Determination of Chlorine Content in Refined Palm Oil

Muhammad Syamim bin Rasidi, Dr. Nurul Fadhilah Kamalul Aripin

Faculty of Chemical Engineering, Universiti Teknologi MARA

***Abstract*—Chlorine always detected as the contaminant as it can cause plugging, fouling and corrosion in the pipeline and other equipment during processing of refined palm oil and higher chlorine content can cause trouble in human health. Thus, method of determination of chlorine content for water soluble chlorine sample and water insoluble chlorine sample in refined palm oil was important as the prevention acts using XRF, GC-MS and DPD colorimetric kits as testing method. Based on the testing method, GC-MS is very suitable for determination of higher organic chlorine content whereas XRF method was very easy to monitor the organic chlorine content in refined palm oil but the method for XRF is not complete as the unavailability of the standard. For wet chemical analysis method, the water soluble chlorine sample method is easiest to use to detect the inorganic chlorine content.**

***Keywords*— refined palm oil; total chlorine, GC-MS; XRF; DPD colorimetric kits**

I. Introduction

Malaysia is one of the largest producers and exporters of palm oil that supply vegetable oil around the world so it the most important industries in Malaysia. At 2016, a total of 5.74 million hectares were planted with oil palm in Malaysia, with 2.68 million hectares in peninsular Malaysia, 1.55 million hectares in Sabah, and 1.51 million hectares in Sarawak (Din, 2017). The focus on plantation growth has now moved to the East Malaysia states of Sarawak, with significant increase in planted areas of 4.7% over the period of 2015 to 2016.

The palm oil milling industries also increase as demand of the vegetable palm oil in the world are increase. Malaysia largest export destination in 2016 is India that need around 2.83 million ton of palm oil followed by Europe that need around 2.06 million tons. This cause a tremendous expansion on the palm oil milling industry. The number of palm oil mills in Malaysia in 2016 currently stands at 453, increase about 58 mills from 2009. Total capacity of the mill around 110.33 million tonnes of fresh fruit bunches (FFB) were processing annually (Din, 2017). The total crude palm oil (CPO) and palm kernel oil (PKO) production was 17.32 million tonnes and 4.19 million tonnes.

Refining is the important process to remove all impurities from crude oils such as undesirable flavour, odour and to remove colour pigment. This benefit of the process is to improve taste, appearance and to keep the content in the palm oil such as anti-oxidants and vitamins. There are two routes on refining the palm oil such as chemical refining or physical refining. In physical operation, the phosphatides and free fatty acids (FFA) are removed during degumming process through steam refining at higher temperature treatment (Gibon, De Greyt, & Kellens, 2007). The important of physical refining process such as reduction of water and effluent, better oil yield and reduction of use the chemical. At the opposite, in a chemical refining, alkali pre-treatment and deodorization method are used to degumming the oil and de-acidified at lower temperature. At physical refining, the modification of the triacylglycerol (TAG) matrix and reactions of TAGS with other component existing in the oil occur at high temperature during deodorizing (Hrncirik & van Duijn, 2011).

The undesirable reaction occurring during refining at high temperature are formation of 3-monochloropropane-1,2-diol (3-MCPD) and glycidyl esters. 3-MCPD was found in refined oils last few years that containing one or two fatty acid at the sn-1 and sn-2 position of the glycerol backbone (Velišek et al., 1980). 3-MCPD is identified as a substance which shows genotoxic effects in-vitro tests but not in in-vivo studies (Franke, Strijowski, Fleck, & Pudel, 2009). The researcher recommended a maximum tolerable daily intake of 2 µg/kg body weight (bw) of 3-MCPD (SCF Scientific Committee on Food, 2001). Refined palm oils generate higher levels of 3-MCPD-esters compared to rapeseed oil or maize oil (Zelinková, Svejkovská, Velíšek, & Doležal, 2006).

3-MCPD are classified as a chloropropanol or glycerol chlorohydrin. It is because of the substitutions of a chlorine atom with 3-hydroxyl group in glycerol. In the form of oil-soluble, the reaction can be done when chlorine present in the form of oil can react with other precursors (Matthäus, Pudel, Fehling, Vosmann, & Freudenstein, 2011). They found amounts between 1 and 6mg water soluble chlorine /kg in different palm oils. The content of unknown chlorine is the most highest in refined palm oil (Nagy, Sandoz, Craft, & Destaillats, 2011). Moreover, in palm oil there are so many organic chlorine compounds such as magnesium chloride, calcium chloride, iron [III] chloride, and iron [II] chloride in palm oil. According to Nagy et al. (2011), during processing, the relatively polar chlorinated constituents in the palm oil could be transformed into and more lipophilic forms such as MCPD esters along the oil processing chain. Figure 1 shows the chemical structure of 3-MCPD in refined palm oil.

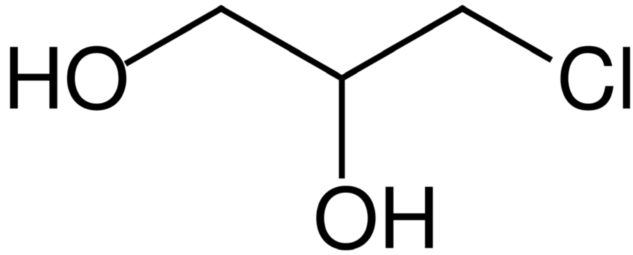

Fig. 1 Chemical structure of 3-MCPD

To increase the quality of the oil, fertilizer is used to grow the oil palm. The fertilizer contains inorganic chloride compound in the form of potassium chloride or ammonium chloride to help the bunch yield and growth of oil palm. The nutrient of the fertilizer such as chloride compounds are absorbed by the plant and gathered in the fruits bunch. The organochlorides seem to be endogenously produced by the oil palm during ripening (Nagy et al., 2011). Nagy also stated that organochlorides might start to decompose at temperature greater than 120°C and the formation of 3-MCPD esters start at temperature greater than 150°C.

Chlorine is used widely in organic and inorganic chemistry as an oxidizing agent (i.e., water disinfectant) and as a leaving group in substitution and elimination reactions. Around 63% of the chlorine is used in the manufacture of organic compounds, and 18% in the manufacture of inorganic chloride compounds. The balance of 19% are used for disinfection and bleaches product. Chlorine compounds discover use as intermediates in the production of a number of important commercial products that do not contain chlorine. Primary examples that do not contain chlorine are polycarbonates, polyurethanes, silicones, polytetrafluoroethylene, carboxymethyl cellulose, and propylene oxide. Sodium chloride also contains chlorine that are used as an electrolyte that have a chemical reaction in its that can cause contamination to produce sodium hydroxide. This contamination can cause severe corrosion and to narrow the market for the sodium hydroxide. For example, the mercury cell cannot achieve high current density cause of disturbance of chloride ion (Ito, Yoshizawa, & Nakamatsu, 1976).

When chlorine react with dissolved organic matter and bromide ion, it will cause production of harmful disinfection by-products (DBPs), such as trihalomethanes (THMs) and haloacetic acids (HAAs), which have adverse effects on human health(Nieuwenhuijsen, Toledano, Eaton, Fawell, & Elliott, 2000). The chlorine dose and residuals need to be kept low to limit DBPs formation and to reduce odour and taste. Chlorine also can cause a problem in crude oil transportation and refining in the presence of salt which cause corrosion, fouling and the deactivation of catalyst employs at the refinery which can cause loss in profit (Doyle, Saavedra, Tristão, Nele, & Aucélio, 2011).

Chlorine always detected in industrial in manufactured product and it is usually evaluated as contaminant (Medeiros, Souza, Araújo, da Silva, & Maranhão, 2018). Chlorine is most abundant halogen in the earth's crust. For regulation of osmotic pressure, water and pH balances, the chloride are needed (Machyňák, Čacho, Němeček, & Beinrohr, 2016). The chloride is easily found in sea food, egg and milk. Excess intake of chloride can cause high blood pressure, headache or mental confusion. Chlorine in the form of salt can cause corrosion, fouling and plugging in the pipeline and other equipment. For these reasons it is necessary to control the presence of chlorine at trace levels in a wide variety of samples. Chloride has been determined by volumetry (argentometric titration), potentiometry (ion-selective electrode), ion-chromatography (IC) and inductively coupled plasma (ICP) techniques. However, all those methods are sensitive to free ions. Therefore, covalently bonded chlorine cannot be determined. In addition, severe interferences highly influence the accuracy of the method.

Inorganic compound is easy to identify the quantity of chlorine rather than organic compound as inorganic compound do not have C-H bond. Furthermore, inorganic compound like salts made from only one element. For organic compound it need special instrument such as Gas chromatography–mass spectrometry (GC-MS) and x-ray fluorescence (XRF) which using a wavelength-disperse spectroscopic principles. Each instrument is suitable to use as it have high stability and easy to use.

From this study, it is expected that the organic and inorganic chlorine can be found in refined palm oil by using several techniques. The importance of this study is to find a new method to estimate the volume of total chlorine in fastest way and comparing the different testing method to achieve accurate reading. Only a few analytical techniques that can measure the chlorine accurately by using direct determination. The technique that are used in this experiment are XRF, GC-MS and N-diethyl-p-phenylenediamine (DPD) colometric test kits. The XRF method is possibly the simplest and the easiest to achieve, however, its sensitivity may be insufficient to assure the safety of the refinery process (Wolska, Kwiatkowski, & Kaminski, 2009). For low concentrations of chloroorganic compounds, the XRF method is also characterised by relatively low precision (Wolska et al., 2009). The instrument such as atomic absorption spectrometry (AAS) cannot be used for the direct determination of non-metal such as chlorine (Cheremisinoff, 1996). Usually analysis of halogens such as chlorine in organic substance are conducted by decomposition of the samples or salt extraction and further analysis as inorganic ions. As we know, as there involve additional method such as decomposition method, it will increase the time and cost of the analysis and the error maybe occur because of the sample contamination. However, the use of these atomic and mass spectrometric techniques for the determination of chlorine without or with minimum sample preparation might be afflicted by matrix interferences (Wolska et al., 2009).

II. METHODOLOGY

A. *Materials*

For the experimental investigations in laboratory scale refined palm oil (RBDPO) were used. Meanwhile, the main solvent used were distilled water, diethyl ether, and n-hexane and other additional chemicals used in solution preparation were sodium hydroxide powder, paraffin wax (food grade) and DPD Total Chlorine Powder Pillow.

B. *Methods*

There are around three methods for the determination of chlorine in refined palm oil which are wet chemical analysis and instrumental analysis that are used in this experiment. For the wet chemical analysis, DPD colorimetric kit was used to determine the chlorine content in water soluble. For instrumental analysis, XRF and GC-MS were used to determine the chlorine content in its.

1) Preparation of water extraction using Diethyl ether

In this method, the refined palm oil was dissolved by using Diethyl ether as solvent. Firstly, the refined palm oil was heated under heating plate at 80℃ for 30 minutes. Then, about 50 ml of distilled water, and 20 ml of diethyl ether were added into separating funnel. Next, the 20 ml of refined palm oil was mixed into the separating funnel and shaken slowly for 5 times to form the layer between solution at the top. The solution was separated between upper layer and bottom layer of the mixture. The solution at the bottom layer was called as water soluble chlorine sample and solution at the top layer was called as water insoluble chlorine sample. The water insoluble chlorine solution and refined palm oil was sent to rotary evaporator and analyzed using GC-MS. The water soluble chlorine sample solution was sent and analyzed using DPD colorimetric test kits.

2) Combustion technique of refined palm oil

Firstly, the refined palm oil was heated under heating plate at 80℃ for 30 minutes. The concentration of NaOH solution was prepared which is 0.1 M NaOH by dissolving the NaOH powder with distilled water for 1 hour using magnetic stirrer. Then, 10 g of refined palm oil was combusted in the furnace. The combustion parameter was set as follows: Temperature: 600℃ and Time: 1 hour. Next, the ash that came from refined palm oil was added into the 0.1 M NaOH solution and was stirred for 1 hour using magnetic stirrer without presence of heat. After that, the mixture was filtered and the solution were analyzed using DPD Colorimetric test kits.

3) Preparation for XRF analysis

Firstly, the refined palm oil was heated under heating plate at 80℃ for 30 minutes. The different weight of refined palm oil was prepared based on percentage of 5 gram of paraffin wax which are 10 %, 20% and 50 % by dissolving the refined palm oil with 5 gram of paraffin wax. Then, the mixture was mixed with 20 ml of n-hexane and was stirred for 1 hour using magnetic stirrer with presence of heat. The sample was sent to rotary evaporator and operated under heat condition and sent to XRF to be analyzed.

C. Characterization

1) DPD colorimetric kit

To measure the chlorine content of the water soluble chlorine sample, DPD colorimetric, Hach DR 2700 was used at 530nm as the measuring wavelength. All of the conductivity was measured at unit of mg/l. to improve the accuracy of the data obtained from the measurement, triplicate measurement was done to obtain the final average chlorine content value.

2) GC-MS

In the scan mode of 49.5-500m/z, the sample were injected to injection port of the GC device and coupled to a mass spectrometer to analyzed the sample. The initial temperature of 80°C were set with a holding time of 5 min, 80-150°C at 1 min, 150-230°C at 3°C min-1 with a holding time of 25 min and 250°C for 0 min. A 1μL refined palm oil and insoluble palm oil was injected to the GC-MS. The carrier gas that are used are helium at head pressure of 100kPa..

3) XRF

In the X-Ray Fluorescence method, the sample was exposed to radiation from an X-ray tube in helium atmosphere. The examined sample was placed in an appropriately prepared vessel with a 0.1 mm thick Mylar foil bottom. The sample was inserted into the measuring chamber of the spectrometer and the reading was taken. At least 2 reading measurements were obtained to determine the average of chlorine content

III. RESULTS AND DISCUSSION

A. The comparison of each method

In this study, a wet chemical and instrumental analysis was performed on refined palm oil to determine its chlorine content. Wet chemical analysis was done to analyze water-soluble Cl originates from inorganic compounds. Instrumental analysis was done to analyze organic compound in refined palm oil. The data of chlorine content of refined palm oil obtained from the analyses of DPD colorimetric kits, XRF and GC-MS are reported. Table 1 presents chlorine concentration measured by DPD for sample preparation of water soluble chlorine sample extraction and furnace. Based on DPD for water soluble chlorine sample, it is used to measure the chlorine content based on chlorine salt that are present in the water. Based on our research, the chlorine content must be higher rather than palm oil seed and palm olein oil as level of 3-MCPD was higher rather than non-refined palm oil (Franke et al., 2009). For the water soluble chlorine sample method, the chlorine content shows an average concentration of 0.37 mg/L which is lower compared to the 3-MCPD chlorine content in commercial production of refined palm oil which is 4.6 mg/L. By using furnace method as sample preparation, it is used to identified the total chlorine content in refined palm oil. For sample preparation on furnace, the average concentration of chlorine was 0.06 mg/L. Its shows that the concentration of total chlorine is below than water soluble chlorine sample. This could be because the chlorine is release to the atmosphere during sampling preparation by using furnace. Another possible reason could be because this type of furnace cannot capture the chlorine gas release from the sample as the gas are release to the atmosphere. Result from this experiment could not be concluded because the decreasing in reading of chlorine content b using furnace as sample preparation.

Table 1 The concentration of prepared sample via different method (Each value based on 3 repetitions)

Method	*Average concentration (mg/L)*
Water soluble	0.37
Furnace	0.06

For the X-Ray Fuorescence (XRF) method, it is used to measure the total chlorine content in the sample. The chlorine content in refined palm oil relatively low because the chlorine has been treated to make sure the food was not contaminated and follow the regulation on food. For low concentrations of chloro-organic compounds, the XRF method is also characterized by relatively low precision (Wolska et al., 2009). Based on the results on table 2, the measurements of each repeated reading was not consistent. This could be because the analysis was done by using the paraffin wax food grade which contains many contaminated compound. From the results, it shows that the paraffin wax contains 1.1278 kcps of chlorine. Another possible reason could be because, the chlorine was not well distributed in the sample preparation, so it does not show the actual result. Results from this experiment could not be concluded because the lack of standardize samples to compare with.

Table 2 Results of reading intensity of chlorine using XRF in refined palm oil

Sample	Weight (g)	Reading of intensity (kcps)	
		1	2
raw wax	5.0	1.1278	1.1278
raw wax + 10% refined palm oil	5.5	1.1935	0.8332
raw wax + 20% refined palm oil	6.0	1.1591	0.9399
raw wax + 50% refined palm oil	7.5	1.0992	0.9724

For GC-MS method, it is used to measure the total chlorine content which is organic chlorine. It is possible to confirm the presence of a certain compound by analyzing SIM chromatogram.

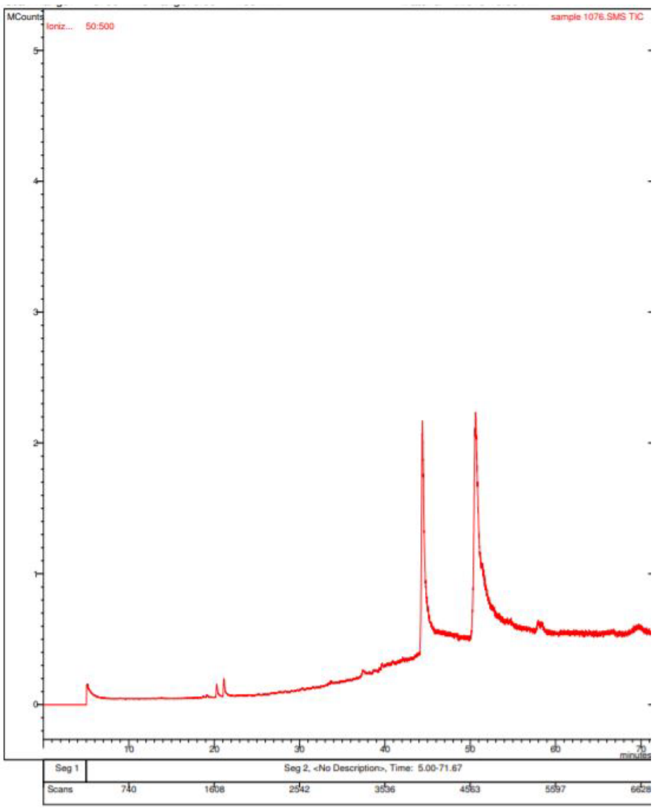

Fig. 2 GC-MS Analysis of chlorine content based on total ion chromatogram from the refined palm oil

GC-MS have the capability in identifying compounds using retention times and the relative abundances of the characteristic product ions, thus increasing the accuracy of the results. Fig.2 shows the total ion current (TIC) chromatograms obtained for the refined palm oil, where 4-Chloro-3-n-butyltetrahydropyran was identified.

Table 3 The chlorine composition of refined palm oil using GC-MS

Retention time	**Component**	**Percentage (%)**
58.314	4-Chloro-3-n-butyltetrahydropyran	0.4

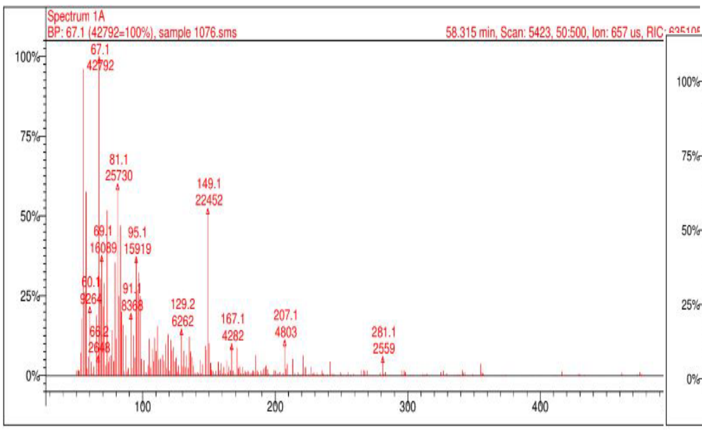

Fig. 3 The spectrum of refined palm oil at retention time of 58.314 (4-Chloro-3-n-butyltetrahydropyran)

Fig.4 shows the total ion current (TIC) of organic chlorine contains in insoluble water sample of refined palm oil. Based on the GC-MS measurement the reading is almost correct as palm oil has a balanced ratio of unsaturated and saturated fatty acids. It contains about 40% oleic acid (monosaturated fatty acid), 10% linoleic acid (polyunsaturated), 45% palmitic acid and 5% stearic acid (saturated fatty acid).

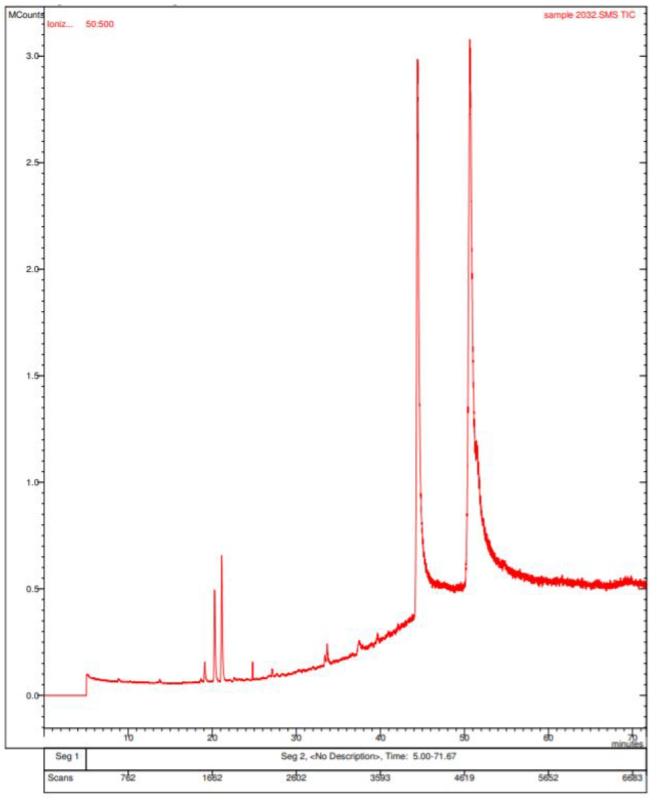

Fig. 4 GC-MS Analysis of chlorine content based on total ion chromatogram from the insoluble water chlorine sample of refined palm oil

Table 4 The chlorine composition of insoluble water chlorine sample of refined palm oil

Retention time	Component	Percentage (%)
39.633	2-Chloroethyl methyl ether	0.323
50.760	2-Chloroethyl oleate	19.473
51.490	7-Heptadecne, 1-chloro-	5.327

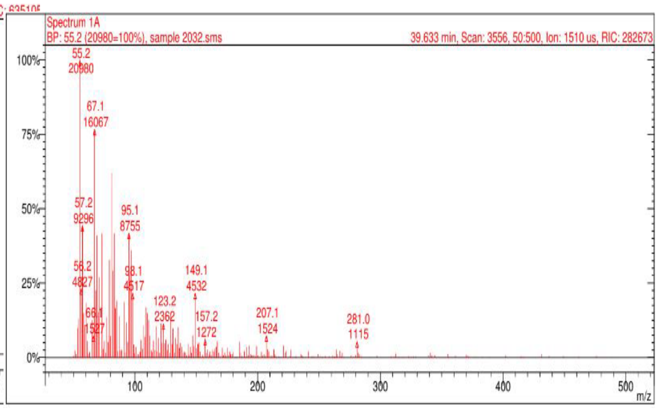

Fig. 5 The spectrum of insoluble water sample of refined palm oil at retention time of 39.633 (2-Chloroethyl methyl ether)

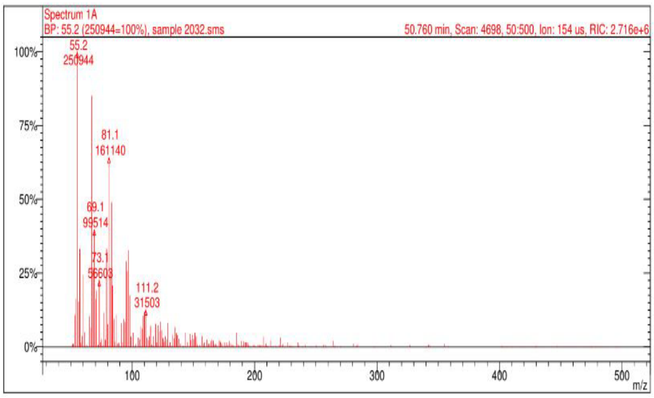

Fig. 6 The spectrum of insoluble water sample of refined palm oil at retention time of 50.760 (2-Chloroethyl oleate)

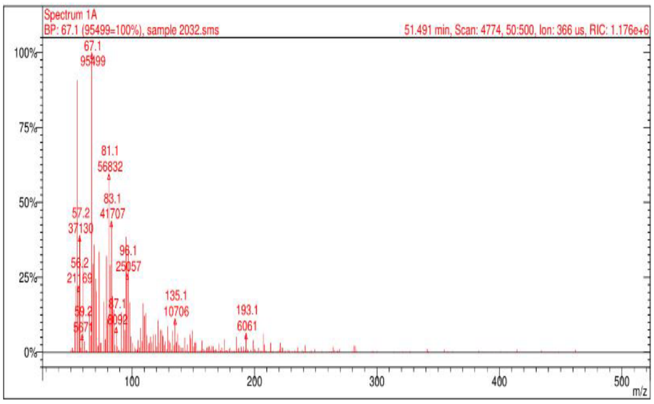

Fig. 7 The spectrum of insoluble water sample of refined palm oil at retention time of 51.491 (7-Heptadecne, 1-chloro-)

IV. Conclusion

Based on the results of this study chlorine content in refined palm oil can be detected on DPD colorimetric method, XRF method and GC-MS method. For the XRF method the actual chlorine content cannot be identified as the standard of the chlorine unavailable. The simplest method for wet chemical analysis method was water soluble chlorine as there's only little preparation that need to be followed. For instrumental analysis, XRF shows the easiest method and accurate but the standard solution unavailable. GC-MS reading is not precise as the chlorine content in refined palm oil is not high enough.

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