QUANTUM ANALYTICS

Material Characterization of Rock Sample using Thermal Vaporization/Pyrolysis-GC/MS Technique

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Introduction

One of the first steps in the standard protocol for geochemical characterization of rock samples is Rock-Eval analysis. In its simplest form, this process entails grinding the rock sample and then determining the amount of free or adsorbed matter by heating the sample in an inert gas flow to 300 °C for 3 minutes (S1) and then ramping the temperature to 650 °C @ 25 °C/min (S2) to pyrolyze the heavier material. The hydrocarbons are measured with an FID and CO_2 (S3) by an infrared detector. The value of S1 is related to the recoverable oil, and S2 of the potential for oil production. A measure of the maturity may be derived from the temperature of the maximum in the S2 curve T_{pS2}.

Key Words

- Rock-Eval Analysis
- Geochemical Characterization
- Mining
- Oil Production

Method

In the Evolved Gas Analysis (EGA) mode, the Thermal Vaporization / Multi-Shot Pyrolyzer (EGA/PY-3030D) system from Frontier Laboratories, paired with a Frontier AS-1020E autosampler, a Frontier SS-1010E Selective Sampler, and a Frontier MJT-1035E MicroJet Cryo-Trap may be used to determine the basic parameters listed above. This is accomplished by coupling with an Agilent 7890B GC-FID/5977 MSD system and an Agilent 3180B two-way splitter with makeup gas. In this configuration, an inert Ultra Alloy capillary is used between the GC injector and the splitter.

It is possible to obtain much more detailed molecular information without extensive solvent extraction to obtain extracted organic material (EOM). Using different modes of operation of the multi-shot pyrolyzer with a GC separation column in place instead of a deactivated EGA tube, this is done in two steps.

In this experiment, a rock sample, referred to as sample A, with a depth of 7845.42 feet is used for material characterization. The ground rock sample is heated to 300 ºC and held for 20 minutes while the evolved gases are cryo-trapped at the head of the column with the MicroJet Cryo-Trap. At that point, the sample is automatically removed out of the furnace to an ambient holding position, the oven and the nitrogen cooling turned off and GC/MS and FID chromatograms are obtained. With the GC/MS operated in SIM/SCAN mode and the split to the FID, three chromatograms with identical retention times, are obtained in a single run. This corresponds to the S1 peak. After this is complete, the nitrogen cooling is turned back on, the sample reintroduced into the oven and the evolved gases ar cryo-trapped as before as the oven is heated from 300 ºC to 650 ºC corresponding to S2. Again, 3 chromatograms are obtained in a single run.

The GC was operated at a constant flow of 1.2 mL min-1 with a temperature program of 70 °C for 3 mins; a ramp of 5 °C per min to 200 °C; a ramp of 4° per min to 320 °C and held at that point for 20 min. The flow was split between the FID and the MSD. The MSD was operated in SIM-SCAN mode.

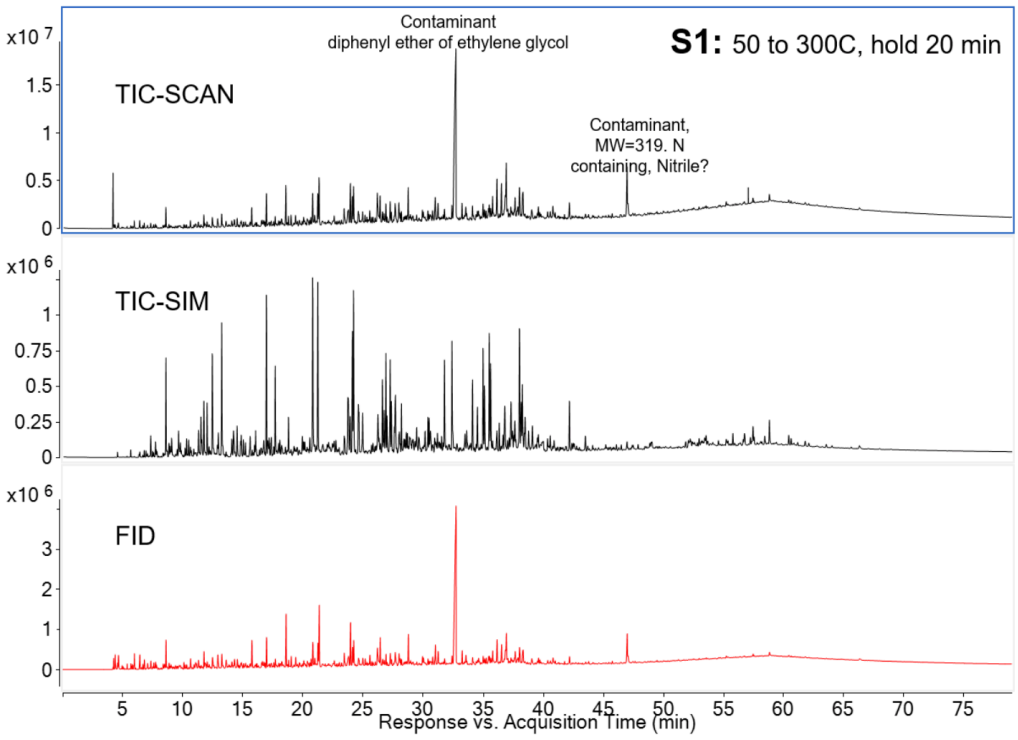


Figure 1. Three Chromatograms Obtained from GC/MS in SIM/SCAN Mode & Split to FID

Results

Figure 1 shows the GC/MS total ion current (TIC) SCAN from m/z=20 to 650 (top), the TIC selected ion monitoring (SIM) chromatogram (middle) and the flame ionization detector chromatogram (bottom) all obtained in a single run. Immediately obvious from the TIC SCAN is the presence of two contaminants. The most prominent is the diphenyl ether of ethylene glycol and the second is (actually 2 peaks) nitrogen-containing compound(s) with nominal molecular weight 319. Neither of these will interfere with further analyses.

The Frontier EGA/PY-3030D Multi-Shot Pyrolyzer can analyze any organic materials using some or all of the following techniques:

- Evolved Gas Analysis (EGA)
- Thermal Desorption (TD)
- Heart-Cutting (HC)
- Pyrolysis
- Reactive Pyrolysis (RxPy)
- Single, Double or Multi-Shot Analysis

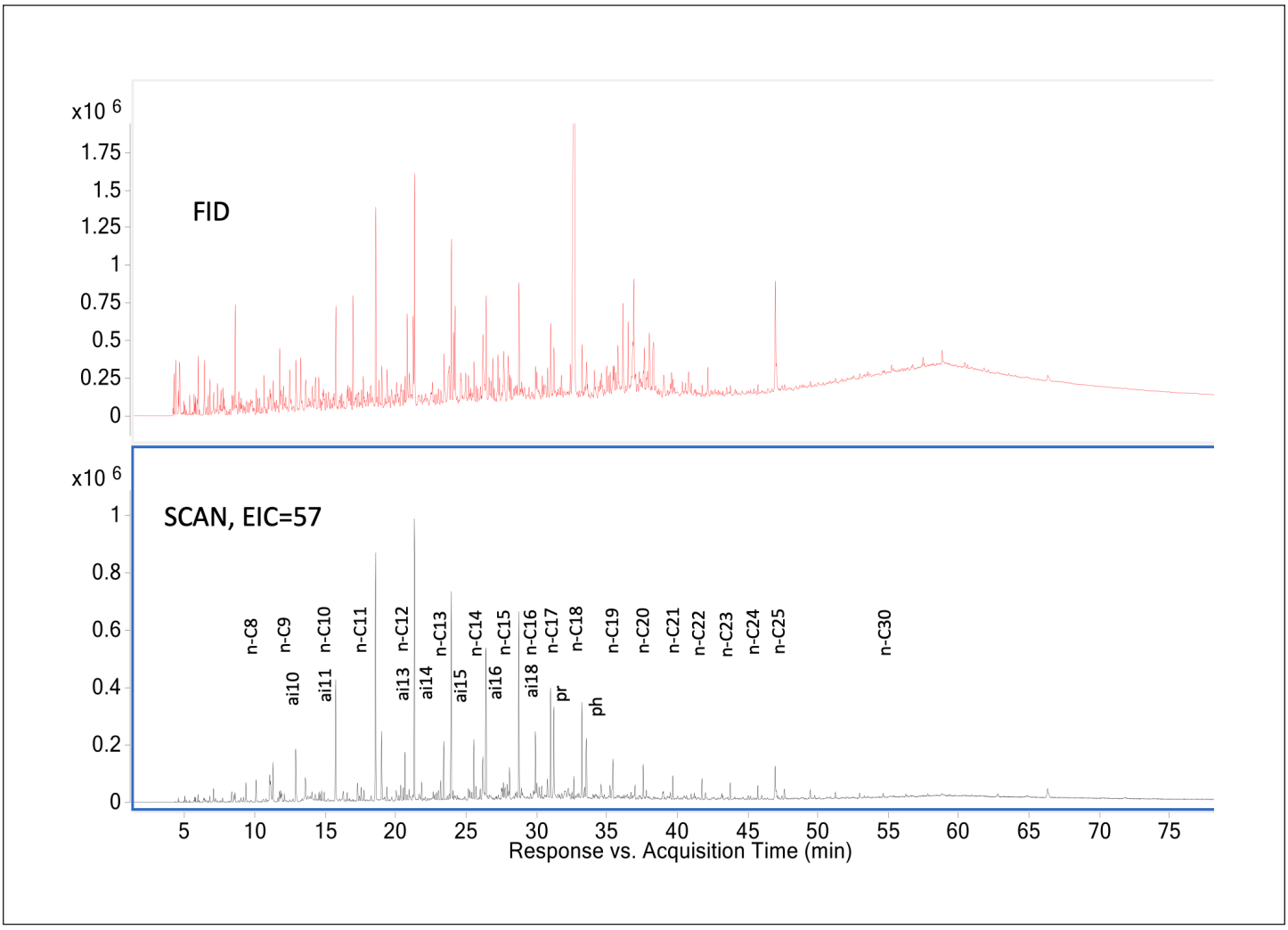


Figure 2. FID & EIC (m/z = 57) for n-alkanes and acrylic isoprenoids (ai).

Figure 2 shows the FID trace (top) and an extracted ion chromatogram (EIC) at m/z = 57, corresponding primarily to alkanes. Assignments for the n-alkanes and some of the acyclic isoprenoids are indicated in the Figure.

Measurements of peak areas from the FID chromatogram, along with an expanded plot of the FID trace from 4 to 9 minutes are given in **Table 1** in **Appendix A**.

Figures 3 and 4 are EIC plots for substituted benzenes, naphthalenes, phenanthrenes, and dibenzothiophenes. The distribution of isomers and ratios among the alkanes and acyclic isoprenoids as well as the various aromatics are used to derive geochemical properties, including thermal maturity. Measurements of SIM areas/heights are used for the aromatics.

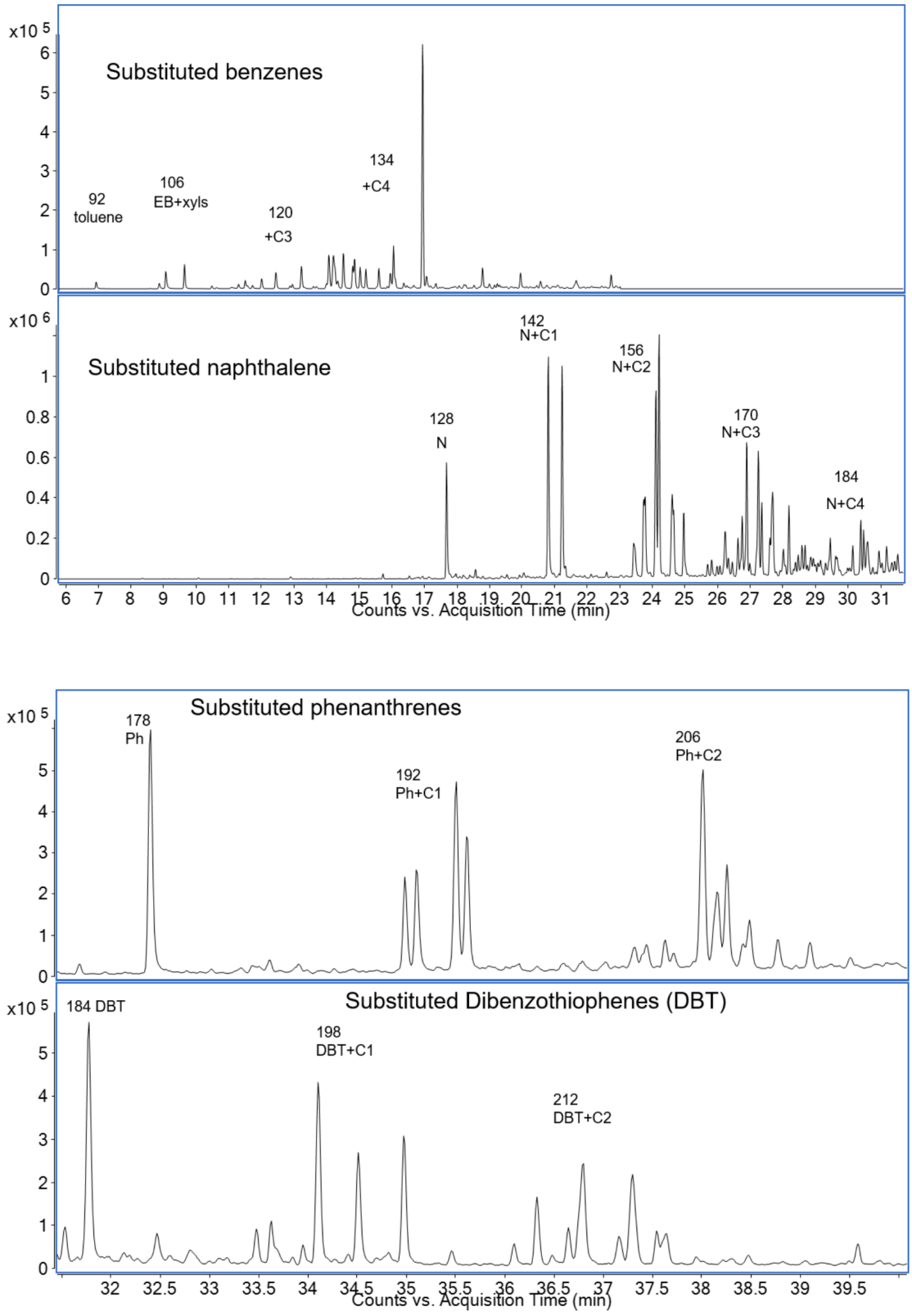


Figure 3 & 4. EIC for Substituted Benzenes, Naphthalene, Phenanthrene, and Dibenzothiophenes.

Even more diagnostic information is obtained from the measurement of biomarkers; terpanes and hopanes, steranes, and mono- and di-aromatic steroids. **Figure 5** shows the fragmentograms for m/z = 191.2, 217.2 and 218.2. The first corresponds to terpanes and hopanes and the last two to steranes.

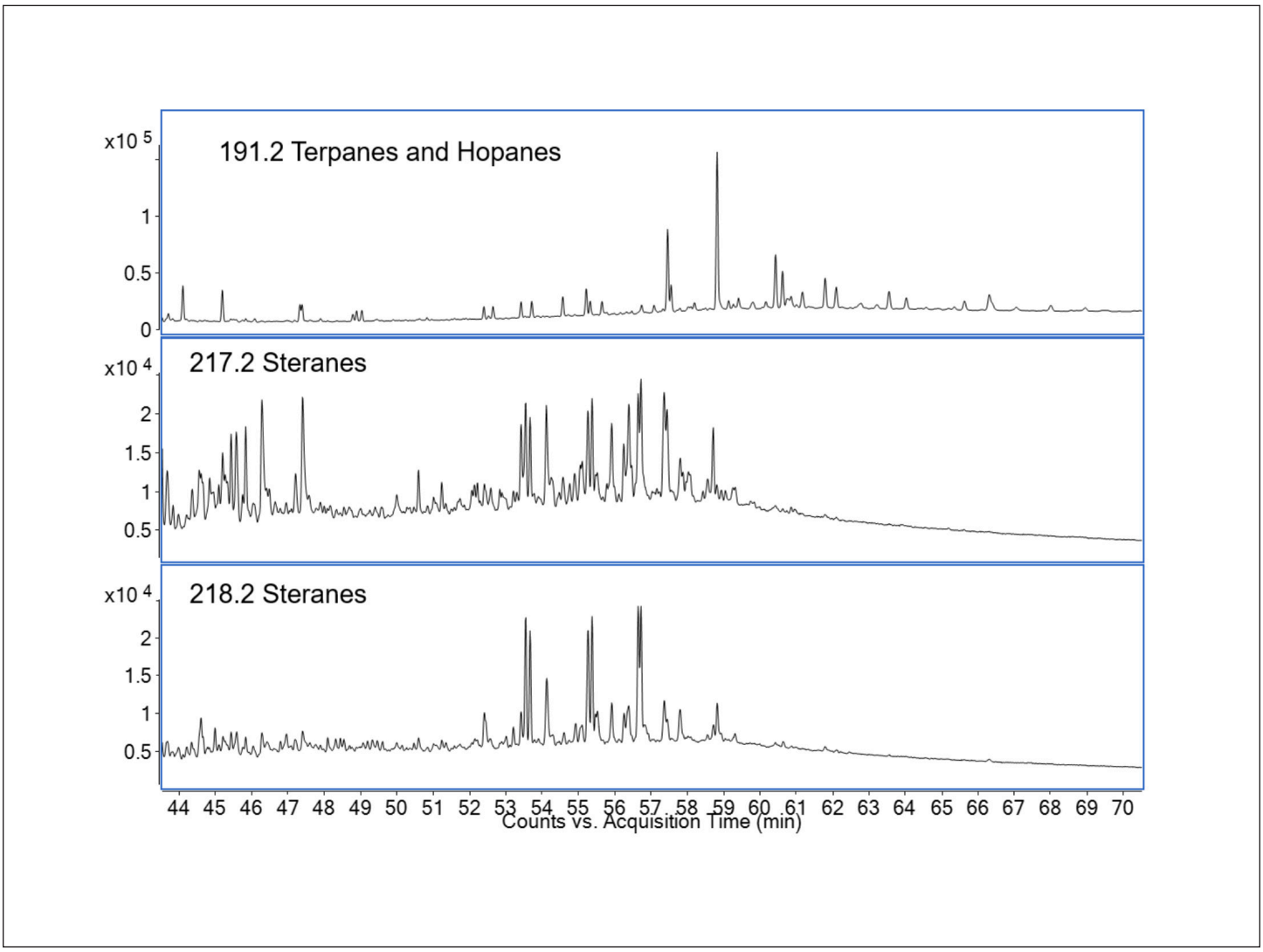


Figure 5. Extracted Ion Chromatograms for Biomarkers (Terpanes, Hopanes, and Steranes).

Figure 6 below shows the fragmentograms for m/z = 231.1 and 253.2, the tri-aromatic and mono-aromatic steroids.

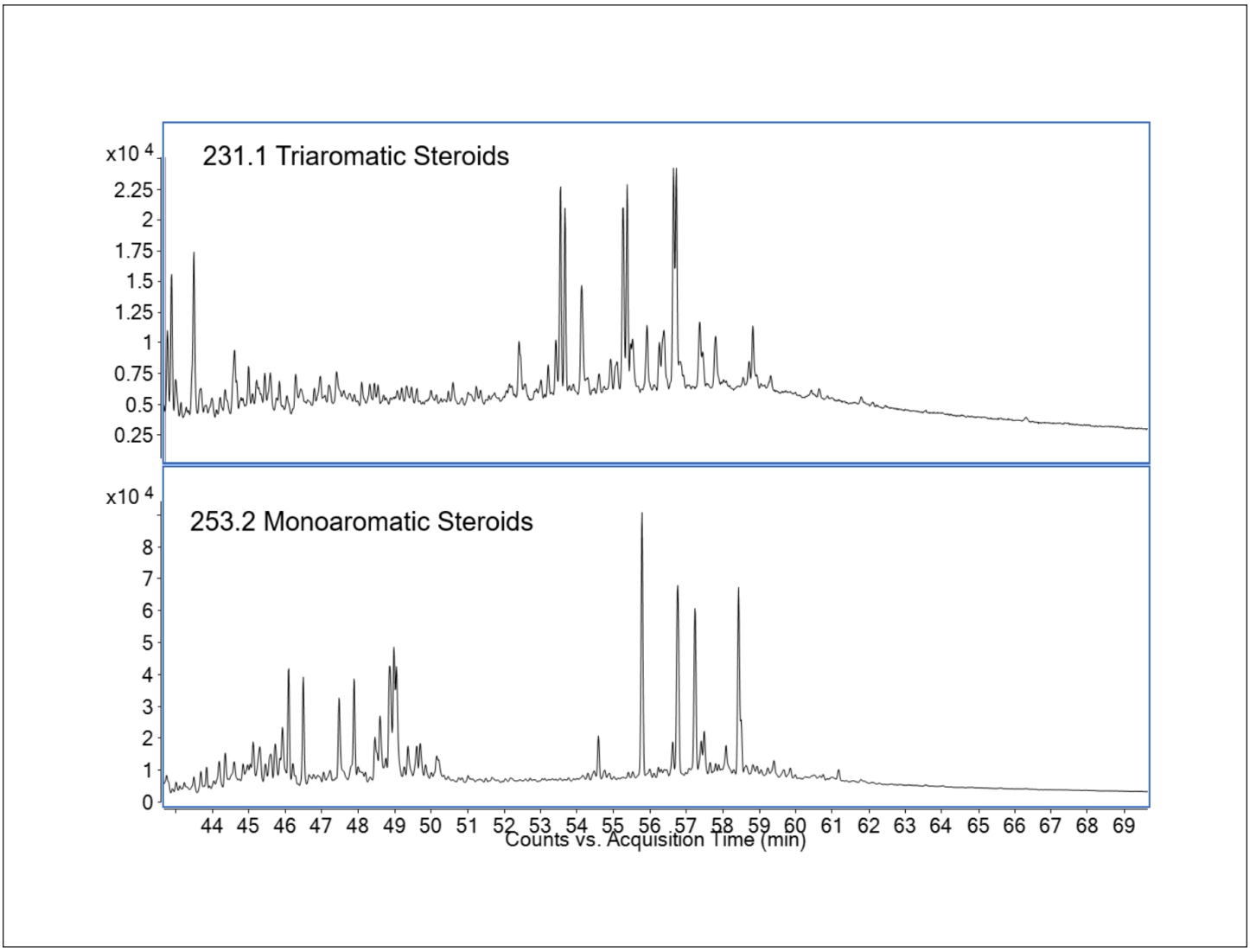


Figure 6. Tri-aromatic & Mono-aromatic Steroids.

Table 2 shows the results for the terpanes and hopanes relative to 30-Hopane normalized to 100 (**Appendix B**). The presence or absence of specific biomarkers and ratios of combinations of biomarkers yields information on the conditions during deposition, age, maturity, and sometimes lithology. **Figure 7** below is a different sample with assignments shown on the Figure for illustration.

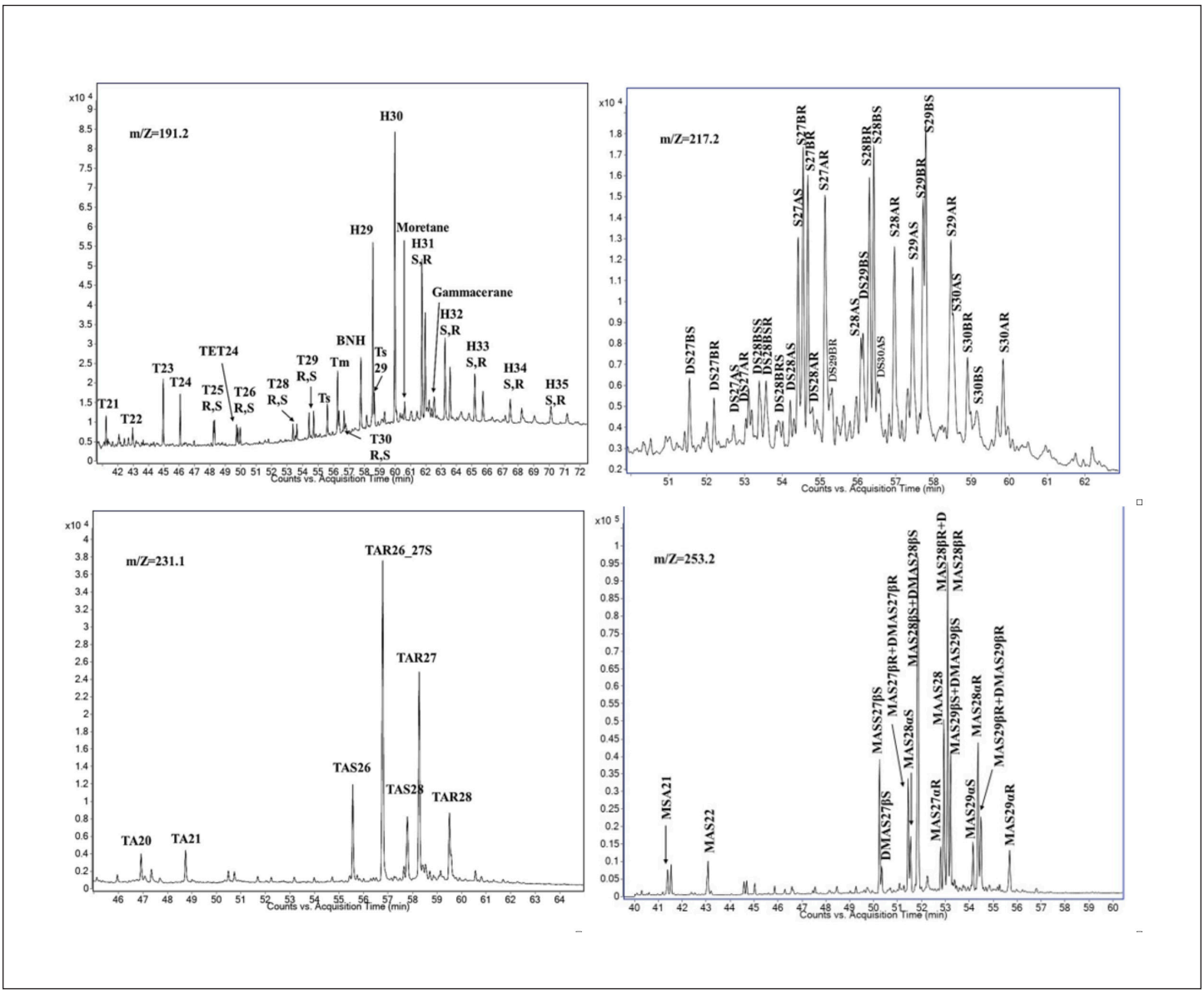


Figure 7. Illustrating Figure for Peak Assignments.

Figure 8 shows the three chromatograms collected for the S2 peak: the TIC SCAN, the TIC SIM and the FID. The TIC SCAN is used along with a library to identify peaks that may be in question. Many small alkenes are observed early on. The progression of alkane peaks is accompanied by the corresponding alkene.

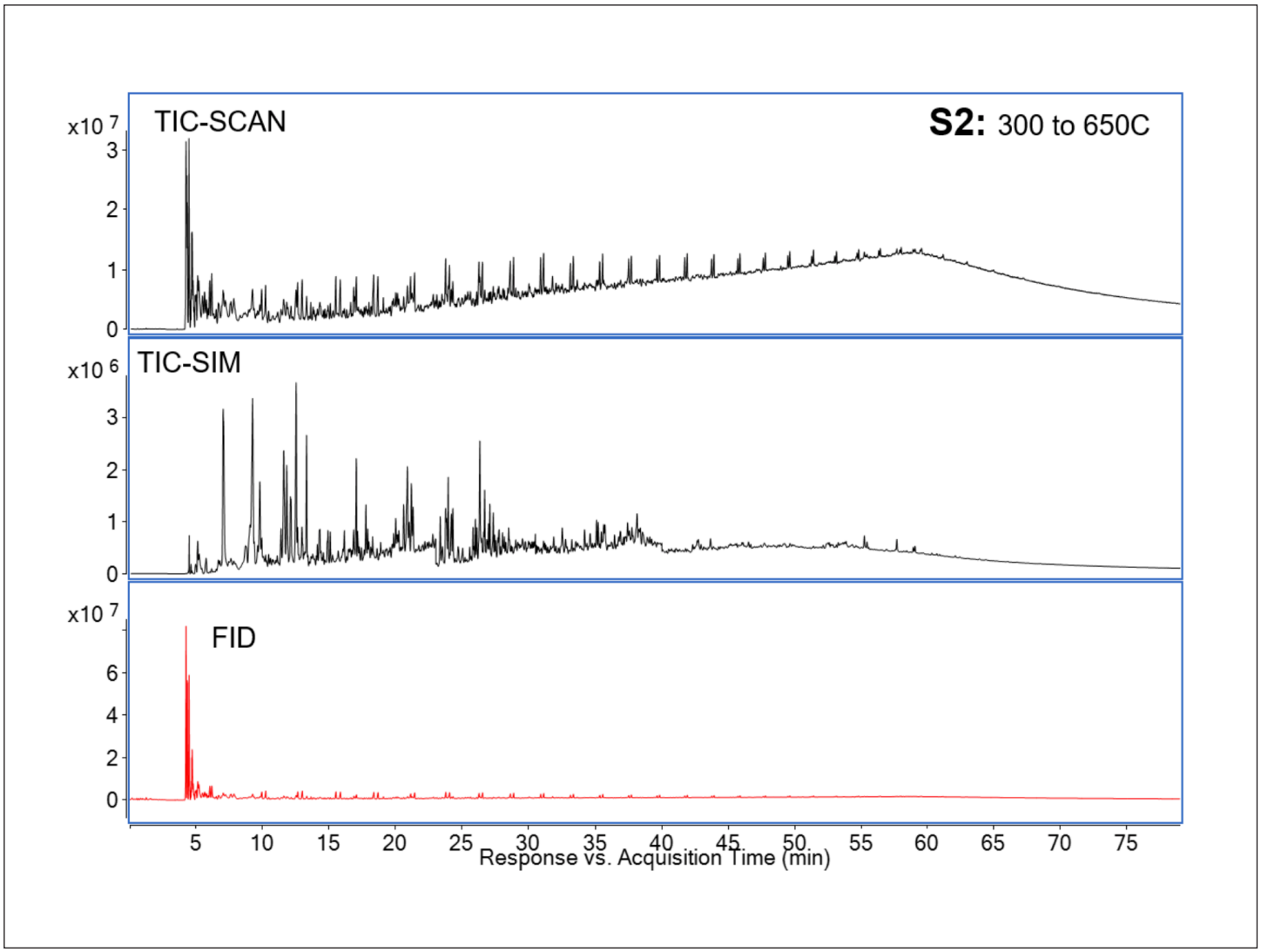


Figure 8. TIC-SCAN, TIC-SIM, and FID of S2.

Figure 9 shows the FID and the m/z = 57 (alkane) and m/z = 55 (alkene) peaks. The same fragmentograms for aromatics and biomarkers plotted for S1 may be plotted for S2. In general, the distributions are quite different, especially for the biomarkers.

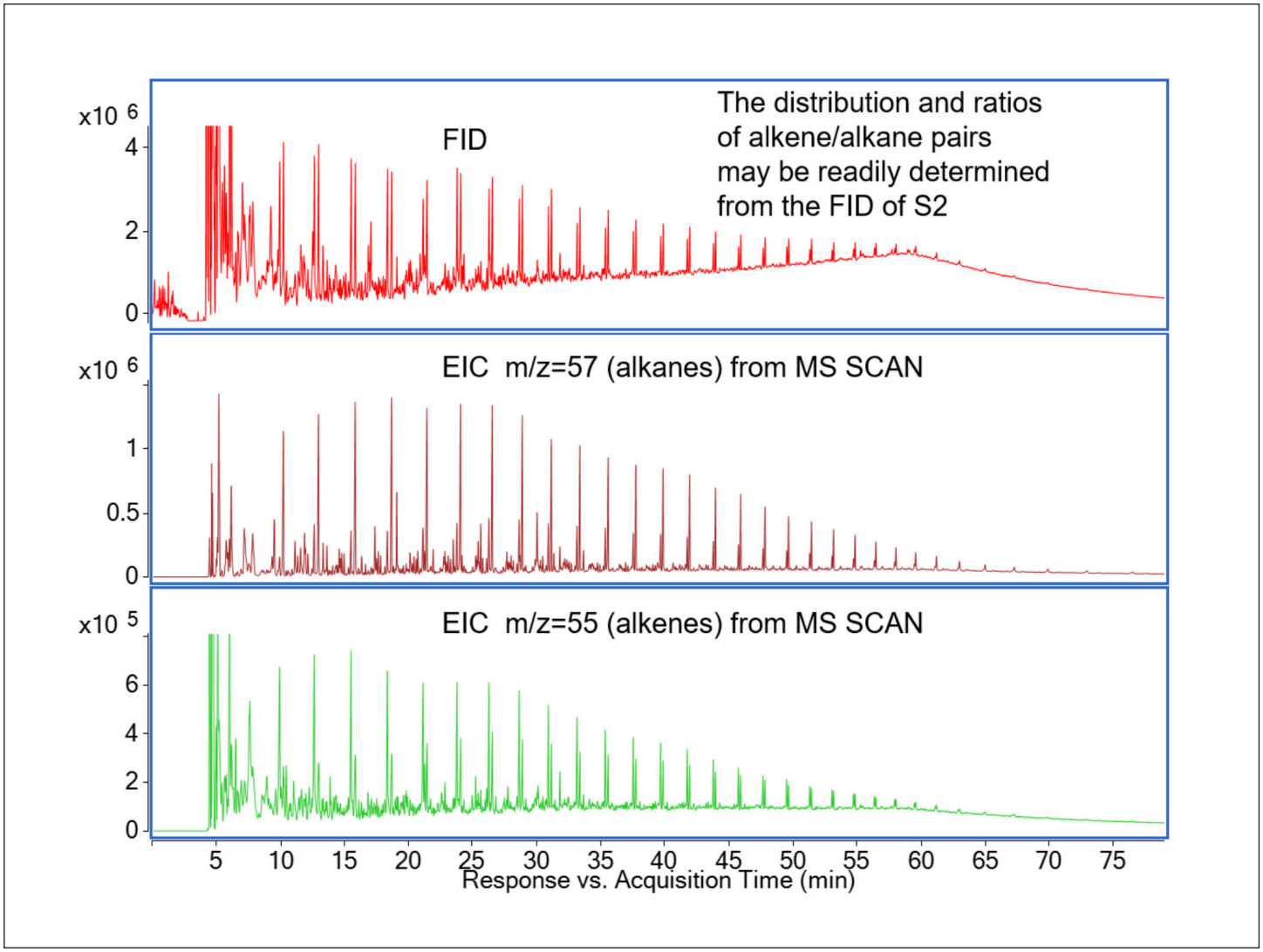


Figure 9. FID and EIC (m/z:57 and m/z:55) of S2.

Summary

In summary, the Thermal Vaporization/Pyrolysis-GC/MS technique using the vertical micro-furnace multi-mode pyrolyzer enables the analysis of S1, S2, and biomarkers present in a rock sample without any solvent extraction or sample preparation. The obtained detailed information from this technique can reveal critical facts about the recoverability and the potential for oil production.

Thermal extraction-GC/MS offers the geochemist a means of:

- ✓ Simplifying sample preparation.
- ✓ Improved accuracy of organic determination.
- ✓ Precise information on chemical species present.
- ✓ Ability to perform Rock Eval pyrolysis and biomarkers speciation on the same system.

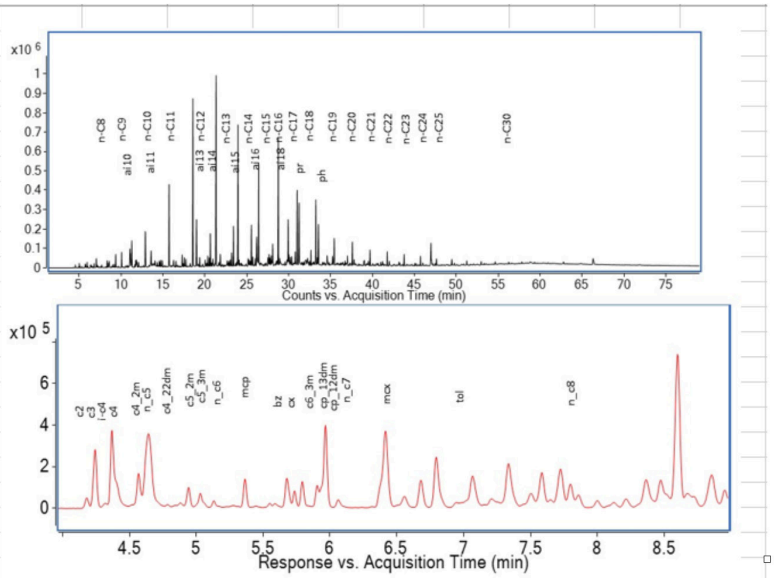
About Quantum Analytics

Quantum Analytics is the authorized distributor for Frontier Laboratories in the United States and Canada. Contact us today to discuss your application needs, or to request a quote for the Frontier Multi-Shot Pyrolyzer.

Visit **www.LQA.com/Pyrolysis** to learn more.

Appendix A

	Compound Method		02x-201910-7845p42-S1-41_034			Area	Height
	Name	MZ	RT	Area	Height	%	%
3	c2	0	4.18	93967	50799	0.25%	0.39%
4	c3	0	4.24	520102	282305	1.38%	2.16%
5	ic4	0	4.32	54509	24016	0.14%	0.18%
6	nc4	0	4.37	959639	372903	2.55%	2.85%
7	c4_2m	0	4.57	361984	167622	0.96%	1.28%
8	nc5	0	4.64	1338352	357308	3.55%	2.73%
9	c5_2m	0	4.94	193839	99774	0.51%	0.76%
10	c5_3m	0	5.03	193510	72470	0.51%	0.55%
11	nc6	0	5.13	91493	36560	0.24%	0.28%
12	mcp	0	5.36	204962	132563	0.54%	1.01%
13	bz	0	5.59	30195	15551	0.08%	0.12%
14	cx+c6_2m	0	5.68	271619	137689	0.72%	1.05%
15	c5_23dm	0	5.73	119962	76392	0.32%	0.58%
16	c6_3m+cp_11dm	0	5.79	218179	122626	0.58%	0.94%
17	c-cp_13dm	0	5.90	0		0.00%	0.00%
18	t-cp_13dm	0	5.90	175396	104368	0.47%	0.80%
19	c-cp_12dm	0	5.97	816522	393100	2.17%	3.01%
20	nc7	0	6.06	77436	35955	0.21%	0.28%
21	mcx	0	6.42	899377	356789	2.39%	2.73%
22	tol	0	6.95	30728	14888	0.08%	0.11%
23	nc8	0	7.58			0.00%	0.00%
24	nc9	0	10.09	293242	143133	0.78%	1.10%
25	a10	0	11.07	455989	142595	1.21%	1.09%
26	nc10	0	12.91	1176992	335208	3.12%	2.57%
27	a11	0	13.61	766430	190763	2.03%	1.46%
28	nc11	0	15.75	1848754	677108	4.90%	5.18%
29	nc12	0	18.59	3648846	1309466	9.68%	10.02%
30	a13	0	19.02	679079	255766	1.80%	1.96%
31	a14	0	20.82	1820364	579711	4.83%	4.44%
32	nc13	0	21.35	4599855	1533013	12.20%	11.73%
33	a15	0	23.43	1300127	324070	3.45%	2.48%
34	nc14	0	23.96	3250270	1075390	8.62%	8.23%
35	a16	0	25.57	739072	248325	1.96%	1.90%
36	nc15	0	26.43	1844967	672595	4.89%	5.15%
37	nc16	0	28.77	2274981	769565	6.03%	5.89%
38	a18	0	29.94	565010	195453	1.50%	1.50%
39	nc17	0	31.02	1596715	474660	4.24%	3.63%
40	pristane	0	31.25	1042841	309093	2.77%	2.37%
41	nc18	0	33.25	877379	334656	2.33%	2.56%
42	phytane	0	33.56	1006006	221482	2.67%	1.69%
43	nc19	0	35.45	486055	157552	1.29%	1.21%
44	nc20	0	37.66	772850	264188	2.05%	2.02%



nc21	0	39.71	311836	98868	0.83%	0.76%
nc22	0	41.77	159689	64983	0.42%	0.50%
nc23	0	43.78	226842	66403	0.60%	0.51%
nc24	0	45.74	170368	58776	0.45%	0.45%
nc25	0	47.63	113403	34189	0.30%	0.26%
nc26	0	49.47	126570	38113	0.34%	0.29%
nc27	0	51.25	96684	26838	0.26%	0.21%
nc28	0	52.97	136297	34518	0.36%	0.26%
nc29	0	54.65	91905	26636	0.24%	0.20%
nc30	0	56.27	36136	12065	0.10%	0.09%
nc31	0	57.82	59834	11368	0.16%	0.09%
nc32	0	59.34	13682	6081	0.04%	0.05%
nc33	0	60.95	52232	9423	0.14%	0.07%
nc34	0	62.80	67123	10278	0.18%	0.08%
nc35	0	64.55	12131	3155	0.03%	0.02%
nc36	0	66.89				
nc37	0	68.32				
nc38	0	71.69				
nc39	0	73.84				
			37697594	13067470		

Table 1. Measurements of peak areas from the FID chromatogram, along with an expanded plot of the FID trace from 4 to 9 minutes.

Appendix B

	Compound Method		201910-7845p42-S1-41_			Area	Height
	Name	MZ	RT	Area	Height	Ratio	Ratio
3	T19- C19 tricyclic terpane	191.2	36.14			Area Ratio=Area*100/Area of 30-Hopane	
4	T20-C20 Tricyclic terpane	191.2	38.00			Height Ratio=Area*100/Height of 30-Hopane	
5	T21-C21 trcyclic terpane	191.2	40.44	55646	17353	11.01	12.50
6	T22-C22-tricyclic terpane	191.2	42.16	71042	20691	14.06	14.90
7	T23-C23-tricyclic terpane	191.2	44.10	104704	30870	20.73	22.23
8	T24-C24-tricyclic terpane	191.2	45.19	86277	27392	17.08	19.73
9	T25S	191.2	47.33	42180	15049	8.35	10.84
10	T25R	191.2	47.39	54777	15002	10.84	10.80
11	TET24	191.2	48.78	20349	6194	4.03	4.46
12	T26S-C26 Tricyclic Terpane(22S)	191.2	48.89	29910	9220	5.92	6.64
13	T26R-C26 Tricyclic Terpane(22R)	191.2	49.03	31700	9512	6.27	6.85
14	25TNH	191.2	54.57			0.00	0.00
15	Ts-C27 17α, 21β-22, 29, 30-Trisnorhopane	191.2	54.57	58347	16815	11.55	12.11
16	Tm-C27 17α, 21β-22, 29, 30-Trisnorhopane	191.2	55.22	79541	22977	15.74	16.55
17	H28-C28 17α, 21β-28, 30-Bisnorhopane	191.2	56.73	29592	6810	5.86	4.90
18	T28R-C28 Tricyclic-Terpane (22R)	191.2	52.64	36979	10855	7.32	7.82
19	T28S-C28 Tricyclic-Terpane (22S)	191.2	52.40	33360	10936	6.60	7.88
20	H29-C29 17α, 21β-Norhopane	191.2	57.45	251989	72290	49.88	52.06
21	Ts29-C29 18α, 30-Norneohopane	191.2	57.55	74250	23406	14.70	16.86
22	NM-C29 17β, 21α-30-Norhopane (Normoretane)	191.2	58.19	26191	6649	5.18	4.79
23	T29R-C29 Tricyclic-Terpane (22R)	191.2	53.71	46498	14162	9.20	10.20
24	T29S-C29 Tricyclic-Terpane (22S)	191.2	53.42	45331	14079	8.97	10.14
25	DH30-C30 Diahopane	191.2	57.79	3623	1551	0.72	1.12
26	OI-C30 18α-Oleanane	191.2				0.00	0.00
27	H30-C30 Hopane	191.2	58.82	505202	138856	100.00	100.00
28	M-C30 17β, 21α-Hopane (Moretane)	191.2	59.40	42933	9521	8.50	6.86
29	G-C30 Gammacerane	191.2	61.17	69250	14523	13.71	10.46
30	T30R-C30 Tricyclic-Terpane (22R)	191.2	55.64	47303	11474	9.36	8.26
31	T30S-C30 Tricyclic-Terpane (22S)	191.2	55.32	41801	12188	8.27	8.78
32	H31S-C31 17α, 21β-Homohopane (22S)	191.2	60.43	185426	47261	36.70	34.04
33	H31R-C31 17α, 21β-Homohopane (22R)	191.2	60.62	128740	32913	25.48	23.70
34	H32S-C32 17α, 21β-Bishomohopane (22S)	191.2	61.79	113442	26413	22.45	19.02
35	H32R-C32 17α, 21β-Bishomohopane (22R)	191.2	62.10	78268	18475	15.49	13.31
36	H33S-C33 17α, 21β-Trishomohopane (22S)	191.2	63.55	67936	15038	13.45	10.83
37	H33R-C33 17α, 21β-Trishomohopane (22R)	191.2	64.03	46776	9846	9.26	7.09
38	H34S-C34 17α, 21β-Tetrahomohopane (22S)	191.2	65.62	40841	7897	8.08	5.69
39	H34R-C34 17α, 21β-Tetrahomohopane (22R)	191.2	66.29	24756	12806	4.90	9.22
40	H35S-C35 17α, 21β-Pentahomohopane (22S)	191.2	68.01	30719	4880	6.08	3.51
41	H35R-C35 17α, 21β-Pentahomohopane (22R)	191.2	68.95	13887	2516	2.75	1.81

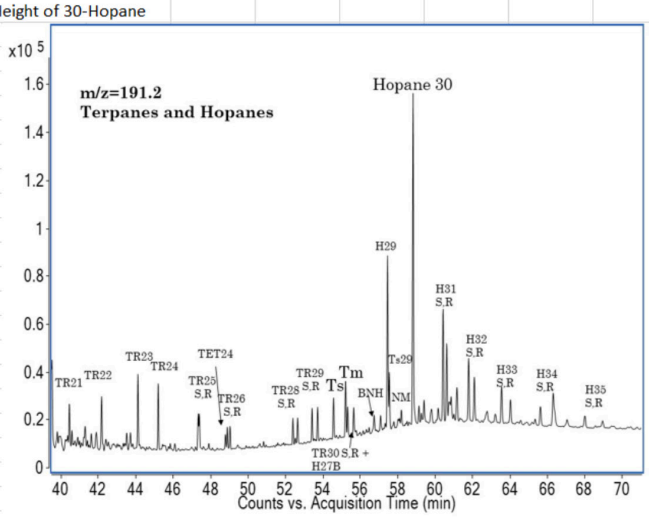


Table 2. Calculated results for the terpanes and hopanes relative to 30-Hopane normalized to 100.

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