

# The Analysis of Tar Balls and Crude Oils\*

by

T.I. BALKAS, A.F. GAINES, I. SALIHOGLU, M. SUNAY, and A. YILMAZ

Middle East Technical University, Marine Science Department, Erdemli, Icel (Turkey)

## Abstract

Despite much work, the general problem of identifying sources of oil pollution of the marine environment remains unsolved. At the same time, the chemistry of the 'weathering' of oils in the sea, in particular, the role of oils in modifying organic-inorganic interactions is poorly understood.

Tar balls (from beaches in southern Turkey, Cyprus and Malta) and a series of crude oils have been fractionated and the fractions have been examined by IR, UV and <sup>1</sup>H nmr spectroscopy. Paraffins have been examined by gas chromatography and gas chromatography coupled with mass spectrometry. Measurements of the trace metal (V, Fe, Ni, Pb) content of some fractions have been made. Middle Eastern crude oils are rather similar and the different techniques of analysis used have been compared to identify the source material of tar balls. UV and IR spectroscopy distinguish between crude and refined oils. Precise identification of the source material requires consistent evidence from <sup>1</sup>H nmr spectroscopy, gas chromatography and fluorimetry. Investigation of a large number of samples so as to establish the composition limits of each source material is most desirable.

\* \* \*

Introduction

Despite much work, the general problem of identifying sources of oil pollution of the marine environment remains unsolved. Other than rare cases where spillage is either witnessed or easily deduced, few sources of pollution have been identified after the causative event. The methodology of MED POL I, based on fluorescence measurements at fixed wave lengths, is insufficient to characterise the constituent hydrocarbons, let alone identify their source. The present work forms part of an attempt to examine and solve these methodological problems. One notes that crude and refined oils not only cover a wide range of composition but, in addition, are very similar, and their composition is subject to change with minor fluctuations in feedstock, refinery or storage conditions. Under such circumstances, there is no optimal method of fingerprinting the source of a pollutant; instead, a variety of techniques should be used together to simplify the identification of the source. The chemistry of the 'weathering' of oils in the sea, in particular their role in modifying organic-inorganic interactions, is poorly understood. Evidently, there is a need for an intermediate level of analysis which is reasonably rapid, which does not pretend to be exhaustive, but which nevertheless characterizes oil fractions in some detail.

## Materials and methods

Hydrocarbons were separated into hexane-soluble, benzene-soluble (but hexane-insoluble) and methanol-soluble (but hexane and benzene-insoluble) fractions. Hexane-solubles were further separated

\* Communication présentée oralement par les auteurs.

<sup>1</sup> Journées Étud. Pollutions, pp. 25-32, Cagliari, C.I.E.S.M. (1980).



by column chromatography (using alumina freshly heated at 120°C for 4 hours) into hexane, benzene and methanol eluates.

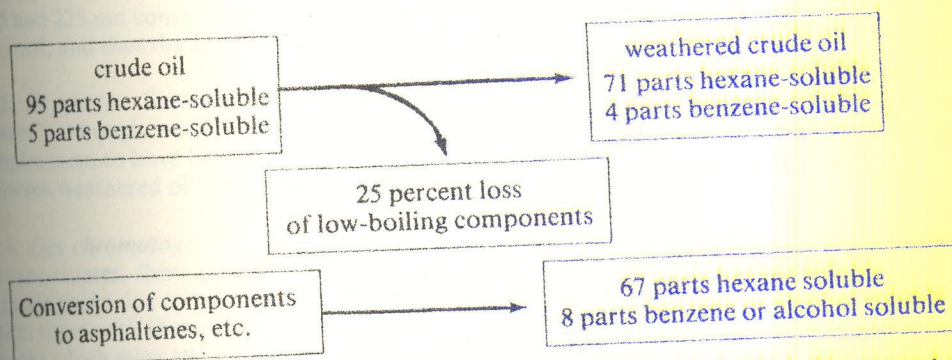
IR spectra were obtained by the potassium bromide disc technique using a Beckmann Acculab. 2. Routine <sup>1</sup>H nmr spectra were obtained in carbon tetrachloride using a Varian EM 300. TMS was used as an external standard.

UV spectra of hexane solutions were obtained using a twin beam Varian Techtron 635 recording spectrophotometer. Gas chromatograms were generally obtained using a Packard Becker model 421. Eight foot columns coated with 3 % SE 30 or 3 % SP 2100 were heated at a rate of 3°C/min from 100 to 250°C with isothermal heating at the lower and upper ranges. Nitrogen (30 mls/min) was used as the carrier gas. In some experiments a Finnegan 3000 quadrapole mass spectrometer was coupled to the exit of a gas chromatograph via a glass capillary jet separator. Ionisation with 70 EV electrons was carried out at about 10<sup>-6</sup> mm Hg while the gas chromatograph was operated according to the usual program. Fluorescence was excited by emission from a high pressure Xenon lamp and was measured using a Turner model 430 spectrofluorometer. Flameless atomic absorption spectrometry employed a Varian AA6 with a carbon rod atomizer.

## Results and discussion

### 1. Weathering

The yields shown in Table I reveal, not unexpectedly, that all materials examined were largely soluble in hexane. IR spectra summarised in Table II and the absence of UV absorption near 260 nm indicated that the hexane eluates were overwhelmingly paraffinic, and Table I indicates that over two thirds of all the materials examined were paraffinic. IR spectra showed that weathered and crude oils contained rather similar structures, thus the ratios shown in Table II are averages for both weathered and crude oils. Weathered oils differed from crude oils in containing less paraffinic, somewhat more aromatic material soluble in benzene but not in hexane (asphaltenes), and a small percentage of material that was insoluble in both hexane and benzene which IR spectra show to be highly aromatic and to contain oxygen groups. Weathering in the sea consists mainly of the loss of low boiling hexane-soluble material, primarily by evaporation (BUTLER, 1975) and when the softening point of the remaining mixture exceeds the temperature of its surroundings, the mixture congeals and a tar ball forms. In boreal waters this has been observed to take only a few hours (DUDLEY, *Private communication*). In the regular sequence of *n* paraffins which dominated the gas chromatograms, the first member which could be picked out in crude oils was *n*C<sub>9</sub>, or *n*C<sub>10</sub>, whereas from tar balls from Malta or from Erdemli the sequence appeared to start with *n*C<sub>12</sub> or *n*C<sub>13</sub> and for tar balls from Cyprus, *n*C<sub>14</sub>. Consideration of boiling point : composition diagrams of crude oils, the boiling points of the paraffins which have been 'lost' in tar ball formation, and the changes in peak heights at the beginning of the gas chromatograms, suggest that about 25 % of the parent oils evaporated or dissolved during weathering. The weathering of a crude oil may be expressed approximately as :



which is equivalent to 88 % hexane-soluble, in approximate agreement with Table I. The second reaction, which in fact occurs simultaneously with the first, is a representation of the small chemical changes that we have shown to be caused by weathering.



Table I  
% Recoveries

Source	IRAN C.O.	KUWAIT C.O.	TURKEY C.O.	CYPRUS T.B.	ERDEMLI T.B.	MALTA T.B.
Hexane-solubles	97	96	96	87	92	86
Benzene-solubles	4	4	4	8	8	10
Methanol-solubles	0	0	trace	3	2	4

From consecutive soxhlet extraction C.O. = crude oil T.B. = tar ball

Source	IRAN C.O.	KUWAIT C.O.	TURKEY C.O.	CYPRUS T.B.	ERDEMLI T.B.	MALTA T.B.
Hexane eluate	86	89	84	78	74	84
Benzene eluate	7	6	12	16	14	11
Methanol eluate	3	2	1.5	3	6	2

From consecutive elution of hexane solubles

Table II

Infra red spectra : Average (absorbance at  $1600\text{ cm}^{-1}$ /absorbance at  $1450\text{ cm}^{-1}$ ).

Hexane solubles	Benzene solubles	Methanol solubles
$0.17 \pm 0.05$	$0.38 \pm 0.06$	$2.7 \pm 0.2$
Hexane eluate	Benzene eluate	Methanol eluate
$0.045 \pm 0.015$	$0.21 \pm 0.02$	2.4 *

\* Error uncertain

## 2. Characterisation of crude and weathered oils

2.1. *General.* The discussion of weathering suggests that if chemical structures characteristic of a particular crude oil persist in tar balls derived from the oil, it would be appropriate to look for such structures from among the higher boiling hexane-soluble material.

2.2. *UV.* In general, all hexane-soluble material gave similar UV absorption spectra showing a pronounced maximum at 225-230 nm and a smaller maximum or a shoulder at 255-260 nm, characteristic of benzenoid material. Absorption was always broad and the spectra were very similar to those recorded by LEVY (1972) who used UV absorption to distinguish crude oils from their refined products. Although the spectra obtained from weathered oils did show some variation between samples, the relative absorption at 255 and 225 nm considered by LEVY varied little from one crude oil to another in the samples we have examined, and thus the spectra cannot be used to identify the source material of tar balls.

2.3. *IR spectra.* Similarly, whereas IR spectra were sufficient to distinguish between a crude oil and a 'mazot', although most samples of weathered oils examined were derived from crude oils and only a few samples seem to have been derived from 'mazot' or fuel oils, there were insufficient spectral differences between weathered oils to permit the identification of their source material.

2.4. *Gas chromatography.* Gas chromatograms of hexane-soluble components and in particular of the hexane-eluates, show peaks which mass spectrometry reveals to be aliphatic hydrocarbons. Most prominent are peaks due to normal paraffins, confirmed both by mass spectrometry and by comparison of retention times with those of reference compounds. Between the n paraffin peaks there are series of smaller peaks which mass spectrometry shows to be branched but not cyclic paraffins. Few of these have as yet been identified precisely although it is well known that terpenoids are present, in particular, pristane and phytane. These two compounds have retention times similar to those of  $nC_{17}$  and  $nC_{18}$  paraffins and their mass spectra are well established. None of the resolved gas chromatographic peaks are due to aromatic compounds. Most crude oils give similar gas chromatograms but the proportions of the com-

Table III

**<sup>1</sup>Hnmr Analyses of Benzene, (B), and Methanol, (M), Eluates**

Upper figures give number of hydrogen atoms of the type specified for every 100 hydrogen atoms.

Lower figures give average numbers of the group specified (or of aromatic hydrogen atoms) per benzene ring. Thus  $\text{ArCH}_2 + \text{ArH}$  numbers add to 6.

When only one figure is given, it is an upper figure.

Source of Eluate	$\text{CH}_3$	$\text{CH}_2$	$\text{CH}$	$\text{CH}_2\text{-O}^a$	$\text{CH}_2\text{OAr}^b$	$\text{ArCH}_2^c$	$\text{Ar H}$
(B)	11.1	44.4	11.1	3.7	0	22.2	7.4
ICO	1.2	7.2	3.6	0.6	0	3.6	2.4
(B)	8.6	31.0	5.2	10.3	6.9	24.1	13.8
KCO	0.62	3.6	1.2	1.2	0.84	2.8	3.2
(B)	7.9	31.6	10.5	9.2	2.6	26.3	11.8
TCO	0.63	3.8	2.5	1.1	0.3	3.2	2.8
(B)	8.6	42.8	14.2	5.7	8.6	14.2	5.7
CTB1	1.35	10.0	6.18	1.33	2.02	3.3	2.7
(B)	5.1	30.8	16.7	8.9	5.1	17.9	15.4
CTB2	0.4	3.8	4.1	1.1	0.65	2.2	3.8
(B)	7.3	51.2	7.3	4.9	0	19.5	9.8
ETB	0.74	7.8	2.2	0.45	0	3.0	3.0
(B)	5.9	41.2	11.8	11.8	0	23.5	5.9
MTB	0.67	7.1	4.03	2.01	0	4.03	2.01
(M)	4.3	21.7	4.3	4.3	4.3	8.7	52.2
ICO							
(M)	8.7	17.4	4.3	21.7	8.7	21.7	17.4
TCO							
(M)	7.1	← 7.1 →		← 28.6 →			57.1
CTB1							
(M)	8.3	33.3	8.3	16.7	16.7	8.3	8.3
CTB2							

a = includes  $\text{O-CH}_3$ ,  $\text{CNH}$ ,  $\text{CSH}$  ;

b = may include  $\text{ArOH}$  ;

c = includes  $\text{ArCH}$  and  $\text{ArCH}_3$  ;

Ar = Aromatic group ;

other symbols as in Tables I and V.

Table IV

**Summary of Gas Chromatography : Ratios of Peak Heights**

Hexane solubles	$n\text{C}_{18}/n\text{C}_{17}$	$n\text{C}_{18}/n\text{C}_{19}$	Phytane/ $n\text{C}_{18}$	Pristane/Phytane
IRAN C.O.	$0.86 \pm 0.06$	$1.2 \pm 0.1$	$0.65 \pm 0.01$	$1.3 \pm 0.1$
KUWAIT C.O.	$0.87 \pm 0.02$	$1.14 \pm 0.02$	$0.48 \pm 0.05$	$0.95 \pm 0.03$
TURKEY C.O.	$0.82 \pm 0.03$	$1.03 \pm 0.03$	$0.47 \pm 0.02$	$2.0 \pm 0.1$
LIBYA C.O. T.B.	$0.96 \pm 0.03$	$0.97 \pm 0.04$	$0.56 \pm 0.04$	$1.3 \pm 0.1$
CYPRUS T.B.	$1.85 \pm 0.2$	$0.65 \pm 0.05$	$0.55 \pm 0.05$	$0.60 \pm 0.05$
ERDEMLI T.B.	$1.0 \pm 0.1$	$1.0(5) \pm 0.1$	$0.45 \pm 0.05$	$1.25 \pm 0.1$
MALTA T.B.	$1.00 \pm 0.04$	$1.03 \pm 0.02$	$0.36 \pm 0.02$	$1.02 \pm 0.05$
TURKEY FLOATING T.B.	$0.94 \pm 0.02$	$1.05 \pm 0.02$	$0.27 \pm 0.05$	$1.87 \pm 0.05$



Table V  
Trace Metal Analyses (ppm)

	I.CO			K.CO			T.CO			C TB1			C TB2			E TB			MA TB		
	H	B	M	H	B	M	H	B	M	H	B	M	H	B	M	H	B	M	H	B	M
VANADIUM	4	5	68	14	24	105	24	23	41	3	48	20	2	85	65	2	12	34	2	49	44
NICKEL	3	9	10	1.5	11	30	3	-	23	3.5	28	34	2	46	210	5	13	18	1	19	198
LEAD	4	17	6	0.5	14	15	3	-	5	5	21	10	2	26	10	3	5	31	7	3	8
IRON	3	116	50	4	34	76	2	-	42	8	98	148	3	47	63	2	33	48	72	37	144

I = Iran, K = Kuwait, T = Turkey, C = Cyprus, E = Erdemli, MA = Malta, CO = Crude oil, TB = Tar ball, H = Hexane solubles, B = Benzene solubles, M = Methanol solubles, C TB1 and C TB2 are two different balls.

pounds present vary from one crude oil to another. Chromatograms of moderately high boiling hexane-soluble components are thus among the most characteristic 'finger prints' of crude oils that one is able to obtain. It must be remembered however that crude oil samples are not strictly reproducible and that gas chromatograms vary if the temperature program, the detector or the column is changed. Our gas chromatograms are summarized in Table IV, in which we have followed a procedure due to EHRHARDT and BLUMER (1972) and recorded the ratios of the peak heights of pristane and phytane and the  $nC_{17}$  and  $nC_{18}$  paraffins. Although Middle Eastern crude oils that have been examined are rather similar, it will often be possible to distinguish them by their ratio of pristane to phytane as shown by gas chromatography. The present work is being extended to include a much larger selection of crude oils.

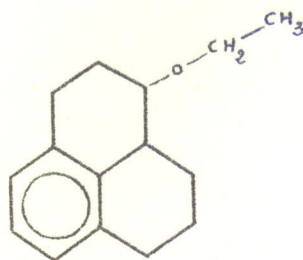
**2.5. Fluorescence.** The results shown in Table VI, similar to those reported by FRANK (1975), indicate that since hexane-soluble fractions of crude oils differ in their polynuclear aromatic hydrocarbon content, they differ also in their fluorescence. Differences occur both in the wavelengths of emission and excitation maxima and in the intensity of emission. Hexane-soluble polynuclear aromatic material is unlikely to be affected by weathering and, indeed, the spectra of the tar balls that have been examined do show differences which appear to offer an excellent means of confirming the identity of the source material. Fluorescence spectra of crude and weathered oils change with concentration and, in confirming identification of source material, care must be taken to compare similar concentrations of material.

**2.6.  $H^{1}nmr$  Spectra of eluates.** Consistent with the philosophy that the higher boiling components of hexane-soluble material may contain characteristic chemical structures is the suggestion that the examination of benzene and methanol eluates might help identify source material. These eluates were rather high boiling and did not give resolvable gas chromatograms. Other techniques were therefore necessary for their characterisation and Table III gives the results of  $H^{1}nmr$  analyses of some of these eluates. The eluates are seen to contain aromatic, aliphatic and hetero (probably oxygen) atom groups, and, while the benzene eluates were all rather similar, they were sufficiently different that such  $H^{1}nmr$  spectro might be used to distinguish crude oils. Thus, the benzene eluates from the Turkish and Kuwait crudes appear rather similar in terms of their  $CH_2/CH_3$  ratio and the numbers of oxygenated and aromatic groups present but differ by a factor of 2 in their  $CH/CH_3$  ratio. Although the benzene eluate from Iranian crude oil possesses the same  $CH_2/CH_3$  ratio as other benzene eluates, it contains about twice as many aliphatic groups and less oxygenated groups per benzene ring.

The results in Table III readily give average structures for the benzene eluates. The relatively high proportions of tertiary  $CH$  to  $CH_3$  groups imply that much of the aliphatic material in these eluates must be alicyclic. Thus, the  $H^{1}nmr$  analyses suggest that might be amongst the many compounds present in the benzene eluate obtained from Kuwait crude oil and such a compound would be reasonably high boiling.

Table I suggests that weathering may cause the formation of additional benzene and methanol eluates; nevertheless, benzene eluates from weathered oils gave  $H^{1}nmr$  spectra similar to benzene eluates from crude oils but there was an indication that the benzene eluates from weathered oils had increased molecular weights, possessing rather more aliphatic groups per benzene ring. The results in Table III





show that <sup>1</sup>Hnmr spectra of benzene eluates may be used to indicate the source material of weathered oils. Since weathering is unlikely to either diminish the number of oxygen groups or augment the number of alkyl groups present, Table III shows that the Erdemli tar balls could have been derived from Iranian crude oil but definitely not from either Kuwait or Turkish crude oil.

Table VI  
Summary of Fluorescence Spectra

	I. CO		K CO		T CO		C TB	E TB	F TB		M TB
Emission Max.	340	405 <sup>a</sup>	410	435	405	425	408	405	415		410
Excitation Max.		365		405		382	366*	368*	364	386	370
Approximate concentration		4 x 10 <sup>-5</sup>		10 <sup>-5</sup>		10 <sup>-5</sup>					

\* = secondary maxima observable

FTB = tar ball floating near Turkish coast ; other abbreviations as in previous tables.

<sup>a</sup> = approximate concentration ml/ml hexane.

Table III shows that methanol eluates possessed much more hydrogen and/or oxygenated groups than did benzene eluates. Where large proportions of aromatic hydrogen were present it is probable that the eluates contained polynuclear aromatic material. The patterns exhibited by these spectra were very different from one other. If the examination of larger numbers of samples confirms this and demonstrate the constancy of the results, then these spectra would prove useful as 'finger prints' characteristic of the material. It is clear that further investigation of <sup>1</sup>Hnmr spectra of benzene and methanol-soluble material would be valuable in distinguishing crude oils and describing their weathering.

2.7. AAS. Table V shows some trace metal analyses for three crude oils and four tar balls. Analyses are given for hexane, benzene and methanol soluble material. It is well known that many metals occur in crude oils associated with polar oxygen groups and as metalloporphyrins and, not surprisingly, it will be seen that, the metals are in general more soluble (sometimes even much more soluble) in the benzene and methanol-soluble material than in the hexane-soluble material. Since the proportion of hexane-soluble material was always the greatest (Table I), the amounts of metal in each fraction were usually comparable. The pattern of trace elements in each crude oil was different and such patterns may be used to distinguish crude oils. Previous workers (OMANG, 1971) have employed vanadium and nickel concentrations. If it may be assumed that the trace metals and the solubility fractions of oils and of tar balls are in thermodynamic equilibrium, then, to a reasonable degree of approximation, the distribution of trace metal concentrations between the solubility fractions of a tar ball should be the same as the oil from which it was derived. That is,  $T_H/T'_H = T_B/T'_B = T_M/T'_M$  (H,B and M = Hexane, Benzene and Methanol respectively), where  $T_H$ , for example, is the concentration of trace metal in the hexane soluble fraction of the tar ball and  $T'_H$  is the concentration of the same trace metal in the hexane soluble fraction of the corresponding crude oil. No such relationship is present in Table V.



The variation of trace metal concentration from one solubility fraction to another differed from trace metal to trace metal. It will be shown that the Erdemli tar ball probably derived from Iranian crude oil. If this is valid, calculations of the total concentration of each trace metal in the tar ball and in the Iranian crude oil suggest that, whereas nickel may be conserved during weathering (its total concentration in the tar ball increased roughly in proportion to the amount of organic material lost by weathering), both vanadium and lead appear to have been lost by weathering. It is clear that a variety of effects determine the trace metal concentrations of tar balls and it will not usually be possible to determine the source material of a tar ball from its trace metal composition.

**2.8. Identification of the source material of tar balls.** One is claiming that consideration of gas chromatograms and fluorescence spectra of hexane-soluble material and of <sup>1</sup>Hnmr spectra of benzene eluates enables one to determine the source material of weathered oils. If an oil is sampled soon after it has entered the sea, then source material identification is straight forward by the three techniques mentioned (other possibilities are inadmissible).

If, however, weathered oils are sampled some time after they have entered the sea (as in our case) some doubt as to the identity of the source material is likely to remain. The problem is more difficult in regions which handle several crude oils having similar chemical structures, or in cases where different samples are used for standardization of the three techniques cited above.

There is also a need for the characterisation of a wider range of crude oils.

The tar ball found floating near the Turkish shore and analyzed here very probably was derived from Turkish crude oil. Gas chromatography gave a pristane/phytane ratio similar to the characteristic high value of Turkish crude oil. The fluorescence spectra of the tar ball and the Turkish crude oil were virtually identical. (Turkish crude oil is among those refined nearby). Gas chromatography of the tar balls found on the Erdemli beach suggests they could have been derived from Iranian or Libyan crude oils. Both the <sup>1</sup>Hnmr spectrum and the fluorescence spectra are in reasonable agreement with the origin of the balls being Iranian crude oil, but a larger range of crude oils needs to be examined. A larger range of crude oils must also be examined before one can hope to identify the source of the tar balls from Malta. Their pristane/phytane ratio was similar to that of Kuwait crude oil and while such an identification is not inconsistent with fluorescence measurements, it is clearly incompatible with the <sup>1</sup>Hnmr spectra of the benzene eluates. The Cyprus tar balls gave unusual <sup>1</sup>Hnmr spectra and their gas chromatograms indicated extensive weathering ; it is probably no longer possible to determine their source.

## Conclusions

Methods of characterising crude and weathered oils have been assessed. It has been confirmed that :

1. Crude and refined oils may be distinguished by their IR and UV spectra.
2. Characterization of those fractions of crude oils which are least affected by weathering by determining (a) gas chromatograms of terpenoids present in hexane-soluble material ; (b) fluorescence spectra of the oils, and (c) <sup>1</sup>Hnmr spectra of benzene eluates of hexane-soluble material, permits the identification of the source material from which these weathered oils were derived (with a degree of uncertainty which obviously diminishes with increasing information on the history of the weathered oils. There is a need to standardize the above techniques and to use them to 'finger print' a range of crude oils.
3. Whereas the crude oil mined in Turkey is similar to other paraffinic Middle Eastern oils, it has a rather high ratio of pristane/phytane and is markedly fluorescent.
4. Weathering of crude oils in the sea involves the loss of low boiling material by evaporation and dissolution. Solubility relationships suggest that about half the crude oil may be lost in this way, but gas chromatography of weathered oils indicates that this estimate is too high and that some hexane-soluble material becomes converted to asphaltenes and to material soluble in methanol (but insoluble in hexane and benzene) by weathering.



5. Determination of the patterns of trace metal concentrations in crude oils by AAS may be used to distinguish crude oils from each other but examination of V, Fe, Ni and Pb concentrations in tar balls suggests that weathering may have affected each metal differently and while the technique may give interesting information about the weathering process, it is not useful for identifying the source material from which weathered oils were derived.

#### Acknowledgments

Mass spectral analyses were obtained by Taner TUGRUL of Ankara University. Suleyman TUGRUL, Gonul OZYILDIZ and Ismail YIGINSU helped us in obtaining AAS, IR and <sup>1</sup>Hnmr results respectively. The tar ball from the fire in Istanbul was collected by A.T. HUR. The work has been generously supported by UNEP (MED POL I) and by the Turkish Scientific and Technological Research Council (TUBITAK).

#### References

- J.N. BUTLER, 1975. — The age of Pelagic Tar, *Marine Chem.*, **3** : 9-12.
- M. ERHARDT & M. BLUMER, 1972. — The Source Identification of Marine Hydrocarbons of Gas Chromatography, *Environ. Pollut.* **3** : 179.
- J.F. RANK, 1975. — Identification of Petroleum Oils by Fluorescence Spectroscopy, *Proc. Conf. Prevention and Control of Oil Pollution*.
- E.M. LEVY, 1972. — The Identification of Petroleum Products in the Marine Environment by Absorption Spectrophotometry, *Water Research*, **6** : 57.
- S.H. OMANY, 1971. — Determination of Vanadium and Nickel in Oils by Flameless Graphite Tube Atomization, *Anal. Chim. Acta.* **56** : 470.