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Origin identification of oil spillage in marine pollution from ships by GC/MS and FTIR analyses

Gemi kaynaklı deniz kirlenmesinde sintine orjininin GC/MS ve FTIR analizi ile tayini

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Abstract

Samples were collected from an oil slick in Tuzla Bay released from two ships. The origin of the oil was identified by GC/MS and FTIR analyses. The aliphatic and aromatic group compounds were detected by GC/MS analysis. Similar FTIR spectra were obtained from the sea water and bilge water of ships. Both analysis methods support each other and they can be used for oil spillage identification. In addition to the Pr/Ph ratio, nor- Pr/Ph and nor - Pr/Ph ratios were used for the first time in the identification of oil spillage.

Key words: Oil spillage, GC/MS, FTIR analyses

Introduction

Oil enters seawater by a number of different routes. Total input of petroleum to seawater from all sources is 3.2 million tonnes a year of wich 1.47 million t/a derives from transportation and 0.7 million t/a from discharge and is referred to as clingage. The distribution of pollution sources of oils is 37% industrial discharges and urban run-off, 33% vessel operation, 12% tanker accidents, 9% atmosphere, 7% natural sources and 2% exploration production (Anon., 1993). As can be indicated above , tank cleaning and de- ballasting operations and bilge waste waters are important factors in oil pollution. According to the "Regulations Prohibiting Pollution of the Environment of Turkish Straits; Article 33: No refuse, ballast, bilge water, domestic and industial waste, ecologically harmful or insanitary material, oil or other pollutants may be dumped or discharged into the sea in the straits and Marmara region" (Aybay, 1995). -Bilge water discharge is a a major problem for the Turkish Straits (the Straits of Istanbul and Çanakkale and the Sea of Marmara).

So far, increase in petroleum hydrocarbon levels mainly from oil spills, sewage outfalls and ship bilge water, has been observed in the sea of Marmara. However, no report is published on this issue.

The methods used for detection and identification of oil spill are the gas chromatography (Johansson *et.al.,*), GC/MS spectrophotometry (Davies and Wolff, 1989; Grahl-Nielsen and Lygre, 1990) and the IR spectrophotometric method (Bean, 1974)

This study is the first of this kind and it was implemented in the Sea of Marmara to investigate oil spillage from ships.

In this study GC/MS and FTIR analyses were used for the identification of de-ballasting operations in Tuzla Bay and their results have been reported.

Material

The samples of seawater near the dockyard and bilge water samples from ship 1 and 2 were taken in Tuzla Bay in 25 July 1997.

Method

Extraction of oil in seawater

Seawater was extracted three times with 50 ml dichlormethan (DCM). The organic phase was combined and then dried over anhydrous sodium sulphate and distilled in a rotary evaporator. The residue was dissolved with hexane and the volume adjusted to 10 ml and subjected to GC/MS and FTIR analyses.

GC/MS analyses were run on an HP 6890 capillary GC connected to a Hewlett Packard Mass Selective Detector (MSD) controlled by an HP ChemStation. Operating conditions were: 50 m x 0.20 mm fused HP PONA, methyl siloxane, glass capillary column; oven temperature programme: 110°C- 290°C at 6° C/min, from 290°C at 15 min, splitless injector temperature 250°C; carrier gas helium, 1.2 flow.

FTIR analysis: The IR spectrum was taken in KBr by using FTIR Shimadzu 8201-PC

Results

The selected GC/MS chromatograms and FTIR spectra of seawater samples near the dockyard and bilge waters taken from ship 1 and 2 are shown in Figure 1, 1a-1c and 2, 2a-2e respectively.

The identified hydrocarbons are;

Aliphatic group:, **2.** Dodecane, **3.** Undecane 2,6 dimethyl, **4.** Undecane 4,6 dimethyl, **5.** Tridecane, **6.** Tridecane- 6 methyl, **7.** Penthyl cyclohexane, **8.**

Dodecane 2,6,10 trimethyl, **9.** Tetradecane, **12.** Tridecane 6- propyl, **13.** Pentadecane, , **17.** Hexadecane. **18.** nor- Pristane (Pentadecane 2,6,10 trimethyl), **19.** Heptadecane, **20.** Pristane, , **22.** Octadecane, **23.** Phytane, **24.** Nonadecane, **26.** Eicosane, **27.** Heneicosane, **28.** Docasane, **29.** Tricosane, **30.** Tetracosane, **31.** Pentacosane, **32.** Hexacosane, **33.** Heptacosane.

Aromatic group: **1.** Naphthalene,**10.** Naphthalene 2,6 dimethyl, **11.** Naphthalene 1,7 dimethyl, **14.** 2- isopropyl naphthalene, **15.** Naphthalene 2,3,6 trimethyl, **16.** Naphthalene 1,6,7 trimethyl, **21.** Phenanthrene, **25.** Anthracene- 1 methyl.

Similar compounds belonging to aromatic groups were found in the cargo sample of ships 1 and 2 and the seawater sample taken near these ships.

The GC/MS chromatograms and the spectra of the peaks for seawater sample and bilge waters of ship 1 and 2 are similar (Fig. 1). The similarity was confirmed by comparison of the spectra of the samples and the spectrum taken from HP memory.

Aliphatic and aromatic groups compounds in both samples were detected by GC/MS. The chromatograms of aliphatic and aromatic groups are shown in Figure 1a-1c.

Spilled crude oil and various oil residues are the unique source of fossil pristane and phytane. Almost C10-C26 alkanes and large amounts of pristane and phytane were detected in the sea water samples and bilge water taken from ships. The ratio of pristane/phytane was a good petroleum marker for the pollution. Pr/Ph, nor- Pr/Ph and nor-Pr/Pr ratios are shown in Table 1. As can be seen from this Table, all the ratios are similar (lower or higher than one), which support that spillage and bilge waters are from the same origin.

Table1. The ratios of nor- Pr/Ph, nor- Pr/Ph and nor- Pr/Pr.

	Pr/Ph	nor- Pr/Ph	nor- Pr/Pr
Near the dockyard	1.293	0.930	0.719
Ship 1	1.858	0.960	0.516
Ship 2	1.416	0.979	0.691

FTIR spectra of seawater near the dockyard and bilge waters of ship 1 and 2 are shown in Figure 2. Partial spectra at 4000-3600 cm^{-1}, 3200-2200 cm^{-1}, 2000-1700 cm^{-1}, 1700-1300 cm^{-1}, 700-400 cm^{-1} are shown in Figure 2, 2a-2e.

It was observed that the bands in total IR spectra at 4000 cm^{-1} - 400 cm^{-1} near the dockyard and spillage waters were similar.

Finally, the profiles of GC/MS chromatograms and FTIR spectra are very similar to those observed in bilge water of ships 1 and 2 and sea water taken near the ships. According to these findings the seawater samples and bilge water taken from ships 1 and 2 are obviously from the same origin.

Discussion

GC/MC and FTIR spectrometric methods are an important tool used for the detection of oil spillage.

For the identification of oil spillage, it is seen that the combined usage of GC/MS and FTIR analyses give reliable results.

In addition to the Pr/Ph ratio, nor- Pr/Ph and nor - Pr/Ph ratios were used for the first time in the identification of oil spillage.

Özet

Tuzla Körfezi'ne sintine basan iki gemiden alınan örnekler ile bu gemilerin yanından alınan su örnekleri GC/MS ve FTIR analizine tabi tutuldu. Bunlara ait kromatogramların ve IR spektrumlarının incelenmesinde sintinenin bu gemilere ait olduğu saptanmıştır. Bu şekilde kombine analiz ile sintine basan geminin tesbiti sağlanmıştır. Bu çalışmada Pr/Ph oranı yanında yeni olarak önerdiğimiz nor-Pr/Pr , nor-Pr/Ph oranlarının bu petrol kirliliğinin orjininin saptanmasında yardımcı bir oran olarak kullanılabileceği gösterildi. Bu çalışma sintine tesbiti için ülkemizde yapılan ilk çalışmadır.

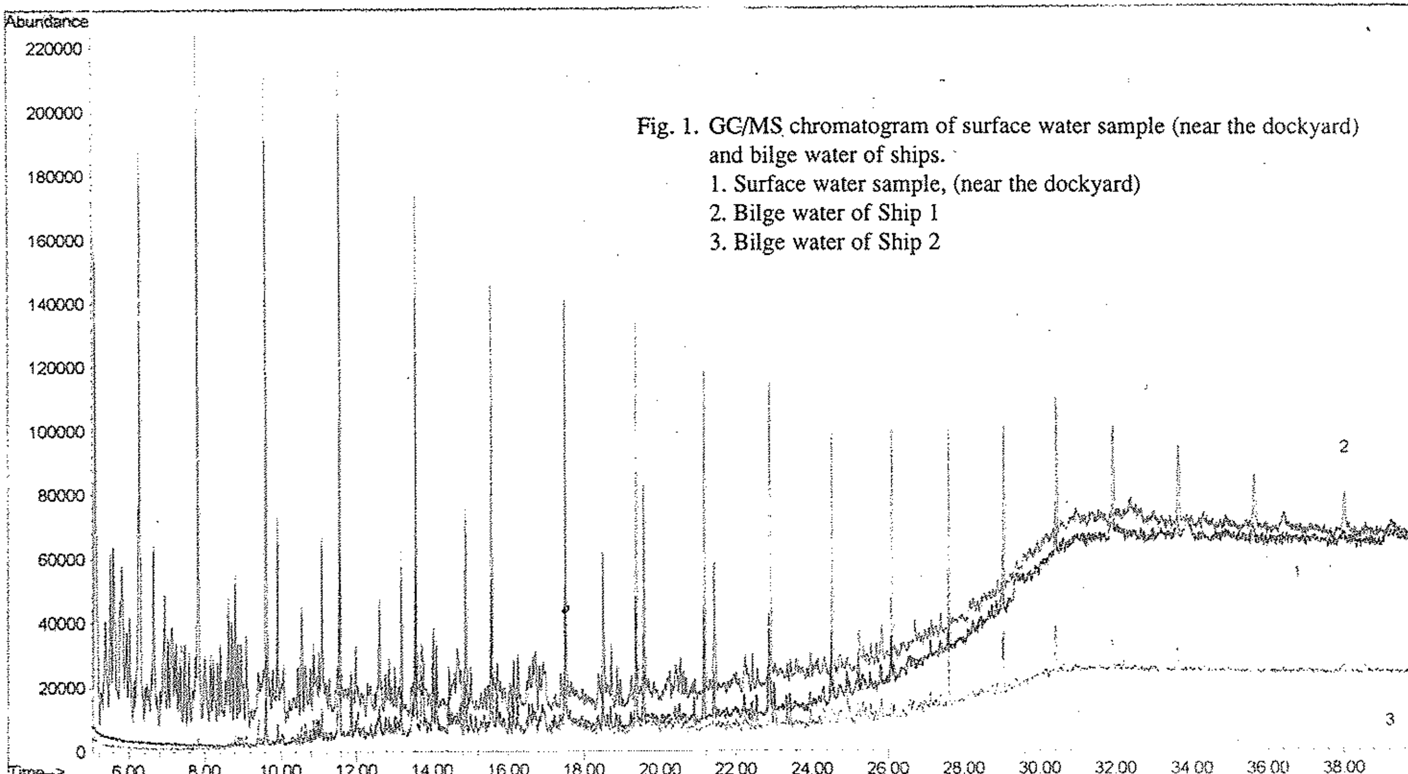
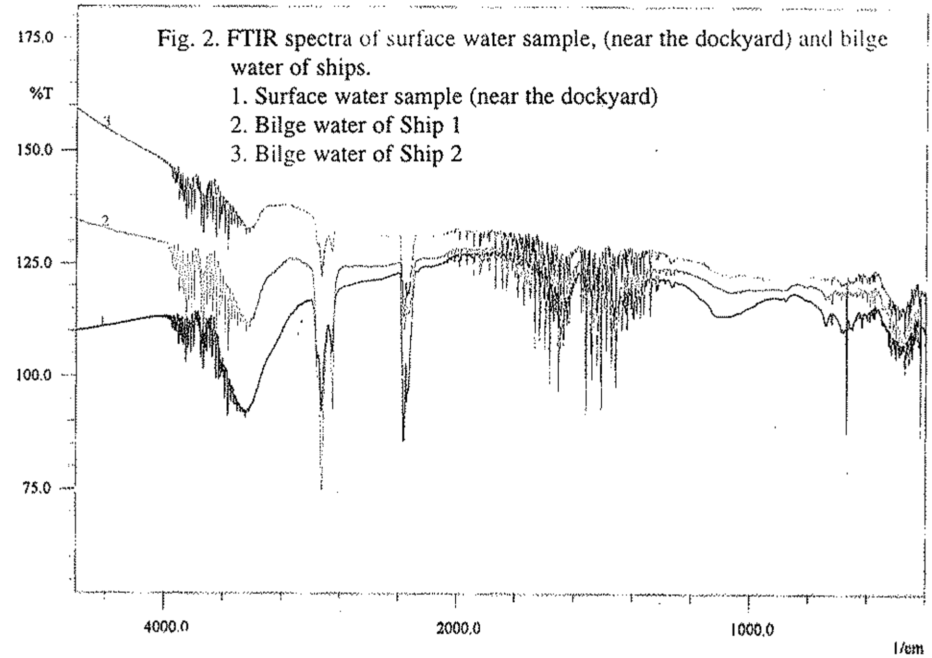


Fig. 1. GC/MS chromatogram of surface water sample (near the dockyard) and bilge water of ships.

1. Surface water sample, (near the dockyard)
2. Bilge water of Ship 1
3. Bilge water of Ship 2

Fig. 2. FTIR spectra of surface water sample, (near the dockyard) and bilge water of ships.
1. Surface water sample (near the dockyard)
2. Bilge water of Ship 1
3. Bilge water of Ship 2



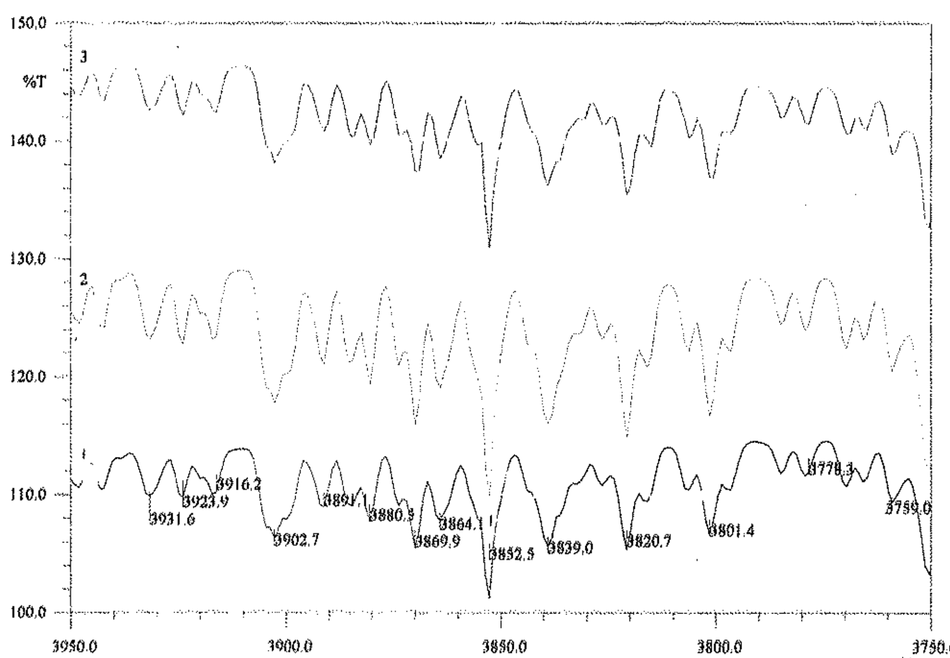


Fig. 2a. FTIR Spectra for 1, 2, 3 at 3950 - 3750 cm^{-1}

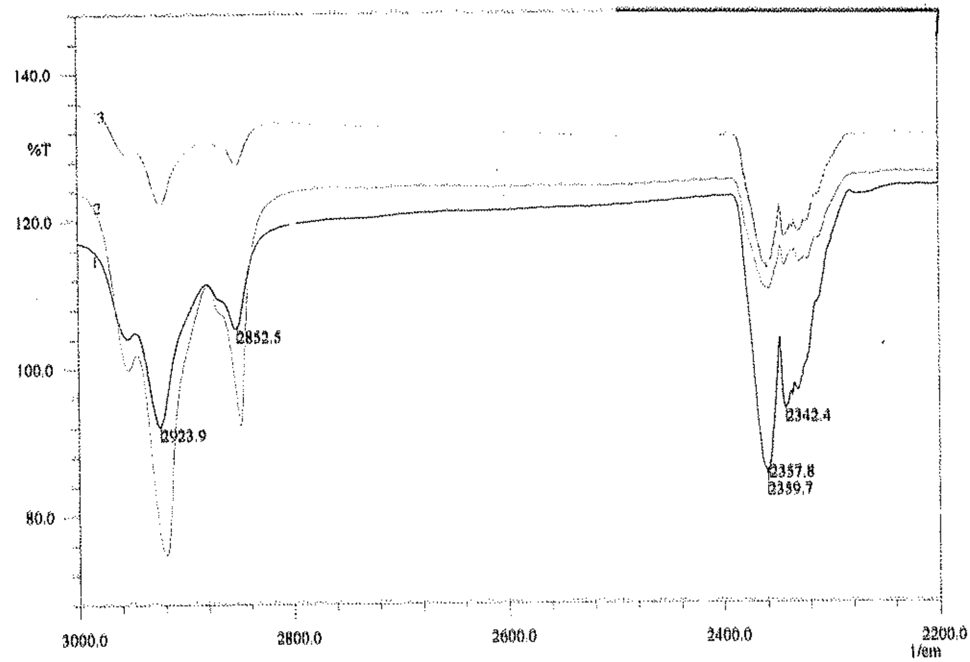


Fig. 2b. FTIR Spectra for 1, 2, 3 at 3000 - 2200 cm-1

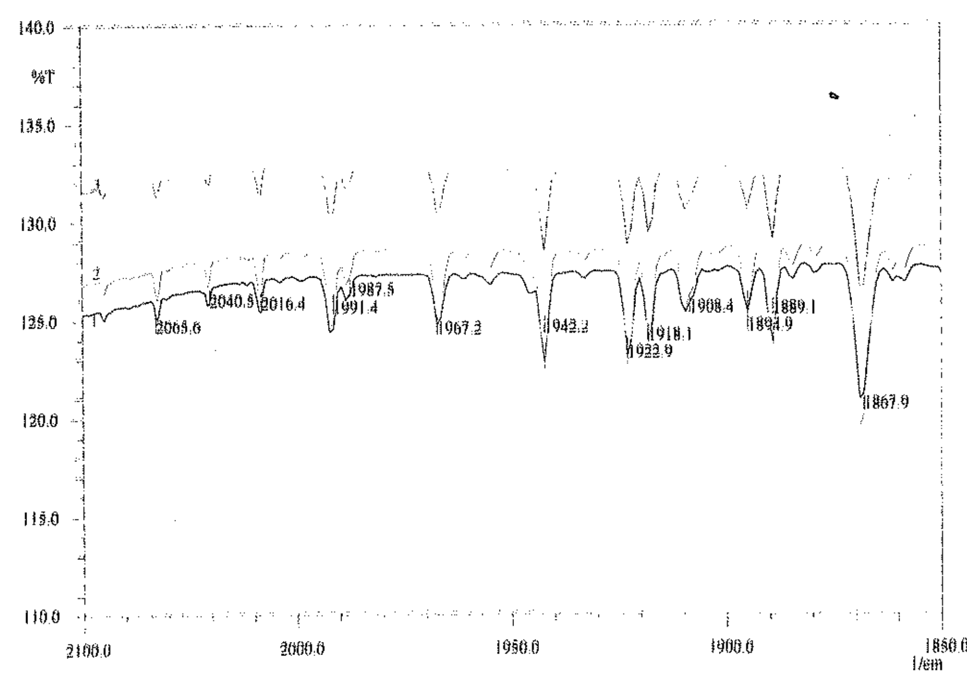


Fig. 2c. FTIR Spectra for 1, 2, 3 at 2100 - 1850 cm-1

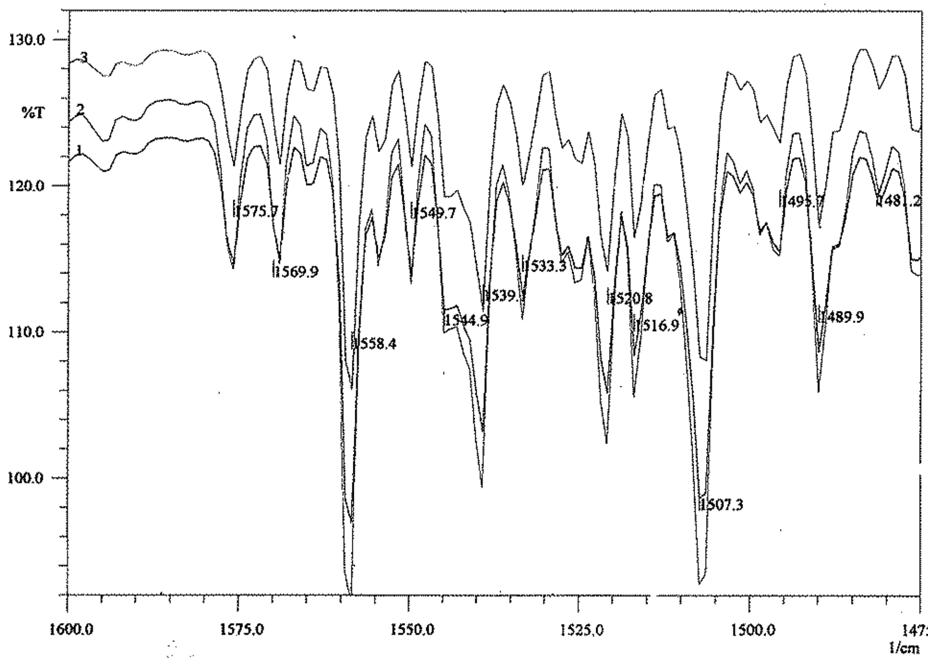


Fig. 2d. FTIR Spectra for 1, 2, 3 at 1600 - 1475 cm-1

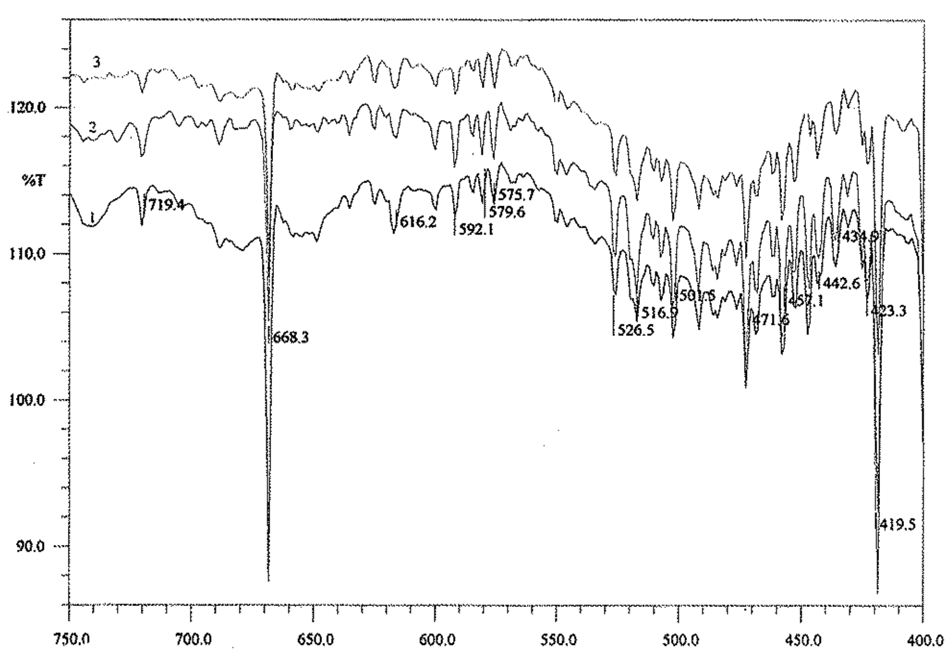


Fig. 2e. FTIR Spectra for 1, 2, 3 at 750 - 400 cm-1

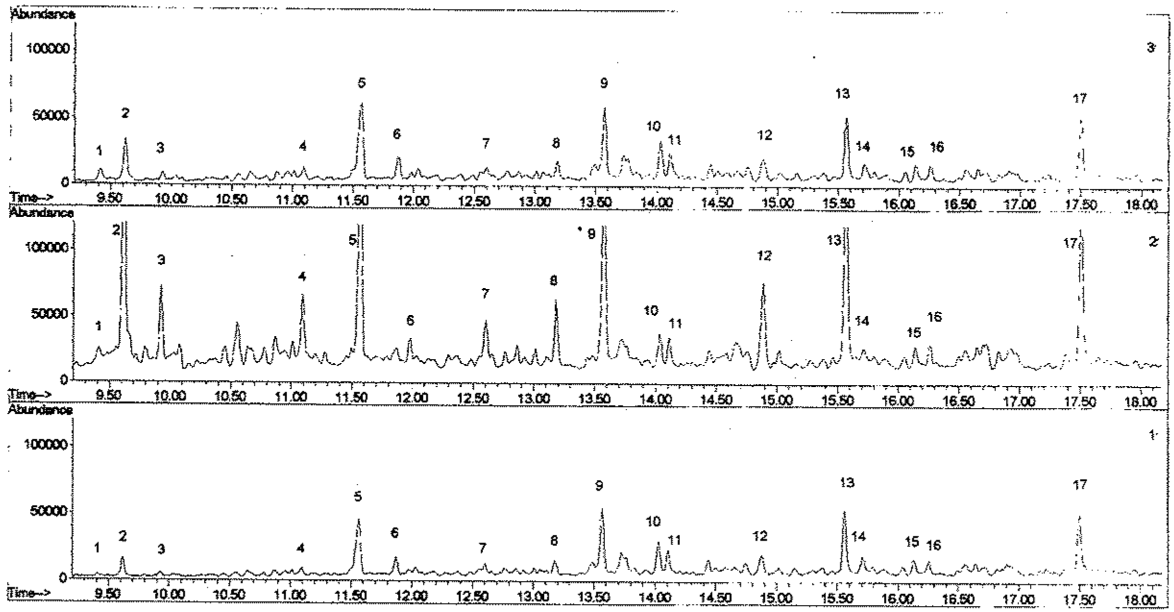


Fig 1a. GC/MS chromatograms for 1, 2, 3, Rt. 9.5 - 18.00 min.

1. Naphthalene, 2. Dodecane, 3. Undecane 2,6 dimethyl , 4. Undecane 4,6 dimethyl, 5. Tridecane, 6. Tridecane-6 methyl, 7. Penthyl cylohexane , 8. Dodecane 2,6,10 trimethyl, 9. Tetradecane, 10. Naphthalene 2,6 dimethyl, 11. Naphthalene 1,7 dimethyl, 12. Tridecane 6-propyl, 13. Pentadecane, 14.2-isopropyl naphthalene, 15. Naphthalene 2,3,6 trimethyl, 16. Naphthalene 1,6,7 trimethyl, 17.Hexadecane.

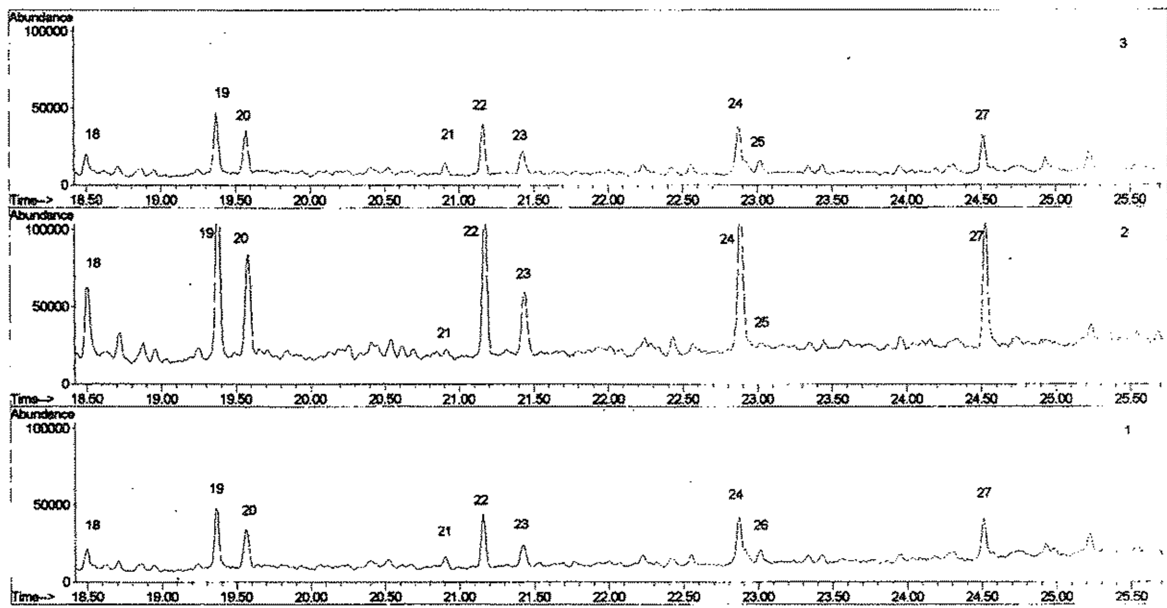


Fig. 1b. GC/MS chromatograms for 1, 2, 3 , Rt. 18.50 - 25.50 min.
18.Nor-pristane (Pentadecane 2,6,10 trimethyl), 19.Heptadecane, 20.Pristane, 21.Phenanthrene, 22.Octadecane, 23.Phytane, 24.Nonadecane, 25. Anthracene-1 methyl , 26. Eicosane, 27. Heneicosane.

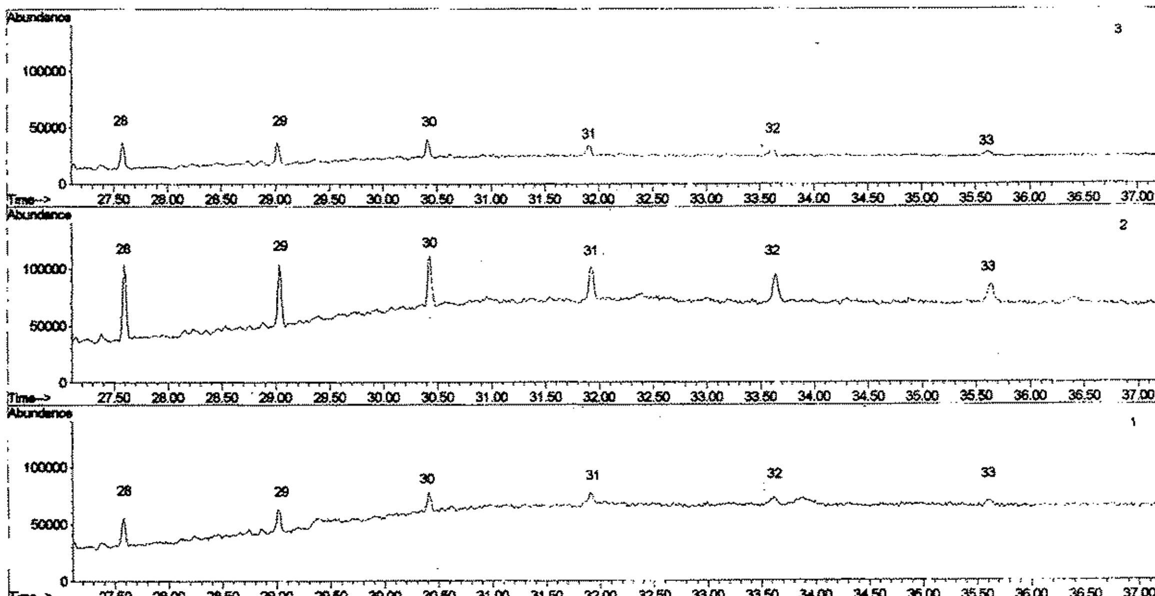


Fig. 1c. GC/MS chromatograms for 1, 2, 3, Rt. 27.50 - 37.00 min.
28.Docascne, **29**.Tricosane, **30**.Tetracosane, **31**.Pentacosane, **32**.Hexacosane,
33. Heptacosane.

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