

Supplementary Material

The novel chemical pre-pyrolysis treatment of waste tyre crumbs: a viable way for low temperature waste tyre pyrolysis

Phuti Cedrick Tsipa^{1,2*}, Mapoloko Mpho Phiri¹, Samuel Ayodele Iwarere^{3*}, Ntandoyenkosi Malusi Mkhize², Mohau Justice Phiri¹, Shanganyane Percy Hlangothi¹

¹Nelson Mandela University, Centre for Rubber Science & Technology; Department of Chemistry, P O Box 77000, Port Elizabeth, 6301,

²University of KwaZulu-Natal, Chemical Engineering Discipline, 348 Mazisi Kunene Road, Glenwood, 4041

³University of Pretoria, Department of Chemical Engineering, Faculty of Engineering, Built Environment, and Information Technology, Lynnwood Road, Hatfield, Pretoria, 0028, South Africa

* samuel.iwarere@up.ac.za; s215375548@mandela.ac.za

SM-1: Chemical mixture for waste tyre treatment.

Different protonic acids and organic solvents were tested to find the best combination, Table S1 contains the lists.

Table S1: Chemical mixture for waste tyre chemical treatment

Acids			
IUPAC name	CAS number	Chemical formula	Chemical structure
Sulphuric acid 96%	7664-93-9	H ₂ SO ₄	
Hydrochloric acid 35%	7647-01-0	HCL	
Acetic acid	64-19-7	CH ₃ CO ₂ H	
Nitric acid 69%	7697-32-2	HNO ₃	
Organic solvents			
IUPAC name	CAS number	Chemical formula	Chemical structure
Hexane	110-54-3	CH ₃ (CH ₂) ₄ CH ₃	
Dichloromethane	75-09-2	CH ₂ CL ₂	
Acetone	67-64-1	CH ₃ COCH ₃	
ethanol	64-17-5	CH ₃ CH ₂ OH	

*Nitric acid and dichloromethane

SM-2: Chemical mixture treatment

The chemical mixture from the treatment was prepared with nitric acid and dichloromethane solvents with 95:5 ratio. The chemical mixture follows phase-transfer catalysis principle, meaning the two chemicals do not mix and there is a transportation of compounds from one liquid phase to the other. Nitric acid has the ability to cleave sulphur bonds from the vulcanised polymer via oxidation process, while dichloromethane in solution produces halide chlorines which are proton acceptors. They bond with the broken bonds from the polymer, preventing them from re-combining.

SM-3: Compounds identification and estimate area percentage

Table S2: GCMS compounds from the treated waste tyre oils

Peak #	Retention time (RT)	*Compound identification	Area %		
			**C1	**C2	**C3
1	1.629	Ethyne, fluoro-	-	0.31	-
2	1.811	Butane	3.69	5.28	1.54
3	1.845	Acetone	-	-	0.22
4	1.900	Pentane, 2-methyl	-	3.20	0.06
5	1.934	Sulfur dioxide	1.63	1.22	1.11
6	2.194	Propanenitrile	0.36	0.52	-
7	2.254	Acetic acid	0.69	10.20	2.20
8	2.321	2-Butanone	0.42	1.55	0.05
9	2.860	-Pentadiene, 2,4-dimethyl-	-	-	0.32
10	3.014	Benzene	4.36	1.23	3.43
11	5.234	Toluene	1.22	0.42	2.75
12	9.547	Ethylbenzene	0.90	0.02	1.53
13	10.997	styrene	1.30	0.65	2.61
14	11.001	2,6-Lutidine	-	-	0.19
15	11.472	o-Xylene	2.30	0.32	-
16	11.673	p-Xylene	0.95	0.12	2.26
17	18.010	Benzene, 1-ethyl-3-methyl-	1.01	0.50	3.00
18	18.144	Benzene, 1-ethyl-2-methyl-	1.32	0.27	2.50
19	21.536	Mesitylene	-	-	0.02
20	25.701	o-Cymene	1.00	-	1.44
21	26.226	D-Limonene	4.20	1.71	-
22	26.881	Sulfurous acid, cyclohexylmethyl dodecyl ester	2.90	0.68	0.87
23	33.410	p-Cymene	0.59	-	-
24	44.074	Benzene, 1-methyl-2-(2-propenyl)-	0.31	-	2.36
25	52.063	1H-Indene, 2,3-dihydro-1,6-dimethyl-	0.32	-	-
26	52.529	1-Tridecene	1.00	-	1.23
27	53.077	Dodecane	2.00	4.30	1.00
28	53.518	Benzothiazole	1.30	-	1.30
29	54.334	2-Ethyl-2,3-dihydro-1H-indene	0.60	-	-
30	55.134	Naphthalene	1.30	-	-
31	55.325	1H-Indene, 1,3-dimethyl-	0.20	-	-
32	57.271	Naphthalene, 1-methyl-	0.80	-	-
33	57.571	Naphthalene, 1,2,3,4-tetrahydro-1,5-dimethyl-	0.12	-	-
34	57.789	2-methyl-1-Tridecene	1.12	-	2.30
35	58.196	Tridecene	-	1.50	1.20
36	59.011	Naphthalene, 1,2,3,4-tetrahydro-6,7-dimethyl-	0.56	-	-
37	60.360	Sulfurous acid, cyclohexylmethyl pentadecyl ester	1.00	-	0.12

38	61.364	1,2,3-Trimethylindene	0.20	-	-
39	61.448	1H-Indene, 1,1,3-trimethyl-	0.01	-	-
40	61.696	Benzothiazole, 2-butyl	0.20	-	0.21
41	62.256	1-Pentadecene	1.20	1.00	3.20
42	62.439	Naphthalene, 1,5-dimethyl-	0.32	-	-
43	62.596	Tetradecane	1.00	-	2.00
44	64.056	Quinoline, 2,4-dimethyl-	0.22	-	-
45	64.188	Naphthalene, 1,2,3,4-tetrahydro-2,5,8-trimethyl-	0.10	-	-
46	64.305	Farnesol isomer a	0.62	-	0.32
47	65.956	Benzene, 1-(1,5-dimethyl-4-hexenyl)-4-methyl-	-	-	1.00
48	66.655	Pentadecane	1.31	2.00	1.00
49	67.636	Naphthalene, 1,6,7-trimethyl-	0.12	-	-
50	68.257	Naphthalene, 2,3,6-trimethyl-	0.32	-	-
51	70.183	Trichloroacetic acid, tridecyl ester	0.45	1.00	-
52	70.481	Hexadecane		0.90	1.30
53	70.640	Phenol, 2-(1,1,3,3-tetramethylbutyl)-	1.02	0.91	1.61
54	73.418	Bis(2-ethylhexyl)methylphosphonate	1.01	1.41	0.32
55	73.871	1-Nonadecene	2.01	0.70	1.00
57	74.139	Heptadecane		1.27	2.35
58	74.615	Naphthalene, 1,2,3,4-tetramethyl-	0.46		-
59	74.697	2,4,4-Trimethyl-1-pentanol, chlorodifluoroacetate	0.20	0.40	-
60	77.69	Heneicosane	-	0.70	1.00
61	80.968	Heptadecanenitrile	0.20	0.12	-
62	81.531	Cyclohexane, 1-ethenyl-1-methyl-2-(1-methylethenyl)-	-	-	1.20
63	83.157	n-Hexadecanoic acid	-	-	1.86
64	84.218	Eicosane	-	0.20	0.32
65	86.827	9-Octadecenenitrile	0.23	0.70	0.12
66	87.301	Tetracosane	1.00	-	1.32
67	89.222	Octadecanoic acid	-	-	3.90
68	89.230	Octadecanamide	2.03	1.00	0.24
69	90.230	Pentacosane	-	-	0.32

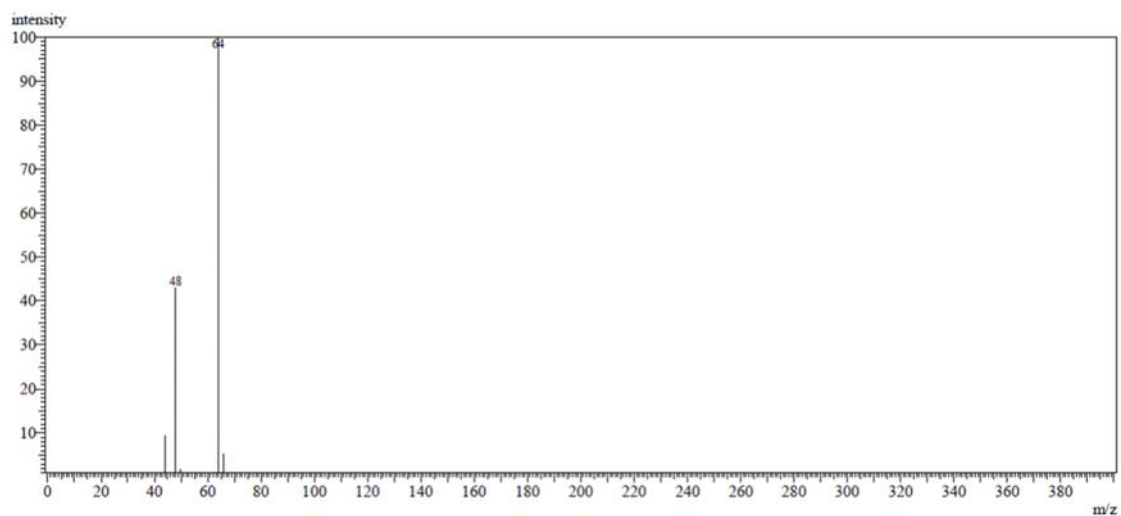
*The compounds documented in the table had a similarity of 90 % and above from NIST library.

**C = Collector

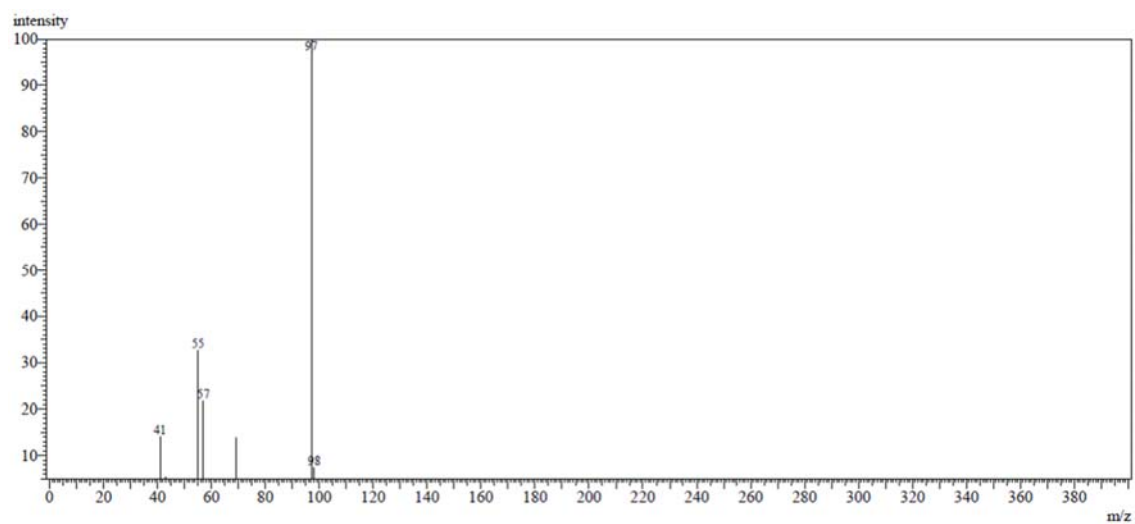
SM-3.1 M/Z- spectra of compounds of interest

SM-3.1.1 Sulphur compounds

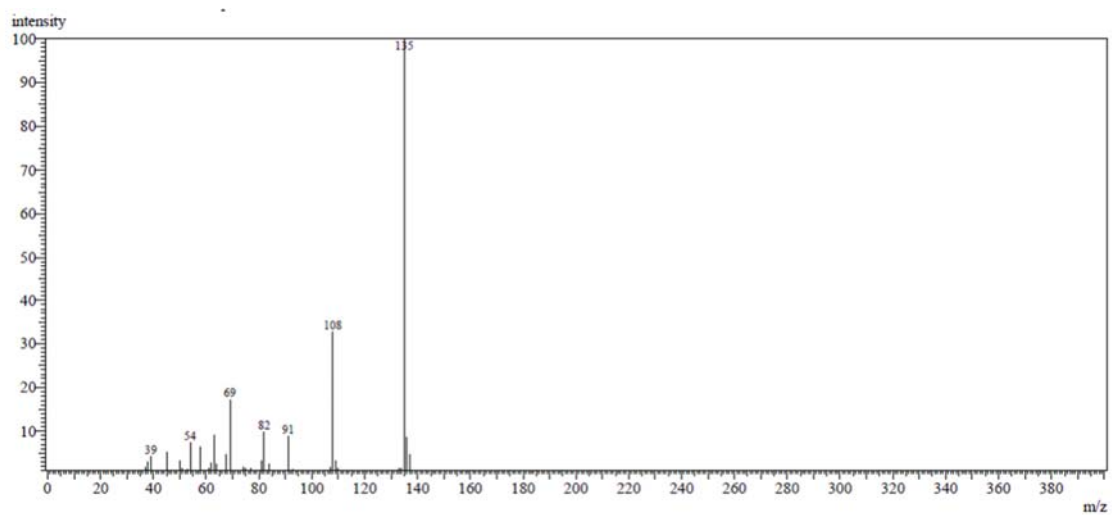
1. Sulphur dioxide: peak no. 5



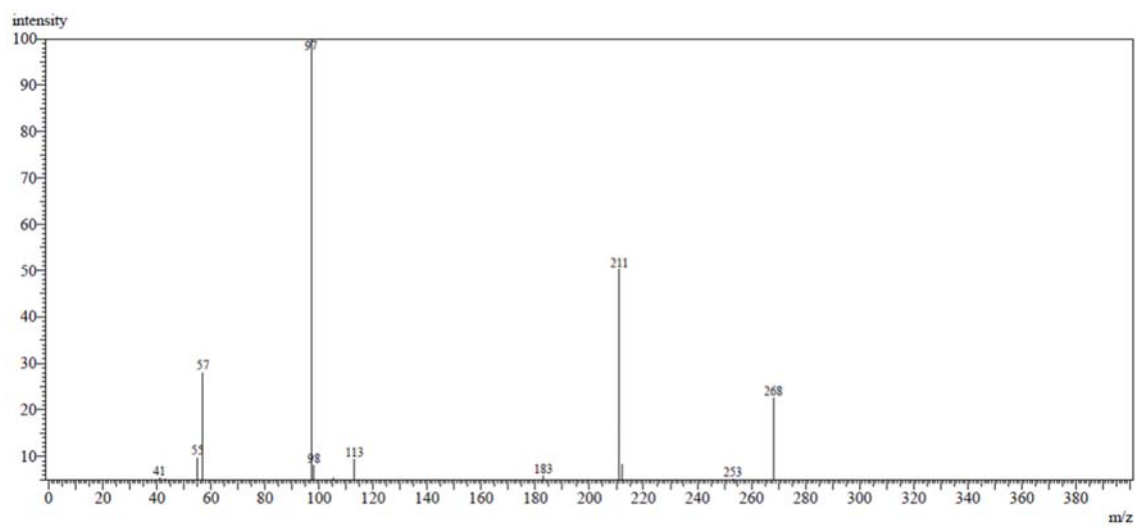
2. Sulphurous acid, cyclohexylmethyl dodecyl ester: peak no. 22



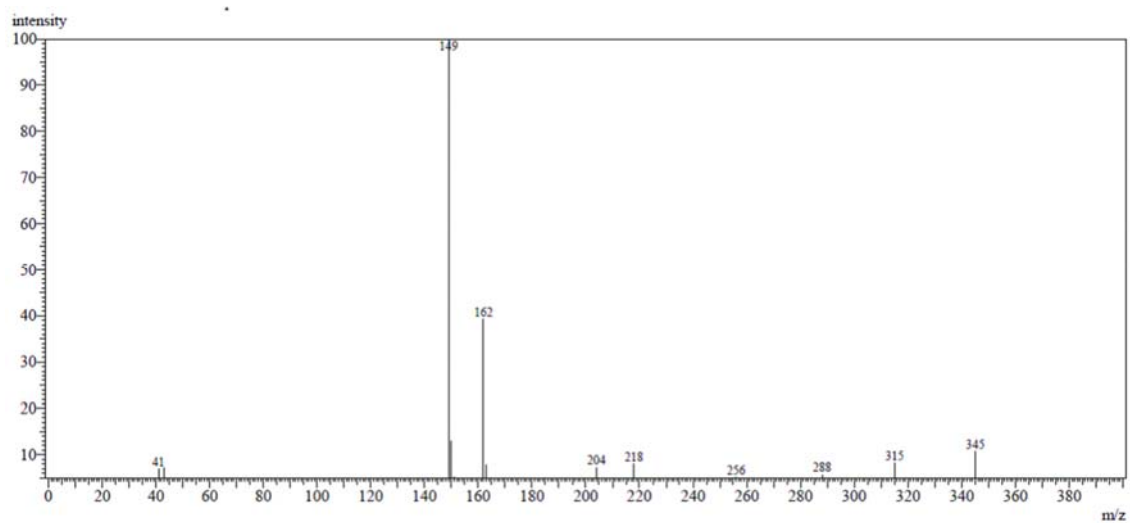
3. Benzothiazole: peak no. 28



4. Sulphurous acid, cyclohexylmethyl pentadecyl ester: peak no. 37

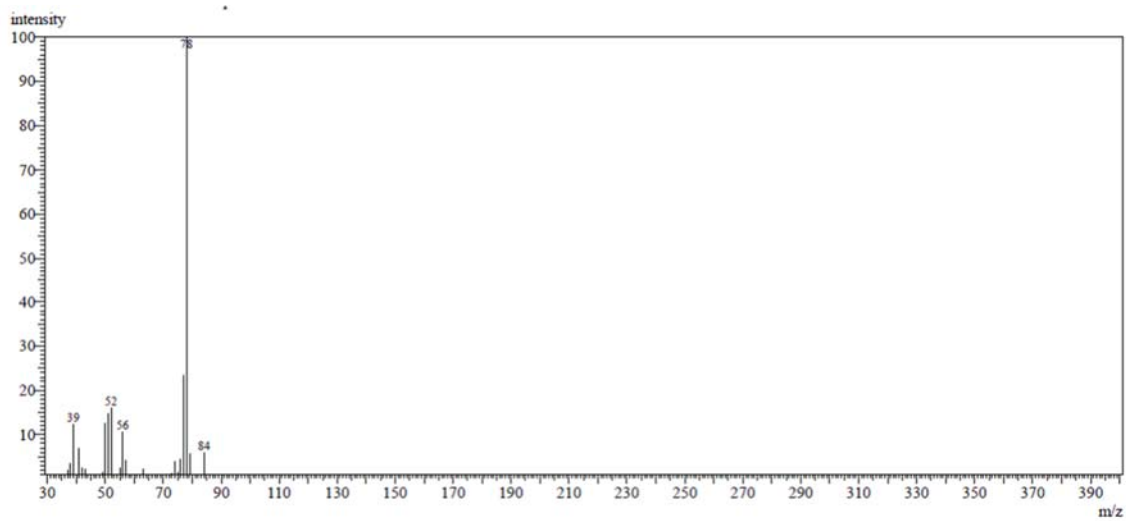


5. Benzothiazole, 2-butyl: peak no. 40

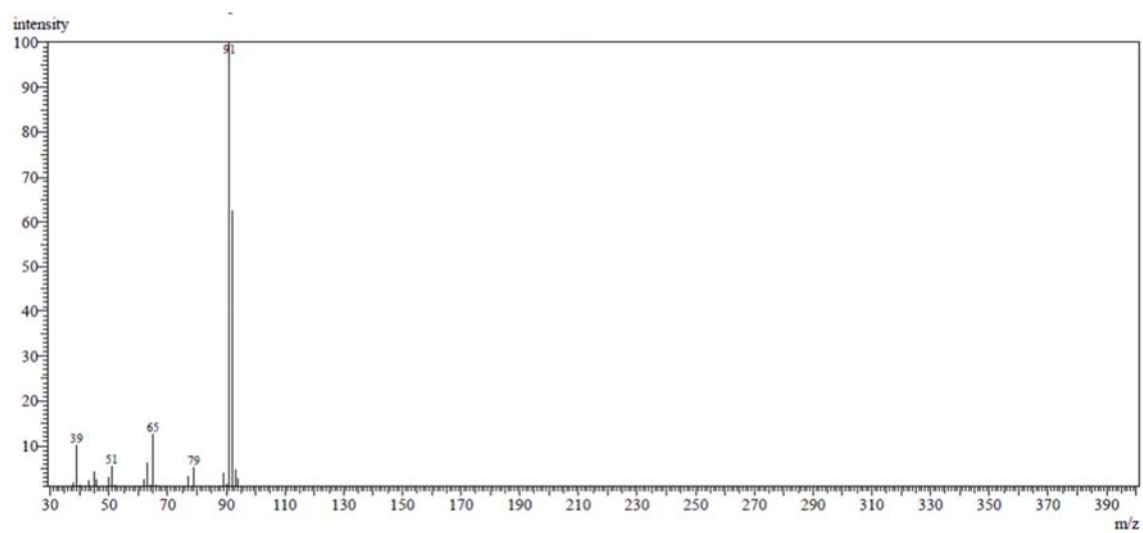


SM-3.1.2 BTX compounds

1. Benzene: peak no. 10

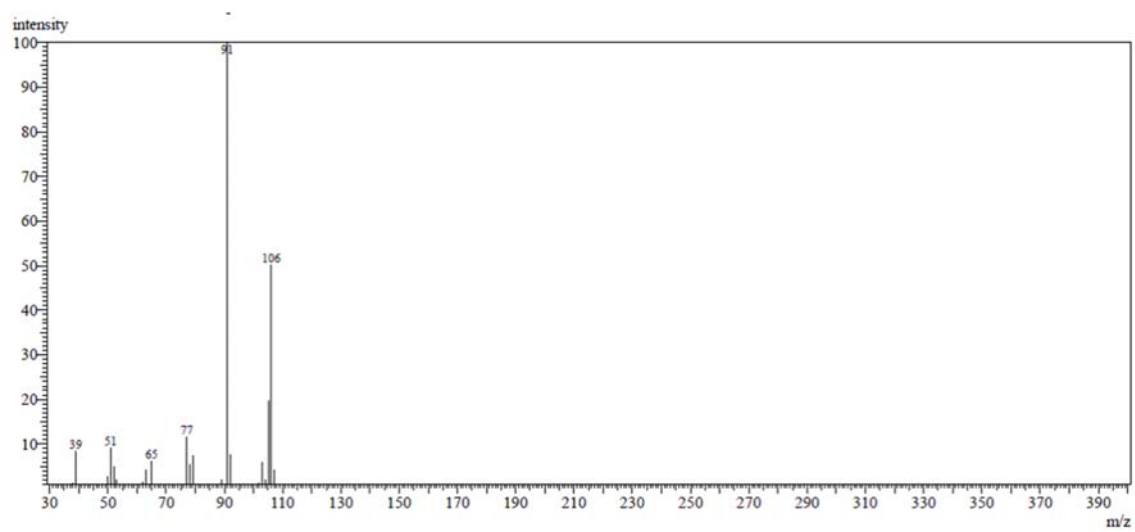


2. Toluene: peak no. 11

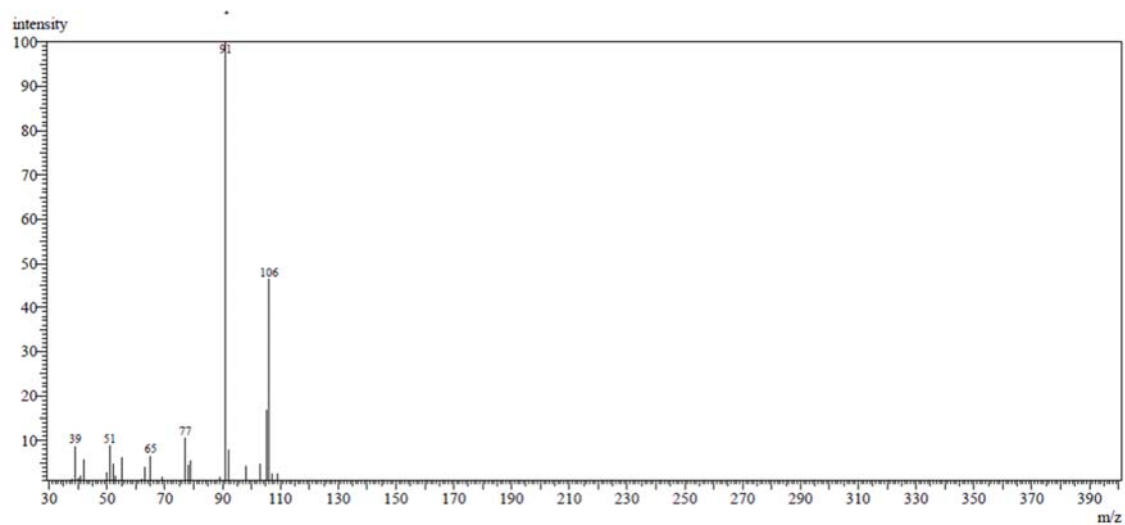


3. Xylene derivatives:

3a. o-Xylene: peak no. 15

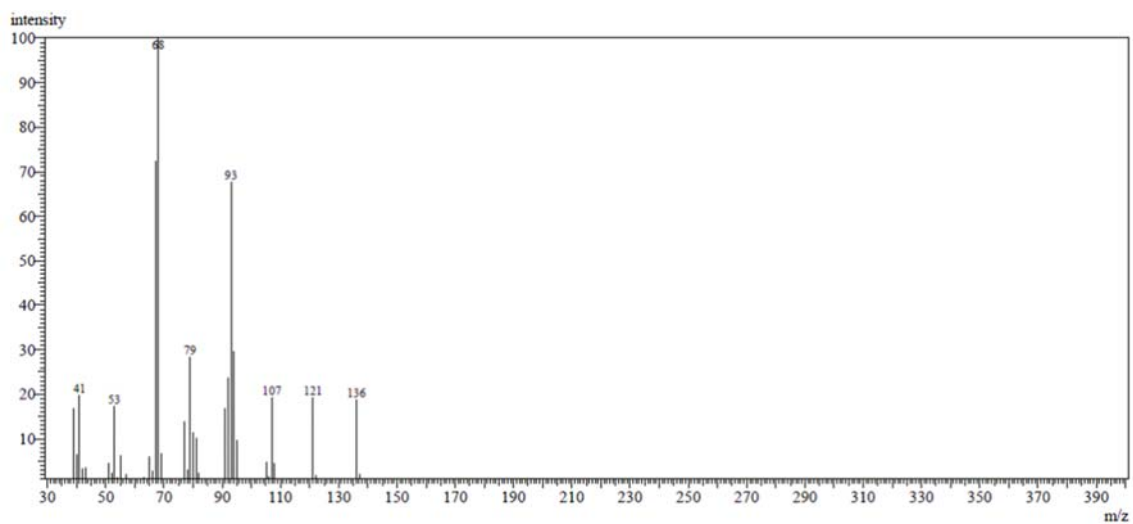


3b. p-Xylene: peak no. 16



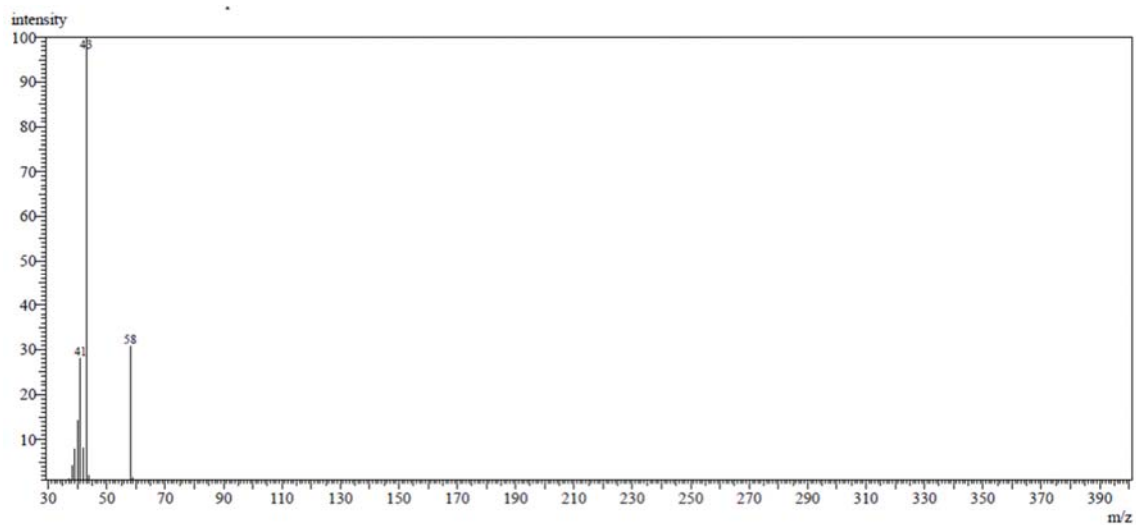
SM-3.1.3 Alkenes

1. D/L Limonene: peak no. 21

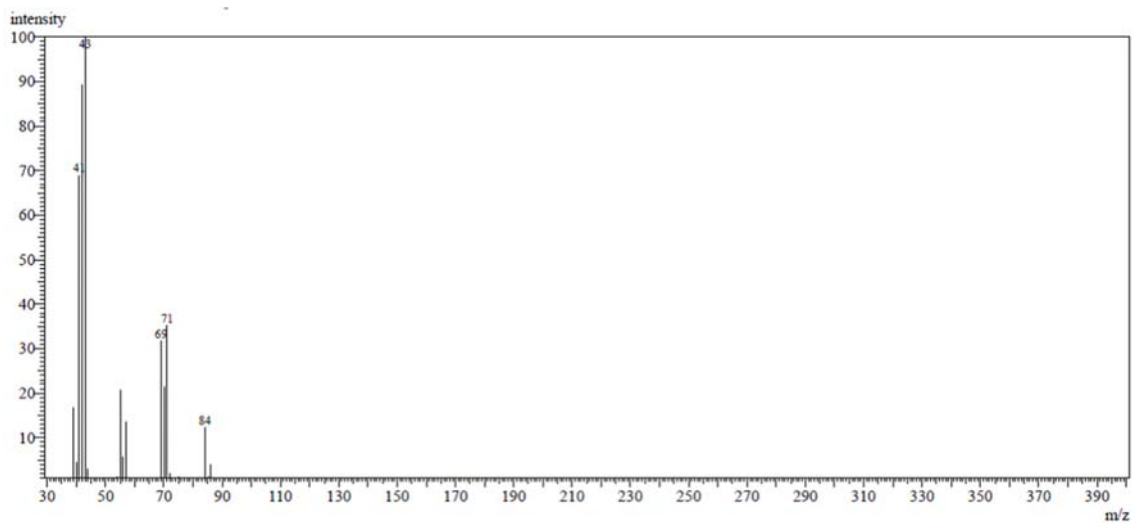


SM-3.1.4 Alkanes

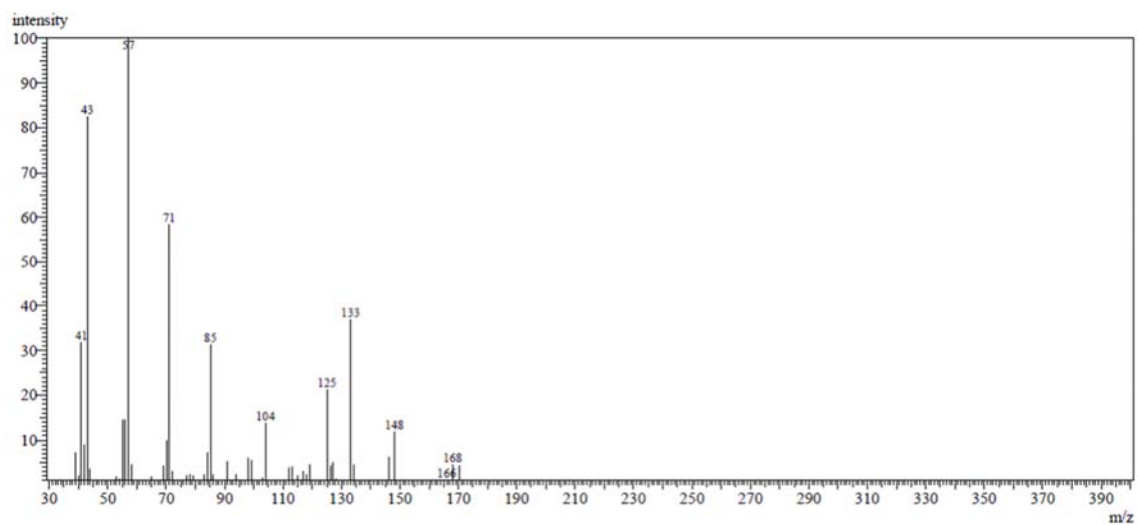
1. Butane: peak no. 2



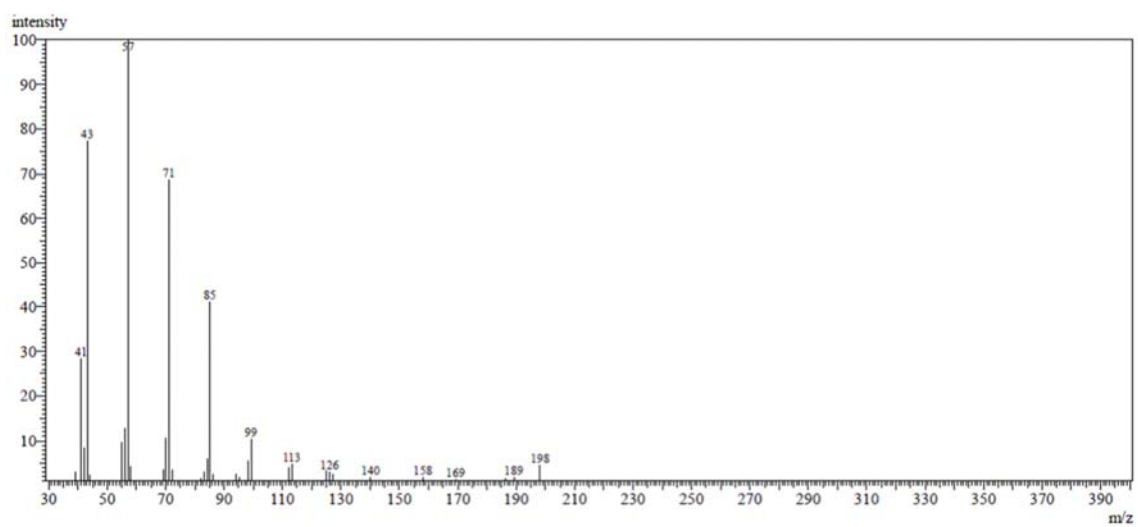
2. Pentane, 2-Methyl: peak no. 4



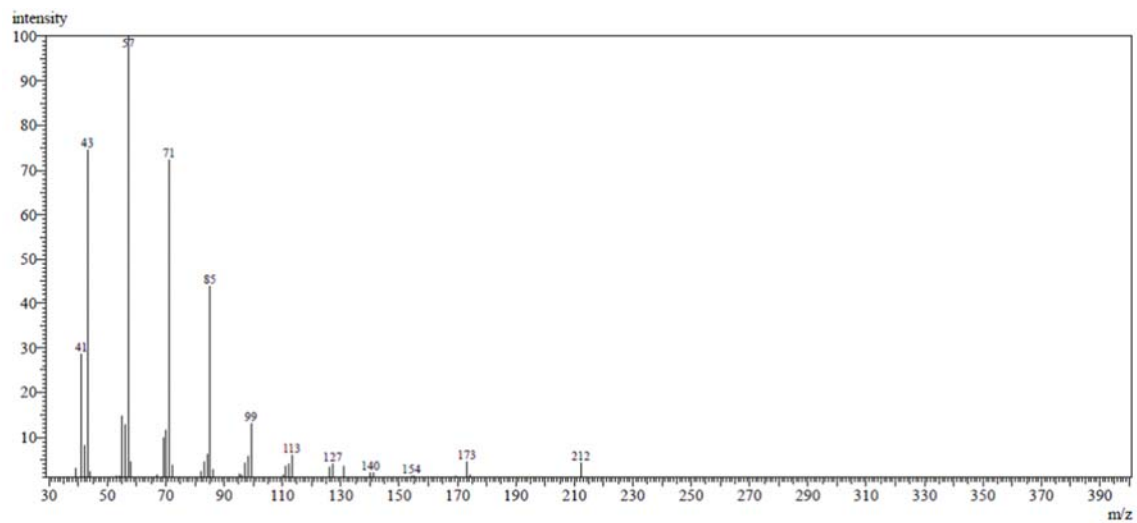
3. Dodecane: peak no. 27



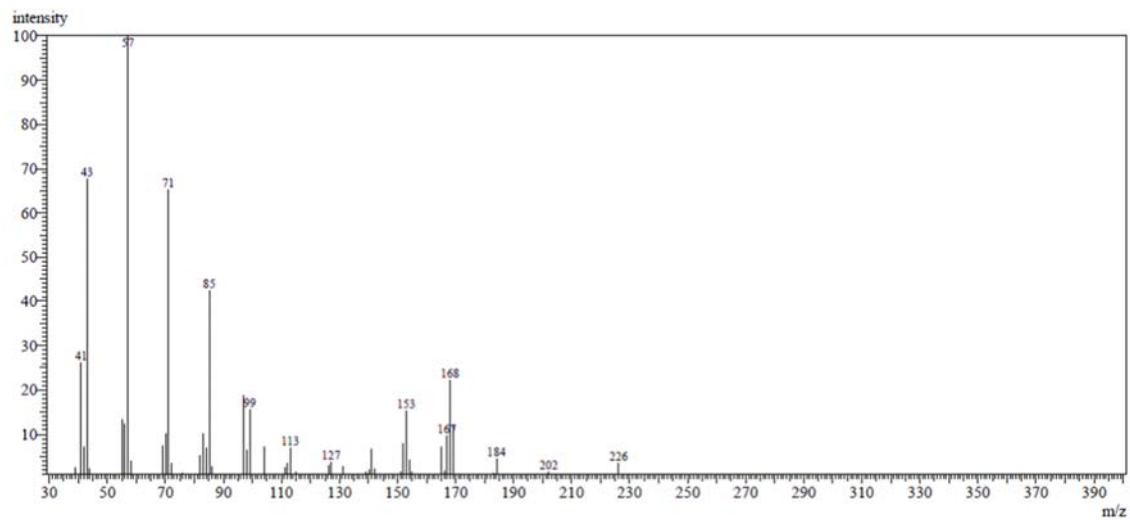
4. Tetradecane: peak no. 43



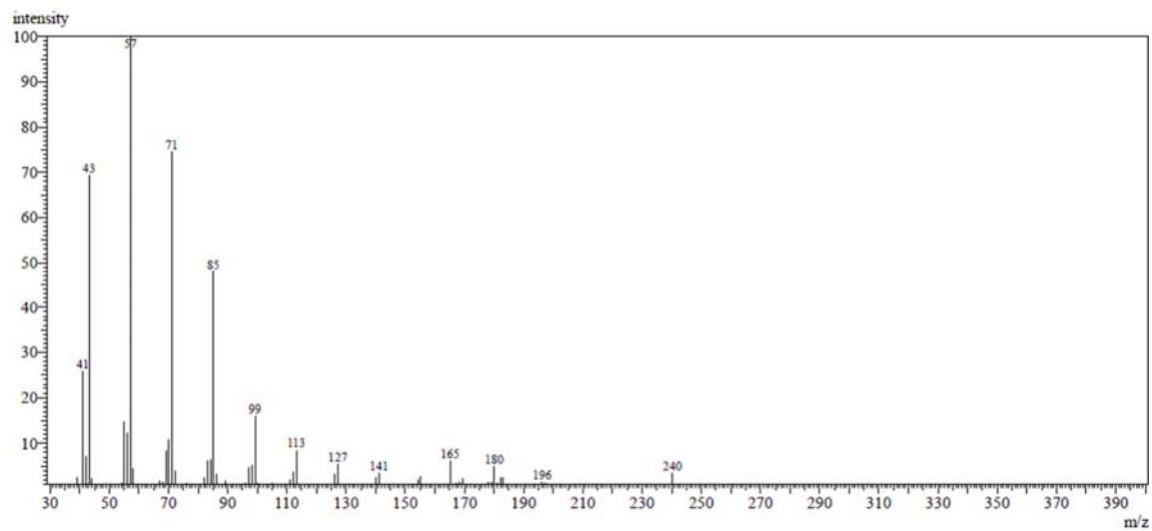
5. Pentadecane: peak no. 48



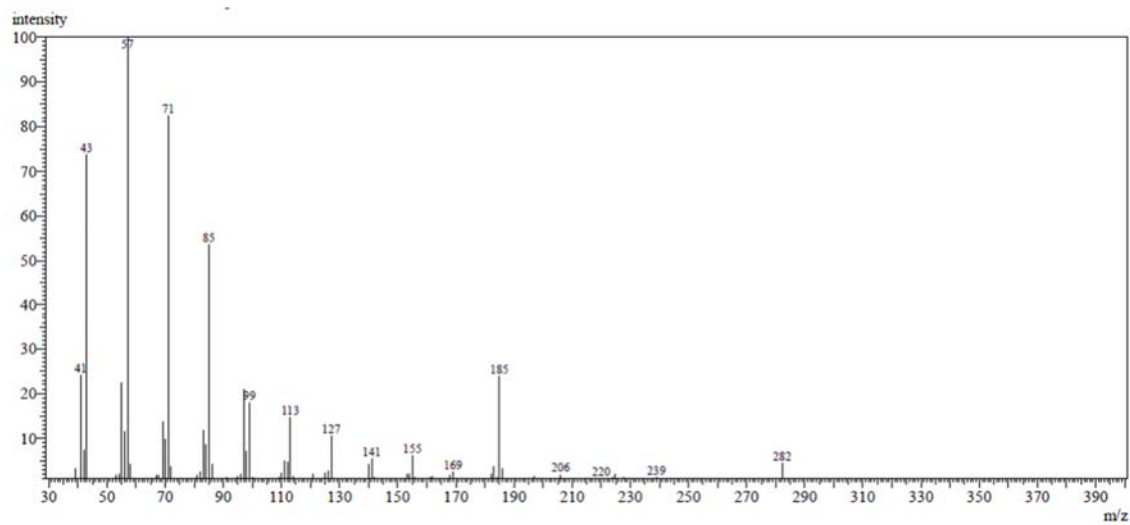
6. Hexadecane: peak no. 52



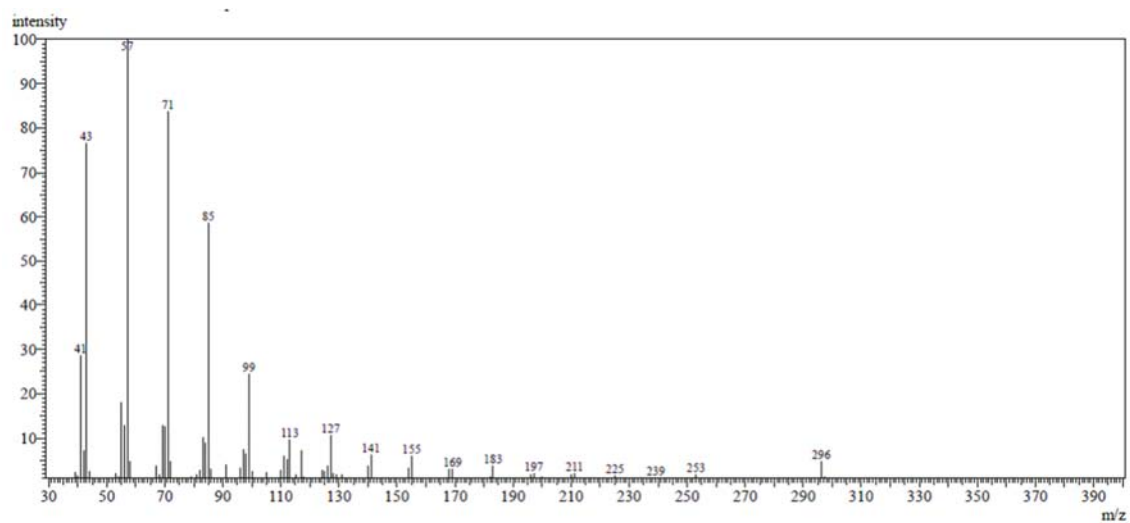
7. Heptadecane: peak no. 57



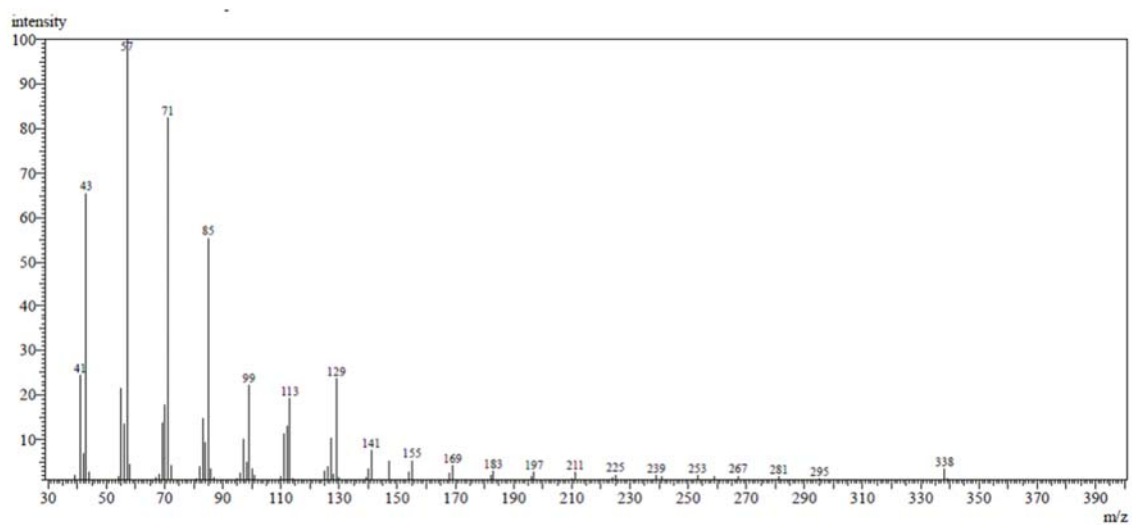
8. Eicosane: peak no. 60



9. Heneicosane: peak no. 64

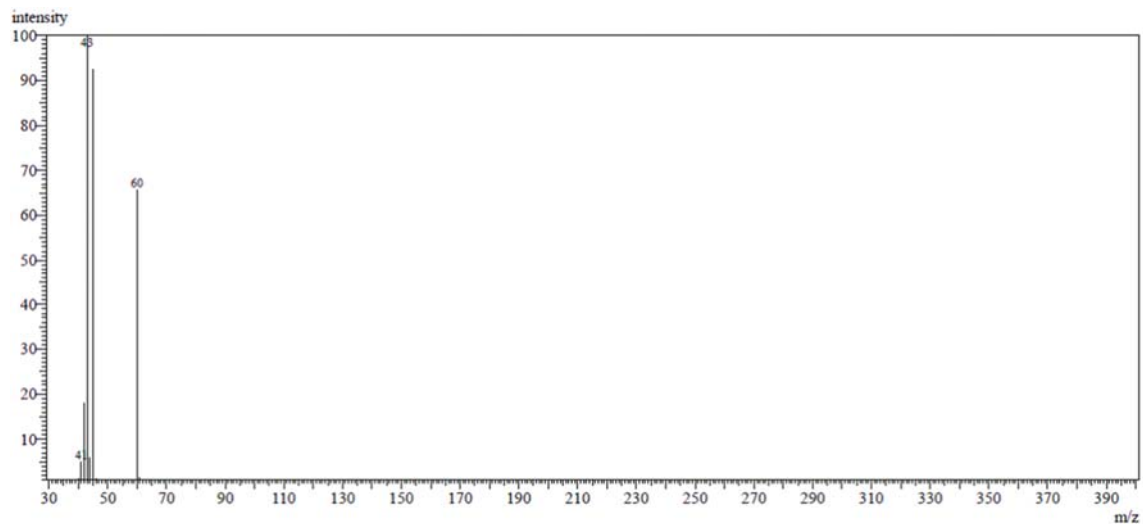


10. Tetracosane: peak no. 69

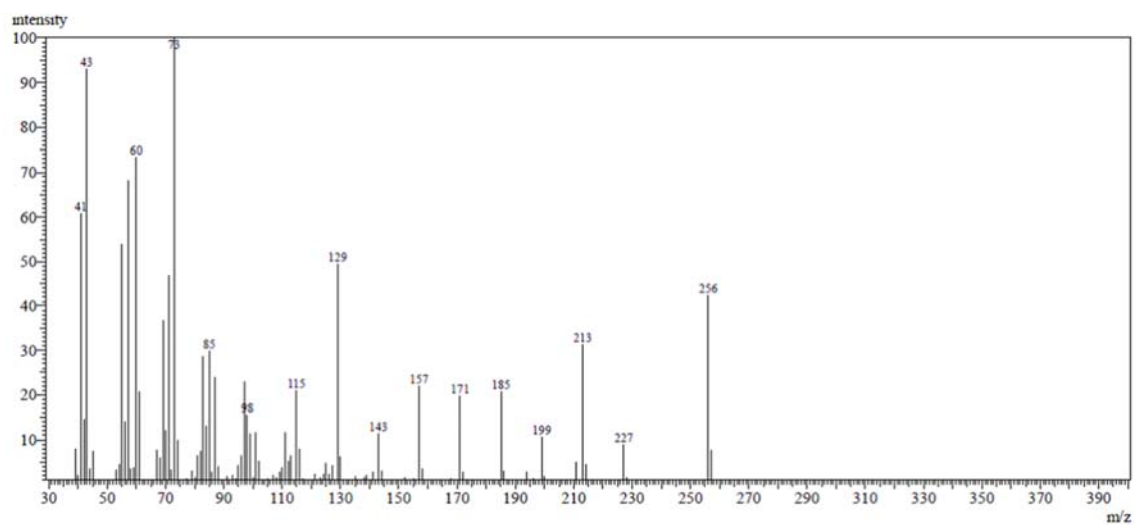


SM-3.1.5 Acids

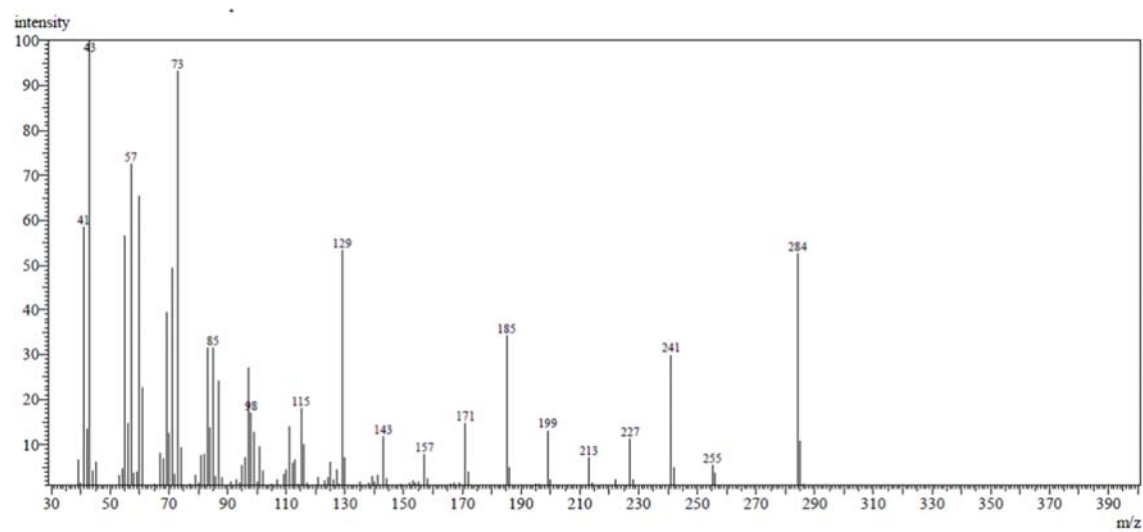
1. Acetic acid: peak no. 7



2. Hexadecenoic acid: peak no. 63

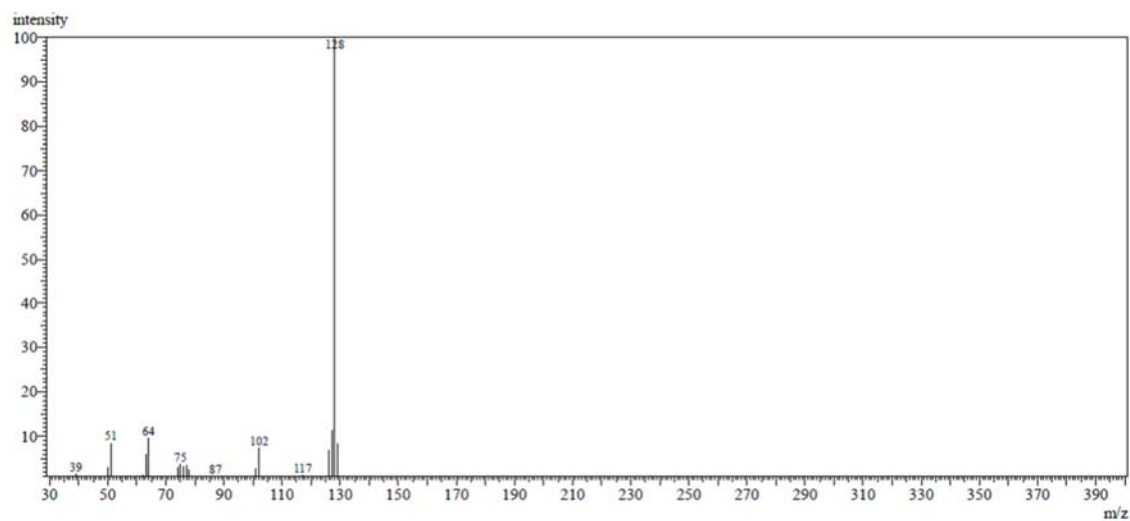


3. Octadecanoic acid: peak no. 67

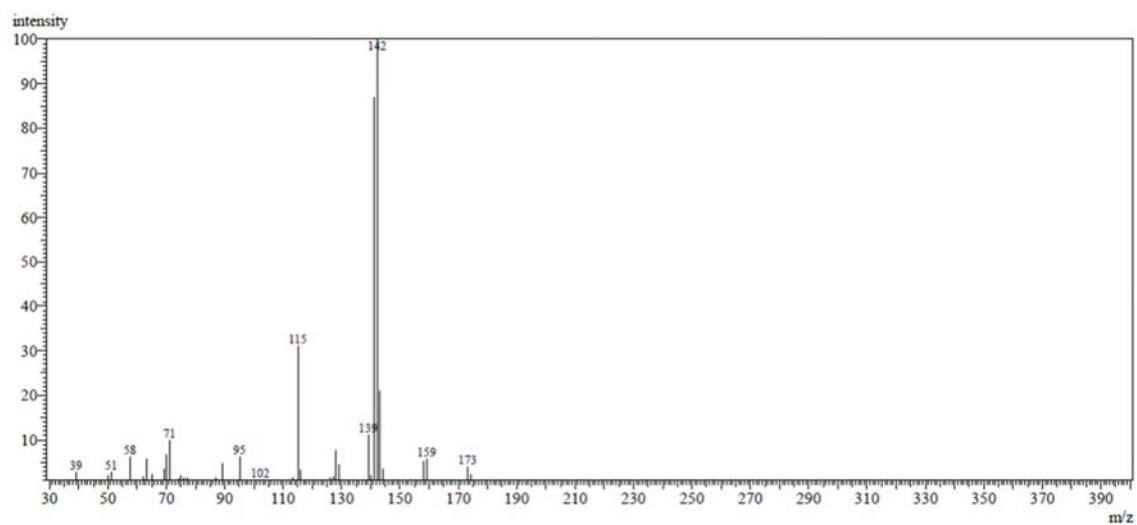


SM-3.1.6 Polycyclic aromatic hydrocarbons (PAHs)

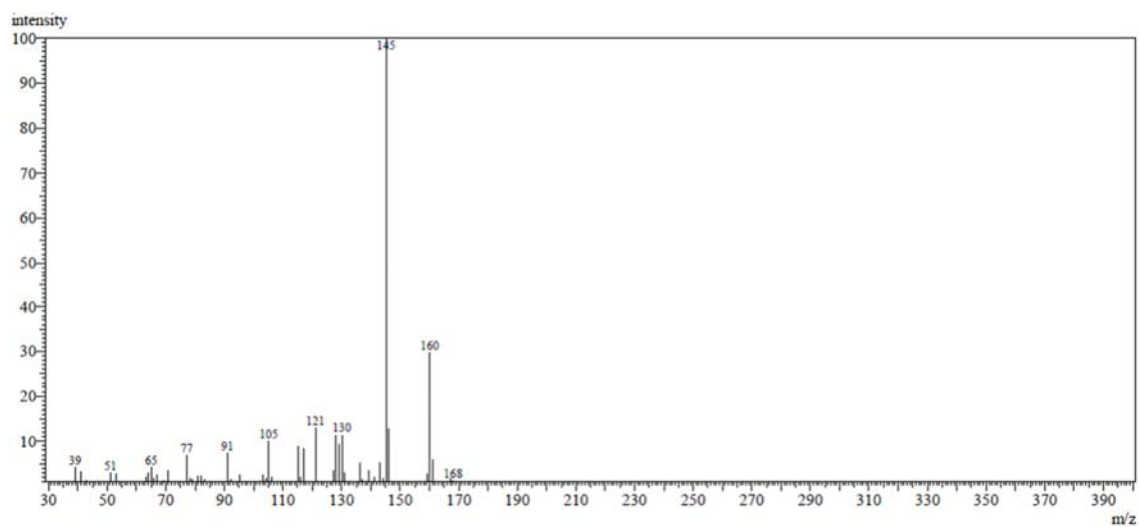
1. Naphthalene: peak no. 29



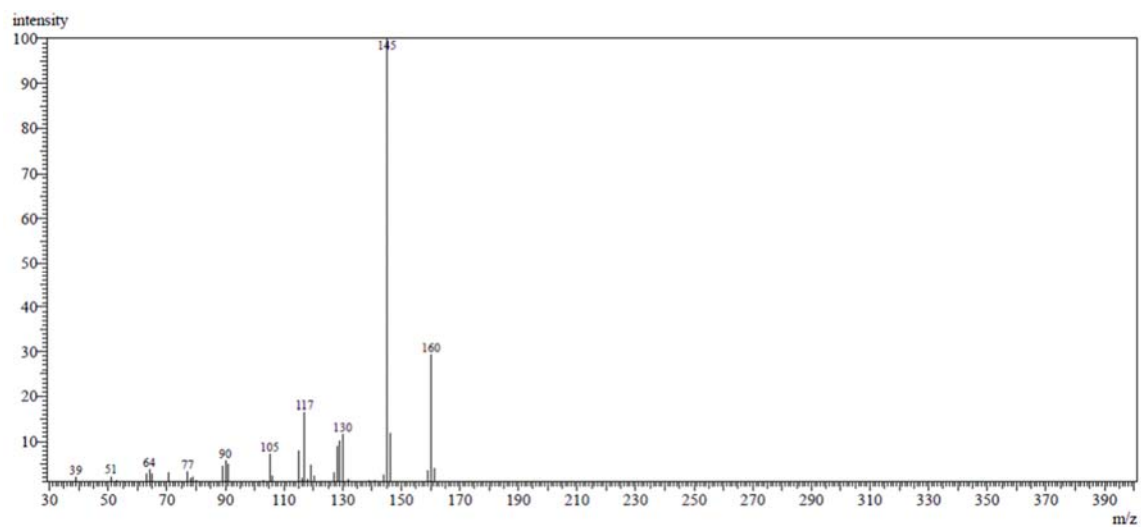
2. Naphthalene, 1-methyl: peak no. 31



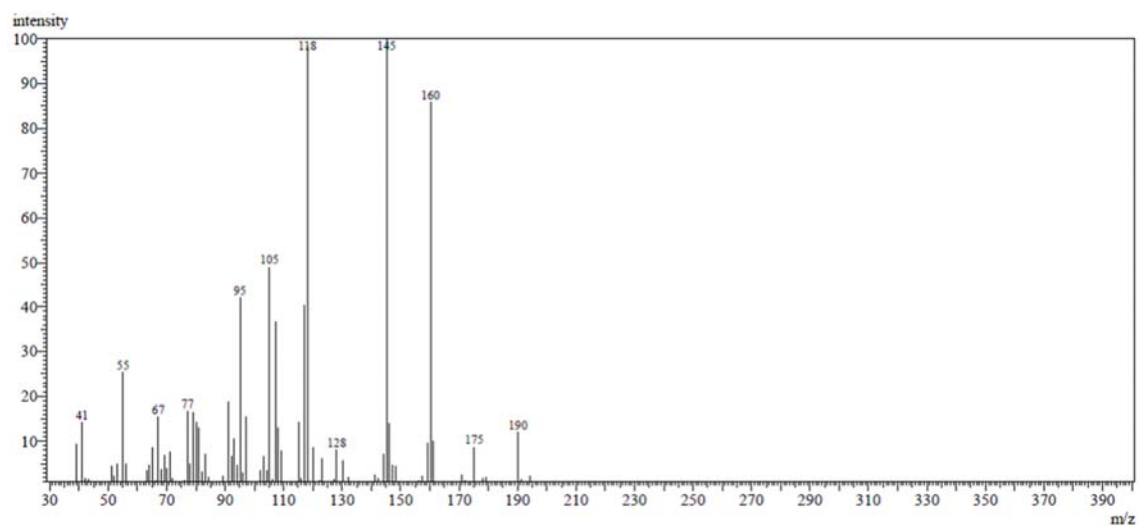
3. Naphthalene, 1,2,3,4-tetrahydro- 1, 5-dimethyl: Peak no. 32



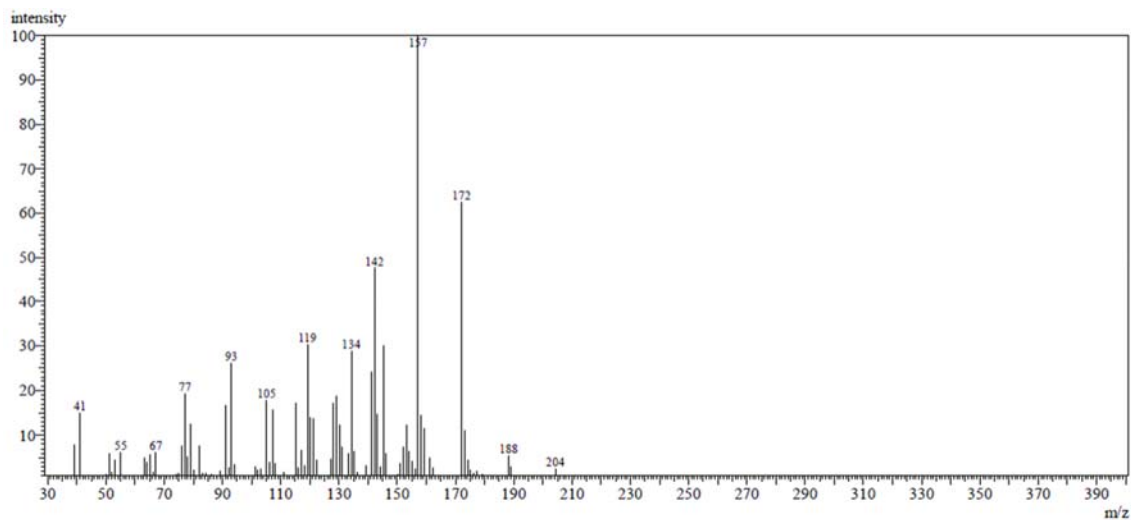
4. Naphthalene, 1,2,3,4-tetrahydro- 6,7-dimethyl: Peak no. 35



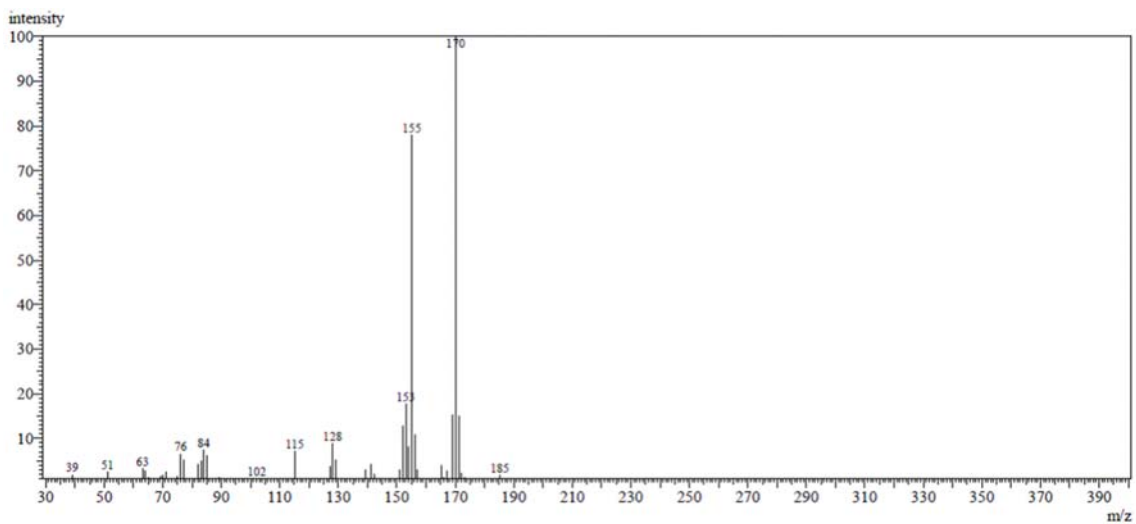
5. Naphthalene, 1,5-dimethyl-: peak no. 41



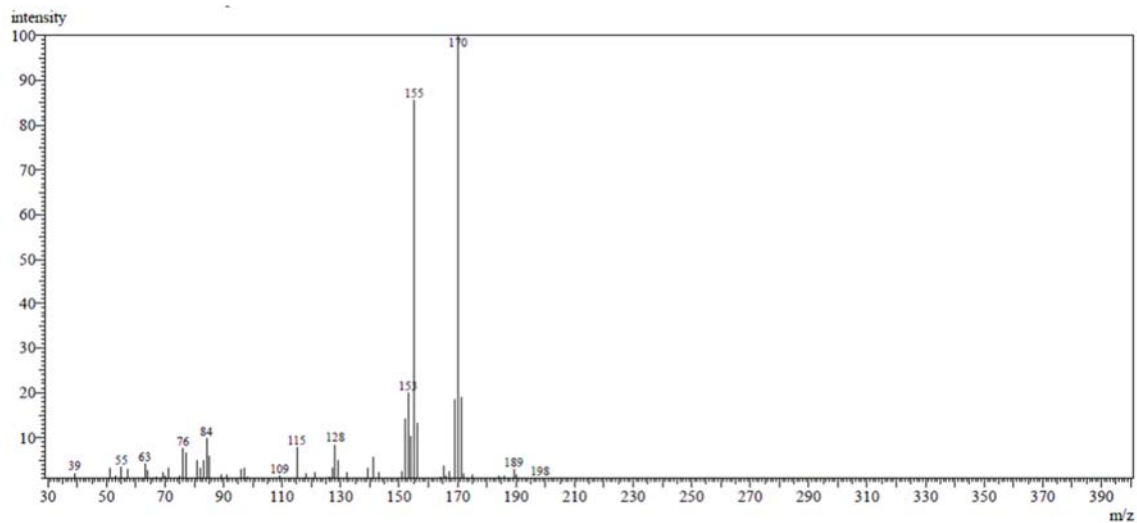
6. Naphthalene, 1,2,3,4-tetrahydro-2,5,8-trimethyl-: peak no. 44



7. Naphthalene, 1,6,7-trimethyl-: peak no. 48



8. Naphthalene, 2,3,6-trimethyl-: peak no. 49



9. Naphthalene, 1,2,3,4-tetramethyl-: peak no. 57

