

Gas Chromatography Analysis of a C1-C5 Hydrocarbon Column

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Abstract: A gas chromatography (GC) equipment was used to classify chemical elements in a sample through a separation method based on the relative molecular mass. This paper describes the replacement of a capillary C5 and above Hydrocarbon Column of a Perkin Elmer Clarus 500 GC with a capillary C1-C5 hydrocarbon column from a different manufacturer. The use of appropriate carrier gas and a new standard procedure for C1-C5 hydrocarbons column, which manage to yield the largest, short time appearance and most stable detector signal area's patterns microVolt-seconds as qualitative and quantitative results were analysed. Several injector temperatures, sample split ratios, carrier gas flow rates and detector temperature were experimented. The effectiveness of nitrogen, helium and hydrogen as carrier gas were observed. The outcome showed that the combination of different column and GC equipment manufacturer works properly without any error. From the qualitative analysis of element configuration, the optimum setting found are; 250°C injector temperature, 1:15 split ratio, 2.5 ml / min flow rate and 275 ° C detector temperature. Hydrogen gas was found to be the best carrier for natural gas samples containing compounds that allot over a wide temperature range. In addition, a quantitative reference standard, the detector signal area microVolt-seconds against concentration of Methane gas was prepared to be used as a benchmark for C1-C5 hydrocarbon conversion reaction analysis.

Keywords: Carrier gas flow rate, split ratio, injector temperature, detector temperature.

1. Introduction

Gas chromatography (GC) equipment serves as a tool to classify the chemical elements in a sample through a separation method based on the relative molecular mass. This equipment can analyse all types of samples and is very suitable for small molecules. Due to the high sensitivity factor and effectiveness in separating components of a mixture, gas chromatography had become one of the important tools in the world of chemistry [1-4]. One of the most popular application of GC is steam reforming of natural gas, also known as Steam Methane Reforming (SMR) which produces synthetic gas based on Methane conversion. Hereby GC plays the main role to analyze the quantitative and qualitative of SMR yield [5-6].

This GC consisted of injector, carrier gas, column, oven, detector and recorder for information processors. This hardware has its their own settings to optimize the analysis of various samples [7-9]. This research has been conducted due to the replacement of a capillary C5 and above hydrocarbon column of a Perkin Elmer Clarus 500 GC with a capillary C1-C5 hydrocarbon column of a different manufacturer. Currently the Clarus 500 GC, had an existing column

of C5 and above hydrocarbon, and its usage is limited. Therefore, a detailed study was carried out so that the existing GC can be fully utilized to analyse the qualitative and quantitative characteristics of SMR's yields which are C1-C5 hydrocarbon.

A replacement was made by installing a new column to measure C1-C5 hydrocarbon. Therefore, the main parameter which is the type of carrier gas and a new experimental procedure for analysing samples should be studied to ensure consistency and accuracy of the GC measurement. The consequences of using a different brand column to different brand equipment are knowledgeable to ensure it will work properly and simultaneously [8,10-11].

The carrier gas functionally brings the sample through the column and selection of a suitable carrier gas for every column is important to ensure its work properly. Some of inert gas, which can be used as a carrier gas for gas chromatography are helium, nitrogen and hydrogen. Each carrier gas has its own unique advantages and benefits and impact of the output gas chromatography [3-5,9-11]. For Thermal Conductivity Detector (TCD) type, helium is the most popular. Meanwhile, for hydrogen is commonly used in some parts of the world (helium is very expensive), but this hydrogen is not recommended because it has

the potential to ignite fire and explode. For Flame Ionization Detector (FID) type, helium or nitrogen gas can be used and this nitrogen is more sensitive but slows in the analysis compared with helium. [9-11].

Hence a comparison has been analysed to create benchmarks on the standard setting of the GC operation. There are four main factors which can potentially give a big effect to the qualitative GC result; injector temperature, split ratio, carrier gas flow rate and detector temperature [10-12]. The area pattern of microVolt-second indicate the total amount of element's signal which been traced by detector through separation and absorption by column. Therefore, the area pattern of microVolt-second is proportional to the concentration absorbed by the column. The faster appearance, largest and stable area pattern show that the column is working in optimum condition for the variable element sample [3,7,9,11-16].

The purpose of this study is to identify and verify the appropriate carrier gas and new standard procedure for C1-C5 hydrocarbon column for qualitative and quantitative analysis. In this paper, the qualitative validation is FID retention time response, carrier gas and sample's mass fraction ratio impact on peak determination. Meanwhile, for the quantitative analysis, is only involving C1 hydrocarbon of Methane gas as the blank and standard library reference of GC systems which represent in concentration percentage [12-15, 17-18].

2. Experimental

2.1 Materials and Instrument

This study used a GC equipment of Clarus 500 from Perkin Elmer, C1-C5 hydrocarbon Column CP 7565 of Agilent as the medium for qualitative and quantitative measurement device. Nitrogen, Helium, Hydrogen and Methane gas are obtained from Air Product (M) Sdn Bhd. Meanwhile, for the Natural Gas is obtained from Petronas Dagangan Berhad.

2.2 Column Installation

The installation between column, injector and detector had been done accordingly to the standard operating procedure provide by Perkin Elmer [16]. These injectors are programmed to split/split less method and adjusted to the optimum operating pressure of 4-6 bar. Visual inspection for any leak at column connectivity had been done by using leak detector spray with a circulation of Nitrogen gas. The conditioning test which involve oven temperature setting of 50°C and elevated at 5°C/min till 200°C for 4 hours. This is to ensure that the C1-C5 hydrocarbon column complied and working accordingly to the GC setting parameter.

2.3 Sample's Injection

The sample is collected in the Tedlar Sampling Bag and manually injected into the GC system by using 250µl gastight needle syringe. This syringe was cleaned and rinsed by Nitrogen gas for each time of sample injection.

2.4 Qualitative Analysis

The qualitative analysis of C1-C5 hydrocarbon involved basic GC operating condition, type of carrier gas and element configuration through ASTM D1495 standard. In order to determine the optimum setting of C1-C5 hydrocarbon column qualitative parameter, a gap analysis had been done and a new setting has been proposed as shown in Table 1. There are four basic standard setting that needs to be tested in order to compare the results for reproducibility, recovery and the possibility of discrimination of the column efficiency. The others setting of Clarus 500 GC Perkin Elmer is using existing Standard Operating Procedure. Currently Flame Ionization Detector (FID) as existing detector and Natural Gas (NG) is used as the test sample.

Table 1 Variability of operating condition setting

Parameter	Split Ratio	Basic standard setting			Detector temperature
		Injector Temperature	Flow Rate	Detector temperature	
i Oven temperature	40°C, 3°C/min, 170°C.	40°C, 3°C/min, 170°C.	40°C, 3°C/min, 170°C.	40°C, 3°C/min, 170°C.	
ii Split ratio	1:50, 1:25, 1:15	1:15	1:15	1:15	
iii Injector temperature	250°C	225, 250/275°C	250°C	250°C	
iv Flow rate	2.5 ml/min	2.5 ml/min	2, 2.5, 3ml/min	2.5ml/min	
v Detector temperature	275 °C	275 °C	275°C	250/275/300°C	
vi Carrier gas	Nitrogen	Nitrogen	Nitrogen	Nitrogen	
vii Detector	FID	FID	FID	FID	
viii Sample	NG	NG	NG	NG	

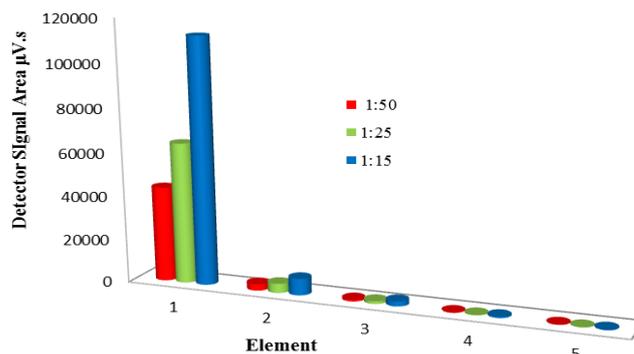


Fig.1 Effect of split ratio on element's detector signal area (µV.s)

Once optimum combination setting had been identified from Table 1, it proceeds with different carrier gas of Helium and Hydrogen. This is important to determine the optimum carrier gas usage for this “in house” configuration.

2.5 Quantitative Analysis

Since this paper is purposely to identify element of SMR's yield, therefore only involving C1 hydrocarbon which is Methane gas. This Methane gas is used as blank and memory reference for peak determination. The quantitative analysis was based on the variable concentration of Methane gas and was plotted against detector signal area in microVolt-second, which is suited for the SMR analysis of Methane conversion. The peak determination is done by comparing the similarity of retention times range, between NG and Methane gas sample [12].

3 Results and Discussions

3.1 Conditioning Test

This test had proven that the combined usage of different column brand to different brand equipment GC was working properly with zero error. This zero error is represented that all tested and setting parameter is successfully working without any machine failure and complied the Standard Operating Procedure of ASTM D1945.

3.2 Split Ratio

Fig. 1 shows three split ratios 1:50, 1:25 and 1:15 effect on the detector signal area in microVolt-second. All split ratio managed to detect up to 5 elements. It is observed that the 1:15 yield the highest area value for every element. This area indicates the efficiency of adsorption columns condition, whereby the column efficiency is proportional to the area. A unique calibration factor can be applied from this optimum FID's signal with deviation of a few percent. The lowest split ratio lead to the increasing of split flow injected sample, therefore the largest sample division carries along inside the column and have sufficient time for element separation and absorption [3,7, 13,15].

3.3 Injector Temperature

As shown in Fig. 2, all temperatures of 225, 250 and 275 °C manage to gain 5 detected elements. Unfortunately, the injector temperature is not proportional to element's detector signal area. This is because only a certain temperature will activate the instantaneous evaporation of the entire sample [7,9]. Therefore, the temperature of 250°C is most optimum setting to be used as an injector temperature because it manages to yield the highest element's detector signal area [3, 7, 9].

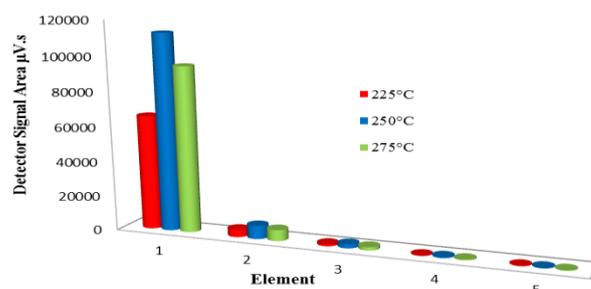


Fig. 2 Effect of injector temperature (°C) on element's detector signal area (µV.s).

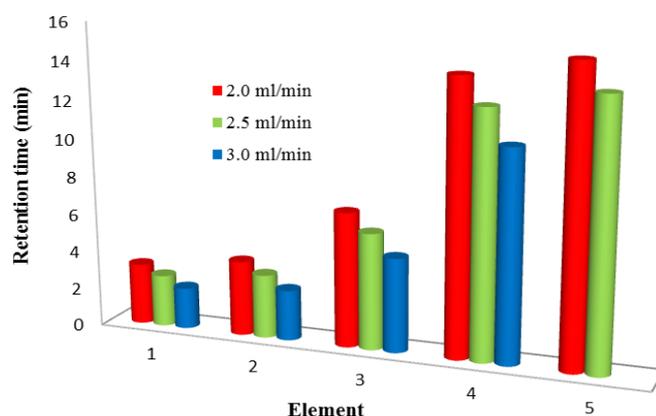


Fig. 3 Effect of carrier gas flow rate (ml/min) on element's retention time (min).

3.4 Carrier Gas Flow Rate

Fig 3 shows a graph of the carrier gas flow rate (ml/min) effect on element's retention time (min). The carrier gas flow rate directly influences the retention time and column efficiency. The proper selection and setting of the flow rate is essential in order to obtain the best analysis times (lowest retention time) and most efficient of detector signal area microVolt-seconds [3,4,11,12]. The flow rate of 3.0 ml/min detected the lowest retention time, unfortunately only manages to detect 4 elements as compared to the others flow rate, which managed to detect up to 5 elements. This indicates that the 3.0ml/min is too fast to work as sample carrier and less efficient for column separation and absorption processes. Meanwhile, the 2.5 ml/min had managed to detect almost the lowest retention time at all 5 elements. Therefore, this setting is more suitable to be used because of less retention time of the most efficient of column separation and absorption.

3.5 Detector Temperature

Analysis of the relationship between detector temperatures against detector signal area of the element can be observed in Fig 4. It is shown that all detector temperature managed to detect all 5 elements. Generally, the detector temperature affects the FID response values which represent as the detector signal area in the unit of microVolt-second. These detector signal areas are indicating the efficiency of absorption and separation column, whereby the column efficiency is proportional to the detector signal area [3, 7, 13]. The graph also shown that the detector temperature effect is not proportional to element's detector signal area. The detector temperature at 275 °C yield the highest detector signal area compared to the other. The detector functionally works at optimum temperature that allows the sample to be recorded simultaneously at separation and absorption stage [13].

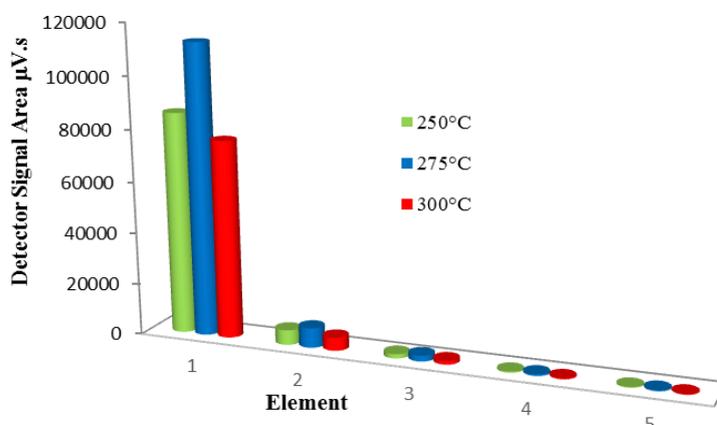


Fig. 4 Effect of detector temperature (°C) on element's detector signal area (µV.s).

3.6 “In house” Configuration Based on ASTMD1945

After several tests have been conducted to assess the appropriate settings for all basic parameters, a summary of the “in house” configuration of Agilent’s C1-C5 hydrocarbon column has been successfully established. As shown in Table 2, the hydrocarbon column Agilent instrument successfully can be applied into the Perkin Elmer Clarus 500 GC and accepted as “in house” configuration based on ASTMD1945 and ASTMD2597.

Table 2: “In house” configuration based on ASTMD1945

Parameters	Setting
i. Oven temperature	40°C, 3°C/min, 170°C
ii. Split ratio	1:15
iii. Flow rate	2.5 ml/min
iv. Injector temperature	250°C
vi. Detector temperature	275°C
v. Volume	200µl

3.7 Optimum Carrier Gasses

Next, the carrier gas for Agilent’s C1-C5 hydrocarbon column and Perkin Elmer Clarus 500 GC by “In house” configuration as in Table 2 was experimented. Two main parameters were considered as judgmental criteria, which are element’s detector signal area and retention time. For this parameter, there are three different carrier gases were tested; nitrogen, helium and hydrogen.

Fig 5a and 5b clearly shown that hydrogen gas manages to detect 6 elements compared to the nitrogen and helium gas which only detect 5 elements. The numbers of element detected is an indication that the sample carry along inside the column for reproducibility, recovery and the possibility of discrimination at most optimum condition. Furthermore, hydrogen gas also yields the highest element’s detector signal area and lowest retention time. According to van Deemter curve [3,13], hydrogen’s maximum efficiency is the highest compared to the others due to its curve is very flat and not easily effluence by any changes. Moreover, hydrogen’s high efficiency results in the shortest analysis times. Also, the wide range obtained makes hydrogen gas as the best carrier for samples

containing compounds that allot over a wide temperature range [3,4,6,8].

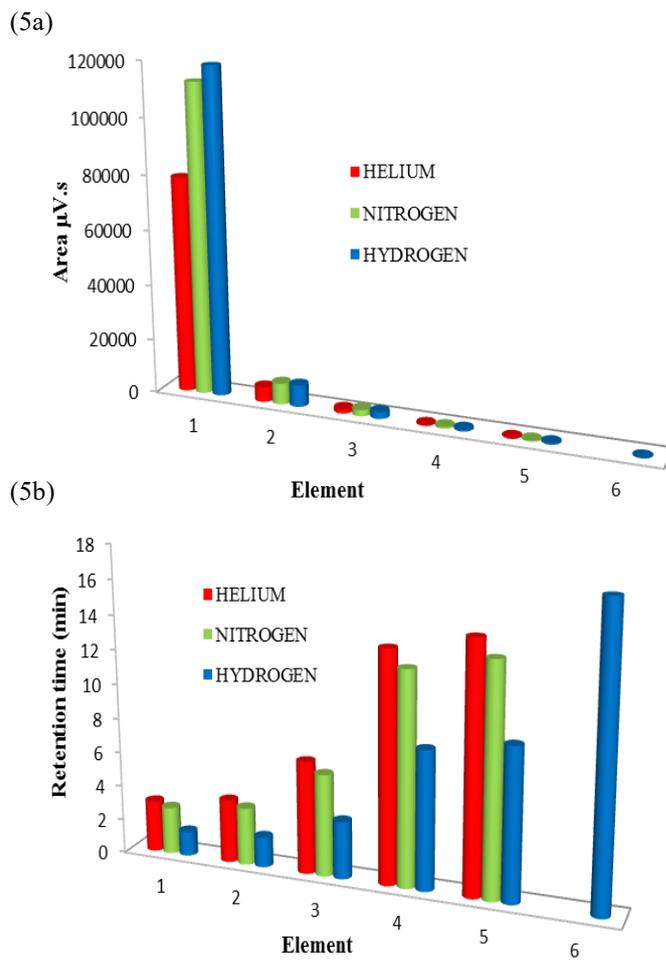


Fig. 5 a) Effect of carrier gas on element’s area; b) Effect of carrier gas at an element’s retention time

3.8 Element Configuration

In order to identify mass spectrometer for detecting element, configuration of element library was done according to the ASTMD1945 and ASTMD2597. Therefore, based on Fig 5a and 5b, detected element is identified and matched accordingly to the retention time and shown as in Table 3. This Table 3 is representing the peak of component’s appearance time.

Table 3 Detected element accordingly to retention time

Element	Component	Retention time (min)
1	Methane	1.30 – 1.45
2	Ethane	1.65 - 1.80
3	Propane	3.20 – 3.35
4	Iso Butane	7.90 – 8. 05
5	Normal Butane	8.65 – 8.80
6	Iso Pentane	16.90 – 17.05

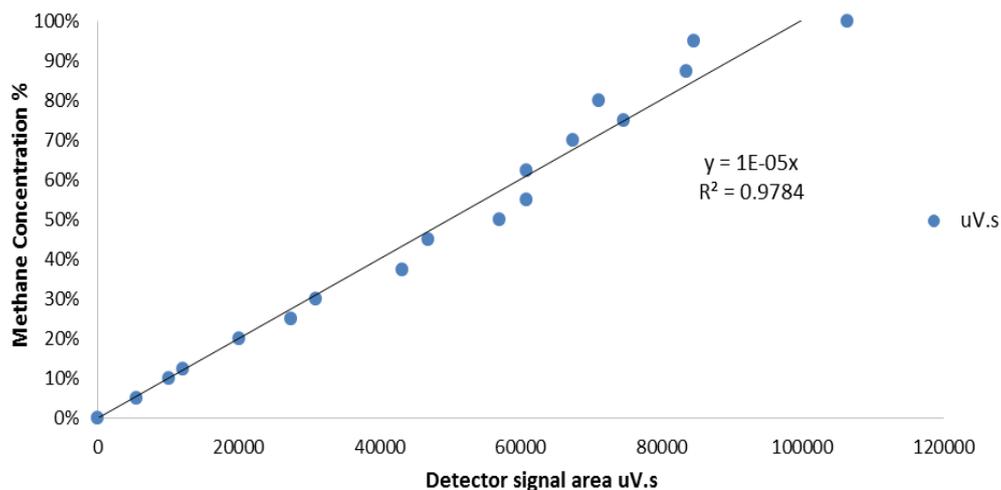


Fig. 6 Standard quantitative analysis of Methane concentration.

3.9 Standard Quantitative Analysis of Methane Concentration

In Fig 6, a graph of a standard reference for Methane concentration (ppm) against detector signal area was plotted. This standard reference was developed as a quantitative analysis because the gas chromatography Clarus 500 is only designed to produce qualitative analysis. The graph shows a straight line trending with $R^2=0.9784$ value. Methane variable concentration is proportional to the detector signal area microVolts.seconds with a function of $y = 0.00001x$.

4 Conclusion

The appropriate carrier gas and standard procedure for C1-C5 hydrocarbon column for SMR's yield quantitative and qualitative analysis were successfully investigated. The optimum main factor setting which is 250° C injector temperature, 1:15 split ratio, 2.5 ml / min flow rate and 275 ° C detector temperature for Agilent's C1-C5 hydrocarbon column. Meanwhile, hydrogen gas was found to be the best carrier gas due to its capability to produce the fastest appearance, largest and most stable area's patterns microVolt-seconds for qualitative parameter. Moreover, configuration of element library is done accordingly to the ASTM D1945 and ASTM D2597 for identifying and matching detected elements accordingly to the retention time. A quantitative reference standard, detector signal area patterns microVolt-seconds against concentration of Methane gas was prepared to be used as a benchmark for any C1-C5 hydrocarbon conversion reaction analysis.

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