

# IDENTIFICATION OF SPILLED CRUDE OILS FROM SIMILAR ORIGINS

Jacob Shen,\* Richard J. Engen, and Nadim K. Saadeh

Laboratories Department, Arabian American Oil Company,  
Dhahran, Saudi Arabia

الخلاصة :

هذا البحث يصف تطوير أساليب العمل الضروري لتمييز زيوت الخام المتسربة والتي هي متشابهة في مجمل تركيبها . إن قياس بعض المركبات البيولوجية ، في الزيوت الخام المتسربة ، بواسطة الجهاز المشترك لتحليل الغازات الكروماتوغرافي والتحليل الكتلي ، يعطي معلومات الأكثر نوعية للتمييز بين الزيوت الخام السعودية التي تعرضت للعوامل الجوية . بالإضافة ، إن قياس بعض المعادن المنتقات ، والتحليل السبكتروسكوبي للإستشعاع المتزامن المسح والتحليل الكروماتوغرافي الشعري للغازات ، هي أيضاً مفيدة بإعطائها دلائل داعمة . إن فائدة وتحديد كل من هذه الأساليب مناقش في هذا البحث .

## ABSTRACT

This paper describes methods, and the development work necessary, for identification of spilled crudes whose gross compositions are similar to one another. Measurements of petroleum biomarkers in spilled crudes by combined gas chromatography/mass spectrometry provides the most specific information for distinguishing weathered Arabian crudes. In addition, measurements of selected metals, synchronous scan fluorescence spectrometry, and capillary gas chromatography are also useful in providing supporting evidence. The usefulness and limitations of each of these methods are discussed.

\* Mailing address for correspondence: Box 8745, Dhahran, Saudi Arabia.

## IDENTIFICATION OF SPILLED CRUDE OILS FROM SIMILAR ORIGINS

### INTRODUCTION

Input of undesirable hydrocarbons into marine environments has been a major concern in the last decade. For example, the U.S. Coast Guard and the National Academy of Sciences have estimated that each year 1.4 to 2.1 million tons of oil are being discharged deliberately as a result of tanker cleaning operations [1]. To trace both the source and the fate of spilled oils, it is necessary to have reliable analytical methods.

Many methods have been developed and used in the past decade for identification of spilled oils [1-4]. However, two main challenges have remained. First of all, it is still difficult to distinguish weathered oils similar in gross composition. For example, while a number of methods can distinguish an Alaskan crude from Arabian crudes (i.e. major types of export crudes from Saudi Arabia), few can distinguish weathered Arabian crudes from one another.

Secondly, almost all methods currently in use are subject to interference from weathering effects. As a result, whenever reference samples from suspected sources are used for comparison, artificial weathering of these samples is necessary. It is often tedious and time consuming to simulate weathering, either in the field or in the laboratory. In addition, interpretation of the differences between spilled oil data and reference sample data can be difficult because of uncertainties introduced as a result of weathering.

In the surveillance of marine environments of the Arabian Gulf, it is important to be able to distinguish major types of export crudes from the region. The Arabian crudes such as Arabian Heavy ( $^{\circ}$ API 27), Arabian Medium ( $^{\circ}$ API 31), Arabian Light ( $^{\circ}$ API 34), and Extra Light ( $^{\circ}$ API 39) become increasingly similar to one another after losing lighter components in weathering. Properties such as specific gravity or viscosity usually become of little use in the identification of weathered Arabian crudes. In spite of the fact that a few methods are available to characterize virgin Arabian crudes, the need exists for methods that can identify weathered Arabian crudes.

We have been developing methods for identification of spilled oils with two major criteria in view:

- (1) the method should be able to distinguish weathered Arabian crudes; and
- (2) the method should not be subject to interference from weathering.

An added advantage in meeting criterion (2) is that all work associated with artificial weathering would become unnecessary. This should shorten the overall analysis time significantly.

Recently, one such method based on selective measurement of petroleum biomarkers by gas chromatography/mass spectrometry (GC/MS) has been reported [5]. The method uses selected ion monitoring (SIM) for better resolution and sensitivity. The relative amounts of biomarker such as pentacyclic triterpanes can be readily used to distinguish the four types of Arabian crude, *weathered or unweathered*. As these biomarkers are, in general, little affected under usual weathering conditions, the method is inherently free of interference from weathering. As a result, samples can be analyzed directly without the need of any prior treatment. The method has been in use successfully for close to a year, and has helped detect major spilled oils of non-Arabian origin in the Gulf area.

It has been a general consensus that the best approach to oil spill identification is to compare the unknown oil with oil from suspected sources (see [6]). Furthermore, reference samples from suspected sources should be taken at the time of the spill for the best results. An oil library can be helpful for screening purposes, but it obviously cannot cover all situations. For example, crudes in a tanker are seldom from a single well or even a single field, but are almost always a mixture of crudes from many different wells and fields. The possibilities are unlimited. No one method has yet been established as being satisfactory in all cases. Consequently, a second general consensus in the field is that a multianalytical approach is always preferred. There would be an increased level of confidence if oil matching were based on multiple data sets. The multimethod approach can be especially important when contaminants in spilled oils may interfere with one or more methods. Besides the GC/MS method mentioned above, we use several additional methods in oil spill identification. These methods include measurements of selected metals, synchronous scan fluorescence spectrometry, and capillary gas chroma-

tography, and are selected as a compromise of equipment availability, speed, and data specificity. This paper describes the usefulness and limitations of each of these methods in the identification of Arabian crudes. Applications of distinguishing Arabian crudes from spilled oils of non-Arabian origins are also discussed.

## EXPERIMENTAL

### GC/MS and GC

GC/MS SIM procedures were as reported previously [5]. For GC analyses, fused silica capillary columns (30 m × 0.25 mm) coated with SE-30 liquid phase were used. The injector port temperature was 350°C. The oven temperature was programmed to rise from 100°C to 300°C at 4°C/min. Typically, 0.3 µl of neat crude, weathered or unweathered, were injected each time at a split ratio of 100:1. The helium flow through the column was 1 ml/min. For ease of data processing and peak identification, GC data reported in this work were obtained from JEOL's DX-300 GC/MS system controlled by a JMA 3500 data system. The chromatograms shown in Figures 4 and 5 were reconstructed ion chromatograms (RIC) generated by the data system. For these runs, a mass range of 25 to 500 was used. The multiplier voltage was kept at 1.6 kV. GC peak area integration was also carried out by the data system.

### Selected Metal Analysis

Vanadium and nickel contents were determined by either atomic absorption spectrometry or X-ray fluorescence spectrometry. Samples were typically prepared according to [17]. Standard samples were used to ensure that results from both methods agreed with each other.

### Fluorescence Analysis

A solution of roughly 21 mg/l of the oil was made up in cyclohexane. The Perkin-Elmer MPF-44B spectrofluorimeter was adjusted to a given sensitivity using the Rayleigh scattering intensity at 400 nm from cyclohexane. The synchronous-scan fluorescence (SSF) spectrum was generated starting with the emission monochromator at 260 nm and the excitation monochromator at 235 nm. A blank cyclohexane spectrum was subtracted from each curve by use of a digital spectral-correction attachment.

### Weathering

Field weathering procedures have been reported previously [5]. For fluorescence spectrometric analysis, samples were weathered by placing 2 g of each crude in a 20 × 200 mm petri dish and exposing the open petri dish directly to the sun. The samples were placed so that they received direct sunlight from roughly 06:30 to 17:30 hours. The location of the exposed samples was somewhat sheltered from direct wind. The surface temperature of the bench upon which they sat was sometimes as high as 60°C. The weathering was continued for three days for each sample.

### Selected Metal Measurements

The measurement of selected metals is often an effective way of characterizing virgin crudes. Work in ARAMCO's laboratory has established that vanadium and nickel contents can be characteristic of major types of Arabian crude. Table 1 lists some historical data on vanadium concentration in Arabian crudes. The total amount of vanadium increases in the order

$$\text{Extra Light} < \text{Arabian Light} < \text{Arabian Medium} < \text{Arabian Heavy}.$$

Table 1 shows there is a spread of vanadium concentration within each category of crude. This reflects the fact that the four major types of Arabian crude are actually crude blends, i.e. mixtures of crudes produced from various zones and fields. As a result, the final composition of a crude blend depends on the types of crude available for blending at the time of sampling. The spread in vanadium content is especially pronounced for Arabian Medium, reflecting a wider range of vanadium level in base crudes available for blending in this category. This again demonstrates the importance of taking reference samples from suspected sources at the time of the spill so that any uncertainty as to actual crude compositions will be minimized.

Historical data for nickel in Arabian crudes are not available. Our recent work, however, shows an increase in nickel of the same order as that for vanadium (see Table 2).

Vanadium and nickel are mostly present in crudes as complexed porphyrins, which have relatively high boiling ranges. As evaporation is usually the major process during short-term weathering, the total relative amounts of nickel and vanadium often become

**Table 1. Vanadium Content of Arabian Crudes**

Date	Vanadium ( $\mu\text{g/g}$ Oil)			
	Berri Light	Arabian Light	Arabian Medium	Arabian Heavy
2 July 1975	2		24*	93
2 July 1975			62†	
5 July 1975		18		
5 January 1976	2		27*	93
8 January 1976			59†	
18 January 1976		17		
3 July 1976	1	20	26	93
2 January 1977	2	20	28	94
2 July 1977	1	20	20	96
2 January 1978	1	20	24	94
12 March 1978			31*	
12 March 1978			67†	
6 January 1980	4	23	26*	87
6 January 1980			64†	
6 July 1980	3	15	38*	84
6 July 1980			67†	
5 January 1981	2	28	47	93
1 July 1981	1	24	58	96
4 January 1982	1	20	63	98

\* Blend of crudes from two fields.

† Blend of crudes from four fields.

**Table 2. Nickel and Vanadium Contents\* of Arabian Crudes**

	Extra Light			Arabian Light			Arabian Medium			Arabian Heavy		
	V†	W‡	V280§	V	W	V280	V	W	V280	V	W	V280
Nickel ( $\mu\text{g/g}$ Oil)	2.3	3.7	3.8	4.6	6.6	6.6	11.6	16.8	16.5	19.2	23.2	28.1
Vanadium ( $\mu\text{g/g}$ Oil)	7.3	10.6	11.3	17.7	26.7	28.4	35.8	52.5	54.2	66.9	83.4	104
Ni/V	0.32	0.35	0.34	0.26	0.25	0.23	0.32	0.32	0.30	0.29	0.28	0.27

\* Nickel and vanadium were measured by atomic absorption spectrometry.

† V  $\equiv$  virgin crudes.

‡ W  $\equiv$  weathered crudes.

§ V280  $\equiv$  280°C-plus bottom cuts of virgin crudes.

higher in weathered crudes. While it is difficult to predict the exact extent of weathering in each case, previous studies and experience show that compositional changes occur mostly in the first 24 to 48 h of exposure. A collaborative study led by the American Society for Testing and Materials has suggested that an oil weathered for two or three days may be simulated by a 280°C-plus bottom cut of its unweathered counterpart. To test its validity, we have carried out a field weathering study, and compared both nickel and vanadium contents in weathered

Arabian crudes to those in the bottom cuts (280°C plus) of unweathered counterparts. The field weathering procedures were as reported previously (see [5]) but were carried out in winter time (January). The results are listed in Table 2.

As expected, Table 2 shows an increase in the relative amounts of nickel and vanadium in weathered crudes as well as in the bottom cuts of the same crudes. In addition, the extents of their increase were similar in both sets of samples. For example, the amount of nickel (3.7 ppm, wt/wt) and vanadium

(10.6 ppm) in weathered Extra Light were similar to those in the bottom cut of the same crude: 3.8 and 11.3 ppm, respectively. For Arabian Heavy, however, nickel and vanadium were somewhat less in the weathered sample than in the bottom cut, indicating Arabian Heavy had less weight loss than other Arabian crudes under the same weathering conditions.

The results in Table 2 show that although nickel and vanadium levels can help characterize Arabian crudes, they will be more useful as negative indicators than as positive indicators. For example, if an unknown oil has a vanadium level of 175 ppm, obviously it cannot be an Arabian crude. However, if an unknown oil has 75 ppm of vanadium, more data would be required to determine if it is an Arabian crude. This is because a number of other oils could also have vanadium levels within a similar range. Furthermore, if it can be established that the unknown oil is of Arabian origin, knowledge of the actual compositions of Arabian crudes at or around the time of the spill would still be needed to determine if the unknown oil is Arabian Medium or Arabian Heavy.

Table 2 also lists nickel to vanadium (Ni/V) ratios in virgin as well as in distilled and weathered Arabian crudes. Weathering has not altered these ratios to any significant extent, but it is obvious that Ni/V ratios would not be useful to distinguish Arabian crudes from one another. However, Ni/V ratios can be useful in distinguishing Arabian crudes as a group from non-

Arabian crudes, so long as the latter have sufficiently different Ni/V ratios.

### Synchronous Scan Fluorescence Spectrometry

Luminescence spectrometry has proven to be a rapid, inexpensive, but useful method for oil spill analysis (see [7–10]). An excellent review is given by Eastwood in [9]. The aromatic hydrocarbon fraction of crude oils is made up of chromophores with favorable fluorescence yields in the ultraviolet through the near visible spectrum. Fluorescence is therefore a specific and extremely sensitive means of fingerprinting crude oils. (Although phosphorescence techniques have been applied to crude oils, fluorescence methods are more commonly used.)

It is known that the geochemical history of a crude oil will be reflected in the makeup and relative amounts of its aromatic hydrocarbons. It follows that not only will crudes from diverse locations have very different fluorescence spectra, but that various grades of crude from within a relatively restricted geographical area can be distinguishable by this method. The ability to distinguish among the grades of Arabian crude is shown in Figure 1 by their synchronous scan fluorescence (SSF) spectra. The synchronous scan technique, first applied to oils by Lloyd [7], and later to crude oils by John and Souter [8], yields a much more detailed spectrum than the common technique of

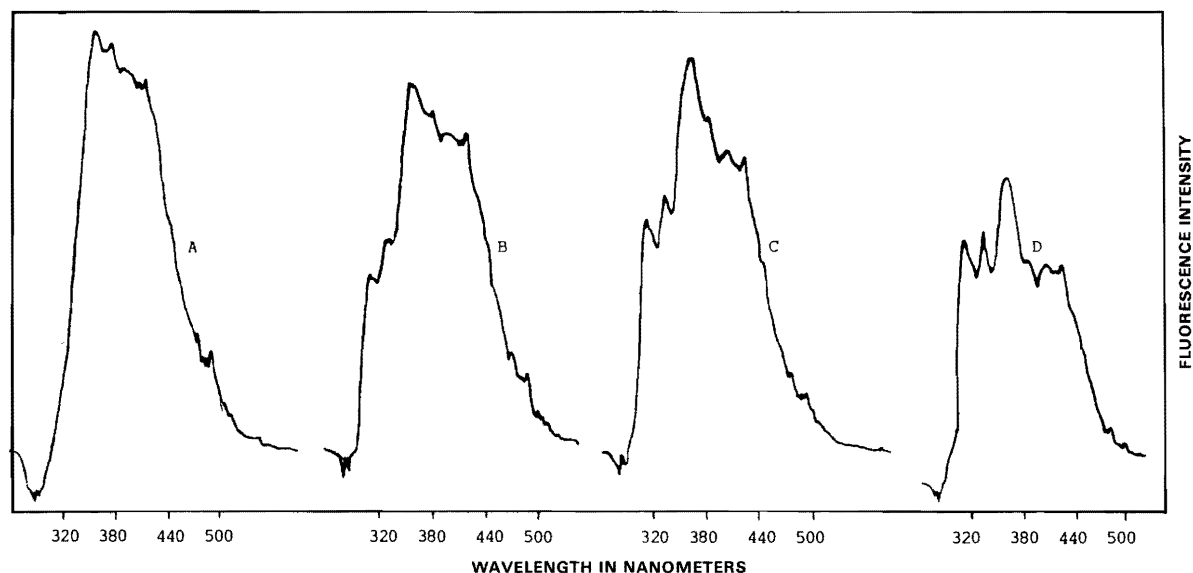


Figure 1. Synchronous Scan Fluorescence Curves of Virgin Arabian Heavy (A), Medium (B), Light (C), and Extra Light (D) Crudes

fixing the excitation wavelength and scanning only the emission spectrum. The general trend with these crudes is that as the °API number increases (specific gravity decreases), there is an increase in the intensity of fluorescence bands below about 380 nm relative to those above 380 nm. There is a great deal of variation in this pattern among SSF spectra of Arabian crudes from single sources. The above pattern is general enough to allow for at least partial discrimination among major grades of crude being shipped through the Gulf. Virgin Arabian Extra Light and Light can be clearly distinguished from one another and from Arabian Medium and Heavy. There are, however, much smaller differences between Medium and Heavy grades. In fact, although Medium and Heavy grades in Figure 1 are distinguishable, we have observed cases where virgin Medium and Heavy grades could not be distinguished. As we have mentioned, this is not surprising because these commercial grades of crude are made up from many individual sources.

Figure 2 shows SSF spectra of the same four crudes following weathering by the petri-dish technique [11]. Although considerable changes can be observed in SSF spectra of Light and Extra Light crudes, they can still be distinguished between themselves and from weathered Medium or Heavy crudes. However, it is not possible to distinguish between weathered Medium and Heavy crudes.

One advantage claimed for the normal fluorescence method in matching spilled oils is that it is relatively

insensitive to short-term weathering changes [9]. Our results show that this lack of sensitivity applies only when photodegradation is absent and when evaporation and/or dissolution are the only important weathering processes. We have found that SSF spectra of crudes subjected to simulated weathering by distillation are remarkably similar to SSF spectra of virgin crudes. Photolysis during weathering, however, does play a predominant role in affecting SSF spectra. Following exposure to sunlight we find that there is a greater decrease in intensity of fluorescence bands at longer wavelengths than at shorter wavelengths. This differential change of intensity with wavelength accounts for the reported greater sensitivity to weathering of the SSF method compared with normal emission fluorescence methods (see [8]). One extracts a great deal more information from SSF spectra, especially at the longer wavelengths, than from fluorescence spectra obtained at a single excitation wavelength. In turn however, this longer wavelength information is more profoundly affected by weathering changes than conventional spectra where such longer wavelength information is much reduced anyway. For short-term weathering, these photolytic changes appear to be consistent enough to allow them to be accounted for in identifying a spilled oil. Also, although many of the influences that come to bear on a crude oil in marine environments are not exerted in open petri dishes, this simulation is apparently a reasonable one for SSF analysis. We have examined several spilled crudes that were satisfactorily identified

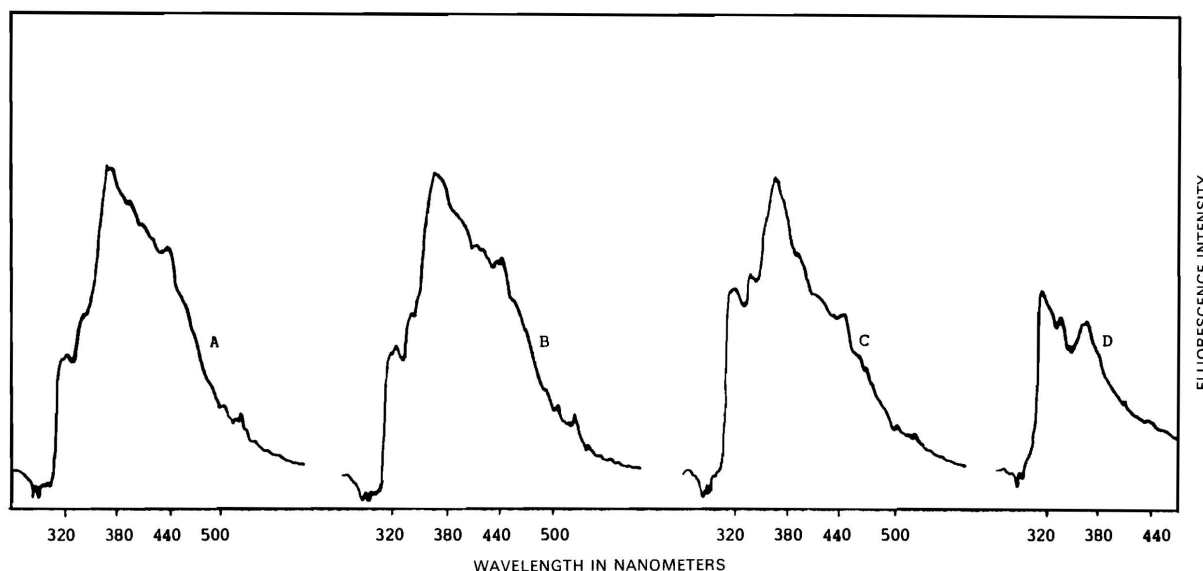


Figure 2. Synchronous Scan Fluorescence Curves of Laboratory Weathered Arabian Heavy (A), Medium (B), Light (C), and Extra Light (D) Crudes

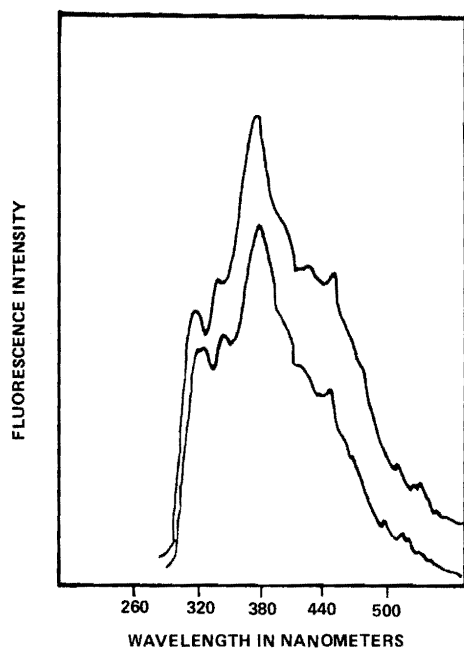


Figure 3. Synchronous Scan Fluorescence Curves of a Weathered Oil Spill Sample Recovered from the Arabian Gulf (upper curve) Compared with Laboratory Weathered Arabian Light Crude

by comparing their SSF spectra with those obtained from crudes weathered by the petri-dish method. Figure 3 shows the SSF spectrum of an unknown spilled crude and that of a suspected light crude that had been weathered in a petri dish. The spectra were similar enough to allow at least a tentative identification. The identification was later confirmed by other data.

We have emphasized throughout this work that it is always best to have samples from suspected sources with which an unknown can be compared. However, even where suspected sources are available, it may not be possible to match unambiguously a weathered spilled crude on the basis of SSF spectra alone. For example, some weathered non-Arabian Heavy crudes from the Gulf area and weathered Arabian Heavy crudes will have very similar SSF spectra. In spite of these limitations, however, the SSF method will for a relatively slight expenditure of time provide valuable supporting evidence to back up selected metals, GC, or GC/MS analysis. In a few cases a reasonably sure identification can be made by SSF spectra alone.

The SSF technique will, as will selected metals analysis, often provide excellent negative evidence. For example, this technique can rule out the possibility that a spilled crude is a Light or an Extra Light grade

without being able to further specify the source. The SSF technique does an excellent job of differentiating between crude oil and petroleum distillates. Most distillates do not show SSF bands above roughly 360 nm. All Arabian and Gulf crudes that we have observed show significant SSF bands to about 500 nm.

### Capillary Column Gas Chromatography

Gas chromatography (GC) has been one of the most useful techniques in fingerprinting complex organic mixtures (see [12]). The technique has been applied extensively in fingerprinting virgin crudes based on either overall profiles of chromatograms or groups of specific peak ratios. It has also been widely used in oil spill identification work in spite of the fact that weathering effects can easily interfere with GC results. Prior treatment of reference samples to simulate weathering effects before GC analysis is essential in order that chromatograms of both spilled and reference samples can be compared on an equal basis. Recent advances in fused-silica capillary column technology and in various types of selective detector have enhanced the usefulness of the technique.

A typical gas chromatogram of a crude is usually dominated by a series of *n*-paraffins that define the gross profile of a chromatogram. Crudes from different regions may often be distinguished from one another based on these gross profiles. For crudes with similar gross profiles, more detailed features in a chromatogram will have to be taken into account. In addition, specific peak ratios such as relative amounts of pristanes and phytanes are often used to aid crude characterization. These chromatographic techniques, however, become more limited when applied to crudes of similar origin such as Arabian crudes.

Figure 4 shows typical chromatograms for Arabian crudes. They are remarkably similar to one another both in gross profile as well as in minor detail. Figure 5 shows chromatograms for weathered Arabian crudes. Weathering has obviously depleted lighter components usually present at the front end of each chromatogram. The altered chromatograms for weathered Arabian crudes, however, are still very similar to each other.

Table 3 lists the relative amounts of pristane and phytane, two isoprenoid compounds often used in crude identification. None of the three ratios evaluated, pristane/ $C_{17}$ , phytane/ $C_{18}$ , and pristane/phytane are specific enough to distinguish Arabian crudes from one another. It is of special importance that weathering affects the relative

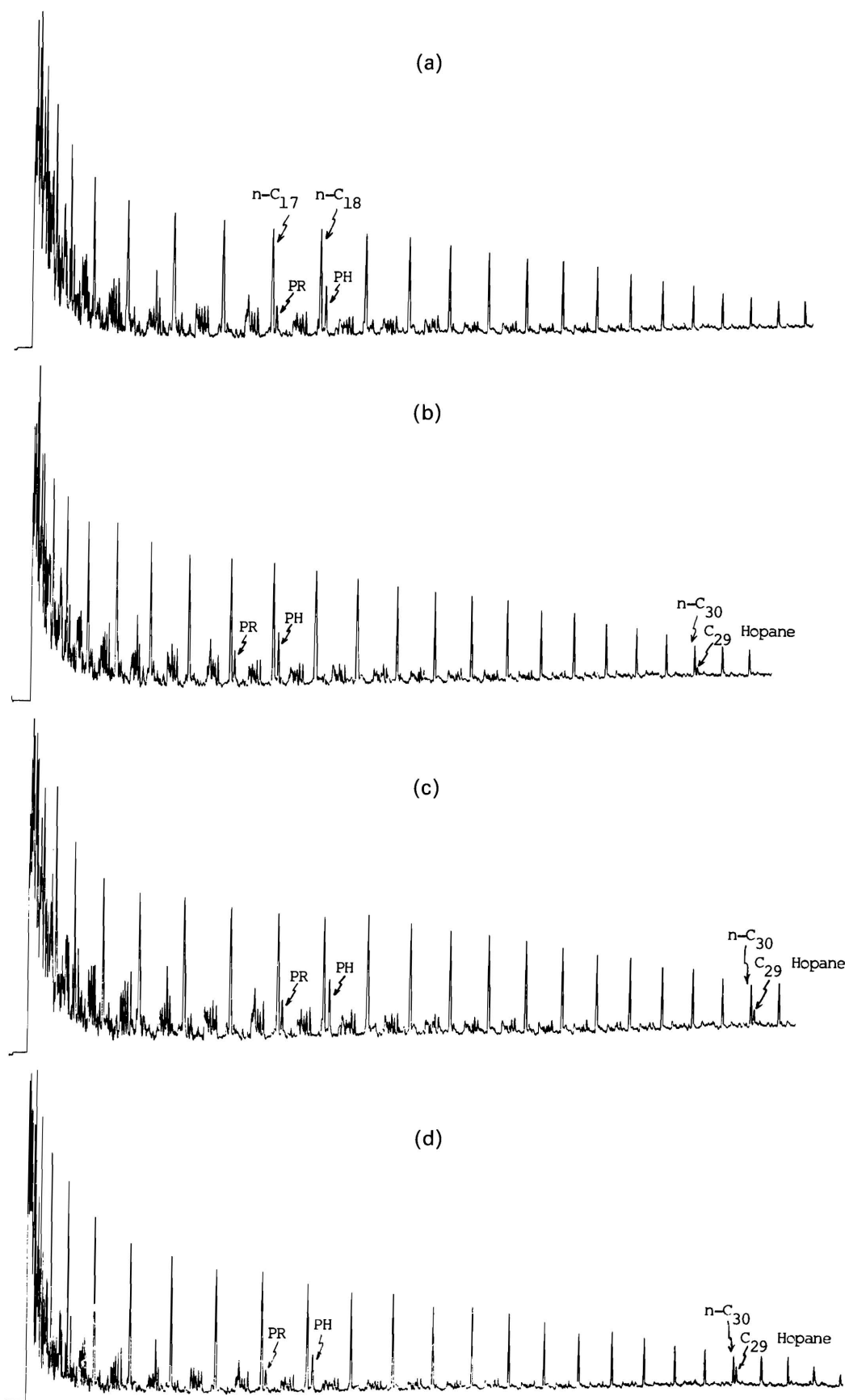


Figure 4. Reconstructed Ion Chromatograms of Virgin Arabian Crudes: (a) Extra Light; (b) Light; (c) Medium; and (d) Heavy (PR ≡ Pristane; PH ≡ Phytane; C<sub>29</sub> Hopane: see text)



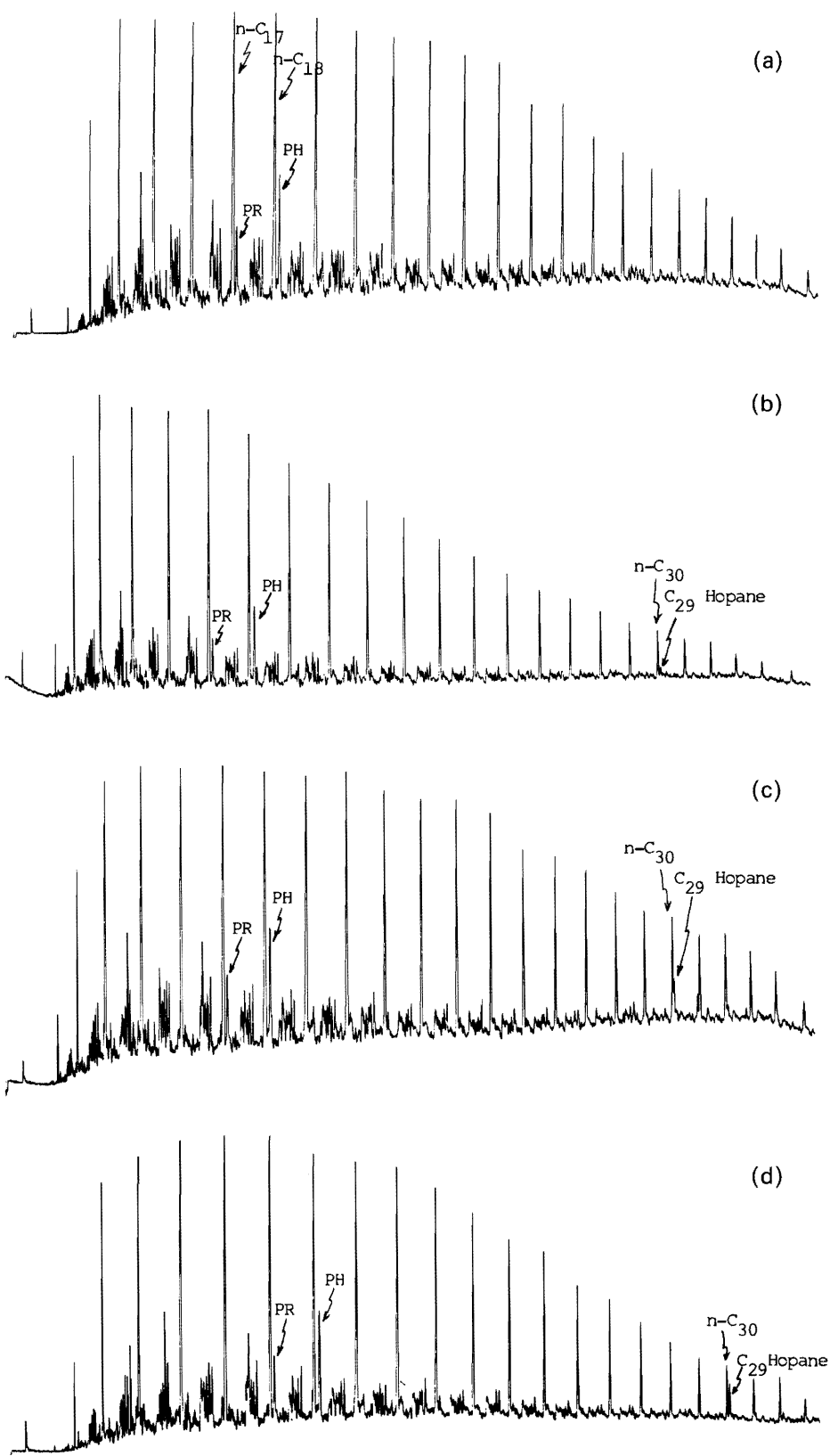


Figure 5. Reconstructed Ion Chromatograms of Weathered Arabian Crudes: (a) Extra Light; (b) Light; (c) Medium; and (d) Heavy (PR ≡ Pristane; PH ≡ Phytane; C<sub>29</sub> Hopane: see text)

**Table 3. Relative Amounts of Pristane and Phytane in Arabian Crudes**

Arabian Crudes	Pristane/ <i>n</i> -C <sub>17</sub>		Phytane/ <i>n</i> -C <sub>18</sub>		Pristane/Phytane	
	V*	W†	V	W	V	W
Extra Light	0.14	0.17	0.30	0.34	0.54	0.48
Light	0.22	0.16	0.40	0.34	0.56	0.49
Medium	0.24	0.17	0.38	0.38	0.63	0.44
Heavy	0.17	0.18	0.41	0.47	0.49	0.47

\* V ≡ virgin crudes.

† W ≡ weathered crudes

amounts of these compounds, and thus introduces uncertainties that at times would be difficult to overcome.

The potentially most useful feature in the chromatograms of Arabian crudes is a doublet at C<sub>30</sub>, which is very strong for Arabian Heavy and Medium, weak for Arabian Light, and extremely weak for Extra Light. The front peak of the doublet is *n*-C<sub>30</sub> paraffin and the second peak is identified as 29-nor-5, 17 (H)-hopane, a pentacyclic triterpane. Figure 6 shows the mass spectrum of this compound, characterized by a molecular ion at *m*/*Z*=398, a fragment ion at *m*/*Z*=383 from loss of a methyl group, and a base peak at *m*/*Z*=191 from C-ring cleavage. Table 4 lists

the peak ratios of this doublet. Weathering has no apparent effect on these peak ratios. This is as expected, since both compounds have relatively high boiling points, and would not be affected significantly during short-term weathering, in which evaporation is usually the dominant process.

It should be noted that under longer-term weathering conditions, especially when biodegradation is taking place which preferentially depletes paraffins, C<sub>29</sub> hopane/*n*-C<sub>30</sub> ratios would be distorted.

The precision of gas chromatographic results are subject to the influence of a number of factors. One of the most important factors is chromatographic resolu-

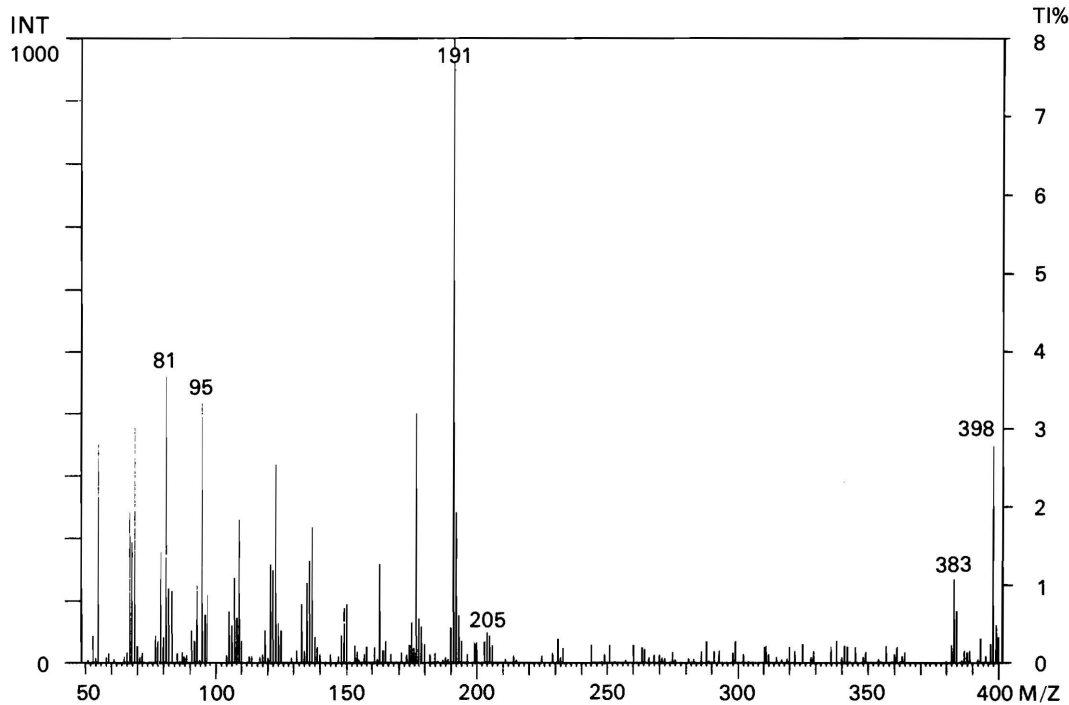


Figure 6. Mass Spectrum of C<sub>29</sub> Hopane

**Table 4. 29-nor-5, 17 (H)-hopane/*n*-C<sub>30</sub> Ratios of Arabian Crudes**

	29-nor-5, 17 (H)-hopane/ <i>n</i> -C <sub>30</sub> (peak area ratios)	
	Virgin crudes	Weathered crudes
Extra Light	—	—
Arabian Light	0.26	0.26
Arabian Medium	0.34	0.33
Arabian Heavy	0.64	0.64

tion of components of interest. Incomplete separation of components of interest would naturally cause variation in results. As crude oil is extremely complex, no one column is able to resolve all components of a crude in a single run. It is therefore often necessary to carry out additional work to ensure the quality of data from GC measurements. Quality assurance aspects of GC work can be time consuming. Use of the GC/MS selected ion monitoring (SIM) technique can often circumvent this type of problem (see [13]).

As mentioned above, chromatograms of Arabian crudes are very similar to each other, and GC fingerprinting would be of limited use in distinguishing Arabian crudes. It is possible to pursue this method further by:

- (1) fingerprinting a selected fraction instead of the entire crude; and/or
- (2) developing pattern recognition techniques for more in-depth data processing.

It has been reported that selected biomarker fractions separated from crudes can be extremely useful in crude characterization [14]. Separation procedures prior to GC analyses, however, are too tedious and time consuming to be considered as a routine method for oil spill identification. Development of pattern recognition techniques could easily involve hundreds of data points, most of which would be minor GC peaks. It would require a great amount of work to monitor the precision of all these GC data points.

### Gas Chromatography/Mass Spectrometry

The best strategy in developing methods for oil spill identification is to focus on specific groups of components in a crude. For example, biomarkers such as pentacyclic triterpanes or steranes are often characteristic of the genetic origins of a crude. In the past decade, biomarkers have been used extensively in oil/oil and oil/rock correlation studies in petroleum

geochemical explorations [15]. In addition to being highly characteristic of an individual crude, these biomarkers have high boiling points, and hence are least subject to loss during weathering. Moreover, owing to their extreme similarities in chemical structure, the distribution pattern of a particular group of biomarkers in a crude remains unchanged under most weathering conditions. Any method based on the use of biomarkers clearly would have the advantage of suffering the least interference from weathering.

Preparation of biomarker fractions from a crude is tedious and time consuming, and has been a major limitation in their application to oil spill identification, which often requires a speedy response. Recent work reported by Shen [5], however, has established that by using GC/MS SIM techniques, measurements of biomarkers useful for spilled oil identification can be accomplished with no prior separation work. Weathered Arabian crudes could be readily identified via relative amounts of methylated phenanthrenes and pentacyclic triterpanes as well as ratios of two C<sub>27</sub> hopanes measured directly from *m/z* = 191 ion chromatograms of crudes. Figure 7 shows such a typical fingerprint of Arabian Light. It was also established that weathering of crudes under typical summer conditions at the Arabian Gulf had little effect on these fingerprints (see [5]). As a result, the method not only requires no prior separation of biomarker fractions, but also requires no artificial weathering of any sample involved.

The pattern of pentacyclic triterpanes as shown in Figure 7 is useful for distinguishing Arabian crudes from crudes of other geographical origin [14]. For example, an unknown spilled oil recovered from Gulf waters clearly had a pattern of pentacyclic triterpanes (see Figure 8) different from those of typical Arabian crudes. Note especially that the relative amounts of C<sub>29</sub> and C<sub>30</sub> hopanes in the unknown oil were the reverse of those in Arabian Light shown in Figure 7.

The ratio of the two C<sub>27</sub> hopanes, designated as Tm and Ts in Figure 7, is specific to each type of Arabian crude. Typical Tm/Ts ratios are shown in Table 5. They have been extremely useful in the identification of Arabian crudes. It is interesting to note from Table 5 that the Tm/Ts ratio of Arabian Medium was 1.7 on 4 September 1982 and 1.9 on 13 December 1982. The difference is significant, as previous work has shown the coefficient of variance of the Tm/Ts ratio for a typical Arabian crude to be about 3.7% (see [5]). The difference actually reflected the fact that Arabian Medium was blended differently on those two days. On 4 September 1982, it was a blend of crudes from four different fields, while on 13 December 1982 it was

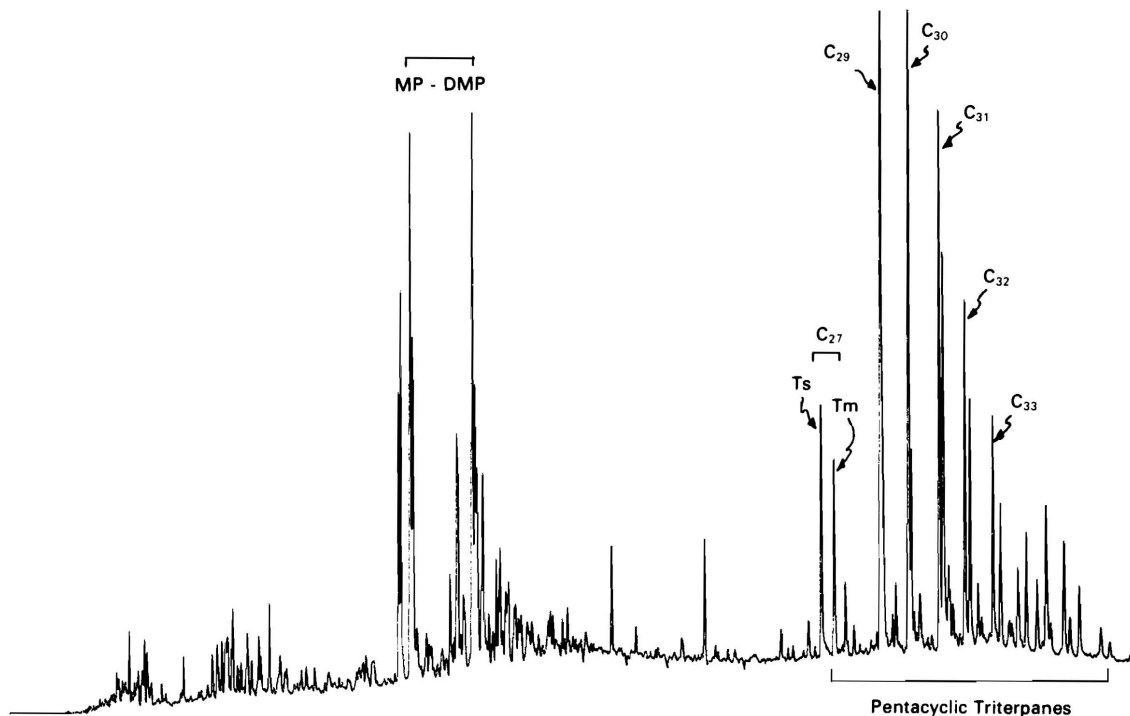


Figure 7.  $m/Z=191$  Ion Chromatogram of a Typical Arabian Light Crude

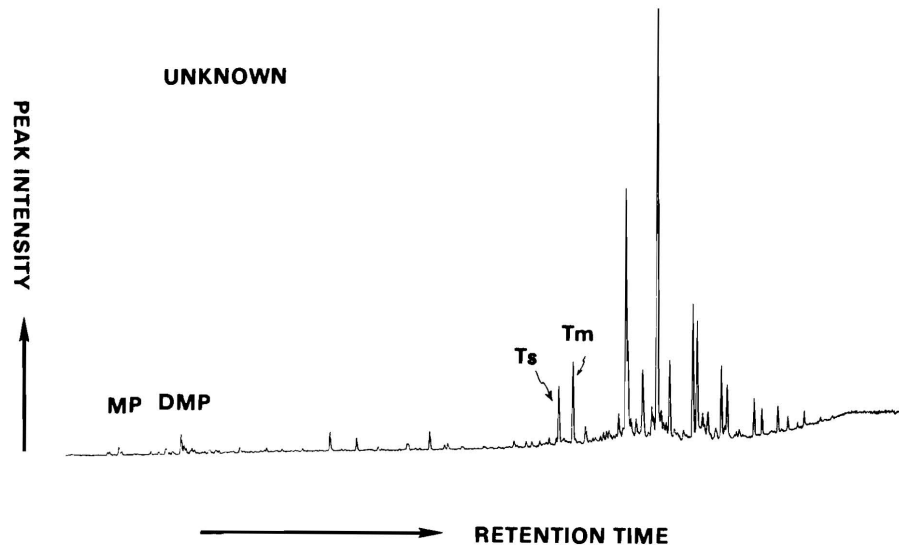


Figure 8.  $m/Z=191$  Ion Chromatogram of an Unknown Oil

a blend of crudes from two different fields. This demonstrates not only the sensitivity of the method in use, but also the importance of having valid reference samples available for comparison.

In addition to pentacyclic triterpanes, other features in  $m/Z=191$  ion chromatograms can also be useful.

For example, the amounts of methyl- and dimethyl-phenanthrenes relative to those of triterpanes are different, and can be characteristic of each type of crude. Comparison of Figure 7 and Figure 8 shows that Arabian crudes have a much higher amount of methylated phenanthrenes than the unknown.

**Table 5. Tm/Ts Ratios of Arabian Crudes**

Crude	Tm/Ts
Extra Light	0.4
Arabian Light	0.8
Arabian Medium, 4 September 1982*	1.7
Arabian Medium, 13 December 1982†	1.9
Arabian Heavy	2.4

\* Blend of crudes from four different fields.

† Blend of crudes from two different fields.

Besides methylated phenanthrenes, the group of small peaks eluted prior to methyl phenanthrenes has been useful in specific instances. For example, Figure 9 shows how this portion of the fingerprint can help match an unknown oil to one of three suspected bilge samples. It is obvious that the reference sample from bilge A matches the unknown much better than the other two bilge samples.

### Monitoring of the Nowruz Spill

The recent spill from Iran's Nowruz field has caused much concern. While the source of the spill is known in this case, it is nevertheless important to ensure that large oil slicks from Nowruz will not cover up other smaller spills that might have occurred.

Virgin Nowruz crude has a much higher specific gravity ( $^{\circ}$ API 21) than Arabian crudes, and has a much higher asphaltene content. It is, however, difficult to distinguish a weathered Nowruz crude from weathered Arabian crudes based on gross physical properties.

Nowruz crude has a significantly higher amount of nickel (52 ppm, wt/wt) and vanadium (130 ppm) than Arabian crudes. Even after severe weathering, Arabian crudes would not be expected to have either nickel or vanadium at these high levels. These metal concentrations, therefore, are useful for rapid screening purposes.

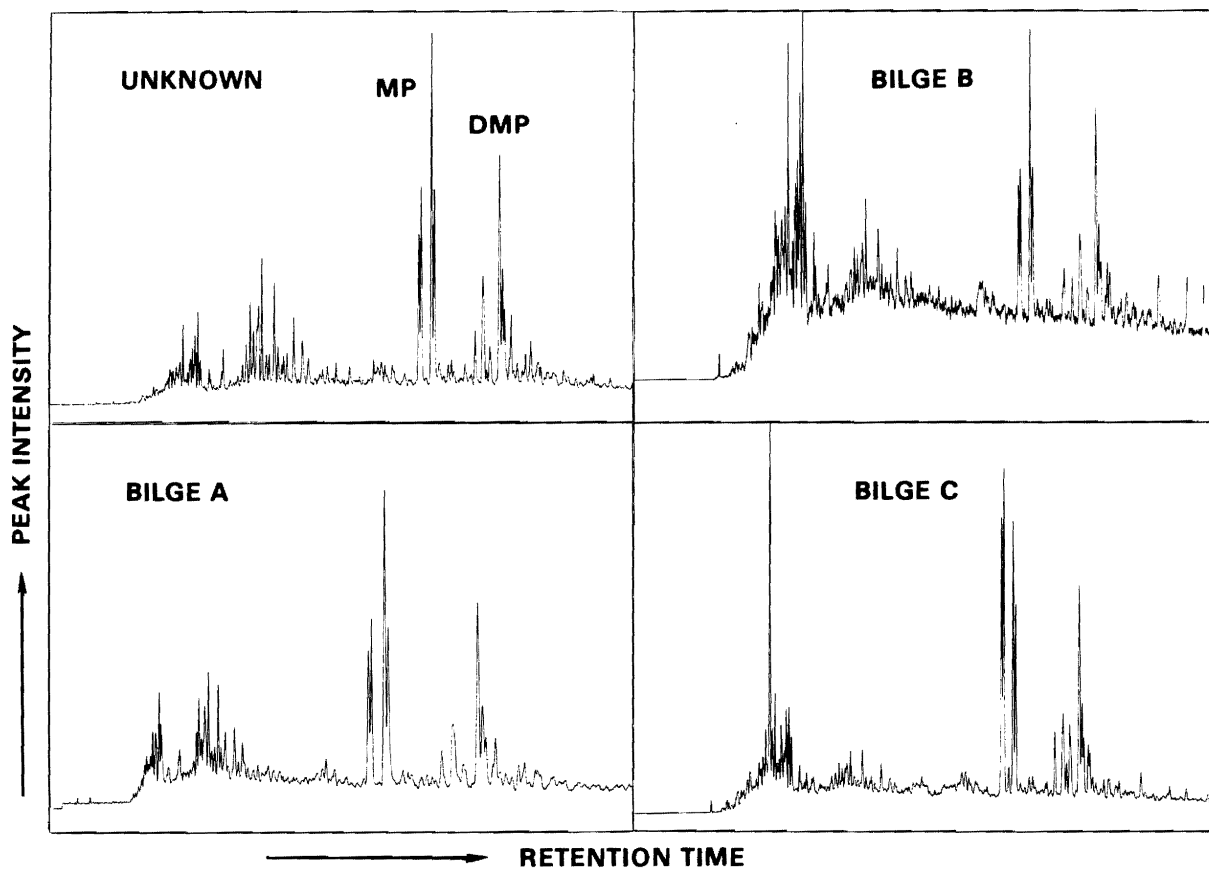


Figure 9. Matching of an Unknown Oil to Three Suspected Bilge Oils

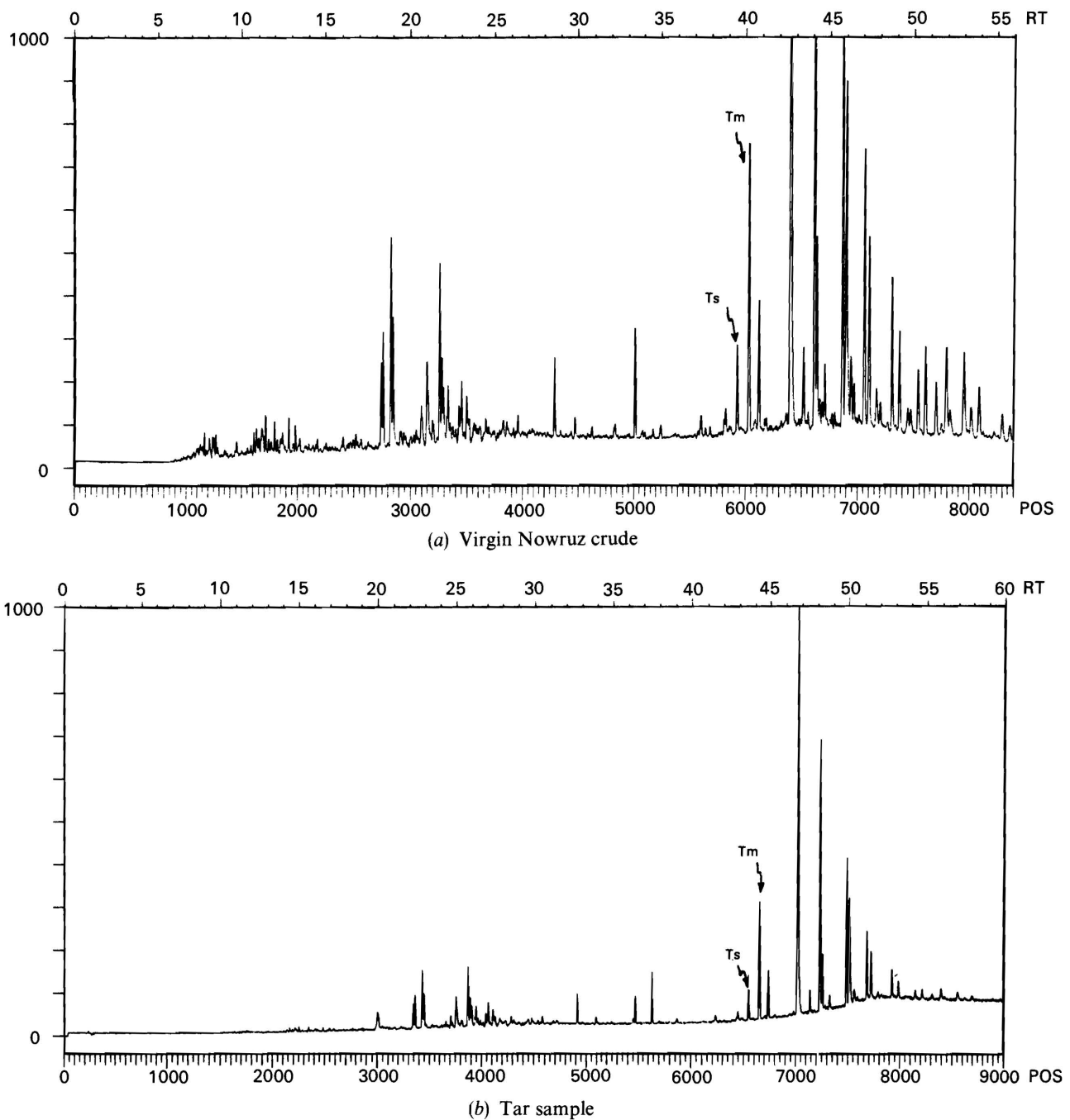


Figure 10.  $m/Z=191$  Ion Chromatograms

Figure 10(b) shows an  $m/Z=191$  ion chromatogram of a spilled sample recovered eight months after the start of the Nowruz spill. It matches well that of a typical Nowruz crude shown in Figure 10(a). The general pattern of pentacyclic triterpanes of a Nowruz crude is quite similar to that of Arabian crudes, except that Nowruz crude has a significantly higher Tm/Ts ratio (3.9) than any of the Arabian crudes (see Table

5). In this case, the unknown tar sample also has a Tm/Ts ratio of 3.9. Previous studies have shown pentacyclic triterpanes were little affected under weathering, even when biodegradation was important [16].

Measurements of selected metals have provided additional data supporting the above identification. The

Table 6. Matching of an Unknown Tar Sample with Nowruz Crude

	Virgin Nowruz	Weathered Nowruz*	Tar Sample
<b>GC/MS</b>			
Tm/Ts	3.9	4.0	3.9
<b>Selected metals (ppm, wt/wt)</b>			
Nickel	52	62	62
Vanadium	130	160	158
<b>GC</b>			
Pristane/ <i>n</i> -C <sub>17</sub>	0.22	0.25	0.34
Phytane/ <i>n</i> -C <sub>18</sub>	0.52	0.51	0.72
Pristane/Phytane	0.44	0.57	0.42
C <sub>29</sub> Hopane/ <i>n</i> -C <sub>30</sub>	0.94	1.64	2.41
C <sub>30</sub> Hopane/ <i>n</i> -C <sub>31</sub>	0.15	0.11	0.17
C <sub>31</sub> Hopane/ <i>n</i> -C <sub>32</sub>	0.27	0.24	0.30

\* Weathered Nowruz crude sample was prepared according to [17].

unknown sample had 62 ppm of nickel and 158 ppm of vanadium, well within the range of those expected of a weathered Nowruz crude. An artificially weathered Nowruz crude obtained by stripping off the light ends under nitrogen [17] had concentrations of nickel and vanadium of 62 and 160 ppm, respectively.

Table 6 summarizes data sets useful in the identification of the unknown sample. Besides Tm/Ts ratios and selected metal contents, several peak ratios extracted from GC measurements are also listed for comparison. In general, the relative amounts of pristane and phytane have been of limited use in distinguishing between Nowruz and Arabian crudes. However, once the origin of the unknown oil is indicated, pristane and phytane ratios may be useful as supporting evidence. The C<sub>29</sub> hopane/*n*-C<sub>30</sub> ratio of Nowruz crude, 0.94, is significantly higher than those of Arabian crudes, and

can be useful in distinguishing the two groups of oil. Similarly, ratios of C<sub>30</sub> hopane/*n*-C<sub>31</sub> and C<sub>31</sub> hopane/*n*-C<sub>32</sub> are significantly more prominent in Nowruz crude than in Arabian crudes. These hopane/*n*-paraffin ratios have not been previously reported for use in oil spill identification work.

Figure 11 shows a typical reconstructed ion chromatogram for the unknown sample. It is important to note that after eight months of weathering the tar sample has suffered no significant amount of biodegradation. This is indicated by the still dominant presence of *n*-paraffins in the chromatogram. The peak ratios listed in Table 6, however, have shown an increase in the tar sample, suggesting the relative amounts of *n*-paraffins have been decreasing. The possible occurrence of some biodegradation in the unknown sample therefore cannot be ruled out.

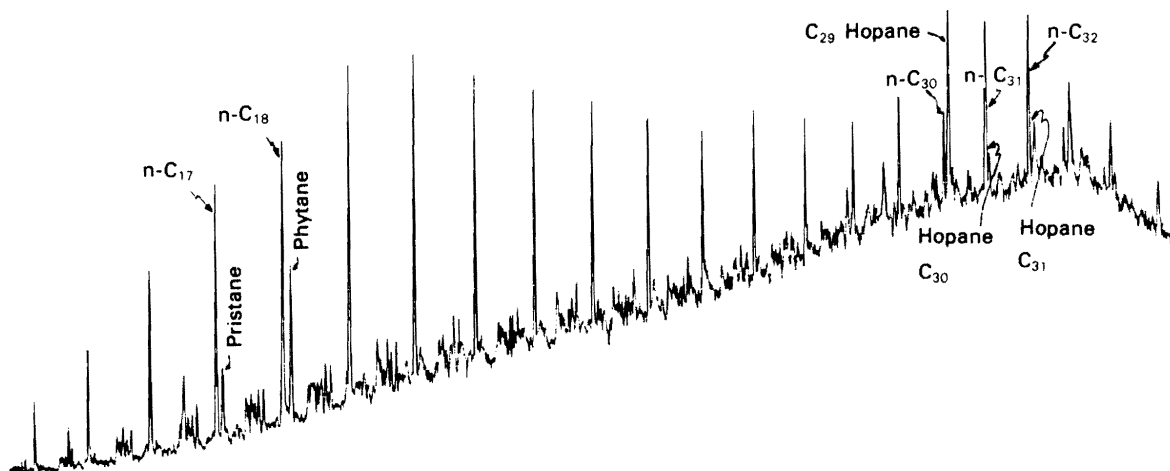


Figure 11. Computer Reconstructed Ion Chromatogram of the Tar Sample

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