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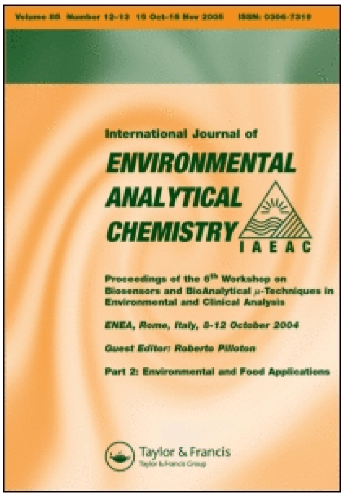

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Fingerprinting Marine Pollutant Hydrocarbons by Computerized Gas Chromatography-Mass Spectrometry

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To cite this Article Albaigés, J. and Albrecht, P.(1979) 'Fingerprinting Marine Pollutant Hydrocarbons by Computerized Gas Chromatography-Mass Spectrometry', International Journal of Environmental Analytical Chemistry, 6: 2, 171 — 190
To link to this Article: DOI: 10.1080/03067317908071170
URL: http://dx.doi.org/10.1080/03067317908071170

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Intern. J. Environ. Anal. Chem., 1979, Vol. 6, pp. 171–190
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Printed in Great Britain

Fingerprinting Marine Pollutant Hydrocarbons by Computerized Gas Chromatography–Mass Spectrometry†

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(*Received October 3, 1978*)

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A series of petroleum hydrocarbons of geochemical significance (biological markers) such as C_{20}–C_{40} acyclic isoprenoids and C_{27^+} steranes and triterpanes are proposed as passive tags for the characterization of oils in the marine environment.

Mass-fragmentography of samples is used to make evident these series of components without complex enrichment treatments. The rational choice of the characteristic ions is discussed and both molecular and stereoisomeric profiles are considered for identification purposes. Furthermore, computerized gas chromatography—mass spectrometry permits multiple fingerprinting from the same GC run. Hence rapid and effective comparisons between samples and long term storage of the results for future examination can be carried out. Differences between oils from the same geographic area and correlations of highly weathered samples are exemplified.

KEY WORDS: Crude oils, acyclic isoprenoids, steranes, triterpanes, mass-fragmentography, marine pollution.

INTRODUCTION

The development of methods for fingerprinting petroleum hydrocarbons in the marine environment, to identify the source of accidental or intentional oil spillages, has been a problem of major concern in the last

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†Presented at the 8th Annual Symposium on the Analytical Chemistry of Pollutants. Geneva, Switzerland, April 1978.

ten years. The need for these methods has arisen due to the increasing quantities of crude and refined oils entering the sea, that have caused extensive damage to marine life, coastal life and recreational beaches. Efficient and unambiguous analytical methods for the characterization of these spillages are also needed from the standpoint of the enforcement of the pollution control laws, designed to protect the public health and the environment.

In this respect Adlard stated in 1972[1] that nearly every known analytical technique has been used or suggested for oil pollutants identification, but, certainly, no one has emerged of such superiority that all the others can be considered as redundant. Therefore, earlier attempts of oil characterization have been performed by a multimethod approach; the particular combination of analytical techniques depends on the facilities and the experience existing in a laboratory and the expenditure which is justified to identify any unknown source.

Representative examples of these overall approaches are reported in Table I. They include analytical determinations such as the IR spectra, asphaltene and paraffin contents, etc., that provide a general classification of the pollutants (crude oils, fuel-oils, oil-sludges, etc...) and others, such as the Ni/V ratio, sulfur content, chromatographic profiles, etc..., that permit, by comparison with reference samples, their precise identification.

However, another approach involving only one analytical technique, but increasing the number of parameters considered, has been emphasized very recently as is exemplified in Table II for trace analysis, IR spectroscopy and gas chromatography. In these cases a multiparametric profile is used for identification, instead of a combination of different analytical

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TABLE I

Overall approaches for identification of oil pollutants

IP Method (1974)[2]	Sp. gr. Asphaltenes S, Ni and V contents TLC/UV GLC
DGMK Method (1973)[3]	IR spectroscopy S, Ni and V (Ca, Ba and Zn) Column chromatography GLC
U.S. Coast Guard (1974)[4]	IR spectroscopy Fluorescence spectroscopy TLC/UV GLC

TABLE II

Multiparametric methods for fingerprinting oil pollutants

Analytical methods	No. of parameters	References
Trace elements	3	Brunnock *et al.*, 1968[5]
	22	Duewer *et al.*, 1975[6]
IR spectroscopy	3	Kawahara and Ballinger, 1970[7]
	18	Lynch and Brown, 1973[8]
	23	Mattson *et al.*, 1977[9]
Gas chromatography	3	Erhardt and Blumer, 1972[10]
	19	Clark and Jurs, 1975[11]
	36	Rasmussen, 1976[12]

determinations and pattern recognition techniques have, often, been applied to improve the diagnostic performance.

The main requirements that must fulfill these fingerprinting parameters, besides their specificity, is that they must remain unaltered during the sea weathering processes affecting the pollutant, namely by evaporation, solution, photo-oxidation and biodegradation. In consequence, both conditions, specificity and stability, need to be investigated in order to evaluate the reliability and the usefulness of any proposed method.

The work reported here deals with the possibilities of computerized gas chromatography–mass spectrometry to afford characteristic profiles for different petroleum products, to be used as a multiparametric method for the identification of marine petroleum hydrocarbons.

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EXPERIMENTAL

Crude oil reference samples were supplied by several refineries and production companies. Weathered samples were obtained directly from the mediterranean coast or by laboratory simulation treatments[13]. Usually, the petroleum residues were gas chromatographed after deasphaltening with *n*-pentane (40 volumes), but when the recovery of the branched + cyclic alkanes was needed for subsequent analysis the saturated hydrocarbon fraction was isolated by conventional silica-gel adsorption chromatography (eluting solvent *n*-pentane) and refluxed in *iso*-octane with 5Å molecular sieves.

The gas-chromatograph (Perkin–Elmer 900) equipped with FI and FP detectors was operated either with 9ft × 1/8″ packed columns (1% Dexsil 300 on Gas-Chrom Q 100–120) from 150 to 300°C at 6°C/min. or with

200ft × 0.02″ capillary columns (OV-101 or Apiezon L) from 120–180°C at 6°C/min. Mass-fragmentographic analyses were performed on an LKB 9000 S/PDP 11 E 10 computerized GC–MS system. The jet-separator was maintained at 290°C and spectra were recorded and disk stored at 4 sec. intervals.

Previously synthesized or isolated hydrocarbons were used as standards for individual identifications.

RESULTS AND DISCUSSION

Gas-chromatographic fingerprinting

Gas chromatographic profiles of petroleum residues, one example of which is shown in Figure 1, exhibit several characteristic features that have been applied for identification or correlation purposes.

Generally, the most apparent is the *n*-paraffin distribution (see the upper trace in Figure 1) that has proved to be useful in differentiating the main types of pollutant samples (crude oils, fuel-oils and tank washings)[14] or even types of crude oils[5], although in this case the method involves the quantification of the previously isolated *n*-paraffins, therefore lengthening the analysis time.

Another relevant feature of the gas chromatographic profile is the acyclic isoprenoid hydrocarbon pattern that is made evident with capillary columns (see the peaks with an asterisk in the upper trace of Figure 1) or by inclusion of the saturated fraction in 5Å molecular sieves or in urea (see the middle trace in Figure 1). The predominant peaks usually correspond to the C_{19} (pristane) and C_{20} (phytane) isomers, which ratio serves as an identification parameter[10], although the series extends to lower and higher homologs.

Finally, the sulfur compounds that are present in minor quantities in petroleum products also exhibit a typical GC fingerprint easily obtained by flame photometric detection (see the lower trace in Figure 1). This fingerprint has been introduced to complement the FID chromatogram with the aim of resolving the ambiguities or increasing the reliability in the identification of the pollutants[15].

All the above fingerprints exhibit a different usefulness for characterizing oils. Their variation between crudes and their resistance to the sea weathering processes are not enough, in many cases, for providing the unequivocal identification of the pollutant. The *n*-paraffins can, apparently, be removed by biodegradation as well as the lower acyclic isoprenoids at respectively slower rates[16]. On the other hand, fractions boiling up to 300°C can be lost by evaporation affecting both the *n*-paraffin and the isoprenoid distributions. The FPD chromatogram is less

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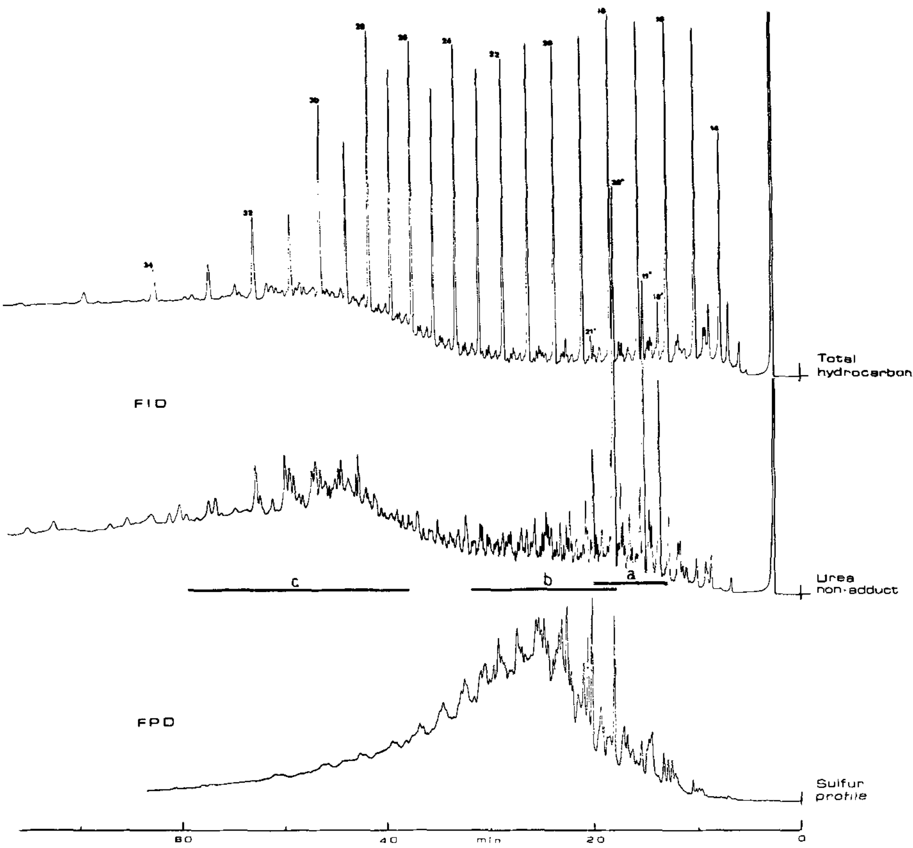

FIGURE 1 FID and FPD high resolution chromatograms of a crude oil residue (b.p. >220 C). Numbers above the peaks (with or without asterisk) indicate the number of carbon atoms of the isoprenoid and the *n*-paraffin hydrocarbons, respectively.

sensitive to modifications by bacterial metabolism but can also be affected by evaporation, in spite of its higher retention range (Figure 1, b), as we will show later. However, the last part of the FID chromatogram (Figure 1, c) appears to be highly promising in overcoming these limitations. In fact, this part corresponds to a hydrocarbon fraction that boils over 400 C, so it cannot be easily evaporated under environmental marine conditions. Moreover, it contains a wealth of compounds of geochemical significance, namely isoparaffins and polycyclic alkanes of isoprenoid, sterane and triterpane structure[17,18], as a result of a complete reduction of precursor isoprenyl alcohols, sterols and triterpenes, respectively. Therefore, their occurrence and final distribution in crude oils will be related to their

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particular genetic history, that is to the original sedimentary organic matter and to the processes undergone during its geochemical cycle. In consequence, we have reasonably assumed that these factors can provide unique hydrocarbon compositions for each crude oil, by which the unambiguous identification of the samples can be brought about. Besides their geochemical stability, these compounds do, also, remain unaltered after biodegradation[19] being, in this respect, valuable passive tags for characterizing marine pollutants.

The problem is that such somponents are present frequently at trace levels, as a part of very complex mixtures and can only be recognized after long and tedious enrichment treatments, that are not practical from the standpoint of the routine or monitoring analysis.

Mass-fragmentographic fingerprinting

Mass-fragmentography provides a satisfactory tool for obtaining specific fingerprints for classes and homologous series of compounds, resolved by gas chromatography. In addition, computerized GC–MS allows multiple fingerprinting from the same chromatogram, that is especially important for a quick survey of any compound class in a scanty sample and permits storing the information for further processing or correlation studies. However, to carry out the analyses successfully a precise knowledge of the nature and the gas chromatographic and mass spectrometric behaviour of such compounds is needed. Our major efforts have been spent, in recent years, in that direction[20–23].

In Figures 2 and 3 the proposed formation pathways of the sterane and hopane hydrocarbons, based on field and laboratory results, are shown, just to illustrate the different type of compounds that can be found in crude oils depending on their particular genetic history.

In short, in the sterane family two series can be expected; the normal and rearranged steranes, the latter as a consequence of the sedimentary acidic catalytic activity[24]. Cholestane, 24-methylcholestane and 24-ethylcholestane are generally the basic components. Variations in the stereochemistry of carbons 5, 14 and 20 have also been detected and contribute to the complex pattern exhibited by this family[25]. A similar scheme could explain the degradation of 4-methylsterols to the corresponding methylsteranes, that occur in some samples[21,23].

The family of the hopanes (Figure 3) originate from two known procariotic source materials, the 3-desoxytriterpanes and the polyhydroxyhopanes, which, by reductive degradation, give rise to the C_{27}–C_{35} members of the series. In this case, the stereochemistry of the C-17 and C-21 in the original compounds is β(H) with one diastereomer at position 22, whilst in petroleum and matured samples, the 17α(H), 21β(H) and

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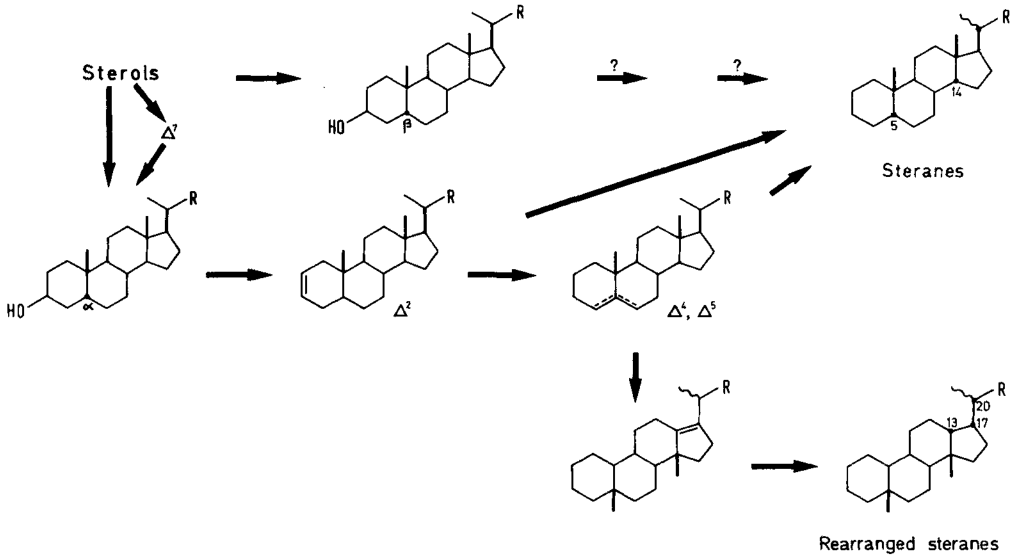

FIGURE 2 Early transformation routes of sterols in the geological environment, based on laboratory and field results.

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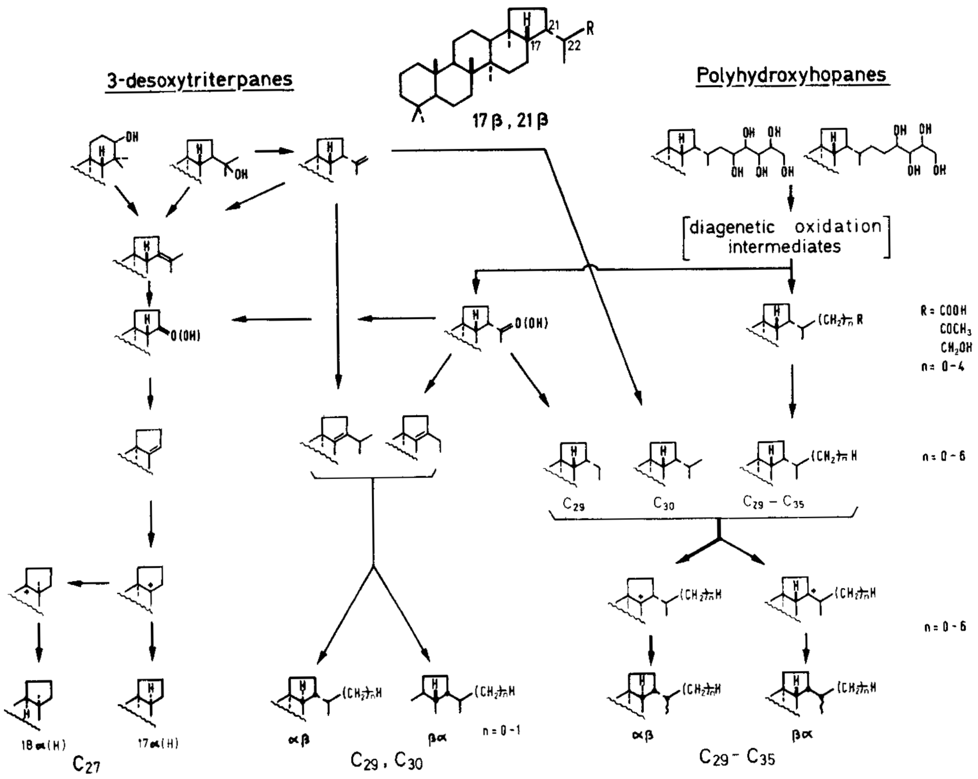

FIGURE 3 Proposed formation routes of the hopane hydrocarbons in the geological environment, based on laboratory and field results.

17β(H), 21α(H), with the 22R + 22S isomers, are found[22]. In addition, two C_{27} members can also be found, the 17α(H) and the 18α(H)-trisnorhopanes, probably formed by acid-catalyzed interconversion[26].

The general distribution patterns of both the sterane and the hopane series are completed, considering variations in side chain length of the isomeric compounds.

Finally, the acyclic isoprenoid hydrocarbon series extends from 10 to 40 carbon atoms[20], according to the earlier environmental occurrence of oligoterpenic alcohol derivatives; the oxydo-reductive deposition conditions being the major factor influencing the ratio of the corresponding parent and nor-hydrocarbon derivatives found in geological samples.

The mass-spectra of these hydrocarbons exhibit fragment ions that are both characteristic and intense for each family, so they fulfill the ideal requirements for mass-fragmentography. The base peak for steranes is 217 (see Figure 4) unless the stereo chemistry of the C-14 would be β in which case it is 218[25]. Other characteristic fragment peaks are 151 for the 5β isomers and 259 for the 13β(H), 17α(H) rearranged steranes [24], so the ratio of the intensities of these peaks can be used for identification purposes. Methylated steranes on ring A (e.g. on C-4) exhibit the peaks corresponding to the above fragmentations but at 14 m/e higher units, therefore the base peak appears at m/e 231 or 232, etc.

Pentacyclic triterpanes are easily distinguished by a base peak at m/e 191 (see Figure 6)[22,23]. Several tricyclic diterpanes that have recently been found in petroleum show the base peak at the same nominal mass but are eluted separately from the hopane series in gas chromatography[27].

Acyclic isoprenoids exhibit prominent ions at m/e 113 + 70n corresponding to the fragmentations induced by the regular side methyl substituents (see Figure 5). To reduce the interferences produced by other isoparaffins we have found suitable the m/e 183 fragmentogram.

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Identification of petroleum pollutants

The characterization of petroleum pollutants using the above heavy hydrocarbon series has been attempted by the mass chromatograms of m/e 183, 191, 217, 231 and 259, which are characteristic for, respectively, acyclic isoprenoids, pentacyclic triterpanes, steranes, 4-methylsteranes and rearranged steranes. Very recently, a similar approach has been applied successfully to problems of geochemical correlation of crude oils[26,28] and to study the chemical transformations in the biodegradation of crude oils[19].

We have previously examined more than fifty crude oils covering most of the commonly used Middle East, African and Venezuelan oils and

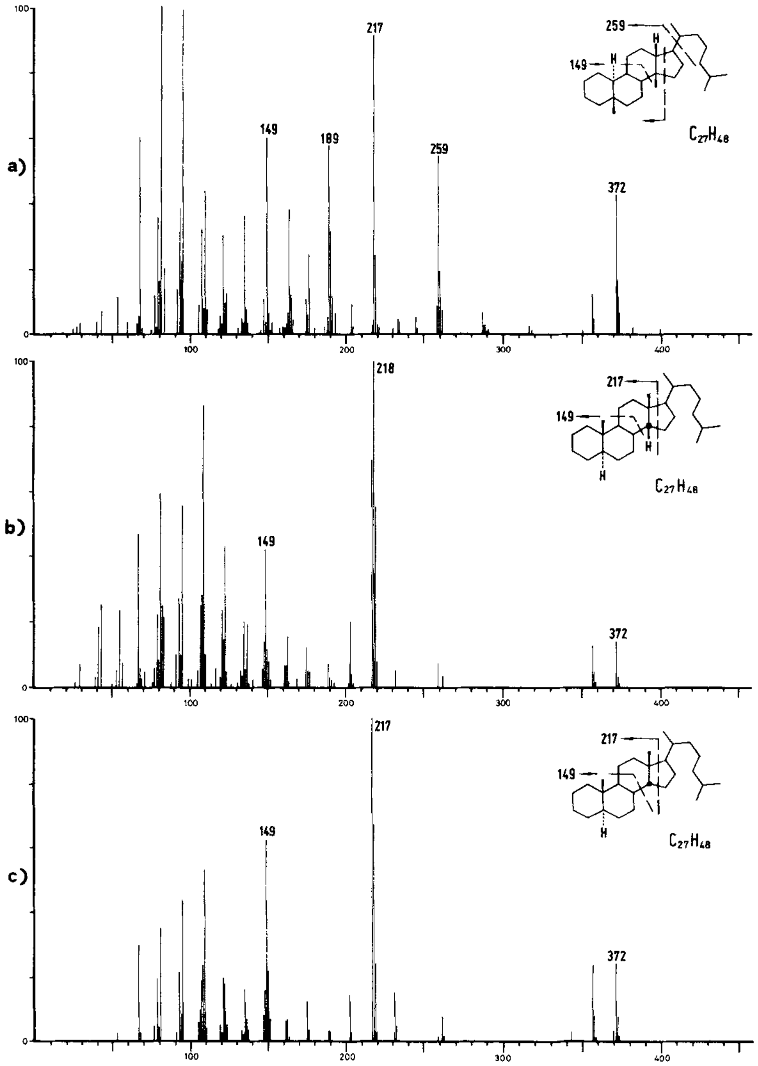

FIGURE 4 Mass spectra of three isomeric steranes obtained by GC-MS-COM of a crude oil extract: 13β,17α-diacholestane (a), 5α,14β-cholestane (b) and 5α-cholestane (c).

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those handled in the Mediterranean sea. Not all provide significant fingerprints for each one of the ions referred, but, in spite of this, relevant differences have been noticed between them. In Figures 5, 6 and 7 are shown examples of individual profiles obtained from petroleum residues of a wide maturity range. Obviously, the fingerprinting capability of the method is largely increased when combined mass-fragmentographic patterns are used.

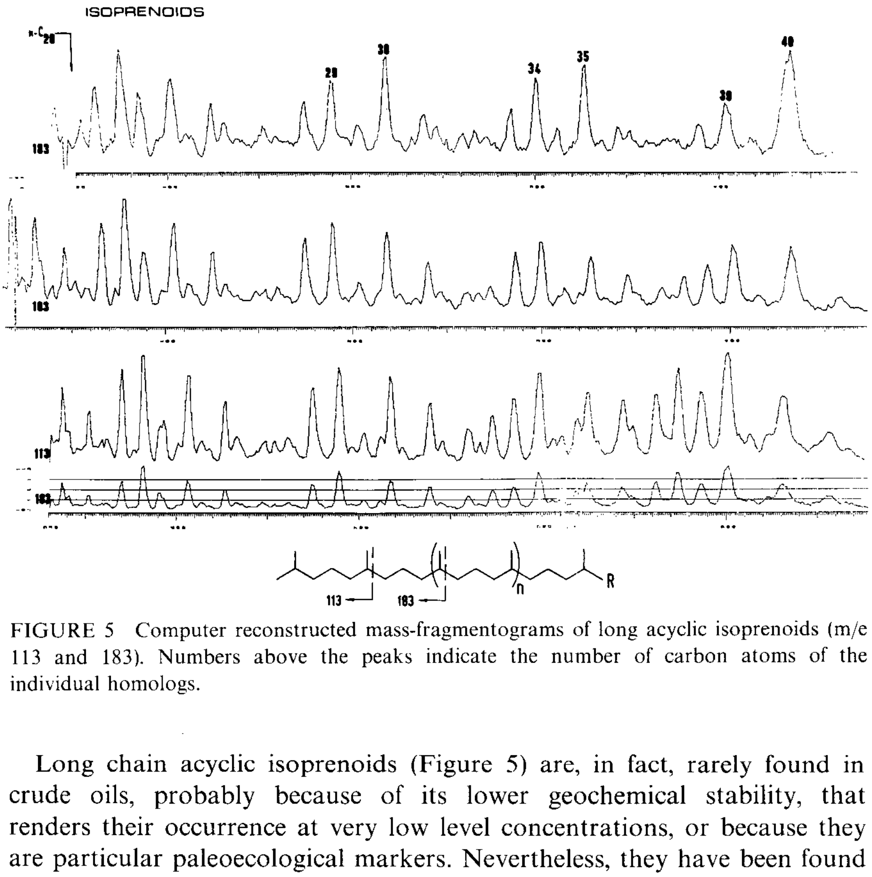

FIGURE 5 Computer reconstructed mass-fragmentograms of long acyclic isoprenoids (m/e 113 and 183). Numbers above the peaks indicate the number of carbon atoms of the individual homologs.

Long chain acyclic isoprenoids (Figure 5) are, in fact, rarely found in crude oils, probably because of its lower geochemical stability, that renders their occurrence at very low level concentrations, or because they are particular paleoecological markers. Nevertheless, they have been found representative of the crude oils produced off-shore in the Mediterranean Spanish coast, oils that, on the other hand, are difficult to differentiate from some of the North-African crudes for their very close values of sulfur, nickel and vanadium concentrations and pristane/phytane ratios. Not only the occurrence but the internal distribution of the several members of the series can be used as identification criteria for these crudes.

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In contrast, pentacyclic triterpanes of the hopane type are ubiquitous in geological samples[22] and generally constitute the most abundant family of hydrocarbons considered here. Some typical crude oil distributions are presented in Figure 6. The m/e 191 reconstructed fragmentograms show the main 17α(H), 21β(H)-hopane series whose individual members are identified by the molecular weight fragmentograms (m/e 370+14n). As it has been

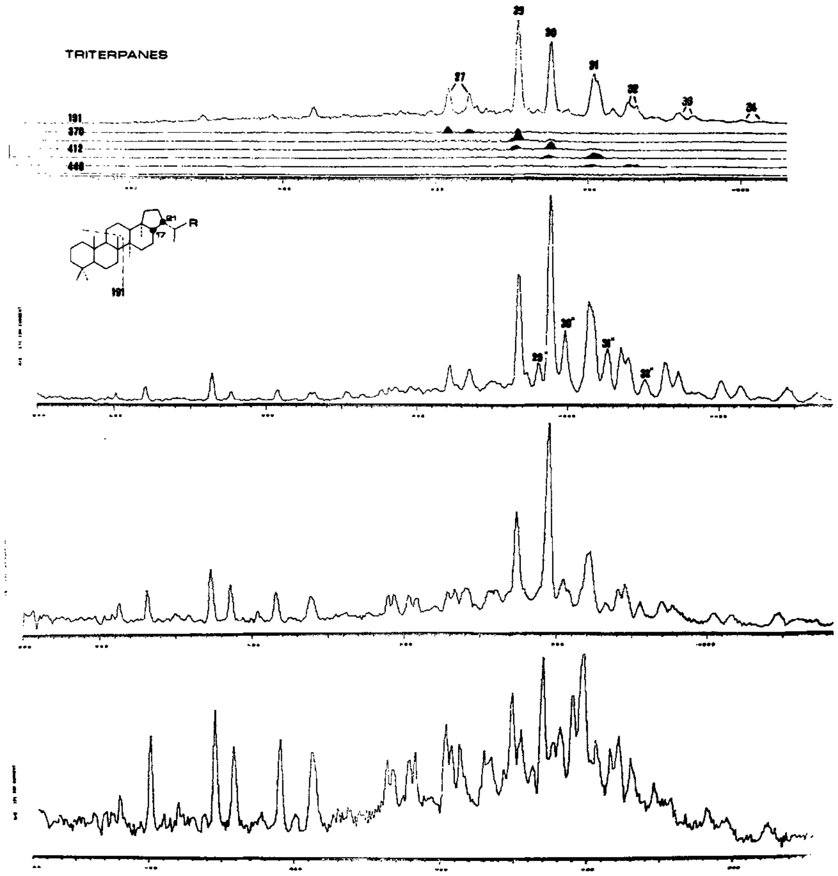

FIGURE 6 As Figure 5 but for triterpanes (m/e 191).

stated before, two C_{27} isomers are present (18α(H) and 17α(H)-trisnorhopanes, in order of elution) as well as two stereoisomers at C-22 (S and R in order of elution) for each one of the homologs from 31 to 35 carbon atoms. The minor series marked with an asterisk corresponds to the moretane family (17β(H), 21α(H)-hopane) and the prominent peaks

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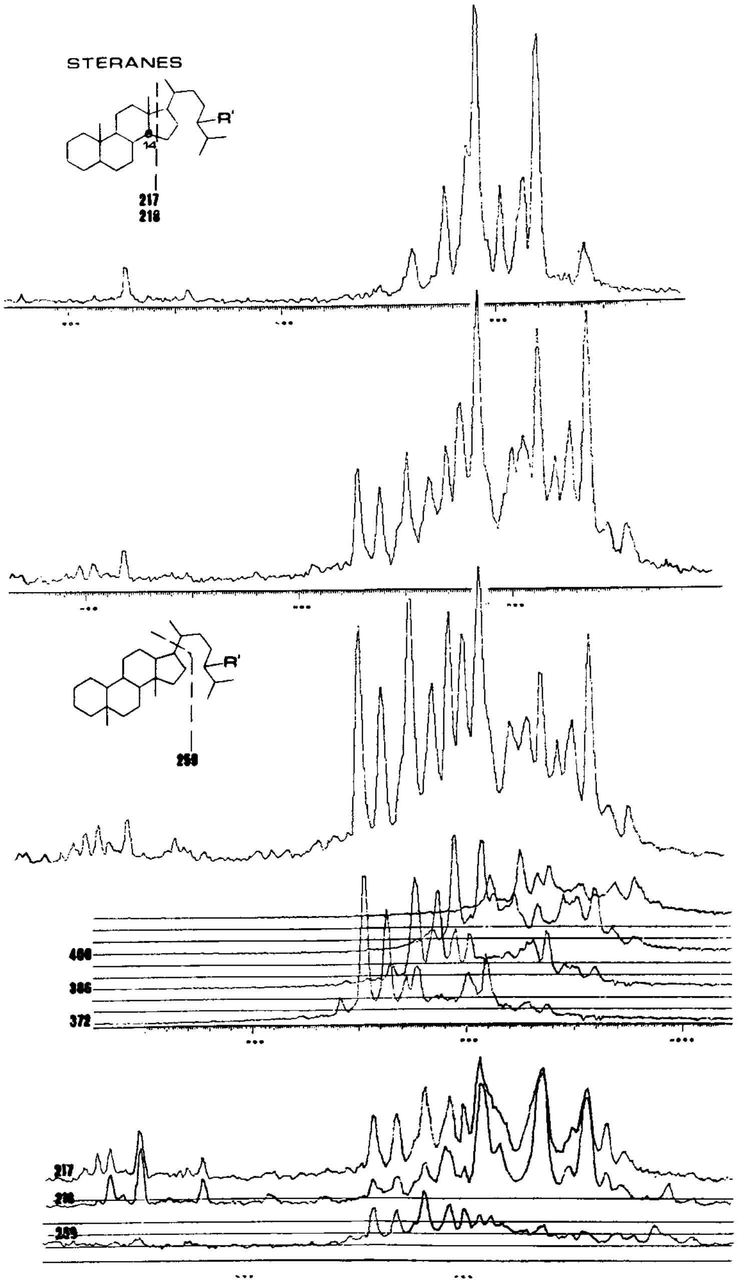

FIGURE 7 As Figure 5 but for steranes (m/e 217, 218 and 259).

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eluting before the hopane series in the bottom fragmentograms appear to be the C_{20}–C_{26} tricyclic alkylated diterpanes previously reported[27]. The identification parameters are apparent from these examples, including those that can reflect the organic source matter and the diagenetic and maturation sedimentary conditions, namely the relative concentrations of diterpane, hopane and moretane hydrocarbon families, the ratios of individual members such as the two C_{27} isomers and the C_{29}–C_{31}, the relative distribution of the higher homologs and the general profile for other unidentified components. Some of these parameters revealed by themselves significant differences between seven Middle East crude oils in a triterpane fingerprinting technique described by Pym *et al.*[29]. We have obtained similar profiles directly from the saturated fraction without problems in sensitivity using the GC-MS-COM technique. The advantages of the latter are obvious as far as the analysis time is concerned, as well as to the new possibilities offered in identification by the multiparametric profiles here being described.

Sterane type hydrocarbons constitute the most complex family of those considered[25]. More than 70 isomers belonging to the C_{27}–C_{30} desmethyl, 4-methyl and rearranged types have been detected by Ensminger in geological extracts[30]. They cannot be fully resolved even by high resolution GC and they elute with triterpanes in the branched + cyclic saturated fraction; however, their characteristic mass-spectrometric fragmentations permit them to be easily distinguished by mass-fragmentography and although many of them have not been conclusively identified, significant profiles can be obtained for fingerprinting purposes.

Figure 7 shows a sequence of m/e 217 crude oil samples. Molecular weight fragmentograms (m/e 372 + 14n) reveal, in contrast with the triterpane profiles (figure 6), complex isomeric mixtures. Important differences in the relative distribution of the various members of the series occur depending on the origin and maturity of the geological sample. Hence, steranic fragmentograms used for identification are those corresponding to m/e 217, 218 and 259 (see the bottom profiles in Figure 7) and to m/e 231, 232 and 273 for the 4-methyl derivatives, respectively. Rearranged steranes (m/e 259) seem to be formed at the same time as the hopane and moretane series, with the two C-20 stereoisomers being formerly present[30], but later on they disappear with the normal steranes (m/e 217), so they are found at trace level in the matured Middle East and North-African crude oils (see Figure 8). The 4-methylsteranes (m/e 231) are, generally, much less abundant than their desmethyl isomers, probably because they have originated in some restricted paleoenvironments. Nevertheless, all of these hydrocarbons are representative of the Spanish off-shore crudes, being useful markers in pollution studies from this area.

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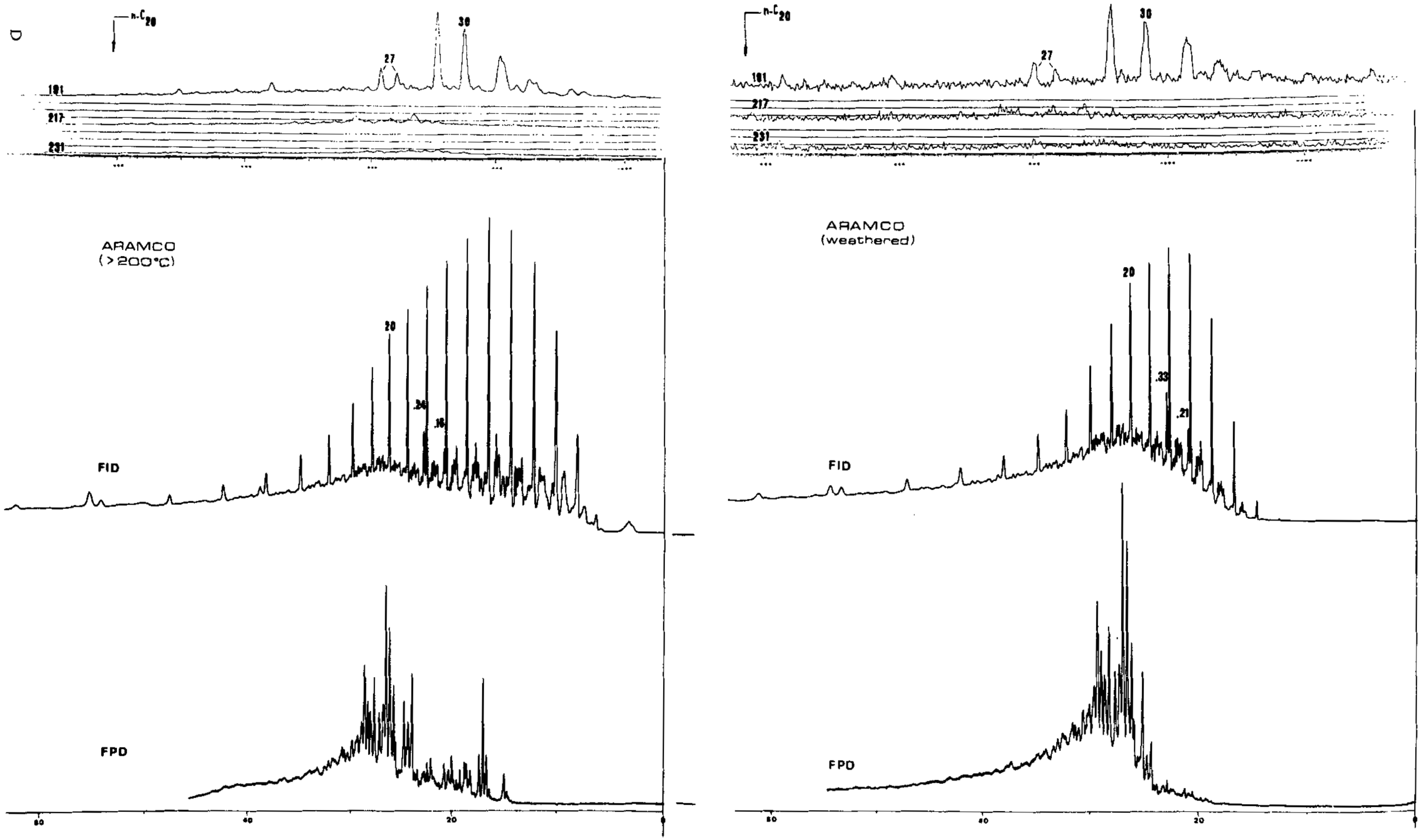

FIGURE 8 Gas chromatographic and mass fragmentographic fingerprints of Aramco residues obtained by distillation (b.p. > 200°C) and simulated weathering. Prinstane/n-C_{17} and phytane/n-C_{18} ratios are indicated.

The most promising results in the application of this fingerprinting method have been achieved in the identification of weathered samples where the commonly used hydrocarbon profiles have been severely modified by evaporation or biodegradation. Figure 8 displays the conventional gas-chromatographic characterization of Aramco crude oil residues, obtained by distillation (b.p. > 200°C) and laboratory simulated weathering (three weeks). From these profiles it can be inferred that the pristane/n-C_{17} and phytane/n-C_{18} ratios are affected by selective biodegradation of linear hydrocarbons. Also, the *n*-paraffin distribution cannot be used satisfactorily for identification. On the other hand, the FPD chromatogram has lost, after weathering, an important part of its fingerprinting pattern and is difficult to ascertain in this sample if the relative distribution of the remaining peaks, mainly the triplet eluting on the *n*-eicosane that can differentiate other Middle East crude oils, have not changed with time. Mass-fragmentograms display only appreciable profiles for triterpanes (m/e 191), as to be expected for the majority of the Middle East crude oils. However, they are sufficiently characteristic of the samples and no detectable changes in the fingerprint have been observed, therefore a satisfactory correlation can be brought about.

Mass-fragmentography also can afford valuable fingerprints with samples whose FI and FP chromatograms exhibit almost featureless profiles, due to the general occurrence of those hydrocarbons in petroleum and to their environmental stability. Figure 9 shows the profiles displayed by the Venezuelan Laguna crude oil. The triterpane mass-fragmentogram (m/e 191) is rather complex but the low retention diterpane series is clearly distinguished, as well as the two C_{27} isomers, that are enhanced in the molecular weight fragmentogram (m/e 370), and the C_{29}–C_{31} homologs. Moreover, the sterane profile exhibits a characteristic predominance of the m/e 218 over the m/e 217 fragmentogram, that is of 14β over the normal isomers. Cholestane and 24-methyl and ethyl derivatives are the three main components. The peak that appears at lower retention time in the fragmentogram has been identified as a pregnane isomer (m/e 288).

A final interesting application is exemplified in Figure 10. A tentative identification of two pelagic tar ball samples, collected on the Mediterranean sea surface, is carried out. Both gas chromatograms are representative of highly biodegraded crude oil sludges[14], but the absence of the original most characteristic part of the chromatogram prevents establishment of their origin, although the similarity of their pristane/phytane ratios permit us to assume a certain correlation between them. Multiparametric mass-fragmentography shows relevant profiles for triterpanes (m/e 191) and to a lesser extent for steranes (m/e 217) that, furthermore, are essentially identical to those presented in Figure 8 for the

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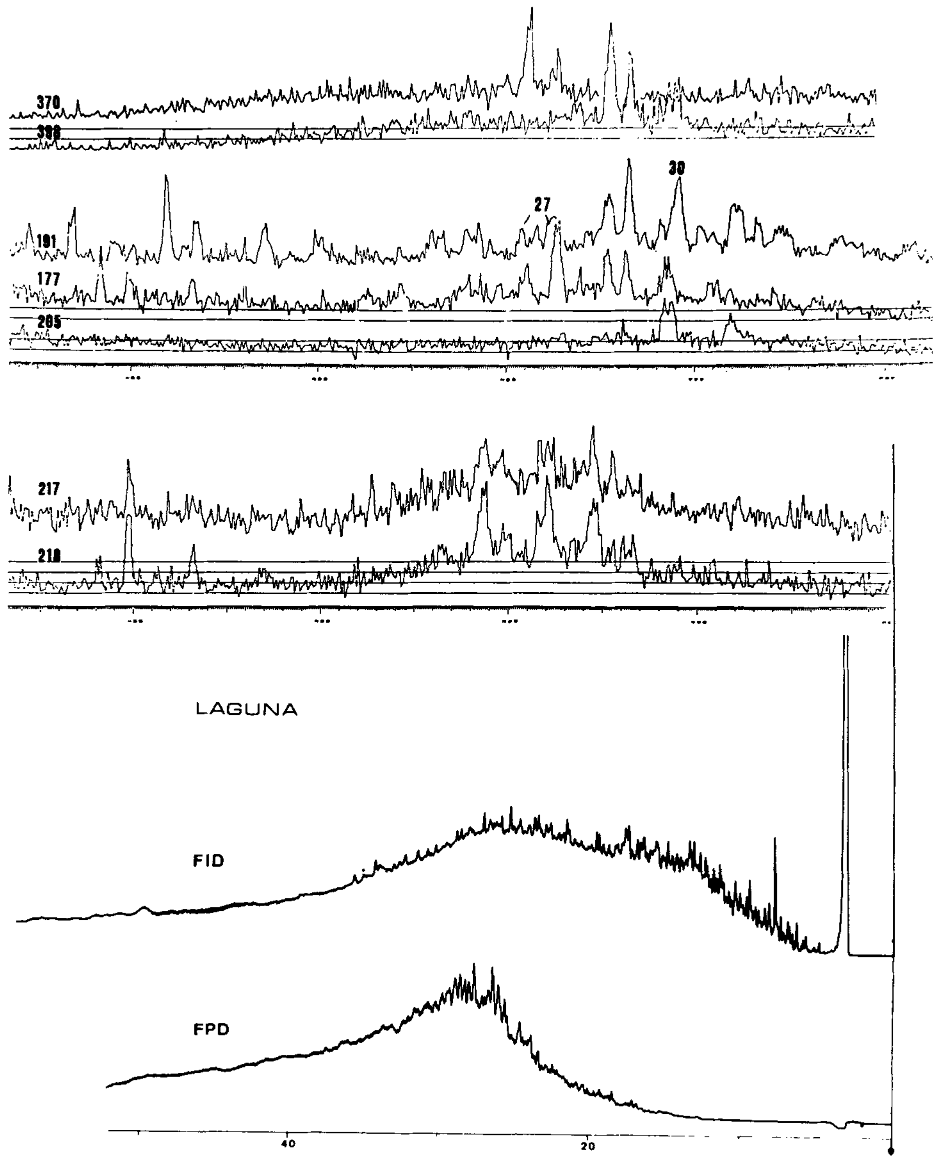

FIGURE 9 Gas chromatographic and mass fragmentographic characterization of Laguna crude oil (Venezuela).

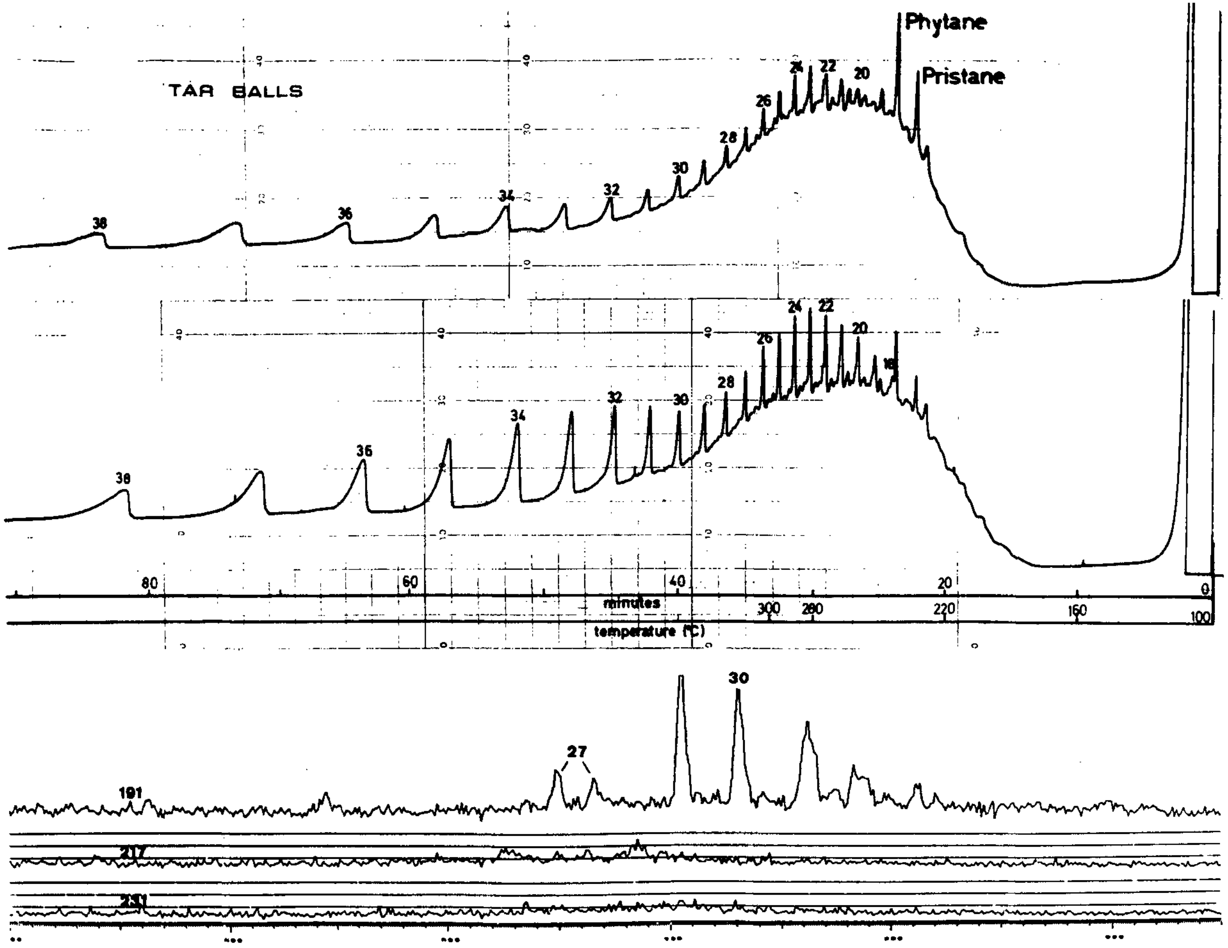

FIGURE 10 Gas chromatographic and mass fragmentographic characterization of two tar ball samples, tentatively identified as an Aramco oil sludge.

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Aramco crude oil. It is interesting to note that this analytical approach could really improve our knowledge about the qualitative input of tar balls on the ocean, which is at present almost exclusively based on quantitative results.

CONCLUSION

From the above results it seems clear that novel molecular fingerprinting techniques have a large application in the identification of petroleum marine hydrocarbons and are expected to be more conclusive than gross compositional parameters used so far. In this respect, acyclic isoprenoids, pentacyclic triterpanes and steranes are hydrocarbon series with high diagnostic values for their variability between crudes and their physicochemical and biological stabilities.

Computerized GC-MS is able to furnish advantageously the corresponding profiles. Firstly, the method as a whole is relatively fast, since it requires only previous separation of total alkanes by adsorption chromatography on silica-gel and, when necessary, a separation of the normal alkanes *via* 5Å molecular sieves. Several characteristic profiles can be obtained from a single chromatogram and can be easily stored for further processing or building a fingerprinting catalogue. Finally, the method can be scaled down and used in the analysis of micropollutants to investigate chronic pollution and to ascertain the origin of trace hydrocarbons present in marine environments, both in water and sediments.

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References

1. E. R. Adlard, *J. Inst. Petrol.*, **58,** 63 (1972).
2. Marine Pollution by Oil, Ed. Institute of Petroleum, *Applied Science*, Essex (1974).
3. Deutsche Gesellschaft Minerolwiss. und Kohle-Chemie, Project 4599 Report (1973).
4. A. P. Bentz, *Anal. Chem.*, **48,** 454A (1976).
5. J. V. Brunnock, D. F. Duckworth and G. G. Stephens, *J. Inst. Petrol.*, **54,** 310 (1968).
6. D. L. Duewer, B. R. Kowalski and T. F. Schatski, *Anal. Chem.*, **47,** 1573 (1975).
7. F. K. Kawahara and D. G. Ballinger, *Ind. Eng. Chem., Prod. Res. Dev.*, **9,** 553 (1970).
8. P. F. Lynch and Ch. W. Brown, *Environ. Sci. Technol.*, **7,** 1123 (1973).
9. J. S. Mattson, C. S. Mattson, M. J. Spencer and S. A. Starks, *Anal. Chem.*, **49,** 297 (1977).
10. M. Erhardt and M. Blumer, *Environ. Pollut.*, 179 (1972).
11. H. A. Clark and P. C. Jurs, *Anal. Chem.*, **47,** 374 (1975).
12. D. V. Rasmussen, *Anal. Chem.*, **48,** 1562 (1976).
13. J. Albaigés, J. Rivera, J. Torradas and M. R. Cuberes, *Rev. Inst. Français Pétrole*, **31,** 427 (1976).
14. S. J. Ramsdale and R. E. Wilkinson, *J. Inst. Petrol.*, **54,** 326 (1968).
15. E. R. Adlard, L. F. Creaser and P. H. D. Mathews, *Anal. Chem.*, **44,** 64 (1972).

16. N. J. L. Bailey, A. M. Jobson and M. A. Rogers, *Chem. Geol.*, **11**, 203 (1973).
17. W. Henderson, V. Wollrab and G. Eglinton, *Adv. in Org. Geochem.* 1968, Eds. P. A. Schenk and I. Havenaar, p. 181, Pergamon, Oxford (1969).
18. E. J. Gallegos, *Anal. Chem.*, **43**, 1151 (1971).
19. I. Rubinstein, O. P. Strausz, C. Spyckerelle, R. J. Crawford and D. W. S. Westlake, *Geochim. Cosmochim. Acta*, **41**, 1341 (1977).
20. J. Albaigés, J. Borbòn and P. Salgre, *Tetrahedron Lett.*, 595 (1978).
21. I. Rubinstein and P. Albrecht, *J. Chem. Soc. Chem. Commun.*, 957 (1975).
22. A. Van Dorsselaer, P. Albrecht and G. Ourisson, *Bull. Soc. Chim. France*, 165 (1977).
23. B. J. Kimble, J. R. Maxwell, R. P. Philp, G. Eglinton, P. Albrecht, A. Ensminger, P. Arpino and G. Ourisson, *Geochim. Cosmochim. Acta*, **38**, 1165 (1974).
24. I. Rubinstein, O. Sieskind and P. Albrecht, *J. Chem. Soc.*, Perkin Trans., **1**, 1833 (1975).
25. L. J. Mulheirn and G. Ryback, *Adv. in Org. Geochem.* 1975. Eds. R. Campos and J. Goñi, p. 173, Enadimsa, Madrid (1977).
26. W. K. Seifert and J. M. Moldowan, *Geochem. Cosmochim. Acta*, **42**, 77 (1978).
27. W. E. Reed, *Geochim. Cosmochim. Acta*, **41**, 237 (1977).
28. A. Van Dorsselaer, J. M. Schmitter, P. Albrecht, J. Claret and J. Connan, Paper presented at the 8th International Meeting on Organic Geochemistry, Moscow (1977).
29. J. G. Pym, J. E. Ray, G. W. Smith and E. V. Whitehead, *Anal. Chem.*, **47**, 1617 (1975).
30. A. Ensminger. Thesis. Univ. Louis Pasteur. Strasbourg. 149 pages (1977).

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