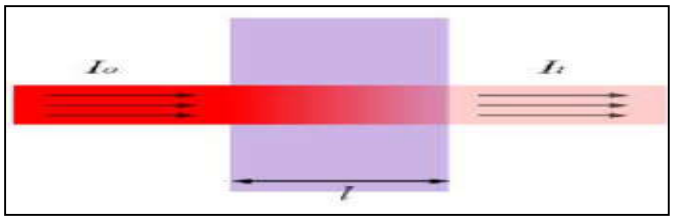

Fig.1. Propagation of light passes through a solution held in a container

The ratio of the intensity of the light entering the sample (I_o) to that exiting the sample (I_t) at a specific wavelength is defined as the transmittance (T). This is often expressed as the percentage transmittance (%T), which is the transmittance multiplied by 100:

$$\%T = (I_o/I_t) \times 100 \quad (1)$$

The absorbance (A) of a sample is the negative logarithm of the transmittance:

$$A = -\log(T) \quad (2)$$

Beer-Lambert law states that, for a given ideal solution, there is a linear relationship between concentration and absorbance provided that the path length is kept constant; the absorptivity, ε is a constant for each molecule for each wavelength [1].

$$A = \varepsilon cl \quad (3)$$

where ε is the absorptivity of the substance, c refers to sample concentration and l is path length. Epsilon, ε in Equation (3) is called molar absorptivity or molar absorption coefficient. The larger the molar absorptivity, the more possible the electronic transition. The unit of molar absorptivity is L/mol.cm. The concentration of the sample solution is measured in mol/L and the length of the light path in cm. Thus, absorbance is unitless.

2. METHODOLOGY

This section summarizes the experimental work and research methodology in characterizing the ethanol-water mixture by using spectroscopy technique. Each of the step is explained in the following subsections.

2.1. Preparation of Ethanol-Water Mixture with Different Concentrations

Water-ethanol mixtures can be regarded as simple model systems for studying the alcoholic strength. For this study, the concentration of ethanol is expressed by the symbol vol %. The percent concentrations of ethanol-water mixtures are determined based on the volume of ethanol and de-ionized (DI) water added. Several concentrations of ethanol in de-ionized water are prepared in the range of 0vol% to 50vol% as in Table 1.

Table 1. Percentage of ethanol-water mixture prepared in vol%

Concentration of Ethanol (Vol)%	Volume DI Water (ml)	Volume Ethanol (ml)
0.0	50.00	0.00
0.1	49.95	0.05
0.5	49.75	0.25
10	49.50	0.50
2.5	48.75	1.25
5.0	47.50	2.50
10	45.00	5.00
15	42.50	7.50
25	37.50	12.50
50	25.00	25.00

2.2. Organization of Spectroscopy Setup and Setting Parameters

The typical spectroscopy setup consists of three main parts; light source, transparent sample holder with internal width of 1cm cell known as cuvette and a light detector or a spectrometer. These can be shown as in Fig. 2 [13]. The light source can deliver a continuous broad spectrum ranging from 0.2 to 2.5 µm and a spectrometer has the detection range of 0.2-1.1 µm. The cuvette was placed in between the light source and the spectrometer. Before making a measurement, spectrometers must be calibrated by means of the absorbency of a reference substance is set as a baseline value, so the absorbencies of all other substances are recorded relative to the initial reference substance. Here, DI water was used as a reference substance. The ratio of the sample spectrum to the reference spectrum is directly related to the sample's absorption spectrum.

The absorption spectrum for ethanol at UV wavelength was recorded by simply setting up three important spectrometer parameters such as integration time to 1.14ms, scanning averages to 100 times and 10 units of smoothing. This chosen setting parameters was advised by the technical specialist from Aseptec Sdn. Bhd.

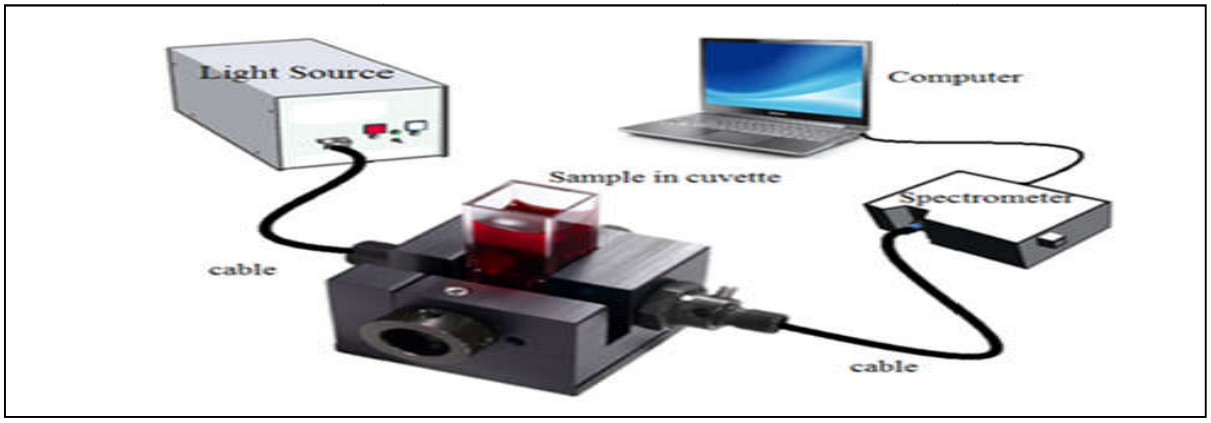

Fig.2. Illustration of fiber optic spectroscopy measurement setup

2.3. Measurement Procedure

The process of taking the ethanol absorbance spectrum can be shown in Fig. 3.

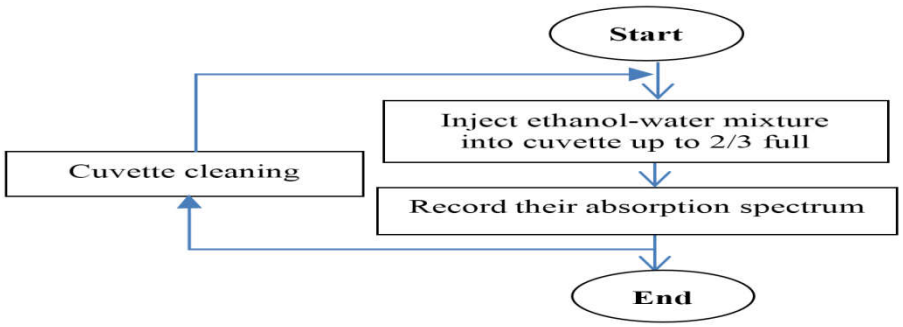

Fig.3. Measurement procedure

The measurement process was started with injecting ethanol-water mixture into the cuvette by using a syringe until two-third full. Spectrometer will qualitatively and quantitatively compare the fraction of the light that passes through a reference solution and the test solution. Their absorbance spectrum was taken once the reading became stabled. After that, the cuvette was rinsed in the way of injecting de-ionized water into cuvette several times. For each measurement, the cuvette was rinse thoroughly with de-ionized water as to ensure no residual particle from the previous test sample. Then, the measurement process was repeated for the whole concentration of ethanol-water mixture samples.

3. RESULTS AND DISCUSSION

The absorbance spectrum of ethanol-water mixture is analyzed based on their wavelength, intensity and the stability of the baseline spectrum.

3.1. Plotting the Absorbance Spectrum for Different Concentration of Ethanol

Fig. 4 shows the results for the absorption spectrum of ethanol-water mixture at the UV wavelength region with difference concentration from 0.5% to 100%. From the figure, notice that, the recorded spectrum data measured at UV wavelength have unstable baseline because the spectra were seemed slanted and not aligned properly at the reference axis.

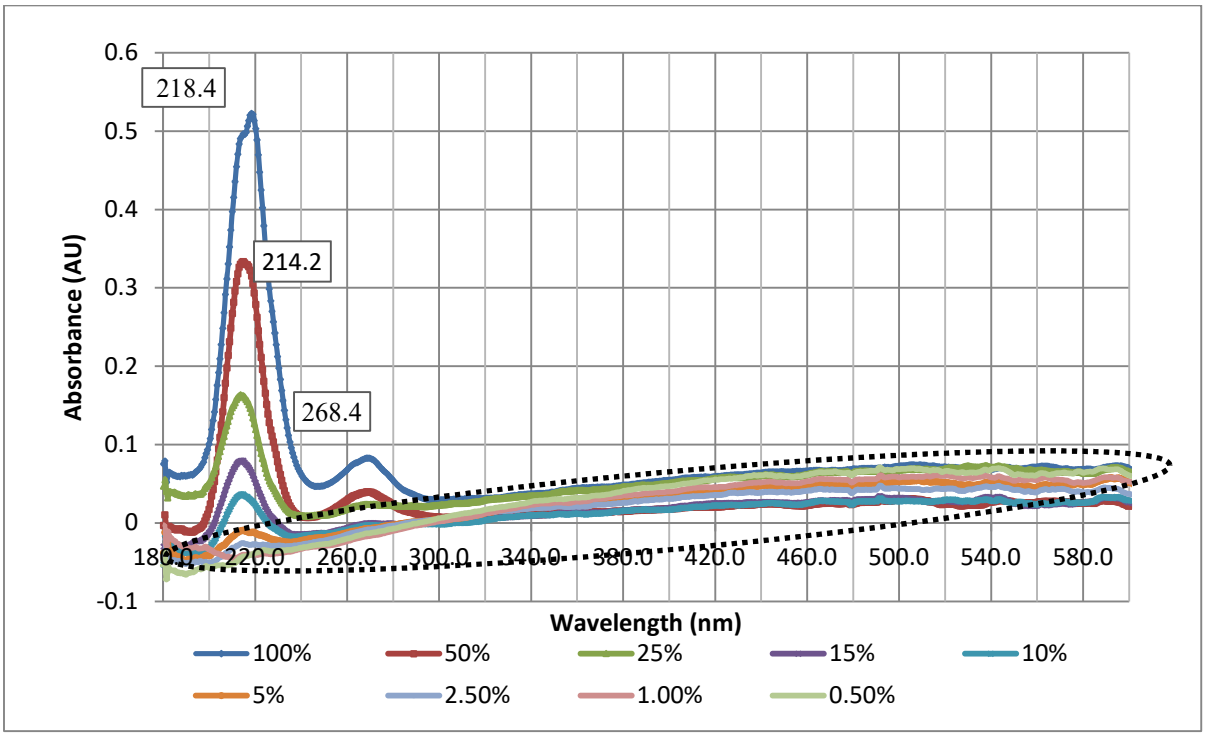

Fig.4. Absorption spectrum of ethanol-water mixture at UV wavelength region

Fig. 5 shows the absorbance spectrum of ethanol after narrowed down at the most significant absorbance wavelength range.

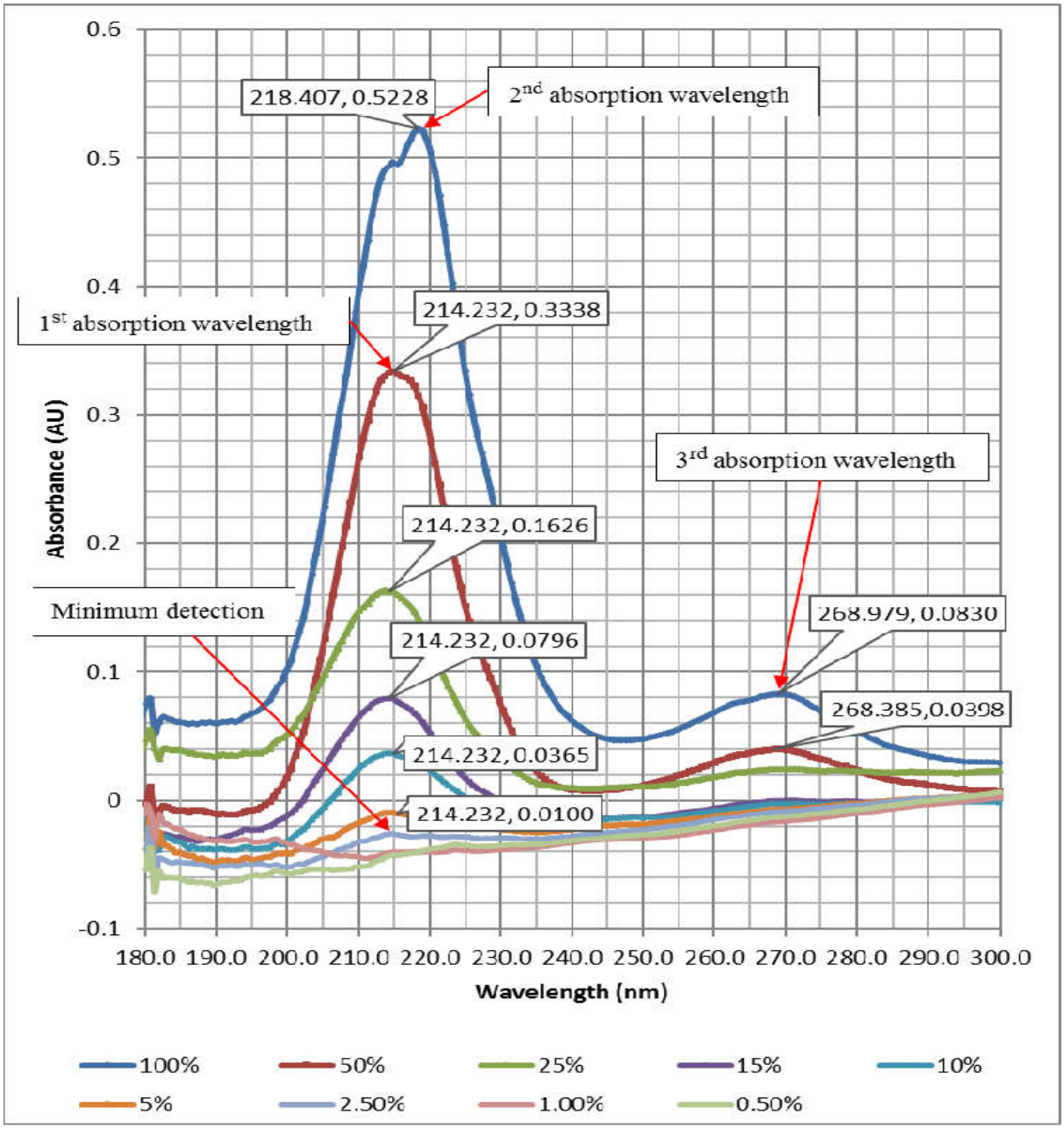

Fig.5. Absorption spectrum of ethanol in the range of 180nm to 300nm wavelength

Obviously, there were double maximum absorption wavelength can be seen for 100% and 50% and ethanol. For 100% ethanol, the first maximum absorption occurred approximately at 218.4nm while the second absorption arisen at 268 nm. However, the first absorption peak for 50% ethanol was shifted to 214.2 nm, while the second absorption peak remained the same as 100% ethanol. However, as the concentration of ethanol decreased, the second absorption wavelength was gradually disappeared. The rest of the concentration only have single absorption peak at 214.2 nm. However, there were no significant peak can be observed for 1%

and 0.5% ethanol. The absorbance intensity for each ethanol concentration at their absorption wavelengths are tabulated in the Table 2.

Table 2. Absorbance intensity at maximum absorption wavelength for different concentration of ethanol-water mixture at UV wavelength region

Percentage of Ethanol (Vol%)	1st Absorbance Wavelength (nm)	1st Absorbance Intensity (AU)	2nd Absorbance Wavelength (nm)	2nd Absorbance Intensity (AU)
100	218.4	0.52	268.4	0.08
50	214.2	0.33	268.4	0.04
25	214.2	0.16	268.4	0.02
15	214.2	0.08	Not significant	Not significant
10	214.2	0.04	Not significant	Not significant
5	214.2	-0.01	Not significant	Not significant
2.5	214.2	-0.03	Not significant	Not significant
1.0	Not significant	Not significant	Not significant	Not significant
0.5	Not significant	Not significant	Not significant	Not significant

From Table 2, as the concentration of ethanol decreased, the intensity of the absorption also decreases. For 100% concentration, the maximum absorption wavelength was occurred at 218.4nm. However, for the concentration from 50% to 0.5% the maximum absorption is aroused at 214.2nm. According to [1, 14-15], the maximum absorption spectrum for ethanol at ultraviolet wavelength was identified at 205nm, 210nm and 304nm respectively. Besides that, in [2] states 202nm, 228 nm and 300nm were identified also as ethanol absorption spectrum. However, the finding found in this research study is a bit shifted away from the reported literature.

From [16] shifting in maximum absorption wavelength can be occurred due to the interaction between water and ethanol. In this study, de-ionized water is a solvent and it was added into the ethanol solution as to vary the concentration. One molecule of water has two hydrogen atoms covalently bonded to a single oxygen atom. Water has maximum absorption spectrum at 190 nm [17] and 191 [15]. The oxygen in one water molecule is attracted to the hydrogen in the hydroxyl group (-OH) in a nearby ethanol molecule, and vice-versa. Then, the H-bonds

pack the molecules together in the liquid phase which produces the macroscopically observed increase in density and total volume reduction of sample [18-19].The interaction between the ethanol and the water itself most probably caused the maximum absorption wavelength varied from 100% to 50% concentration.

3.2. Validation to Beer's Lambert Law

According to the Beer's Lambert law, the absorbance is directly proportional to the path length and the concentration of the absorbing analytes. Therefore, the relationship between absorbance and the concentration of ethanol should be plotted as to see how many percent the samples obeys the law. In order to find the relationship, maximum absorption wavelength at 214.2nm was chosen for all the concentrations since most of the absorption wavelength occurred at this wavelength. Table 3 summarizes the absorption intensity at 214.2 nm.

Table 3. Absorbance and intensity for different concentration of ethanol at 214.2nm wavelength

Percentage of Ethanol (Vol%)	Absorbance Wavelength (nm)	Absorbance Intensity (AU)
100	214.2	0.49
50	214.2	0.33
25	214.2	0.16
15	214.2	0.08
10	214.2	0.04
5	214.2	-0.01
2.5	214.2	-0.03
1.0	214.2	Not significant
0.5	214.2	Not significant

From Table 3, as the concentration of ethanol reduced, the absorbance intensity also reduces. However, at 2.5% and 5% concentration, the absorbance intensity has negative values. According to the Beer's Lambert law, absorbance should be positive if the molar absorption coefficient (ε) and the concentration (c) is both positive. Therefore, this negative absorption reading might be happened if more light is being emitted and detected than the supplied light source.

Fig. 6 shows the relationship between the absorbance intensities and 0.5-100vol% concentration of ethanol at 214.2nm. From the linearity profile, denoted by R^2, it is only 95.72% of the data followed Beer's Lambert Law.

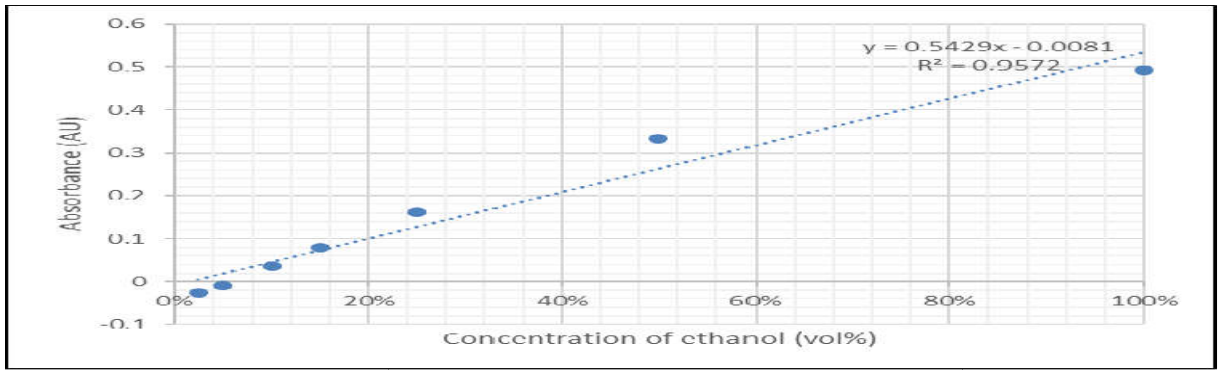

Fig.6. Relationship between absorbance intensities and 2.5%-100% concentration of ethanol at 214.2nm UV region

However, when the range of 2.5-50vol% is considered as in Fig. 7, 99.6% of the data obeyed the law.

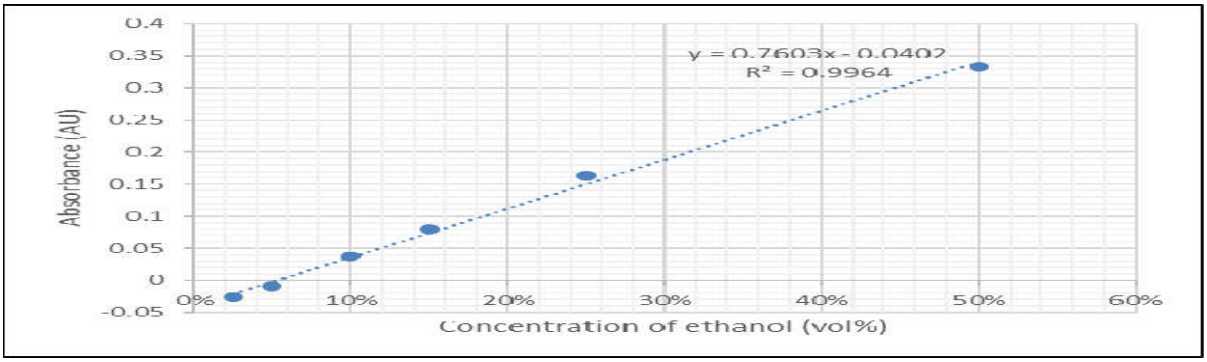

Fig.7. Relationship between absorbance intensities and 2.5%-50% concentration of ethanol at 214.2nm UV region

3.3. Baseline Correction

As mentioned earlier, the baseline of the spectrum data measured at UV wavelength was a bit slanted from the reference axis. This effect mostly might due to the higher energy of UV light source emitted and the stability of the equipment used. Therefore, for this UV spectrum data, the slanted baseline was corrected by using Asymmetrical Least Square algorithm [20]. Unstable/slanted baselines that occurred in instrumental measurements can cause inaccuracy of the reading taken. For this reason, baseline correction is needed for further analysis.

The baseline adjustment method used in this research study was relied on the approach known as asymmetric least squares reported in literature [20]. From this literature, there are two important parameters needed to be tune; p for asymmetry and λ for smoothness. The author found that generally $0.001 \leq \rho \leq 0.1$ and $10^2 \leq \lambda \leq 10^9$. However, the given range value for both parameter was very broad to be varied. Therefore, in this research study, the baseline of each spectrum data was estimated by using polynomial. Here, the degrees of polynomial were

set from 1 to 10. Once the degree of the polynomial has determined, then the parameter ρ and λ from the asymmetrical baseline algorithm was adjusted computationally until it matched enough to the polynomial baseline. The best λ and p was determined based on the calculated Root means square error (RMSE).

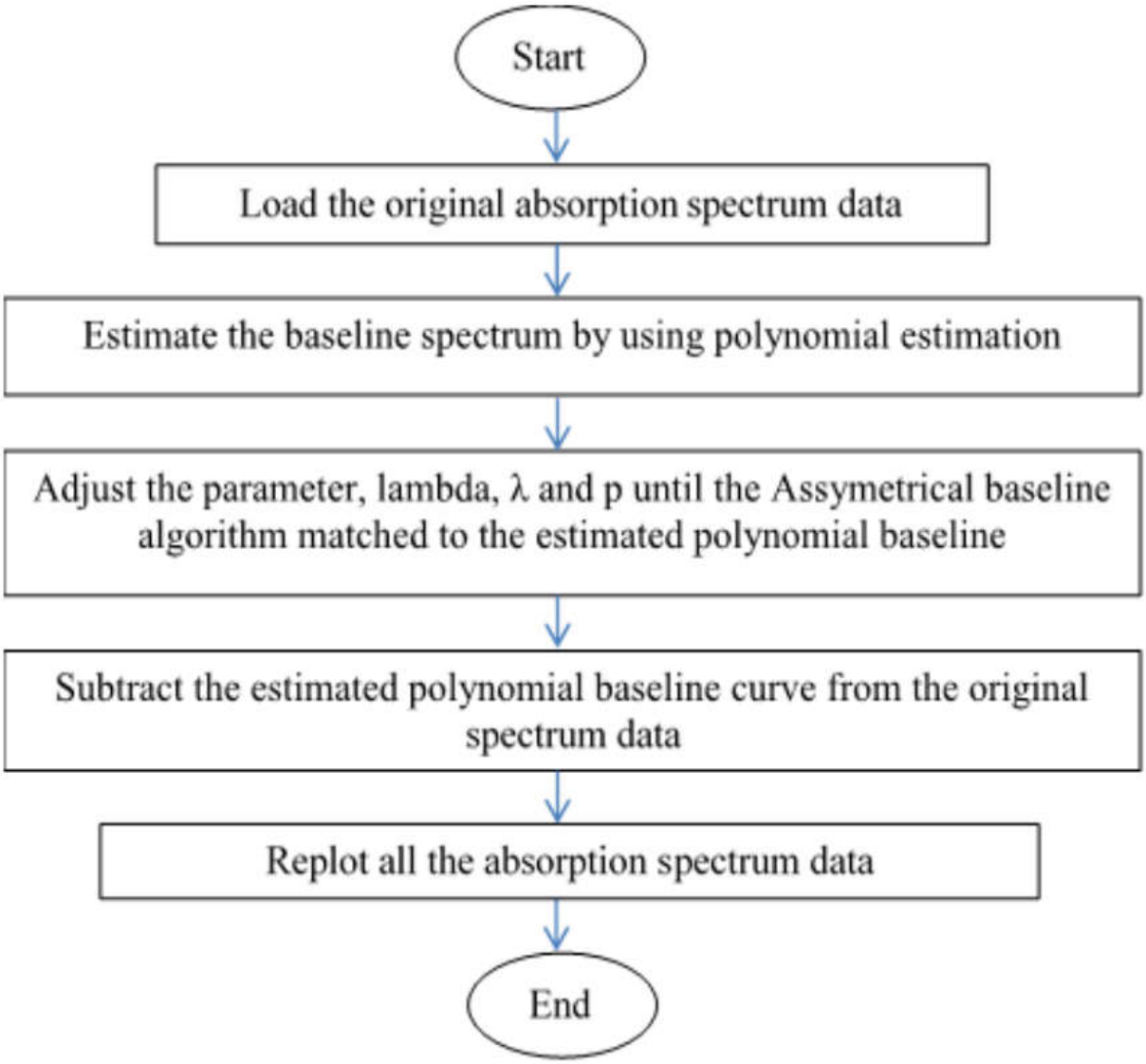

Fig.8. Baseline correction algorithm

After the matching process done, and then the chosen polynomial baseline curve can be subtracted from the original input spectrum. The procedure was repeated and applied for the each of the spectrum signal. Finally, the entire spectrum signal with the corrected baseline was plotted for further analysis. This process can be summarized as in Fig. 8.

The process of proposed algorithm can be described by using the spectrum signal of 100% ethanol concentration as shown in Fig. 9. The spectroscopic signal shows two distinctive peaks which indicate the concentration of the ethanol inside the sample. However, as can be

seen, the baseline of the signal collected from the spectrometer was a bit slanted. Therefore, the baseline should be corrected before the peak data was taken.

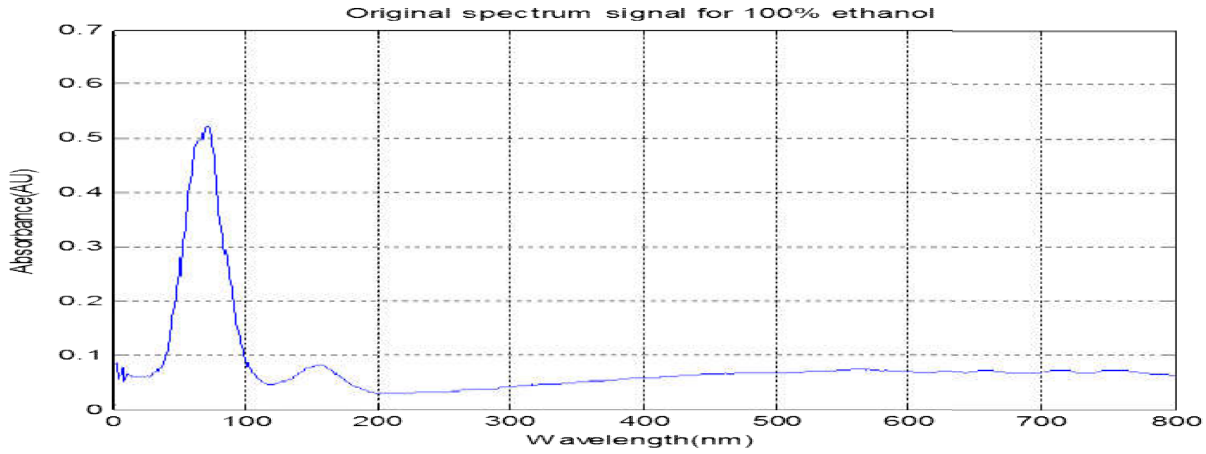

Fig.9. The original spectrum signal

The first step in correcting the baseline of the signal was to estimate the appropriate potential baseline which is suitable to the signal without affecting the information peak. This can be done by determine the suitable upper and lower cut-off values. From Fig. 10, upper cut-off (C_{upper}) and lower cut-off (C_{lower}) was chosen as 0.08 and 0.02. Here, any absorbance values below the cut-off limit will be removed.

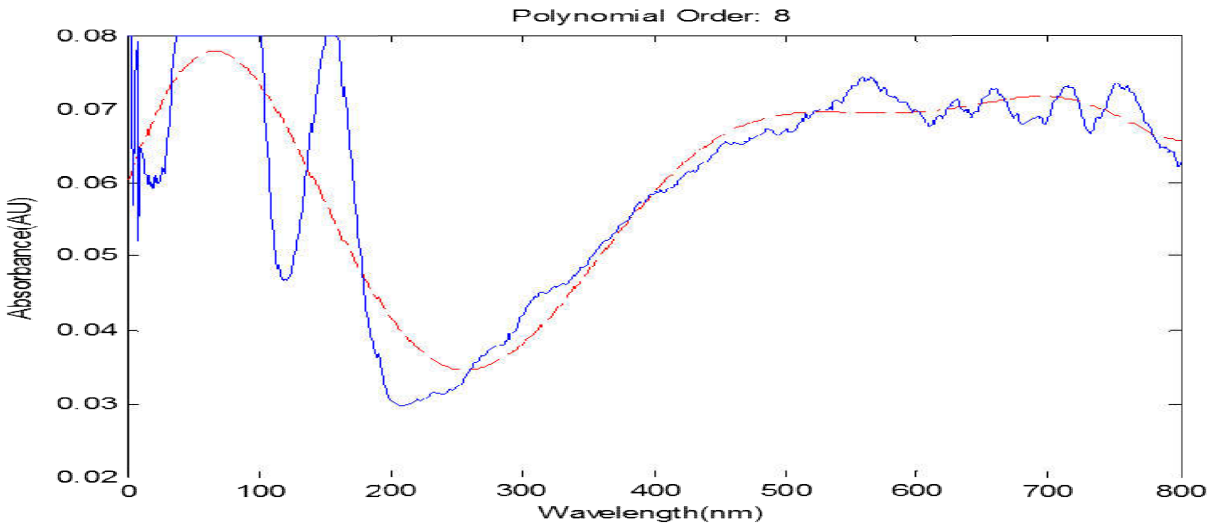

Fig.10. Estimated baseline based on polynomial

The range of estimated baseline should be in the selected cut-off limit as shown in Fig. 10. Next, the degree of polynomial needs to be approximated from the general shape of the clipped signal. Here, the order of the polynomial is varied from 1 to 10. From the figure, polynomial order-8 is the most suitable polynomial to describe the shape of the baseline. The chosen polynomial order should give very minimal effect to the information peak. Once the

polynomial has been approximated, the Asymmetrical Least Square algorithm will generate two values ρ and λ which accordance to the chosen polynomial with a certain acceptable range of RMSE.

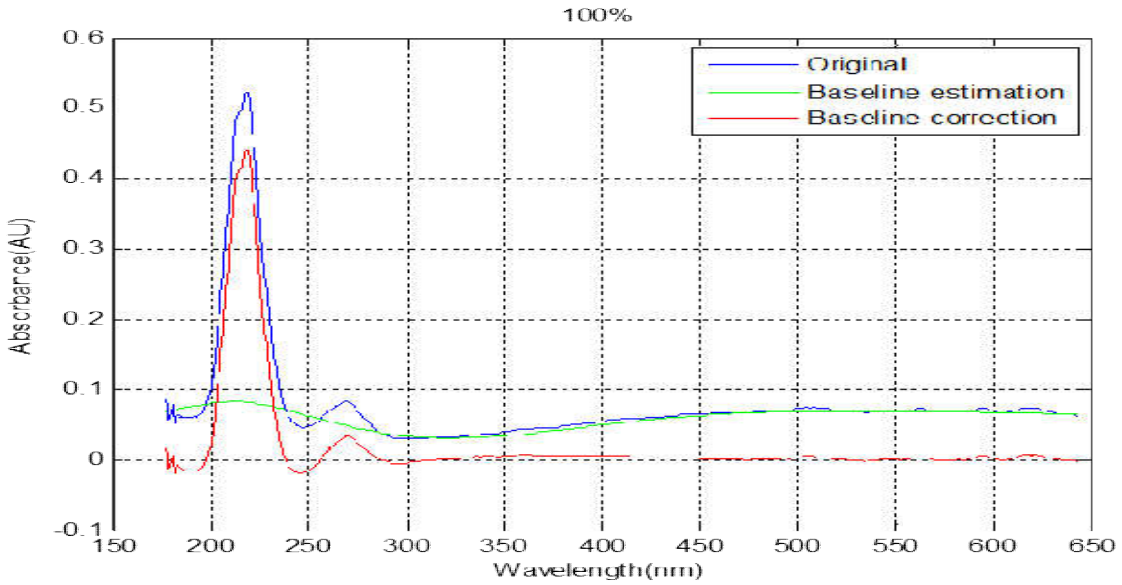

Fig.11. Baseline correction process

Fig. 11 shows the spectrum signal of original signal for 100% ethanol (blue colour), estimated baseline signal (green colour) and the original signal with corrected baseline (red). Any absorbance values below the estimated baseline (green color) were then subtracted from the original signal as shown in Fig. 11. This will result the spectrum signal with a proper baseline (red color). The stabilized signal spectrum for all ethanol concentrations can be shown in Fig. 12. Noticed that, after the baseline was corrected, the baseline of the spectrum was not slanted anymore and it was aligned properly at the reference axis.

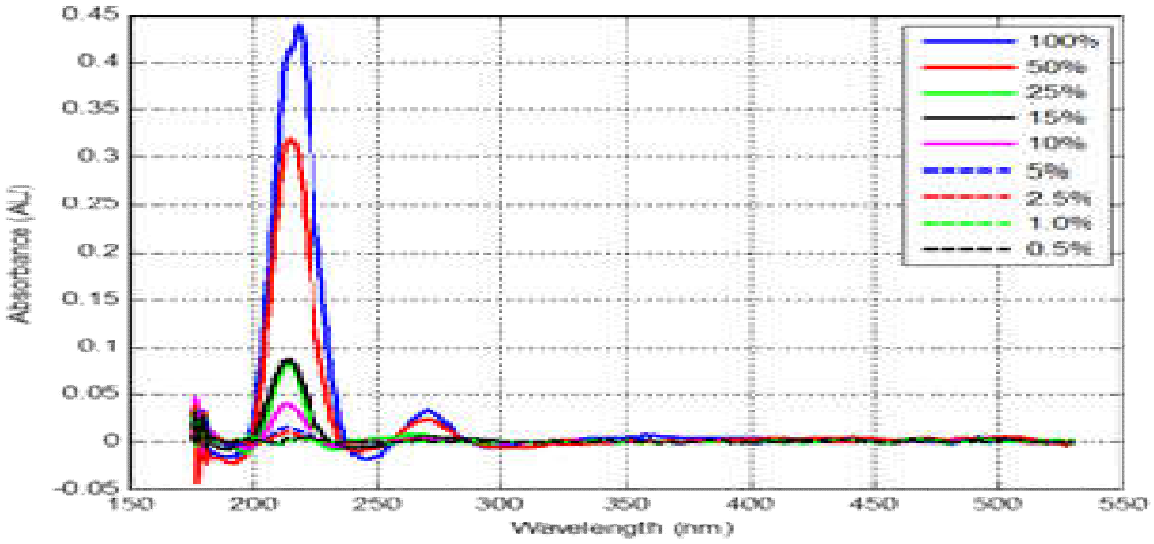

Fig.12. Spectrum signals with stabilized baseline

The value of C_{upper}, C_{lower} and the chosen parameter for p, λ, order of estimated polynomial baseline and the RMSE for each spectrum signal are tabulated in Table 4.

Table 4. Estimated C_{upper}, C_{lower}, polynomial order (PO), **λ**, ρ and RMSE parameters for ethanol spectrum signal

Signal	C_{upper}	C_{lower}	PO	λ	ρ	RMSE
100%	0.080	0.02	8	1010000	0.0500	1.4378×10^{-5}
50%	0.050	-0.05	9	510000	0.0900	9.1106×10^{-6}
25%	0.075	0.01	10	260000	0.0900	3.5365×10^{-5}
15%	0.035	-0.035	4	510000	0.0900	3.1869×10^{-5}
10%	0.040	-0.04	7	10000	0.0900	2.3959×10^{-5}
5%	0.065	-0.05	8	10000	0.0900	8.3994×10^{-6}
2.5%	0.050	-0.06	8	10000	0.0900	4.7497×10^{-6}
1%	0.060	-0.04	8	10000	0.0900	3.3521×10^{-6}
0.5%	0.070	-0.07	7	10000	0.0900	4.2018×10^{-6}

After the baseline spectrum was adjusted, then the relationship between ethanol absorption intensity and their concentration can be replotted as in Fig. 13.

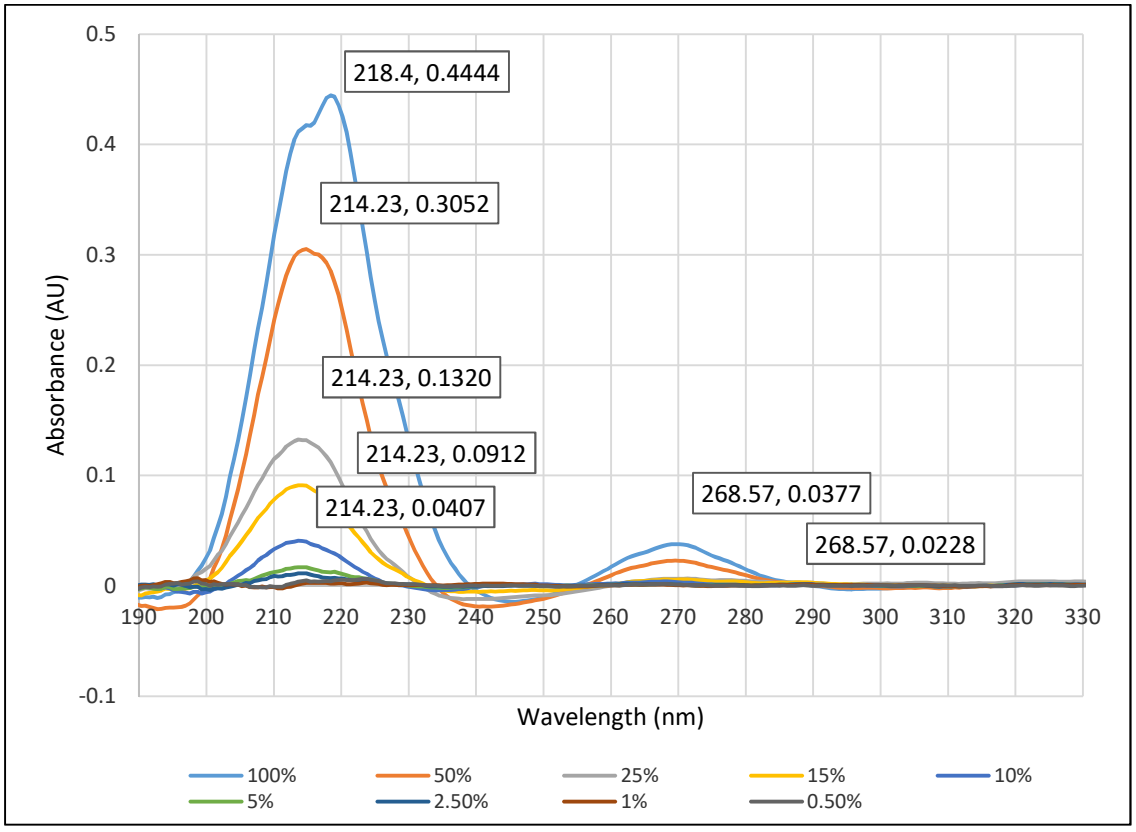

Fig.13. Replotted of ethanol-water mixture absorption spectrum at UV wavelength region after baseline correction

Again, the absorbance intensities at the first maximum absorption peak at 214.2nm were chosen for validation to the Beer's Lambert law. The intensities at this maximum absorption peak for each concentration are tabulated in Table 5.

Table 5. Absorbance intensity at 214.2nm for different concentration after baseline correction

Percentage of Ethanol (Vol%)	Absorbance Wavelength (nm)	Absorbance Intensity (AU)
100	214.2	0.44
50	214.2	0.31
25	214.2	0.13
15	214.2	0.09
10	214.2	0.04
5	214.2	0.02
2.5	214.2	0.01
1.0	214.2	Not significant
0.5	214.2	Not significant

From the table, notice that, after the baseline of the spectrum was stabilized, there is no more negative values for the absorbance intensity. Again, the relationship between absorbance and concentration of ethanol was validated to the Beer's lambert Law. Here, the maximum absorption peak also was chosen at 214.2nm as comparison to the data before the baseline was corrected.

Fig. 14 and Fig. 15 show the relationship between absorbance and concentration of ethanol at 214.2nm after the baseline correction.

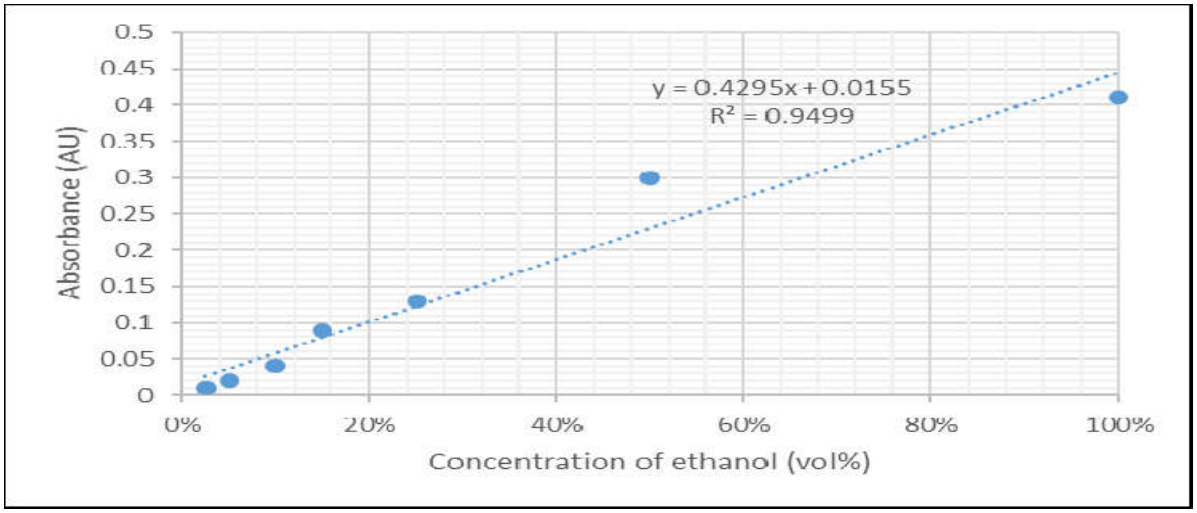

Fig.14. Relationship between absorbance and 2.5%-100% concentration of ethanol at 214.2nm after baseline correction

From the linear plotted data in Fig. 11, 94.99% of the prepared samples obeyed the Beer's Lambert Law when the concentration range was considered in between 2.5% to 100%. Again, when the range of the ethanol concentration were plotted in between 2.5%-50%, as in Fig. 15, the linearity profile was increased to 99.34%.

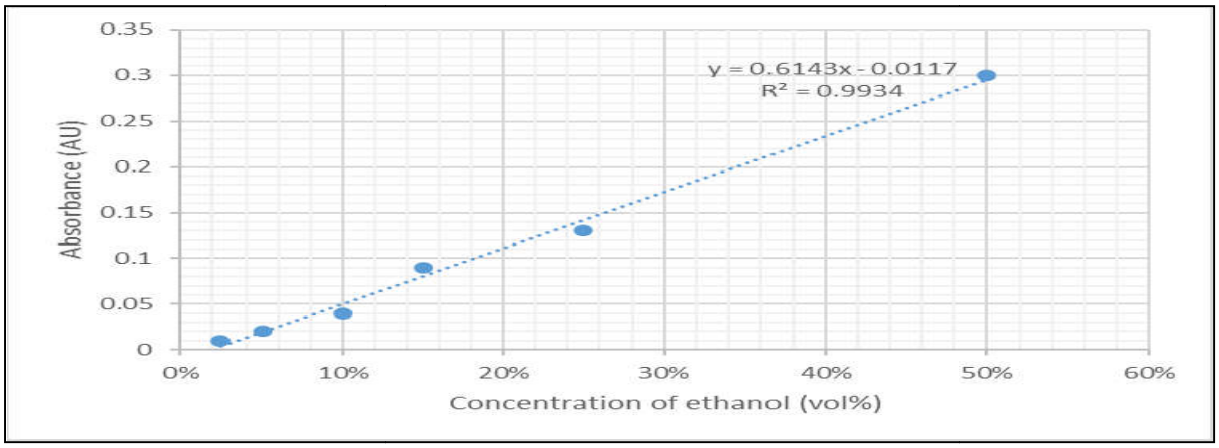

Fig.15. Relationship between absorbance and 2.5%-50% concentration of ethanol at 214.2nm after baseline correction

From both cases, either the ethanol profile was plotted before or after the baseline was corrected, the concentration range of 2.5-50vol% had fulfilled 99% of the Beer's Lambert Law. But, the advantage of correcting the baseline are there will be no negative absorbance value and the spectrum is placed at the proper reference axis.

4. CONCLUSION

The spectroscopy equipment used in this research study has successfully detect ethanol in ethanol-water mixture within the concentration range 2.5-100vol%. However, when validated to the Beer's Lambert Law, concentration range in from 2.5-50vol% has shown 99% of fulfillment. The implementation of Asymmetrical Least Square algorithm assisted with polynomial prediction in correcting the baseline of the absorbance spectrum has been successfully done in this study. The degree of obeyness towards Beer's Lambert Law is 99% achieved.

5. ACKNOWLEDGEMENTS

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