

Gas Chromatography-Mass Spectroscopy for Determining Biomarkers in Crude Oils

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ABSTRACT: Four crude oil samples recovered from some producing wells in the southern part of the Egyptian Gulf of Suez were subjected for measuring some organic geochemical parameters. Biomarkers are biological markers such as Terpanes and steranes of the saturated hydrocarbons obtained by gas chromatography-mass spectrometry (GC-MS). In addition to n-alkanes and isoprenoids distributions obtained by gas chromatography (GC). Terpanes biomarker distributions (m/z 191) mass chromatograms for oil samples is revealing marine organic facies of depositional environmental and maturation parameter. Hopane distributions (m/z = 191) indicates the marine organic sources. The steranes distributions for the oil samples (m/z 217) suggest a pre Tertiary source rocks for these oil samples.

KEY WORDS:- Crude oil, Organic geochemical parameters, Biomarkers, Terpanes, steranes, Depositional environmental, Maturation.

I. INTRODUCTION

Petroleum geochemistry is concerned with the application of chemical principals to study origin of organic matter, migration, alteration, and classification of crude petroleum. Various crude oil classifications have been proposed by geochemists and petroleum refiners. Geologists and geochemists are more interested in identifying and characterizing the crude oils, to relate them to specific source rocks and to measure their grade of maturation [1, 2].

Previous geochemical studies throughout the Gulf of Suez have revealed that the oils are derived mainly from marine sources which may be differentiated into three main groups, designated as I, II and III groups. The distribution of these oil families is consistent with the geographic subdivisions of the Gulf of Suez provinces in the northern, the central and southern. Group I oils are confined to the northern province of the Gulf of Suez and characterized by a C_{33}/C_{34} homohopane index <1 and a relatively heavy carbon isotope composition ($\delta^{13}C$ saturated -27%), suggesting generation from a less reducing marine source rock environment at relatively low levels of thermal maturity. Group II oils are confined to the central Gulf province and are characterized by low API gravity, a predominance of pristane over phytane, a high C_{33}/C_{34} homohopane index and a lighter carbon isotope composition ($\delta^{13}C$ saturated -29%) [3, 4]. Group III oils are located in the southern province and characterized by high API gravity, a low sulfur content and intermediate carbon isotope composition ($\delta^{13}C$ saturated -28 to 29%). This group of oils is believed to be derived from a marine source and exhibits compositional heterogeneity suggesting the presence of a complex petroleum system in the southern Gulf of Suez province.

II. MATERIAL AND METHODS

Samples

Four crude oil samples were collected from wells of El Hamd oil field locates in the central Gulf of Suez, namely: H-1, H-2, H-3 and H-4. These samples are representative for the producing horizon zones of Middle-Lower Miocene age characterized by limestone facies with depths range from 754- 881m. (Top perforation), and 955- 1180m (Bottom of perforation).

Crude oil fractionation

The selected crude oil samples were distilled up to $200^{\circ}C$ at atmospheric pressure in order to separate the heavy oil fractions above $200^{\circ}C$. These residual fractions were deasphalted according to IP-143 standard procedure. The maltene

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fraction (deasphalted) was separated into saturates, naphthenes, aromatics and resins by liquid column chromatography which packed with 1:1 alumina overlying silica gel. Saturates, aromatics and resins fractions were obtained by successive elution with the organic solvents n-pentane, toluene and methanol, respectively.

Chromatography-mass spectrometry (GC/MS)

Saturated hydrocarbon fractions were subjected to gas chromatography – mass spectrometry using Clarus-500 Perkin Elmer in order to investigate the biomarkers of saturated hydrocarbon. Samples were injected onto a fused silica capillary column (30 m x 0.25 mm i.d. and film thickness 0.25 μm) coated with HP-5 MS to determine terpanes (m/z 191) and steranes (m/z 217) distributions.

III. RESULTS AND DISCUSSION

The classification of crude oils is based on the content of the various structural types of hydrocarbons, namely paraffins, naphthenes and aromatics. In addition, bulk composition of the residual fraction and Maltene should be considered. Results of the studied crude oil samples are presented in Tables 1-6. The studied crude oil samples were distilled up to 200°C at atmospheric pressure; the maltene residual fraction (> 200°C) was separated into saturates, naphthenes, aromatics and resins by liquid column chromatography and the data was given in Table 1. It has been found (Table 1) that the aromatic hydrocarbons are the major type (> 50 %) in the four crude oils range from 53.34 to 65.52 % and low saturates/aromatics ratios ranging. Also, the crude oils contain ~ 25 % of naphthenes and paraffins range from 17.75 to 24.06 and 16.73 to 22.60 respectively. Therefore, these crude oils are classified as aromatic intermediate oils. This class contains heavy crude oils of low waxy content (API ranging between 20.80 and 23.45, Table 2).

The complete analysis of crude oil samples was achieved by gas chromatography connected with flame ionization detector and the Pr/n-C₁₇, Ph/n-C₁₈, Pr/Ph and CPI were given in Table 2. Pristine and phytane are isoprenoids of C₁₉ and C₂₀ respectively. The percentages mentioned above reflect some geochemical aspects about the origin and maturation of the selected oil samples.

Carbon Preference Index (CPI) was the first maturity indicator applied to crude oils [5]. The results given in Table 2 indicate the marine organic sources for the studied oil samples.

Table 1: Distribution of Hydrocarbon Types

Well Name	Relative Percentages of Hydrocarbon Types, wt%		
	Paraffins	Naphthenes	Aromatics
H-1	22.60	24.06	53.34
H-2	18.17	20.97	60.86
H-3	18.94	20.35	60.71
H-4	16.73	17.75	65.52

Table 2: Geochemical Parameters Derived from GC Analysis

Well Name	API	Pr/n-C ₁₇	Ph/n-C ₁₈	Pr/Ph	CPI
H-1	23.45	0.423	0.678	0.596	1.003
H-2	22.32	0.398	0.671	0.579	1.054
H-3	20.80	0.384	0.688	0.489	0.997
H-4	21.70	0.400	0.677	0.519	1.009

These biomarker parameters have been used in an attempt to characterize the type of organo-facies, oil classes, depositional environments of the crude oils, and to assess the thermal maturity level for oil generation. Biomarkers in oils are widely used to provide reliable information on depositional paleoenvironments, organic input, and source of organo-facies, kerogen types and the degree of thermal maturity. The biomarker indices are listed in Tables 3- 6. Terpanes biomarker distributions derived from the m/z 191 mass chromatograms are shown in Figs. 1, 2 and peak identifications are given in Tables 3, 4. The ratio of Trisnorhopane /trisnorhopane (Ts/Tm) is considered as a facies and depositional environmental parameter of the relevant source rocks. The results show that the Ts/Tm ranging from

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0.43 to 0.49 for oil samples is revealing marine organic facies of depositional environmental. It is also considered a maturation parameter due to the greater thermal stability of Ts than its counterpart Tm. Ts/Tm ratios for the crude oils are generally consistent with the pristane/phytane ratios and less than unity, indicating an anoxic marine depositional environment.

Hopane distributions (m/z = 191) are characterized by C₂₉ (norhopane)/ C₃₀ (hopane) ratio less than unity indicate the marine organic sources. Depositional environment biomarker parameters based on the terpanes (m/z 191) such as the Oleanane index (Table 8) ranging from 0.08 to 0.12 confirms the previous conclusion [6].

The steranes distributions for the oil samples (m/z 217) are shown in Figs. 3, 4 and compound identifications are given in Table 5. Among the C₂₇, C₂₈ and C₂₉ regular steranes, the pattern shows domination by C₂₉ homologous steranes (Tables 5, 6) suggests a pre Tertiary source rocks for these oil samples. Oils with all these features are believed to be generated from both pre- Tertiary marine shales and carbonates enriched in marine algae with more contribution from terrestrial organic sources, deposited under saline conditions and oxic setting [7].

Steranes biomarkers (m/z = 217) in the oil samples are characterized by a low concentration of diasteranes that could be related to the low maturity level of these oils. Predominance of C₂₇ steranes in the oil samples BK 117 and BK 121 suggests marine marine sources with input from terrestrial organic matters [8].

IV. CONCLUSION

- Normal alkane distribution, isoprenoids (pristane and phytane, isoprenoid/n-alkanes) indicate that the crude oils derived from mixed organic sources (mainly marine with few input from terrestrial origin) belong to carbonate oil type, deposited in transitional environments under reducing-oxidizing conditions.
- Terpanes and steranes biomarkers indicate that mature oils generated from marine shales and carbonates enriched in marine algae with contribution from terrestrial organic matters.

Peak No.	Compound Name
a	13β(H), 17α(H)- diacholestane (20S)
b	13β(H), 17α(H)- diacholestane (20R)
c	13α(H), 17β(H)- diacholestane (20S)
d	24-methyl-13β(H), 17α(H)- diacholestane (20S)
e	24-methyl-13β(H), 17α(H)- diacholestane (20R)
f	5α(H),14α(H), 17α(H)- cholestane (20S) + 24-methyl-13α (H), 17β (H)- diacholestane (20S)
g	24-ethyl-13β(H), 17α(H)- diacholestane (20S) + 5α(H), 14β (H), 17β (H)- cholestane (20R)
h	5α(H),14β (H), 17β (H)- cholestane (20S)+ 24-methyl-13α (H), 17β (H)- diacholestane (20R)
i	5α(H),14α (H), 17α (H)- cholestane (20R)
j	24-ethyl-13β (H), 17α (H)- diacholestane (20R)
k	24-ethyl-13α (H), 17β (H)- diacholestane (20S)
l	24-methyl-5α(H),14α(H), 17α(H)- cholestane (20S)
m	24-methyl-5α(H),14α(H), 17β (H)- cholestane (20R) + 24-ethyl-13α (H), 17β (H)- diacholestane (20R)
n	24-methyl-5α(H),14β (H), 17β (H)- cholestane (20S)
o	24-propyl-13α (H), 17β (H)- diacholestane (20S)
p	24-methyl-5α(H),14α (H), 17α (H)- cholestane (20R)
q	24-ethyl-5α(H),14α(H), 17α (H)- cholestane (20S)
r	24-ethyl-5α(H),14β (H), 17β (H)- cholestane (20R)
s	24-ethyl-5α(H),14β (H), 17β (H)- cholestane (20S)
t	24-ethyl-5α(H),14α(H), 17α (H)- cholestane (20R)
u	24-propyl-14α(H), 17α(H)- cholestane (20S)
v	24-propyl-14β (H), 17β (H)- cholestane (20R)
w	24-propyl-14β (H), 17β (H)- cholestane (20S)
x	24-propyl-14α (H), 17α (H)- cholestane (20R)

Table 4: GC-MS parameters of Terpanes (m/z 191) fragmentogram

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I S	Hopane index HI ^e	Ts/Tm ^k	Oleanane index ^h	C ₂₉ /C ₃₀ ^d	T/S ⁱ
H-1	0.11	0.44	0.11	0.2	0.04
H-2	0.11	0.47	0.12	0.18	0.04
H-3	0.11	0.45	0.09	0.18	0.05
H-4	0.11	0.44	0.10	0.19	0.05

Peak No.	Compound Name
Ts	C27 18 α (H)-22, 29, 30-trisorneohopane
Tm	C27 17 α (H)-22,29,30-trinorhopane
Q	C29 18 α (H)-norneohopane(29Ts)
R	C30 18 α (H)-Oleanane
S	C30 17 α (H), 21 β (H)- hopane
T	C30 17 β (H), 21 α (H)- moretane
U	C31 17 α (H), 21 β (H)- 30 homohopane (22S) C31 17 α (H), 21 β (H)- 30 homohopane (22R)
W	C32 17 α (H), 21 β (H)- 30 bishomohopane (22S) C32 17 α (H), 21 β (H)- 30 bishomohopane (22R)
X	C33 17 α (H), 21 β (H)- 30 trishomohopane (22S) C33 17 α (H), 21 β (H)- 30 trishomohopane (22R)
Y	C34 17 α (H), 21 β (H)- 30 tetrakishomohopane (22S) C34 17 α (H), 21 β (H)- 30 tetrakishomohopane (22R)
Z	C35 17 α (H), 21 β (H)- 30 pentakishomohopane (22S) C35 17 α (H), 21 β (H)- 30 pentakishomohopane (22R)

e C₃₅17 α (H),21 β (H)-30-Pentahomohopane(22S+22R)/ \sum C₃₁to C₃₅ 17 α (H),21 β (H)- 30-homohopanes(22S+22R)

k 18 α (H)-22,29,30-Trisorneohopane/17 α (H)-22,29,30-trinorhopane

h 18 α (H)-Oleanane/C₃₀ 17 α (H),21 β (H)-hopane

pH31:C₃₁17 α (H),21 β (H)-30-homohopane(22S), H32:C₃₂17 α (H),21 β (H)-30-bishomohopane(22S),H33:

C₃₃17 α (H),21 β (H)-30-Trishomohopane(22S), H34:C₃₄17 α (H),21 β (H)-30-Tetrakishomohopane(22S),

C₃₅17 α (H),21 β (H)-30-Pentakishomohopane(22S+22R).

d 17 α (H),21 β (H)-30-norhopane/ 17 α (H),21 β (H)- hopane.

i C₃₀17 β (H),21 α (H)- hopane/ C₃₀17 α (H),21 β (H)- hopane

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Table 6: GC-MS parameters of Steranes (M/Z, 217) fragmentograms

S \ I	Steranes (%) ^a			C ₂₉ diasterane index ^b
	C ₂₇	C ₂₈	C ₂₉	
H-1	32.24	27.03	40.74	0.56
H-3	24.04	35.24	40.72	0.74
H-5	25.83	27.79	46.37	0.98
H-7	17.14	29.27	53.58	0.79

a 5 α (H),14 α (H),17 α (H)-20R-Steranes

b 24-Ethyl-13 β (H),17 α (H)-diacholestane (20R)/ 24-Ethyl-5 α (H),17 α (H)-cholestane (20R)

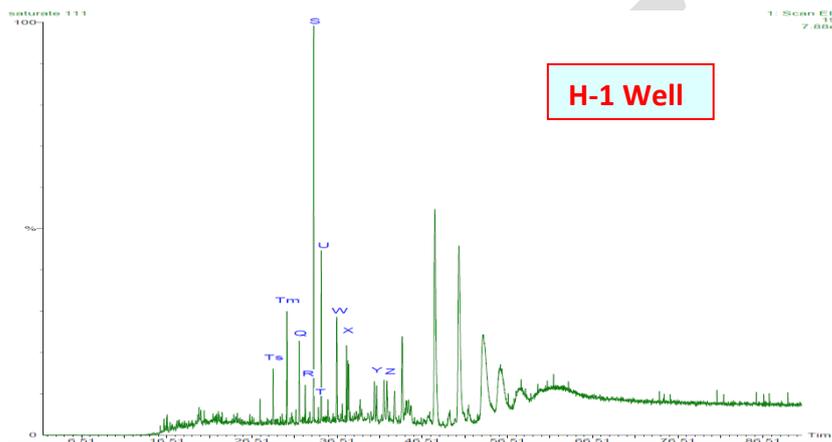
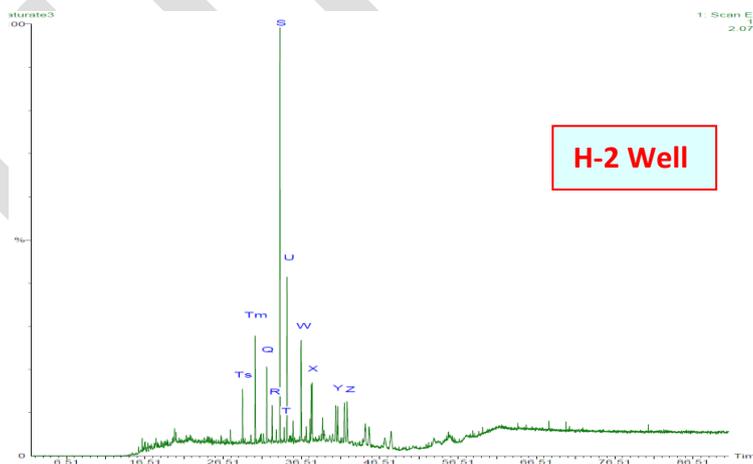


Fig. 1: GC-MS of Terpanes fragmentograms at M/Z 191 for wells H-1 and H-2



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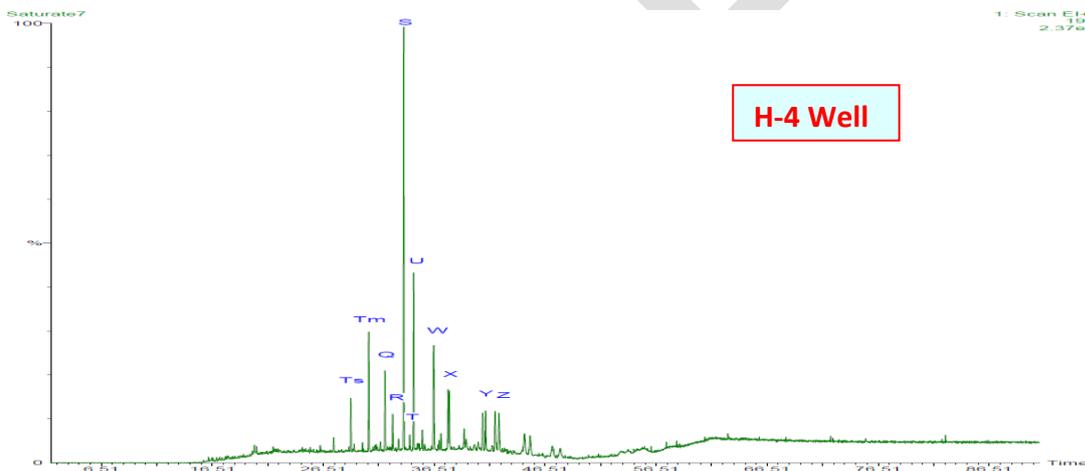
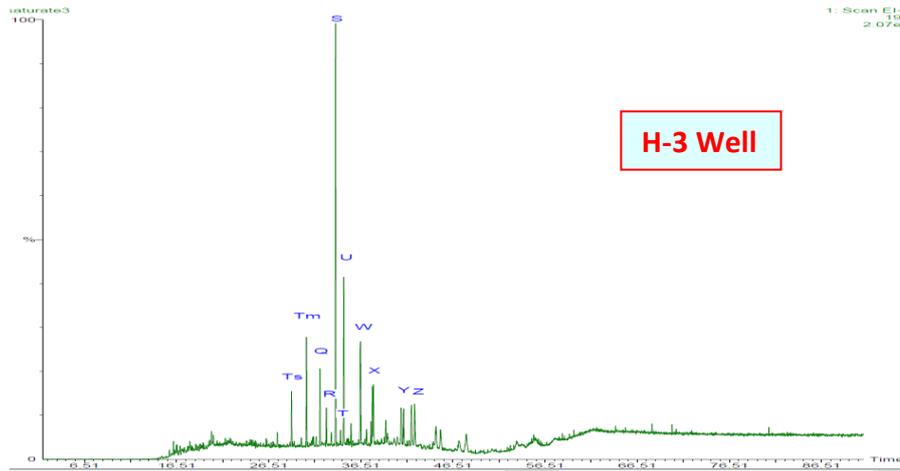
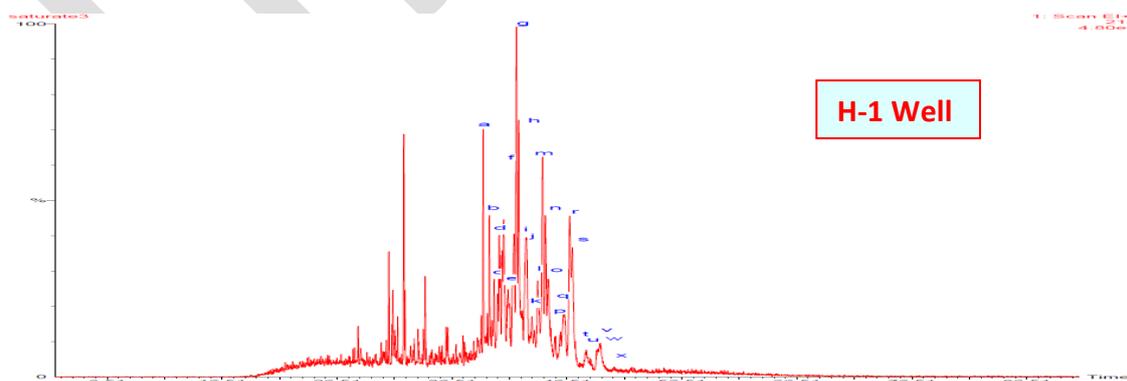


Fig. 2 GC-MS of Terpanes fragmentograms at M/Z 191 for wells H-3 and H-4



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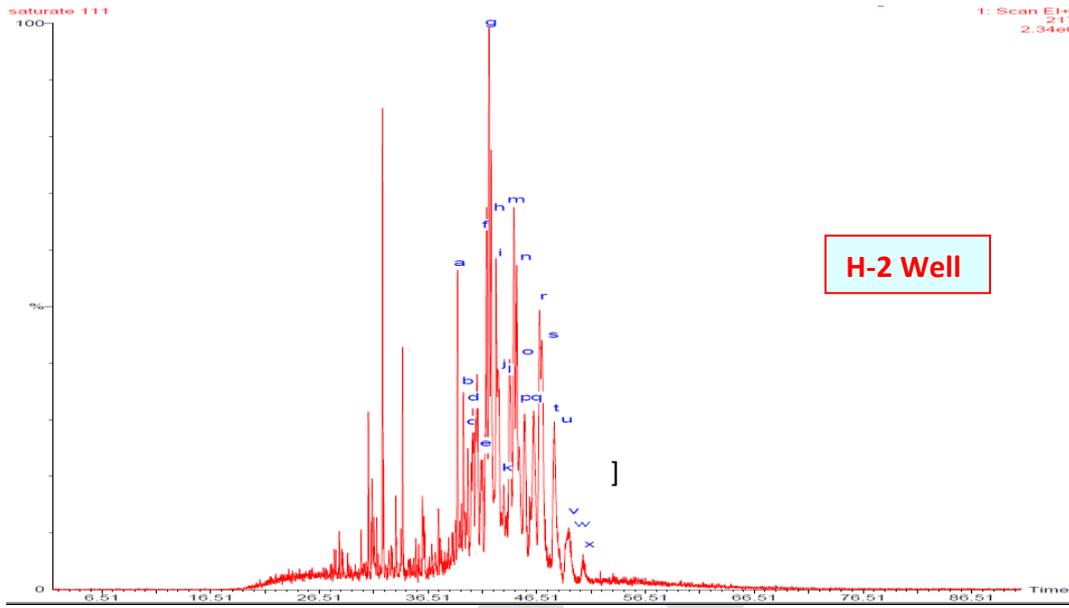
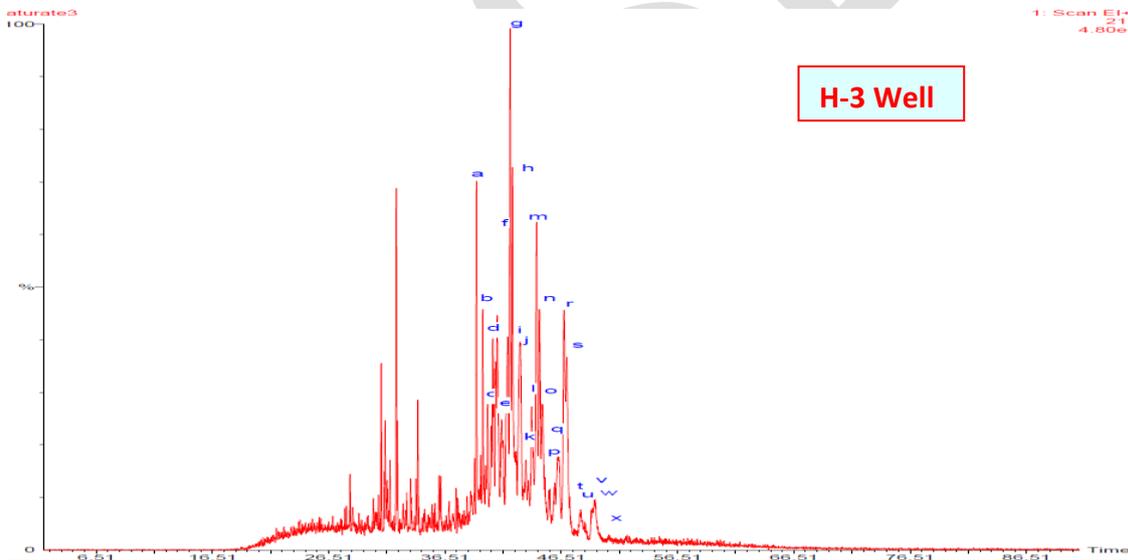


Fig. 3: GC-MS of Steranes fragmentograms at M/Z 217 For wells H-1 and H-2



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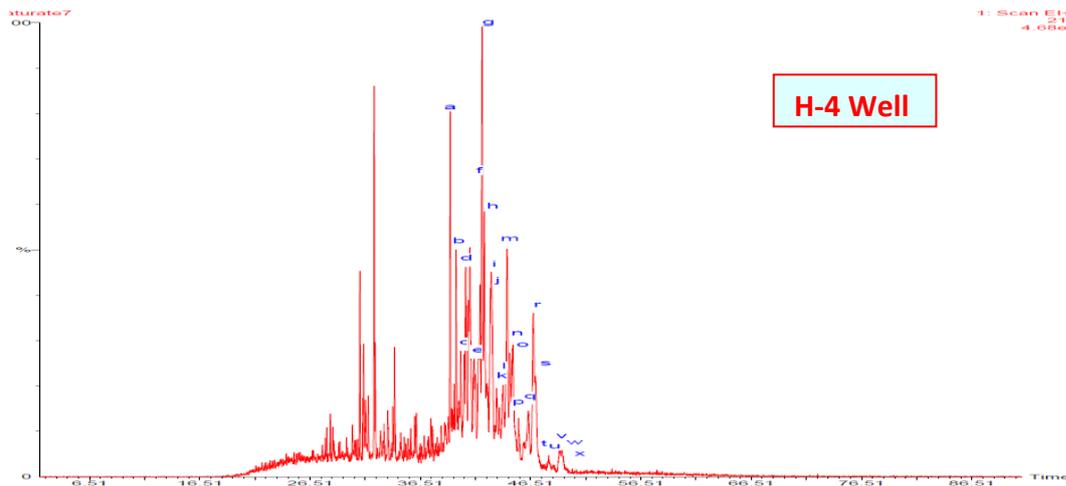


Fig. 4. GC-MS of Steranes fragmentograms at M/Z 217 For wells H-3 and H-4

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