



APPLICATION OF IRAQI RICH-MONTMORILLONITE MINERAL CLAYS DOPED WITH CHROMIUM (III) OXIDE AS CATALYST TO EXTRACT IRAQI VIRGIN OLIVE OIL COMPONENTS BY SOXHLATE TECHNIQUE

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ABSTRACT

Natural Iraqi montmorillonite mineral clay samples, treated chemically and physically, have been doped with Chromium (III) oxide to obtain a catalyst. The chemical composition and structural properties of the clay samples were characterized. They have been applied in extraction of Iraqi virgin olive oil by soxhlate. Four types of solvents were used in the extraction process. Infrared spectroscopy (IR), nuclear magnetic resonance spectroscopy (¹H NMR) and gas chromatography technique built-in to mass spectrometry (GC-MS) were established, in order to identify the components of the extracted olive oil. From results thus

obtained, both the natural and the treated clay have a good efficiency to separate olive oil to their major components which are triglycerides, phenolic and volatile compounds such as aldehydes.

KEYWORDS: Mineral clays, Virgin olive oil, Soxhlate.

INTRODUCTION

Olive oil is the oil obtained from the fruit of the olive tree.^[1] It was available in different qualities. These include (1) cold-pressed extra virgin olive oil and virgin olive oil having a maximum of free fatty acids of 1.0% and 2.0% (as wt % oleic acid), respectively, (2) olive oil, consisting of a blend of virgin olive oil and refined olive oil with a maximal acidity of 1.5% and (3) olive pomace oil which is a blend of, solvent extracted olive-pomace oil and virgin olive oil, having a maximum acidity of 1.5%. Oleic acid (18:1) is the major component

of the olive oil (65-85 wt %).^[2] Olive oil can be divided from the point of view of chemical composition into major and minor fractions. The major components, which include glycerides, represent more than 98% of total oil weight. While the minor components, which are present in very low amounts (about 2% of oil weight), include more than 230 chemical compounds such as aliphatic and triterpenic alcohols, sterols, hydrocarbons, volatile compounds and antioxidants (carotenoids and phenolic compounds).^[3]

Clays such as montmorillonite, widely used in industry for separation, purification and recovery processes. Adsorption with natural clays has great importance due to the ease of operation, comparable low-cost of application, ion exchange properties and high surface areas.^[4] Application of Iraqi raw minerals in industries as adsorbent materials was the interest of many workers. Mineral clays bearing feldspar have been applied to fractionate Iraqi heavy crude oil into its simple and useful components.^[5] Moreover, recently it was reported that doping of Ninivite silica rocks by chromium oxides gel yields active and selective adsorbent catalysts which applied in solid phase extraction fractionation of Iraqi virgin olive oil.^[6] Accordingly and in order to continue searching in this field, many subjects have been tabulated in our laboratories including the present one which is investigating natural mineral clays bearing montmorillonite as major mineral in their composition. Such material has to be characterized physically and chemically via several instrumental techniques and applied in olive oil extraction by using soxhlate.

Experimental

A- Sources and collection of samples

Natural minerals clay, obtained from a village of Aski-Mosul (a suburb of the city of Mosul) Governorate of Nineveh /Iraq. These samples were green-gray in color have (300-425 μ m). Individual samples weighed from 1.0 to 3.0 kg; and were thoroughly mixed to obtain representative samples. At each sampling site, parent rock, samples were also collected. For x-ray diffraction analysis and bulk mineralogy, the raw and the treated samples were powdered by agate mortar and agate tama mill.

Meanwhile, the virgin olive oil sample, which was obtained from a village of Bashiqa (a suburb of the city of Mosul) Governorate of Nineveh /Iraq, was selected to be studied.

B- Methods of study

The identification of clay minerals and their alteration products was carried out by using x-ray powder diffraction method (XRD), which carried out using Shimadzu X-ray Diffraction 7000, 2009 equipment with monochromatic, Cu-radiation.

Meanwhile x-ray fluorescence (XRF) spectrophotometer was employed for the clay samples on OXFORD, X-MET 7500. The thermal analysis was performed by means of METTLER TOLEDO, TGA/DSC STAR^e SW 9.30, each powdered sample was heated by 5°C/min. up to 400°C with α -Al₂O₃ as a reference material temperature, weight, change in wt. and the thermal behavior of the sample is recorded on the chart. Finally infrared spectroscopy was recorded on SHIMADZU, IR Affinity-1, While the physical properties measurements were carried out applying abstracted methods.^[5]

In the other hand, the extracted fractions from virgin olive oil also studied and the infrared spectroscopy were recorded on Nicolet, FT IR Impact 400D, ¹H NMR data were obtained from BRUKER, Ultra Shield 300 MHz. Finally gas chromatography (GC-MS) was recorded on THERMO SCIENTIFIC, TRACE GC ULTRA-ISQ. The above technical studies were performed at AL- Al-Baiyt University/ Jordon.

C- Application

The Chromium (III) Oxide was supported over clay sample by impregnation doping method^[7,8] and further dried and activated at 260°C. Soxhlate technique was applied in order to extract virgin olive oil into its simple components. Temple fractionation column containing clay sample were employed in the extraction process. A known weight (2g) of virgin olive oil was fractionated into four fractions using four eluants of different polarities (petroleum ether, toluene, chloroform and ethanol) in order to evaluate the adsorption capacities of the clay sample.

RESULTS AND DISCUSSION

Physical characterization, structural and chemical analysis of clay sample, acidic and basic treated clay, clay heated at 700°C and the doped sample were studied and to be published recently.^[9] In general, it seems that all those samples show a significant variations in their chemical compositions, physical properties and especially in their structural components. It is therefor, of interest to get benefit of such foundations which evaluate the clay sample as a good adsorbents in the catalytic treatment process.^[10] In our investigation we thought that it is

of interest to concentrate the mineral clays on the doped sample which evaluate the catalytic activity and selectivity in upgrading of Iraqi virgin olive oil.

The infrared spectra for the four eluants resulting on applying doped natural clay sample, which is already activated at 260°C, relying on their infrared data, Figures (1-4) and Table (1). The IR spectra data show bands at (2855, 2921 cm^{-1}) which are corresponding to the stretching vibration of (C-H) in methylene group (-CH₂) and strong band at (1742 cm^{-1}) due to carbonyl group (C=O), in addition to a weak band at (1654 cm^{-1}) due to (C=C) of unsaturated fatty acids. Finally, the spectra revealed three bands at (1100, 1159, 1240 cm^{-1}) which are related to stretching vibrations of (C-O). The above observed bands indeed are attributed to the functional groups of triglyceride compounds and indicate that most of the aliphatic components which represent triglycerides were eluted in petroleum ether and toluene fractions.

Meanwhile, it looks that in chloroform fraction most of the phenolic compounds were eluted. This arises from the spectra data which show a band at (3411 cm^{-1}) due to stretching vibrations of (O-H) and a band at (1595 cm^{-1}) related to stretching vibrations of (C=C) in aromatic ring. Finally, ethanol fraction suggested that band at (2848 cm^{-1}) due to stretching of (C-H) and band at (1720 cm^{-1}) can be assigned to the functional group (C=O) in aldehyde compounds.

Nuclear magnetic resonance (¹H NMR) are shown in Figures (5-8) and data which are presented in Table (2), supported the above observation. Petroleum ether and toluene fractions showed a signal at (0.85ppm) due to proton of methyl group in oleic and linolenic acid, while the signals at (1.6, 1.26 ppm) due to proton of the methylene group and methylene group in beta position for the fatty acid respectively. Whereas the signal at (2.32 ppm) corresponding to proton in alpha position. Furthermore, data show a signals at (4.1-4.32 ppm) due to protons of glycerol's methylene group in triglycerides. In addition to a signal at (5.34 ppm) for proton of olefin in all unsaturated fatty acid.^[14,15] The data obtained from chloroform fraction showed a signal at (7.26 ppm) corresponding to proton of aromatic ring, and signal at (8.1 ppm) due to hydroxyl group in phenols. Finally, from ethanol fraction, it was shown that a signal at (9.7 ppm) due to proton of carbonyl group in aldehyde.^[16,17]

Finally, gas chromatography technique built-in to mass spectrometry (GC-MS) Figures (9-12) were used to identify the eluted fractions, and the result data shown in Table (3).^[18,19] The

results reflect the fact that most of the aliphatic components which represent triglyceride were eluted in petroleum ether and toluene fractions. Meanwhile, it seem that in chloroform fraction most of the phenolic were eluted and finally it was noted that aldehyde compounds eluted in ethanol fraction.

Table (1): IR spectra for eluted fractions of Iraqi virgin olive oil.

Eluted compounds Solvents	Triglycerides					Phenols				Aldehydes	
	C-H CH ₂	C-H CH ₃	C=C	C=O	C-O	O-H	C-H		C-O	C-H	C=O
Petroleum ether	2921.6 2855.4 722.1	1454.8 1367.2	1654.1 966.9	1742.3	1240.6 1159.0 1100.6
Toluene	2920.0 2855.7 727.2	1455.2 1372.2	1653.9 976.4	1735.3	1243.8 1168.8 1106.9
Chloroform	2920.1 2857.1 731.3	1654.1 908.1	1654.1 908.1	1732.4	1260.1 1170.4 1031.0	3411.9	3054.3	1595.2	1100.7
Ethanol	2921.3 723.8	1654.1 976.4	1654.2	1720.4	1262.2 1173.8 1108.8	3353.3	3057.5	1573.3	1108.8	2848.9	1720.4

Table (2): ^1H NMR data for the eluted fractions of Iraqi virgin olive oil.

Solvents	Chemical shift	Protons
Petroleum ether	0.85	-CH ₃
	1.26	-(CH ₂) _n -
	1.6	-CH ₂ -CH ₂ -COOR
	2.01	-CH ₂ -CH=CH-
	2.32	-CH ₂ -COOR
	4.1-4.32	-CH ₂ -O-COR
	5.34	-CH=CH-
Toluene	0.87	-CH ₃
	1.26	-(CH ₂) _n -
	1.6	-CH ₂ -CH ₂ -COOR
	2.01	-CH ₂ -CH=CH-
	2.32	-CH ₂ -COOR
	4.1-4.30	-CH ₂ -O-COR
	5.34	-CH=CH-
Chloroform	0.85	-CH ₃
	1.26	-(CH ₂) _n -
	1.6	-CH ₂ -CH ₂ -COOR
	2.0	-CH ₂ -CH=CH-
	2.32	-CH ₂ -COOR
	3.6	-CH ₂
	4.1-4.27	-CH ₂ -O-COR
	5.34	-CH=CH-
	7.26	Ar-H
	8.1	Ar-OH
Ethanol	0.88	-CH ₃
	1.26	-(CH ₂) _n -
	1.6	-CH ₂ -CH ₂ -COOR
	2.01	-CH ₂ -CH=CH-
	2.32	-CH ₂ -COOR
	3.65	-CH ₂
	4.1-4.27	-CH ₂ -O-COR
	5.34	-CH=CH-
	7.26	Ar-H
	8.12	Ar-OH
	9.7	-CHO

Table (3): GC-MS data for eluted fractions of Iraqi virgin olive oil.

Solvents	Eluted compounds	m/z
Petroleum ether	Olefinic	55.1, 69.0
	R-CHO	83.1, 94.9, 108.9
	Ar-OH	120.9, 137, 165
	R-OH	393.3, 407.2, 423.3
	P	239, 313.4
	L	279.2, 281.2
	O	265.3, 247, 339.2
	PP	551.3
	PO	577.3
	OO	603.4
Toluene	Olefinic	57.1, 69
	R-CHO	83.0, 95, 111.1
	Ar-OH	125.1, 139.0, 165.2, 191.2, 225.2
	R-OH	217, 372.4, 408.5
	P	239
	L	282.3
	O	264.3, 339
Chloroform	Olefinic	57.1, 71.1
	R-CHO	83, 97.1, 111.1, 129.1
	Ar-OH	163.4, 191.3
	R-OH	147.1
	Unknown Compound	207.2
	O	256.4
	L	281.4
Ethanol	Olefinic	57.1, 71.1
	R-CHO	83.1, 98.1, 112.1, 129.0
	Ar-OH	141.1, 191.2, 255
	R-OH
	Unknown Compound	207.2
	O	256.3
	L	281.1

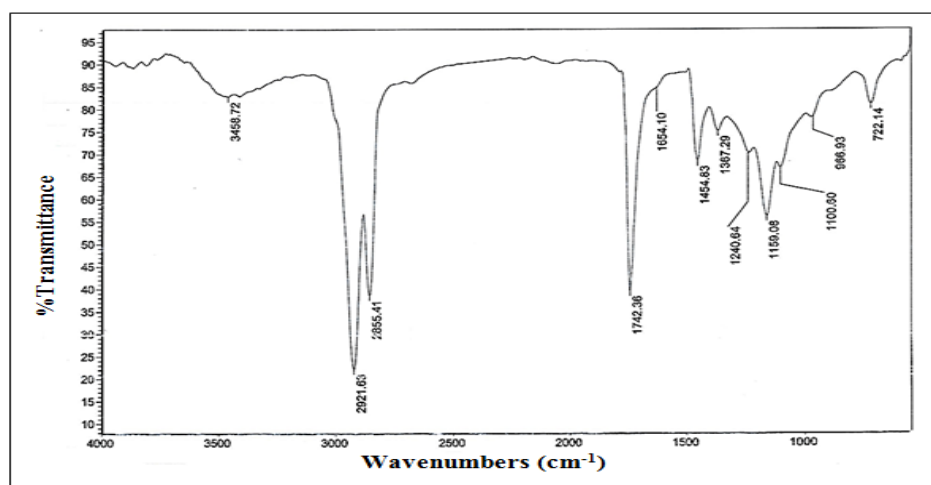


Fig. (1): IR spectra for petroleum ether fraction.

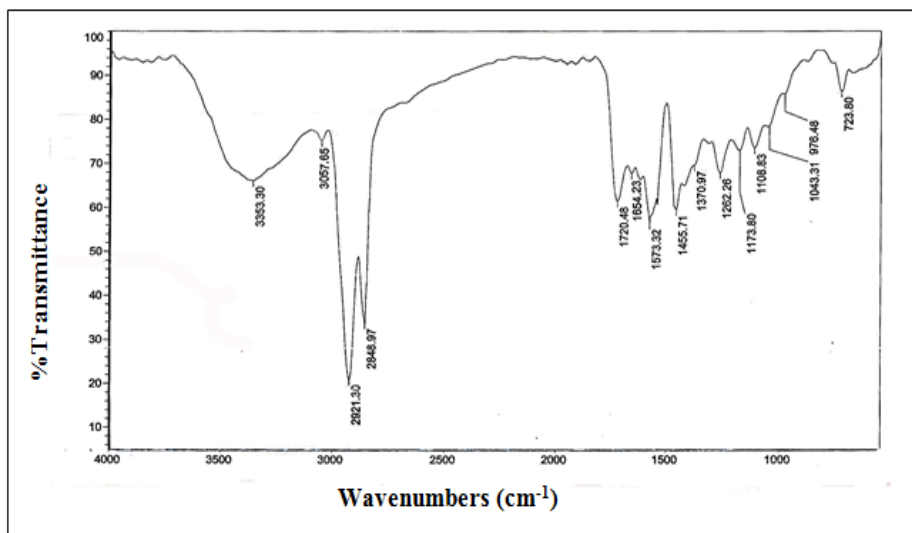


Fig. (5): H^1 NMR spectra for petroleum ether fraction.

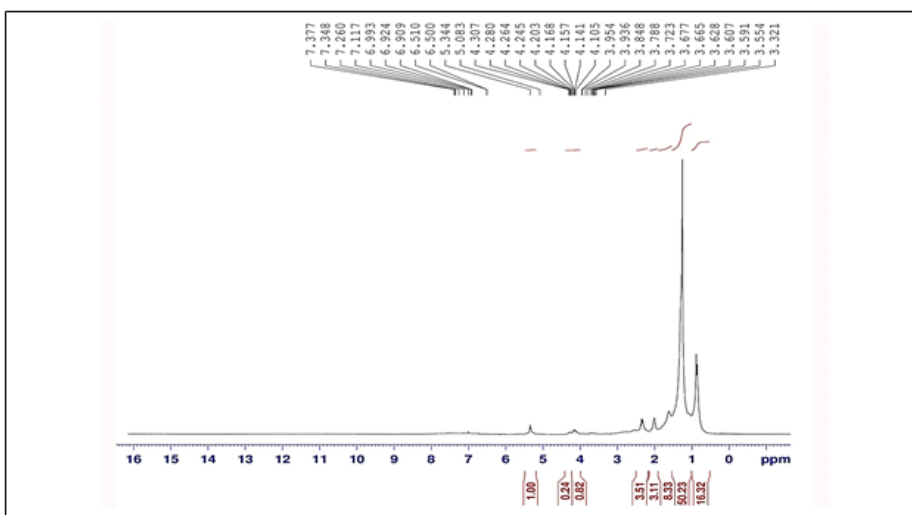


Fig. (6): H^1 NMR spectra for toluene fraction.

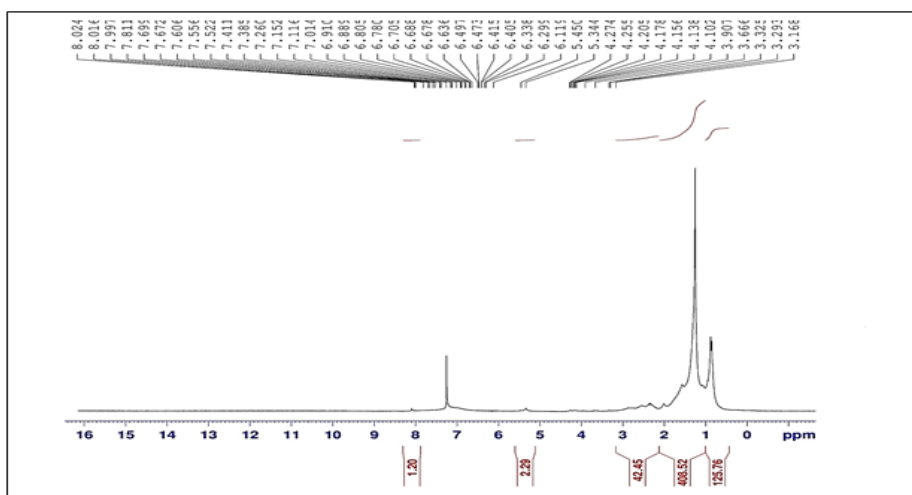


Fig. (7): H^1 NMR spectra for chloroform fraction.

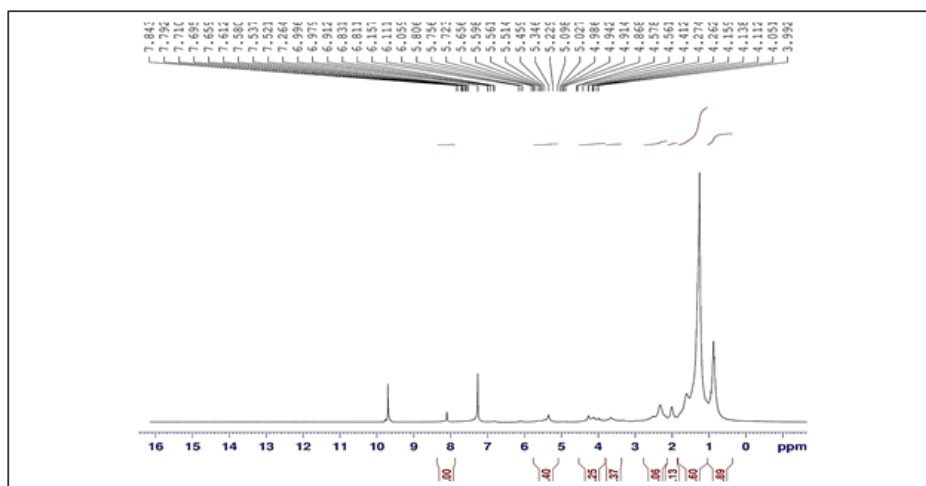


Fig. (8): ^1H NMR spectra for ethanol fraction.

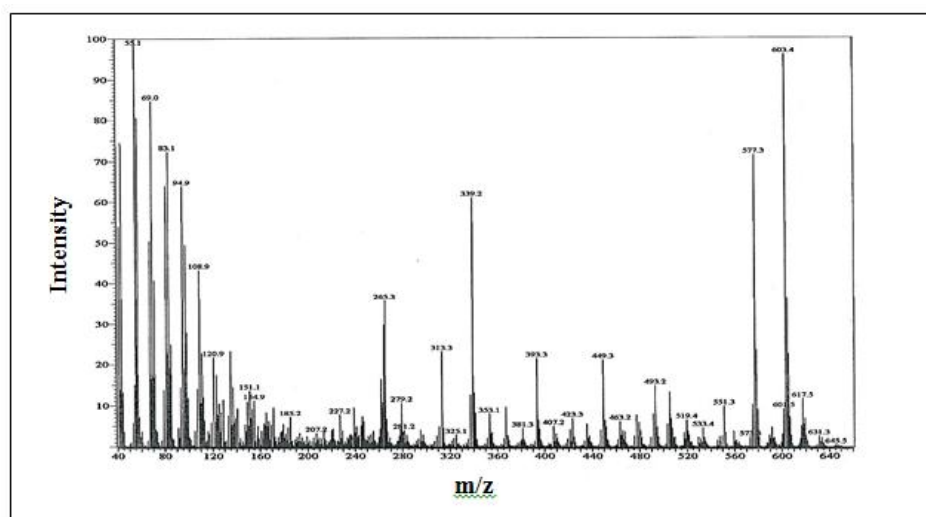


Fig. (9): GC-MS for petroleum ether fraction.

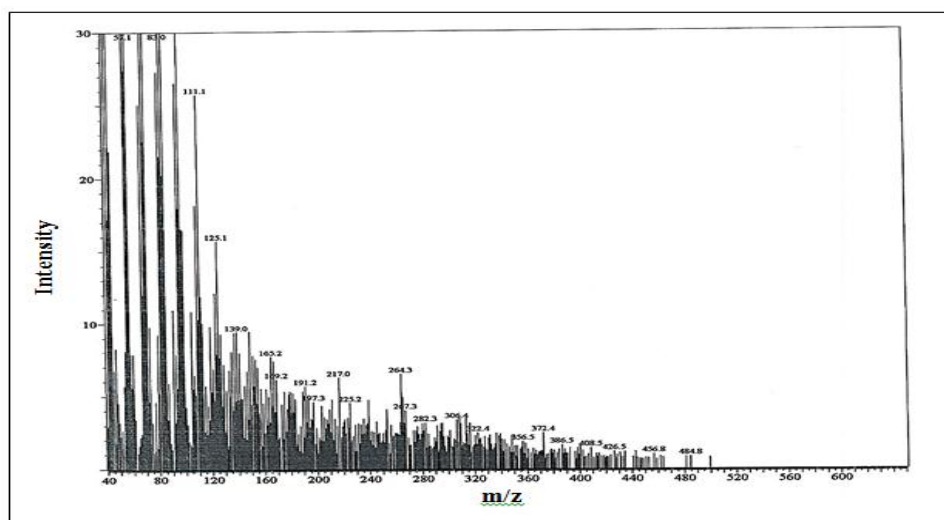


Fig. (10): GC-MS spectra for toluene fraction.

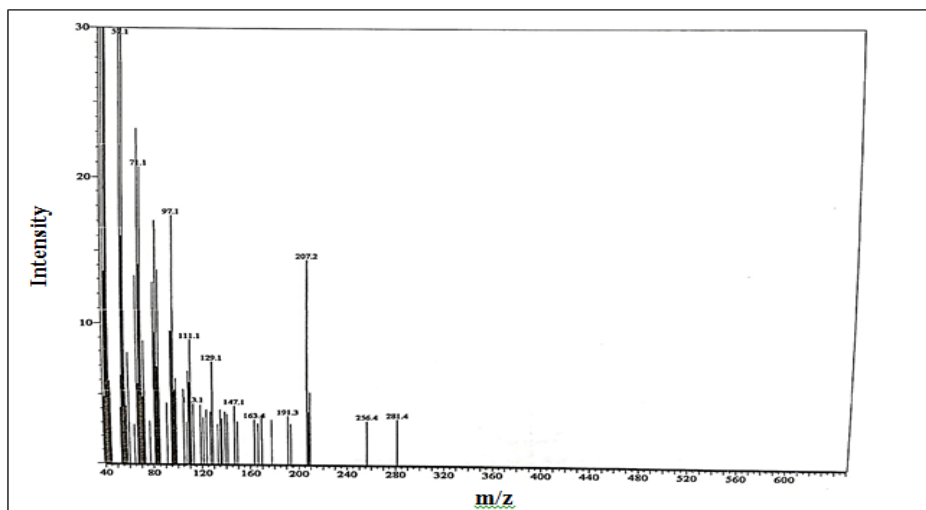


Fig. (11): GC-MS spectra for chloroform fraction.

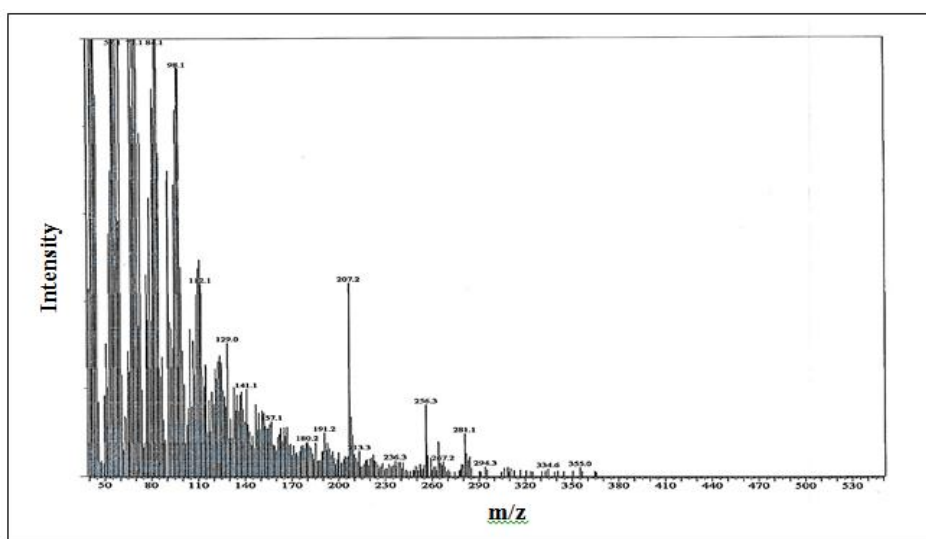


Fig. (12): GC-MS spectra for ethanol fraction.

CONCLUSION

As a result of the above illustration, it is of interest to mention here that naturally occurring clay samples, which are located in our Governorate, were activated to be a good adsorbent in fractionation processes. These samples were natural, treated, doped natural and doped treated clay samples obtained via acidic and basic medium treatment followed by doping by Cr_2O_3 and calcination at 260°C . The 260°C temperature are deduced from differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) studies. One of the above four samples, which is the doped natural, was selected to be applied in soxhlate extraction technique using four solvent which are gradually increasing in their polarities. Therefore, four fractions were resulted have different polarities. From IR, ^1H NMR, GC-MS investigations it

seems that most of the aliphatic compounds which are triglyceride were eluted at the beginning by petroleum ether and toluene solvents. Meanwhile, it looks that this elution followed by phenolic compounds in chloroform fraction. Finally, it was noted that aldehyde compounds supposed to be the ethanol fraction fragments because of their high polarity.

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