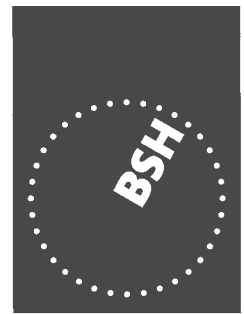


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Characteristic Features of Different Oil Types in Oil Spill Identification



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Author: Gerhard Dahlmann

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Preliminary Remarks

This contribution is based on experience which Bundesamt für Seeschifffahrt und Hydrographie (BSH, Federal Maritime and Hydrographic Agency of Germany) has gained in the identification of oil spills in the past 25 years. Some of the following findings are empirical. They are based on nearly 1,000 cases in which, within the framework of criminal proceedings, oil pollution samples were compared with samples taken from suspected sources of pollution.

The raw data of more than 10,000 gas-chromatograms and mass-chromatograms obtained from different oil spill samples, light fuel oils, heavy fuel oils, lubricating oils, ships' bilge and sludge samples have been stored in a database on a single personal computer. Furthermore, this database includes the corresponding data of 260 crude oils from all over the world.

Characteristic examples thus could be easily chosen, and the various figures of this chapter could be rapidly produced.

The identification scheme itself, given below, has been converted to a computer programme. This programme proved to be valid for all samples in the database.



indicates general remarks, hints, tips, precautions.

Summary

Similarities or dissimilarities in gas chromatograms and mass chromatograms of oils are not easily discernible by non-experts in the field of oil identification. Compound ratios, i.e. relative concentrations of compounds, represent more measurable, objective and defensible means for the verification of results in Oil Spill Identification. A European Standard for Oil Spill Identification is being prepared by CEN Technical Board's Task Force 120 in order to improve existing methods (Nordtest Chem001, ASTM D 3415) especially in this regard.

Based on the revision of the Nordtest-procedure (L.-G. Faksness et. al, SINTEF-Report STF66 A02028, May 2002, <http://www.nordtest.org/register/techn/tlibrary/tec498.pdf>), a set of 23 parameters ("useful minimum set") for comparing two oil samples is proposed. However, this set of parameters has been derived from crude oil research and is based on geochemical findings. In the case of oil products involved in an oil spill, certain parameters simply are not present in the sample, or their meaning, and thus their value for oil identification, has been changed by the production process. But oil products, mainly in form of waste oil, are the major source of oil pollution in all areas of higher shipping traffic. Therefore, guidance is given on how to handle the proposed parameters with respect to the different characteristics of oil types. The identification of the type of oil involved in an oil spill thus is essential, and a step-by-step procedure is provided for identifying the oil type, even in (highly) weathered samples.

But even in a comparison of two crude oil samples, some of the parameters may be much more important than others. Their value is highly dependent on the circumstances of each particular case. Some examples are shown.

1 Introduction

In this contribution, only a rough categorization of oil is made into

- light fuel oil
- lubricating oil
- heavy fuel oil
- mixtures (waste oil such as bilge oil, sludge, slops)
- crude oil

in the context of Oil Spill Identification.

More detailed information about petroleum and petroleum products can be found in literature. Valuable information about product specifications and production techniques is also available on the Internet. A detailed description of oil types, including product descriptions, production techniques, uses as well as physical and chemical properties is given in a series of product dossiers (General Interest Reports) prepared by CONCAWE, Brussels. Most of them (e.g. 98/109 Heavy Fuel Oils, 95/107 Gas Oils, 97/108 Lubricating Oils) are freely downloadable from their server www.concawe.be.

In Oil Spill Identification by chemical analysis, the identification of the type of oil in a sample is essential for several reasons:

- If the origin of an oil pollution is unknown, the investigating authorities must be advised on where to find a possible source. In case of a “mystery” spill, the mere differentiation between pure, unused products or crude oil and waste oil (bilge residues, sludge, slops) is a valuable result. Oils must be identified rapidly in such cases because the chances of identifying sources generally decrease with time.
- The meaning of analytical results, i.e. their contribution to the overall evidence in criminal proceedings, depends very much on the types of oil that are involved in oil spills. Depending on these types, the search can be more or less narrowed down to a few possible sources, or even a single one.
- In court trials, the differentiation between pure products and waste oil may be highly important because it allows conclusions as to the cause of an oil discharge (technical failure, inadvertence, intention).

It is reasonable to expect the responsible analyst to state with fair certainty that either a light fuel oil, lubricating oil, heavy fuel oil, waste oil or crude oil was involved in a particular oil

spill. The analyst may also be able to indicate the general area where a crude oil originated, e.g. North Sea, Middle East, Nigeria, etc.

But even if an oil spill sample is compared with a sample from a suspected source, the oil type must be known because the chemical methodology must be adapted to the peculiarities of different types of oil. This means that different analytical data must be chosen for sample comparison:

In pure light fuels, for example, nearly the whole range of biomarkers are missing. Therefore, only a very limited set of parameters can be used in a comparison of two light fuel oil samples. By contrast, higher-boiling lubricating oils have been found to be rich in biomarkers while most aromatics are missing.

The aromatic hydrocarbons present in the most common types of heavy fuel oil result primarily from production processes (cracking) at the refineries. As identical processes lead to the same, or at least very similar, clusters of aromatic compounds, their value in the discrimination of different HFO samples is rather limited.

Compounds or compound relations in the range of biomarkers may be very characteristic or even “unique” in the case of an unknown crude oil pollution. Examples are:

- 28-bisnorhopane
- oleanane
- gammacerane.

But their significance strongly depends on the circumstances of the particular case. Generally, their rapid recognition may save resources, in case they are present in the spill sample but not in the comparison sample. On the other hand, their presence in both samples may indicate a much stronger connection between these samples than other compounds.



The most suitable strategy for treating analytical data in Oil Spill Identification is different from case to case. Nevertheless, some general guidelines can be given with regard to different oil types and their occurrence and behaviour in the aquatic environment. The more guidance is provided to analysts, the more effective their efforts will be.

Oil identification means, in fact, oil discrimination: generally, differences have to be found or, if there are no differences between two oil samples, they must be considered identical. However, when comparing oil spill samples with samples from suspected sources, it must be taken into account that the composition of an oil changes as soon as it is released into the environment (“weathering” of oil). This means that only those data can be used in the

evaluation of results that are derived from stable compounds which are not affected by weathering processes. In addition, all measurements are subject to an analytical error. Thus, in order to be able to decide whether the data of two samples differ significantly or not, the analytical error of the individual measurement must be known.



When objective numbers, representing compound relations, are used for result verification in Oil Spill Identification, quality assurance plays the dominant role. The analytical error of each parameter must be determined statistically, and it must be ensured that the single measurements are randomly distributed about the mean.

2 Methodology

The method commonly used to identify oil types in Oil Spill Identification is GC screening. GC screening reveals the boiling range of oils, and oil types are – in a first approximation- characterized by their boiling ranges. However, additional GC/MS data are required in doubtful cases. GC/MS is used in any way when samples have to be compared in more detail.

Oil types can be identified using the step-by-step method given below, i.e. by going through paragraphs 2.1 to 2.5, and in many cases a quick look at the screening results (GCs) should be sufficient to answer the question as to whether an unknown sample belongs to a specific type or not.

Changes of spilled oil due to weathering have been particularly taken into account in this scheme, so that it should be possible to identify the type of an oil even in (highly) weathered samples.

2.1 Light fuel oil (gas oil, diesel, fuel No 2)

The vast majority of commonly used light fuel oils consist of “straight-run” gas oils or vacuum gas oils, i.e. products from atmospheric or vacuum crude oil distillation. Light fuel oil thus can be normally regarded as the mid-boiling cut of crude oil (“middle distillate”).

Light fuel oil is ubiquitously used as bunker oil in ships of all sizes, from small pleasure craft to the biggest container ships or tankers. But the origin of light fuel oil may also be land based sources such as storage tanks or diesel engines.

Therefore, the “identity” (or “match”) found between a spill sample and a comparison sample often is not very meaningful because there may be many possible sources of a light fuel oil spill. For example, a particular batch of light fuel oil from a bunker station supplies many

ships, and it is often difficult or even impossible to take samples from all potential sources. In such cases, the “identity” between a spill sample and a sample from a possible source may be virtually meaningless, the only certainty being that the comparison sample has actually been taken from one of the many potential sources.

Because of these limitations, close cooperation with the prosecuting authorities is advisable. After the main characteristics of the light fuel oil have been determined by GC screening (see below) in-depth analyses should only be performed if they are justified by the particular circumstances of the case, in order to save costs and laboratory resources.

Once released onto the water surface, light fuel oils spread very rapidly. In open waters, very large and thin films will form. The large film surface may lead to rapid, severe weathering of the oil.

Because of the thin oil film, only small sample volumes can be obtained from such spills, and there is a high risk of sample contamination by organic pollutants or natural, biogenic compounds from the surrounding water.

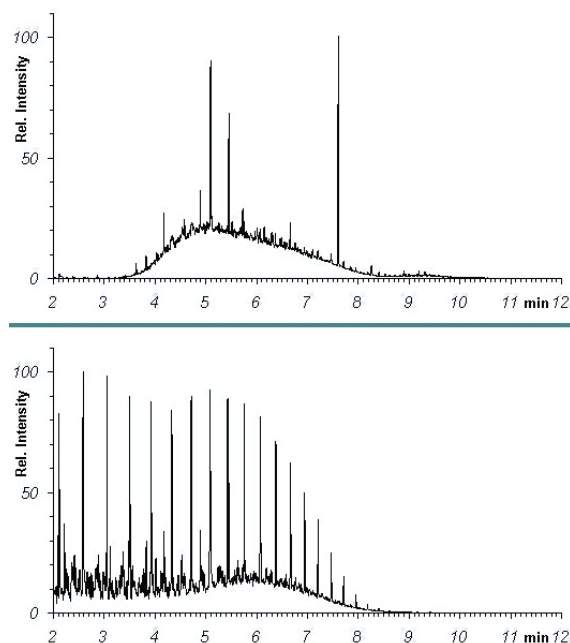


Fig. 1: Gas chromatograms of a heavily weathered light fuel oil (spill sample, above) and the original product (below). Besides strong evaporation which took place in the spill, all of the n-alkanes have been removed by bacterial degradation. Compounds originating from the surrounding water are also present in the spill sample.

2.1.1 Analysis

2.1.1.1 GC screening

Light fuel oil is easily detected in GC screening because of its limited boiling range: compounds end at about n-C₂₅. This n-alkane has a boiling point of about 400 °C (Fig. 2).

Accordingly, the possibilities of comparing two light fuel oil samples are rather limited. Weathering effects, which are quite common (see above), are even more severe in this case because they lead to further limitations in sample comparison.

Light fuel oil samples can be differentiated by the shapes of the envelopes of the n-alkanes, the shapes of the envelopes of the “unresolved complex mixture” (UCM), which mainly consists of naphthenes (cyclo-alkanes), and their C₁₇/pristane, C₁₈/phytane, and pristane/phytane ratios (Fig. 2 and Fig. 3).

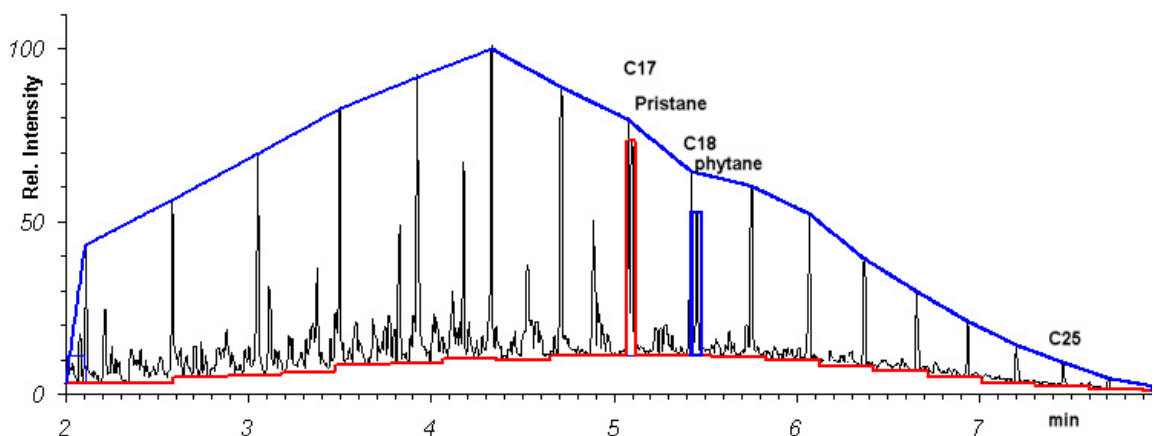


Fig. 2: Gas-chromatogram of a typical light fuel oil. The envelopes of the n-alkanes and the UCM, C₁₇, pristane, C₁₈, phytane and C₂₅ (computer calculations) are shown.



Given here is the general evaluation of the GC screening results of oil samples (“first look”). Further peaks appearing in between the homologues series of the n-alkanes, such as nor-pristane, further isoprenoids and pronounced naphthenes, might provide further information if present.

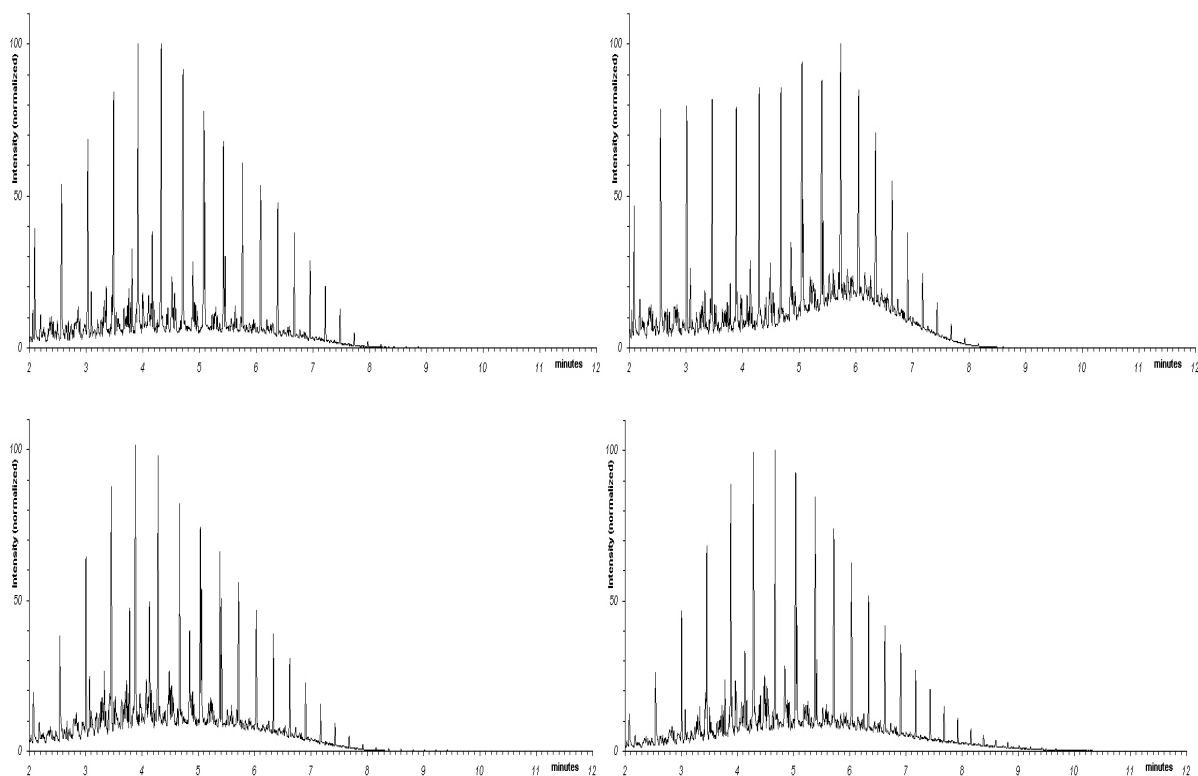


Fig. 3: Gas-chromatograms of light fuel samples showing differences in the parameters given in Fig. 2 (pristane and phytane are found between 5 and 5,5 minutes).

2.1.1.2 GC-MS analysis (alternative parameters)

As higher-boiling biomarkers are rarely present, there is no other way of comparing two light fuel oil samples in Oil Spill Identification than to go deeper into the groups of the remaining aromatic hydrocarbons and sulphur-containing aromatic compounds.

Light fuel oil is subject to rapid weathering once it has been released into the environment. Therefore, it would not be appropriate to base general guidelines for the comparison of two light fuel oil samples on the lower-boiling compounds (such as decalines or low-boiling naphthalenes or thiophenes). Experience has shown that compounds from the higher-boiling end, i.e. the region between n-C₁₉ and n-C₂₅ (boiling range around 320 °C to 400 °C), are more generally suitable for light fuel oil comparisons (Fig. 4).

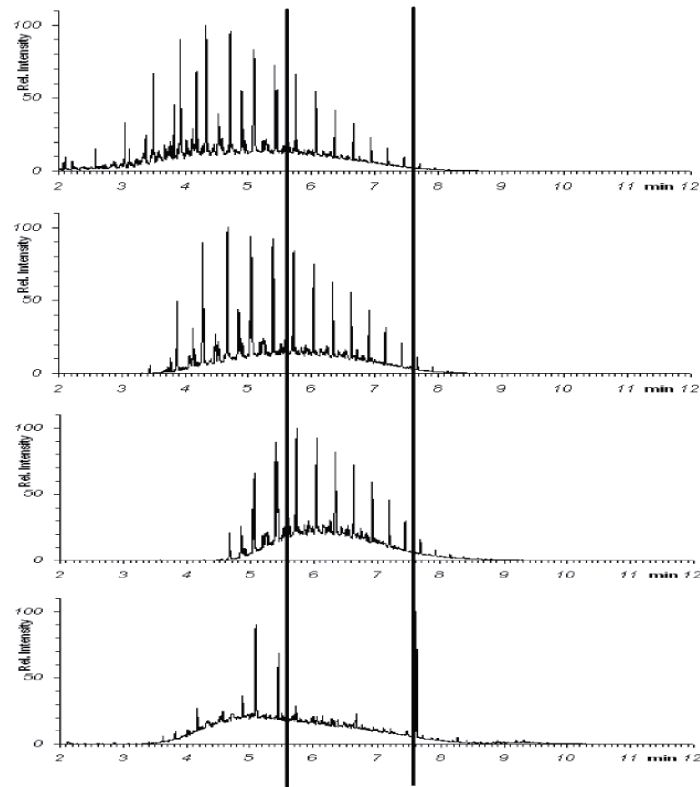


Fig. 4: Spill samples from different light fuel spills showing different degrees of weathering. The boiling range of about 320 to 400 °C is indicated by two lines (see text).

The compound cluster given by the mass 216 has proved to be relatively stable and especially suitable for comparing light fuel oil samples (Fig. 5).

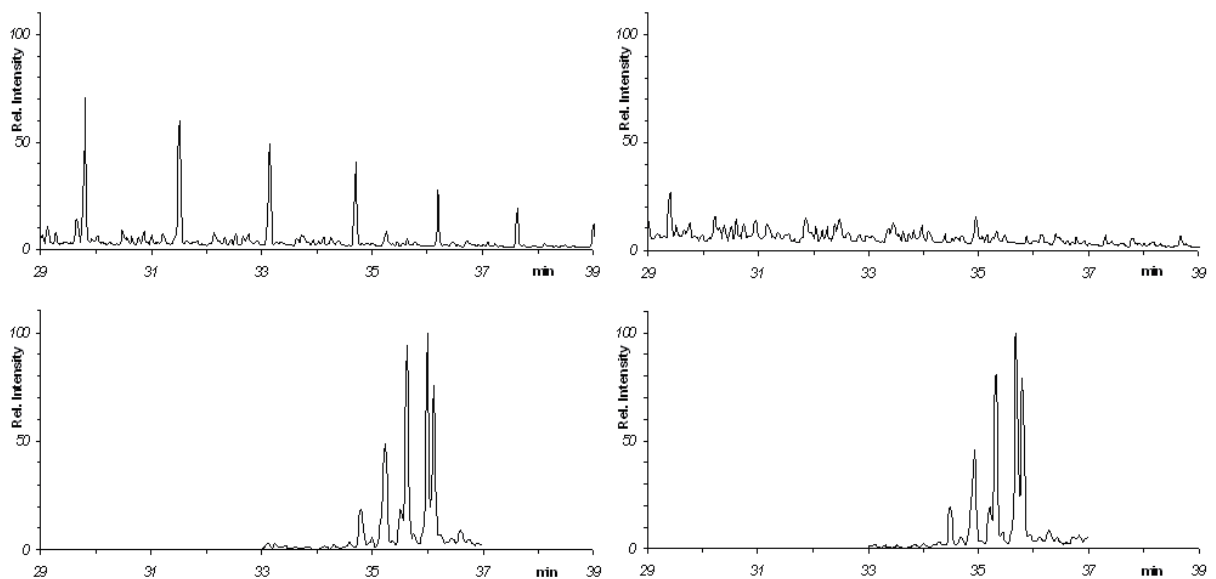


Fig. 5: Compound cluster of aromatic compounds of mass 216 (below) in a fresh light fuel (left) and the same oil heavily weathered (right). Above: mass-fragment 85.

This cluster represents mainly six compounds from different compound classes of aromatic hydrocarbons (Fig. 6). It is, therefore, much more suitable for discriminating between oils than clusters representing only the isomers of a compound within a single compound class.

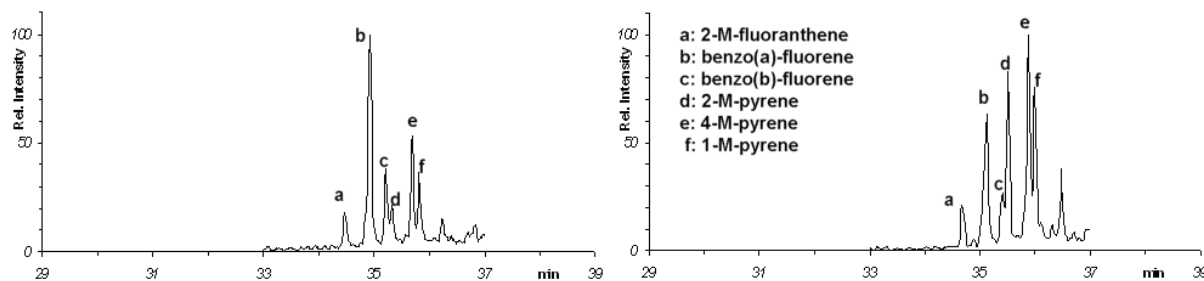


Fig. 6: Mass-chromatograms of mass 216 of two different samples and peak identification.

By normalizing the peak heights on one of these peaks, e.g. on peak “e” (4-M-pyrene), which is often the highest peak of this cluster, a set of five parameters (compound ratios) can be calculated.



In general, compound ratios for verification of the visual findings should be produced by dividing (normalizing) peaks on a peak that is present within the same mass chromatogram and within a narrow boiling range. Variations due to instabilities on the mass spectrometric side as well as variations due to possible compound discriminations on the gas chromatographic side are thus minimized. A high reproducibility is achieved and the resulting compound ratios are even comparable if measurements are made on different instruments (e.g. in interlaboratory comparisons).

In the same boiling region, further masses exist which represent different compound classes within the same mass chromatogram. In the mass-chromatograms of mass 234 and mass 240 even a comparison of aromatics with aromatic sulfur compounds is possible. Here, higher-methylated phenanthrenes and M-benzo-naphtho-thiophenes (mass 234) and higher-methylated naphthalenes and higher methylated dibenzo-thiophenes (mass 240) are indicated (Fig. 7).

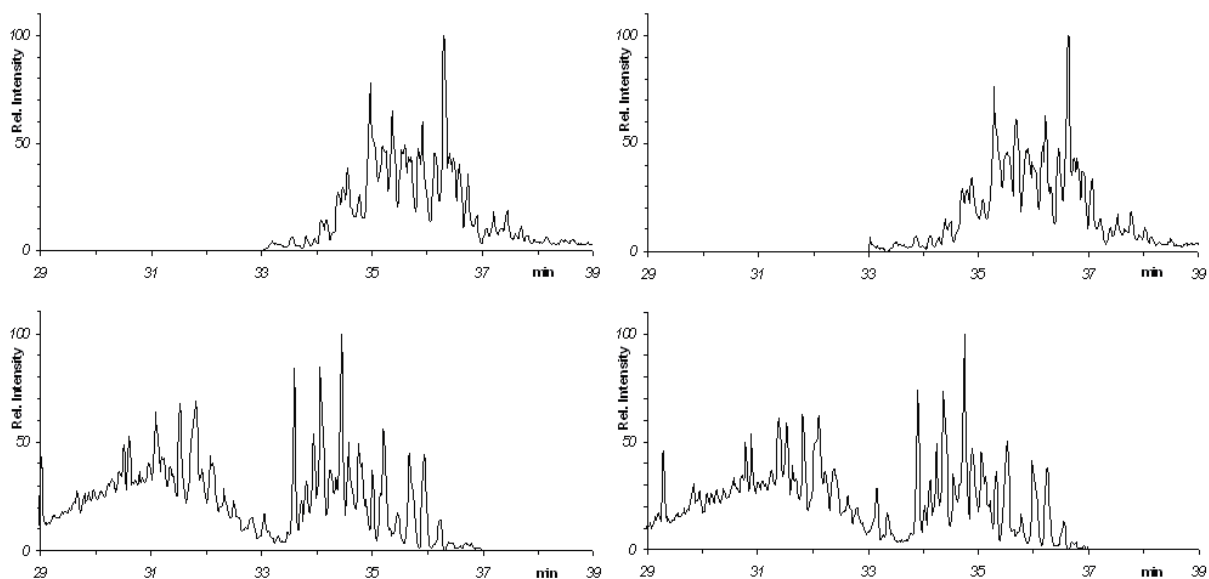


Fig. 7: Comparison of mass-chromatograms 234 (above) and 240 of a fresh (left) and a highly weathered light fuel oil (same samples as in Fig. 5).

Because of the complexity of these chromatograms, one rarely finds any compounds that are suitable for calculating ratios. But, as always when complexity increases, much more information is revealed to the human eye than can be converted into suitable numbers.

Depending on the individual case, i.e. on the particular type of light fuel oil in the spill sample and its degree of weathering, additional parameters that are useful for the verification of results can be found. In the mass chromatogram of mass 220, for example, TM-phenanthrenes appear together with benzo-naphtho-thiophene.

In case the spill sample is only slightly weathered, mass 184 allows a direct comparison of tetra-M-naphthalenes with dibenzo-thiophene. But it must be kept in mind here that this particular relation may have been influenced not only by evaporation of the lower-boiling naphthalenes but also by possible solution of dibenzo-thiophene in water.

2.2 Lubricating oil

Commonly used lubricating oils consist mainly of the residues from atmospheric crude oil distillation, which are further distilled under vacuum conditions to produce a range of vacuum distillates. Solvent extraction and/or hydrofining are then used to increase the viscosity index, enhance the colour and convert undesirable chemical structures such as unsaturated hydrocarbons and aromatics to less chemically reactive species. Finally, solvent dewaxing is

used to reduce the wax content of the base oils so as to prevent wax crystals from forming within the normal working temperature range of the lubricant.

Higher viscosity grades of lubricating oils are produced by solvent deasphalting of the vacuum residue of crude oil with liquid propane. The liquid propane precipitates the resins and asphaltenes to produce a deasphalted residual oil. This is then further treated by solvent extraction and/or hydrogenation to reduce the aromatics content. Residual oils are commonly used in the heavier grades of lubricant, for example, marine diesel engine oils and heavy gear oils.

In this paragraph, no differentiation is made between lubricating oil and hydraulic oil because these oils contain the same base oils.

Pure, unused lubricating oil has been found only in very rare cases of oil pollution because lubricating oil is a valuable, expensive product. On the other hand, it is normal practice on board ships to first collect wastes from all kinds of oil in collecting tanks (sludge tanks, bilge oil tanks). Thus, lubricating oil is often found as part of pollution by waste oil.

The following description, therefore, focuses mainly on possibilities of identifying lubricating oil in waste oil. The presence of lubricating oil together with bunker oil in an oil spill sample is strong evidence of waste oil having been discharged.

2.2.1 Analysis

2.2.1.1 GC screening

Like light fuel oil, lubricating oil is easily detected in GC screening because of its limited boiling range. But in this case, the higher boiling region is covered. N-alkanes are only present in traces, and the whole oil forms a relative narrow UCM in the chromatogram. The boiling range covered is determined by the viscosity of the oil. Fig. 8 shows gas chromatograms of base oils (“base stocks”) with a kinematic viscosity of 90, 130, 150 and 600, respectively (cSt at 40 °C, upper to lower and left to right).

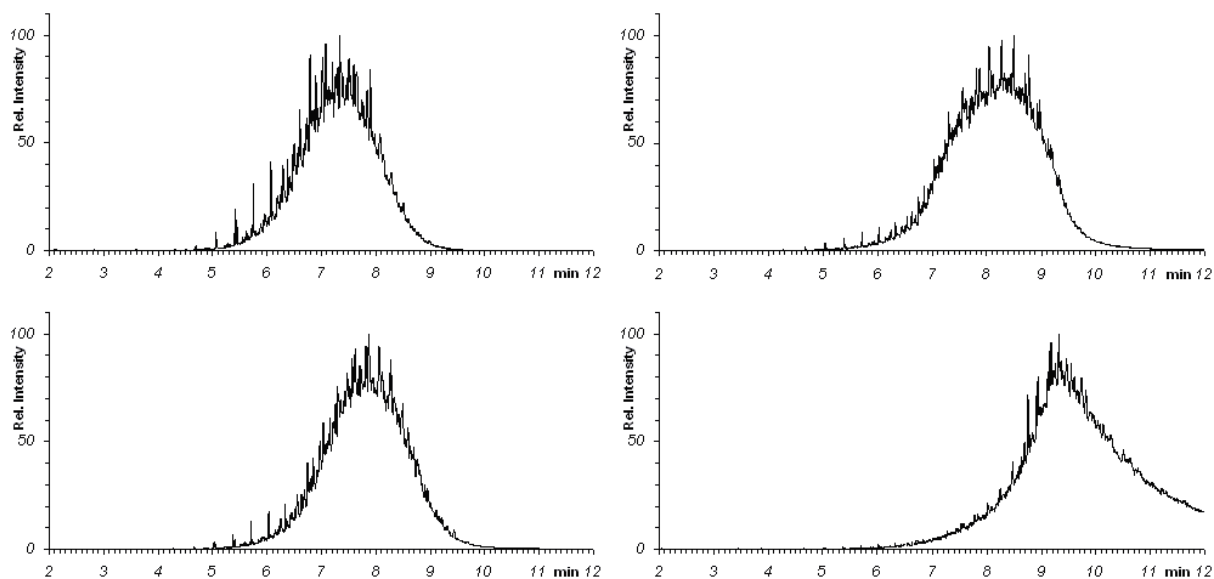


Fig. 8: Gas-chromatograms of different lubricating oils.

2.2.1.2 GC-MS analysis

Lubricating oils have been found to be rich in biomarker compounds. But depending on the boiling range covered, different biomarkers are present in different proportions. Thus, the relation of compounds (or compound ratios) is significantly influenced by the boiling cut of the particular lubricating oil concerned (Fig. 9).

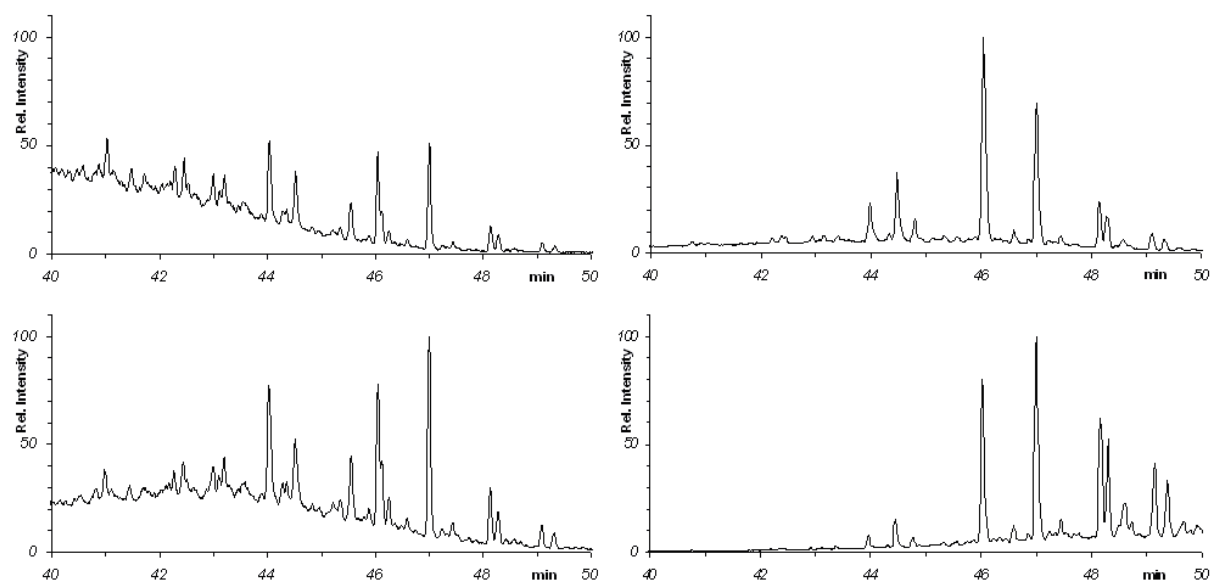


Fig. 9: Hopanes (mass fragment 191) of different lubricating oils (same oils as in Fig. 8).

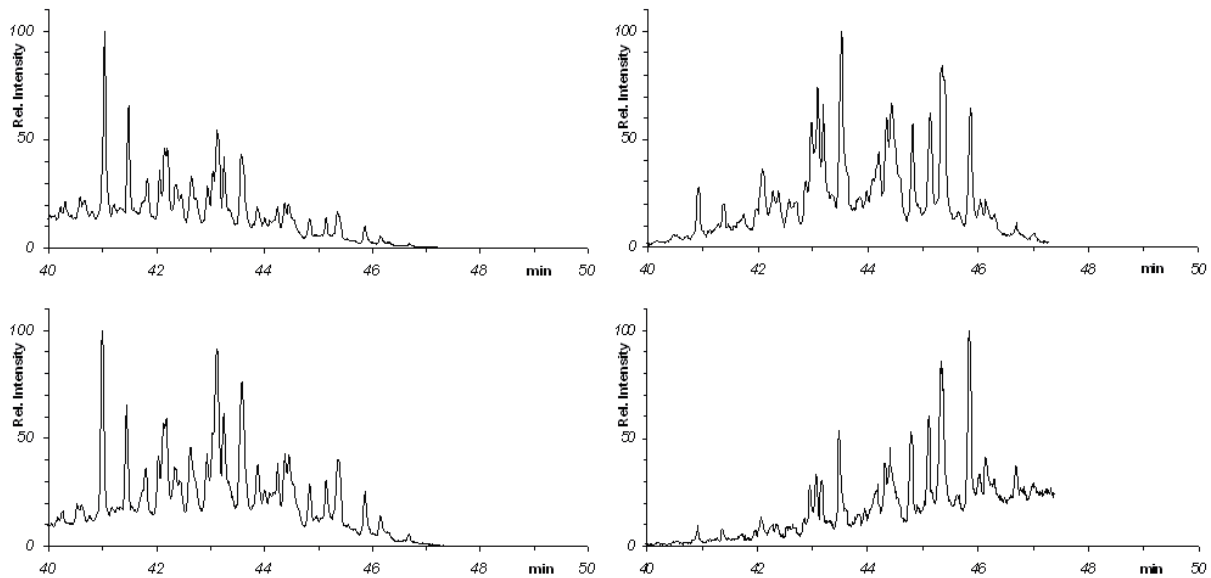


Fig. 10: Steranes (mass-fragment 217) of different lubricating oils (same oils as in Fig. 8).

Lower-boiling biomarkers such as the two C_{27} -hopanes (Ts and Tm) and the two lower boiling diasteranes thus are more pronounced in lower-viscous lubricating oils, whereas the higher-boiling biomarkers are more pronounced in higher-viscous oils.

Especially at this point, it becomes clear that the original meaning and the specificity of the pristine biomarker relations in crude oils are lost totally when oil products or product mixtures (waste oils, see 2.4) are considered. The production (and or mixing) process plays the dominant role here. As can be seen from Figure 10, for example, the important role of the diasterane/regular-sterane relation in crude oils, which is mainly a source indicator but influenced also by maturity, is definitely no longer valid in these cases. This relation is by far much more determined by the (viscosity-) type of the lubricating oil involved.

One of the most significant findings for characterizing oil products is that aromatic steranes (mass fragment 231) are not present in commonly used lubricating oils (Fig. 11 and Fig. 12, see note).

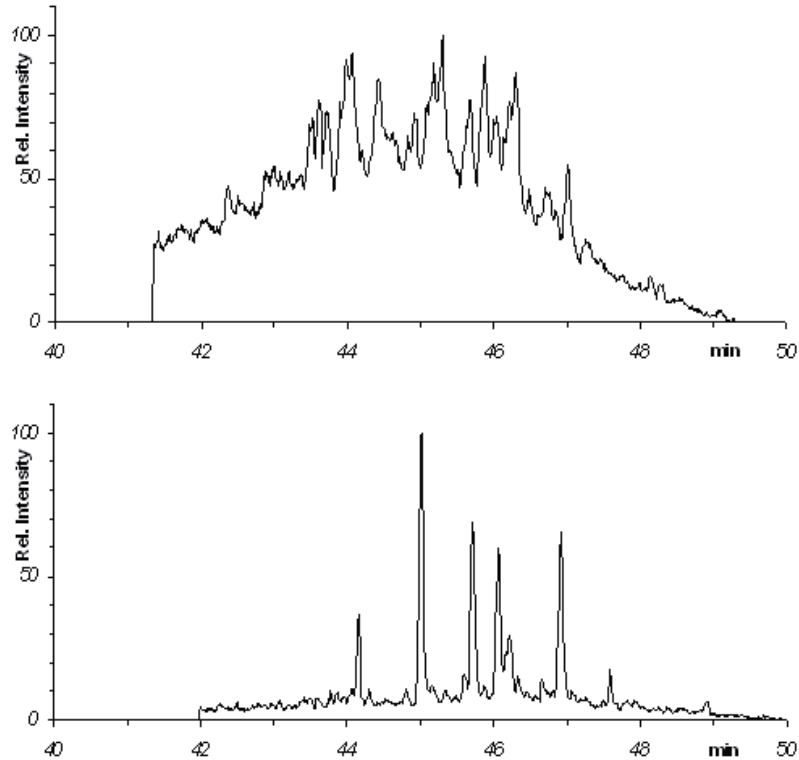


Fig. 11: Mass chromatograms of mass 231. Typical lubricating oil (same as in Fig. 8 upper right) compared to a typical crude oil (Oseberg crude) below.

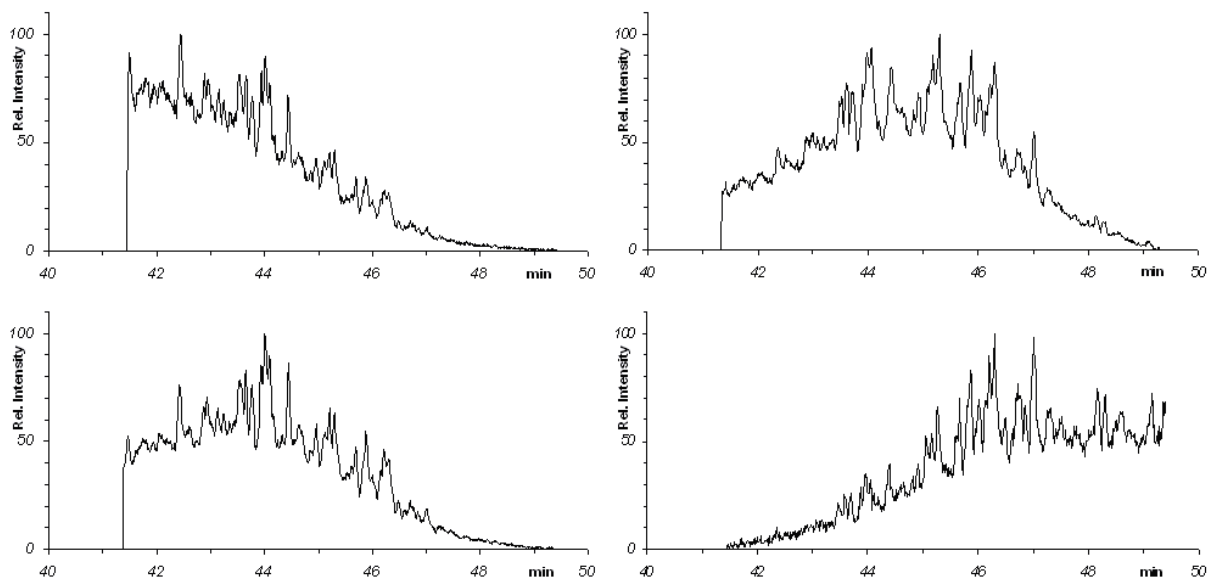


Fig. 12: Mass chromatograms of mass 231 of lubricating oils (same oils as in Fig. 8).



The lack of aromatic steranes in lubricating oils is an empirical finding: aromatic steranes have never been observed in any lubricating oil samples that have been analyzed for oil spill identification. An explanation could be that these compounds are removed from commonly used lubricating oils in de-aromatization processes. The clusters discernible in the 231-chromatogram probably represent 4α -M-steranes (mass fragment 231 caused by an additional methyl group connected to the A-ring of the 217-mass fragment).

Consequently, aromatic steranes are not suitable for sample comparison in cases where pure lubricating oil is found in an oil spill.

But the same applies to light fuel oil/lubricating oil mixtures, i.e. waste oil which is typically present in the bilges of smaller ships. Instead, the finding that aromatic steranes are not present in lubricating oil is particularly useful even in the recognition of waste oil (bilge oil, sludge, see Paragraph 2.4).

2.3 Heavy fuel oil (HFO, Bunker C, Fuel No 6)

Heavy fuel oils are blended products derived from the residues of various refinery distillation and cracking processes. The term Intermediate Fuel Oil (IFO) is often used in this respect. They are highly viscous liquids with a characteristic odour and black colour (black oil) which require heating for storage and combustion. Heavy fuel oils are used in medium to large industrial plants, marine applications and power stations in combustion equipment such as boilers, furnaces, and diesel engines.

Heavy fuel oil consists primarily of residues from the distillation and cracking units of refineries. Historically, fuel oils have been based on residues from the atmospheric distillation column and were also called straight-run fuels. However, rising demand for transportation fuels such as gasoline, kerosine and diesel has increased the value of atmospheric residues as a feedstock in vacuum distillation and cracking processes. As a consequence, most heavy fuel oils are currently based on residues from vacuum distillation units and from thermal and catalytic cracking operations.

Different grades of HFOs are expressed by numbers representing their kinematic viscosity in cSt at 50 °C. The main grades are IFO30, IFO180 and IFO380. Although there may be exceptions, the heavier-grade IFO380 is used as bunker oil by the vast majority of ships over 5,000 tons gross tonnage.

The use of heavy fuel oil as bunker oil on ships has been found to be the main cause of chronic oil pollution:

Heavy fuel oil has to be cleaned of solid contaminants and water on board the vessel before being used (fuel oil separation by centrifuging). The solid contaminants are mainly residual sediments, refinery catalysts and high-boiling asphaltenes and resins. Thus, large amounts of residues and residual oil have to be stored on board until they can be discharged to harbour reception facilities. According to a worldwide study conducted by the International Maritime

Organization in the late 80s, such residues account for about 3% of the originally bunkered fuel oil. Generally, refinery residues appear where they are least usable, i.e. on board ships. Obviously, these residues are often illegally discharged into the sea.

2.3.1 Analysis

As HFOs are blended products, the contents of different compound classes in HFOs may differ widely.



HFOs contain high-boiling compounds which are not analyzable by the GC technique. Therefore, in order to prevent contamination and pollution of the injection system, a sample clean-up is advisable whenever HFO is involved. As a general rule, the extracts of all black samples (“black oil”) should be treated in this way before injecting them into the instruments.

As variable parts of HFO samples thus are not covered by the analysis, it may be hardly possible to differentiate between higher grades of HFOs by application of GC techniques.

2.3.1.1 GC screening

Breaking of the bonds of high-molecular crude oil compounds produces primarily olefins and aromatic hydrocarbons. While olefins react rapidly and disappear, aromatics are stable and remain present.

Therefore, a high content of aromatic hydrocarbons in an oil sample is a strong indicator of a heavy fuel oil (Fig. 13 and 14). However, depending on the different products used for blending and on their amounts, the composition of HFOs may vary widely (Fig. 15). GC-MS analysis thus may have to be performed in order to properly identify the product.

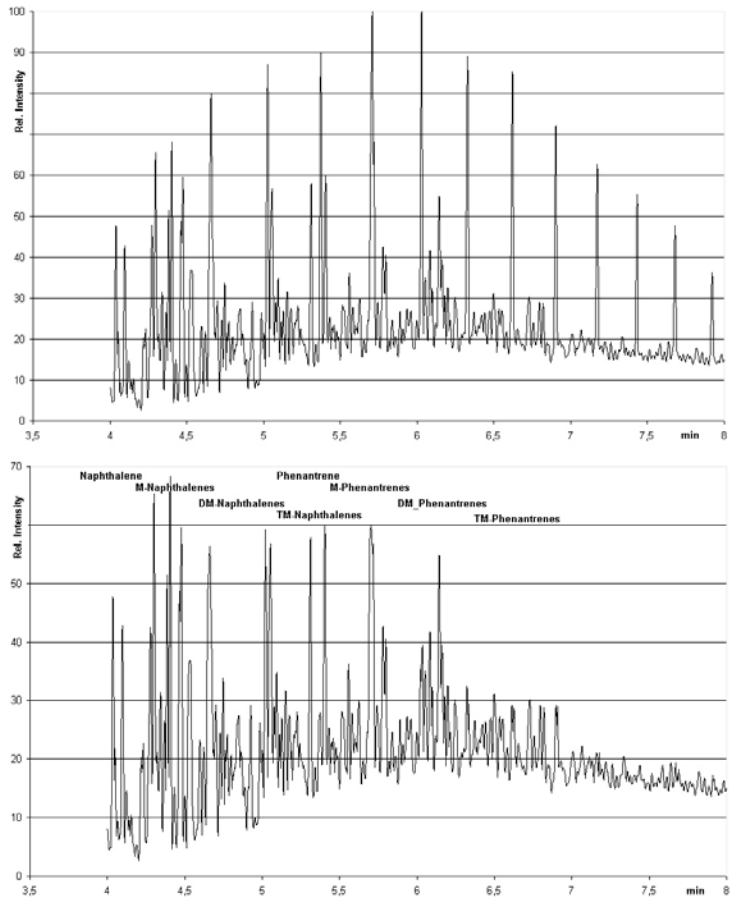


Fig. 13: Upper chromatogram: typical HFO; lower chromatogram: same oil, n-alkanes (virtually) removed and 2- and 3-ring aromatics indicated.

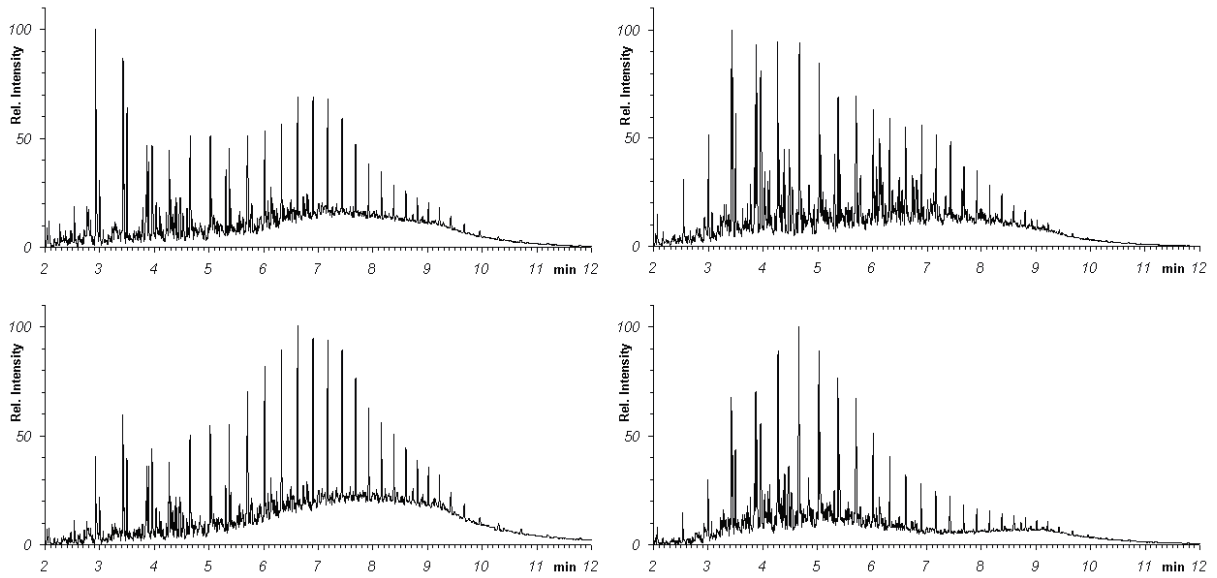


Fig. 14: Gas chromatograms of different HFOs .

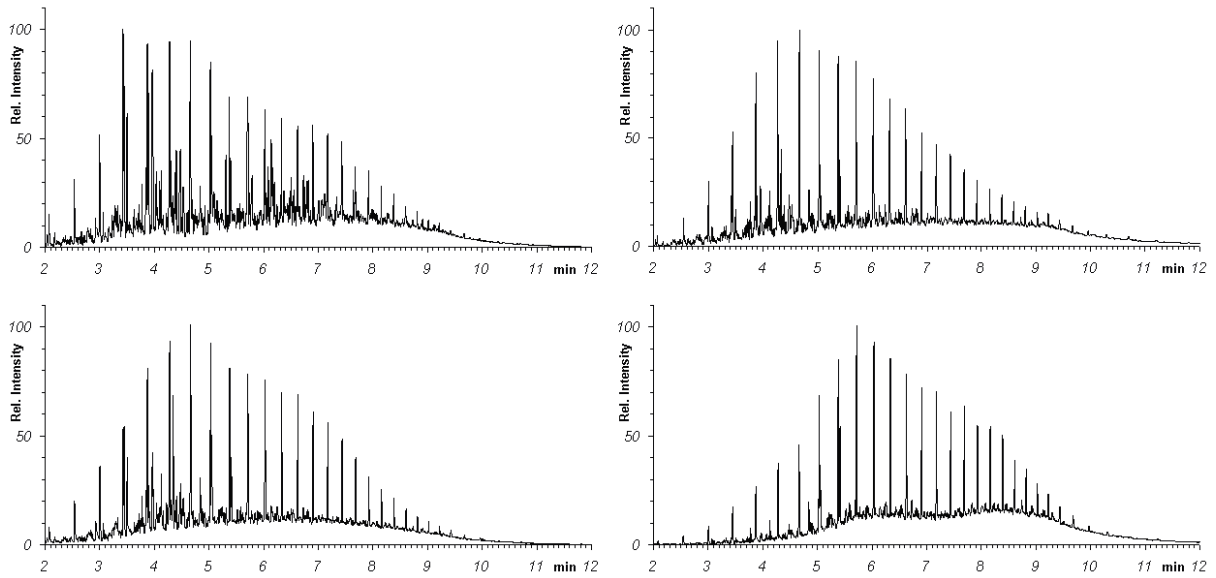


Fig. 15: GCs of HFO samples containing different amounts of aromatics from cracking processes (aromatics are hardly discernible in the upper right sample - and not discernible in the lower right sample).

Since HFOs contain different amounts of high-boiling compounds, which cannot pass the GC (see 2.3.1 Analysis), proper categorization of higher HFO grades by means of GC techniques is hardly possible. The IFO380 in Figure 16 (upper left chromatogram), can hardly be differentiated from the IFO180 (upper right sample). As a very vague rule, it can be stated that higher-boiling grades are often recognized by a higher and broader UCM in the high-boiling region. The two IFO30 (lower samples) can be easily distinguished from such oils because of their limited boiling range.

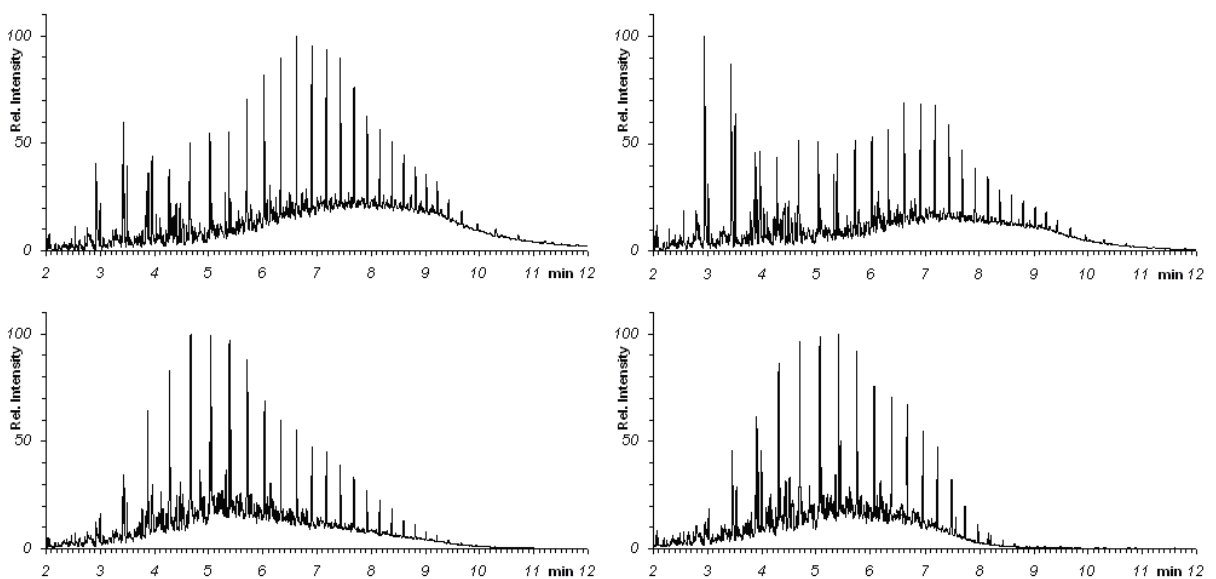


Fig. 16: Gas-chromatograms of IFO380 (upper left), IFO180 (upper right) and two IFO30 bunker oils (below).

2.3.1.2 GC-MS analysis

Cracking processes lead to distinct clusters of isomers. The cluster of isomeric M-phenanthrenes, for example, is typical of the high-temperature production of aromatics (Figure 17). It is generally found, e.g., in soot particles of diesel exhaust gases. Retene is not present (Figure 18) because aromatics with slightly longer side chains are not produced in higher-temperature processes.

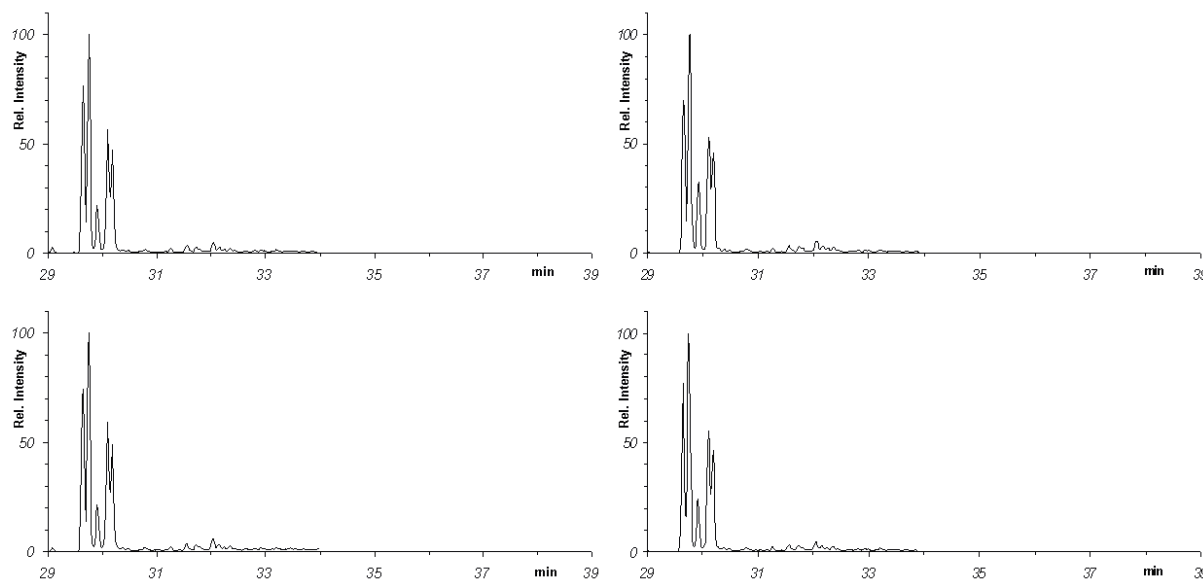


Fig. 17: Mass-chromatograms of mass 192 (M-phenanthrenes, M-anthracene) of HFOs (same samples as in Fig. 14).

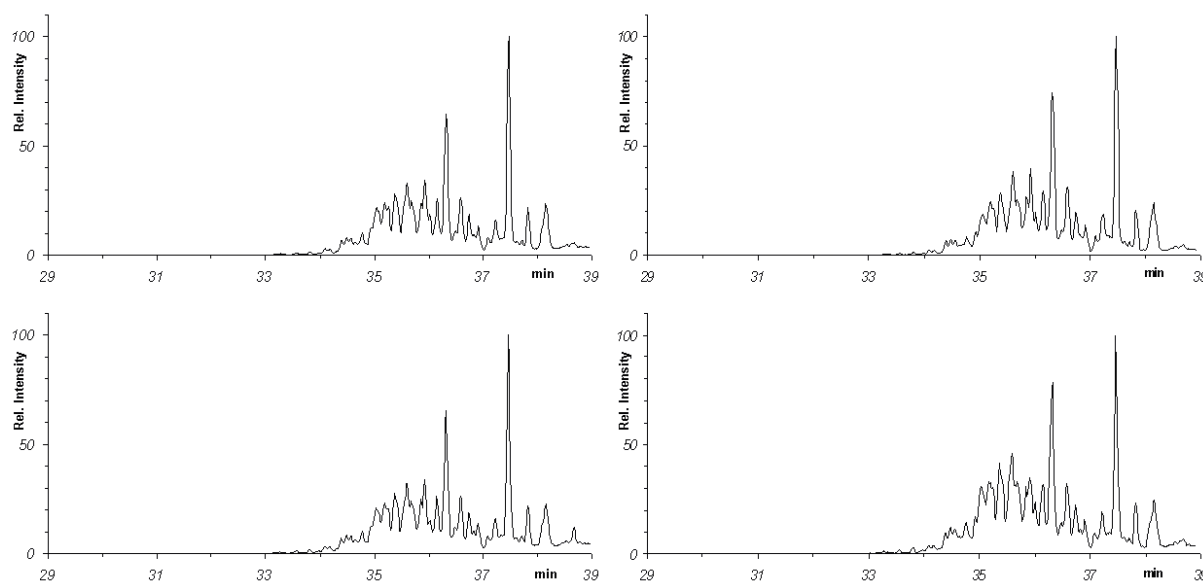


Fig. 18: Mass-chromatograms of mass 234 (tetra-M-phenanthrenes, M- benzo-naphthothiophenes) of HFOs (same samples as in Fig. 14).

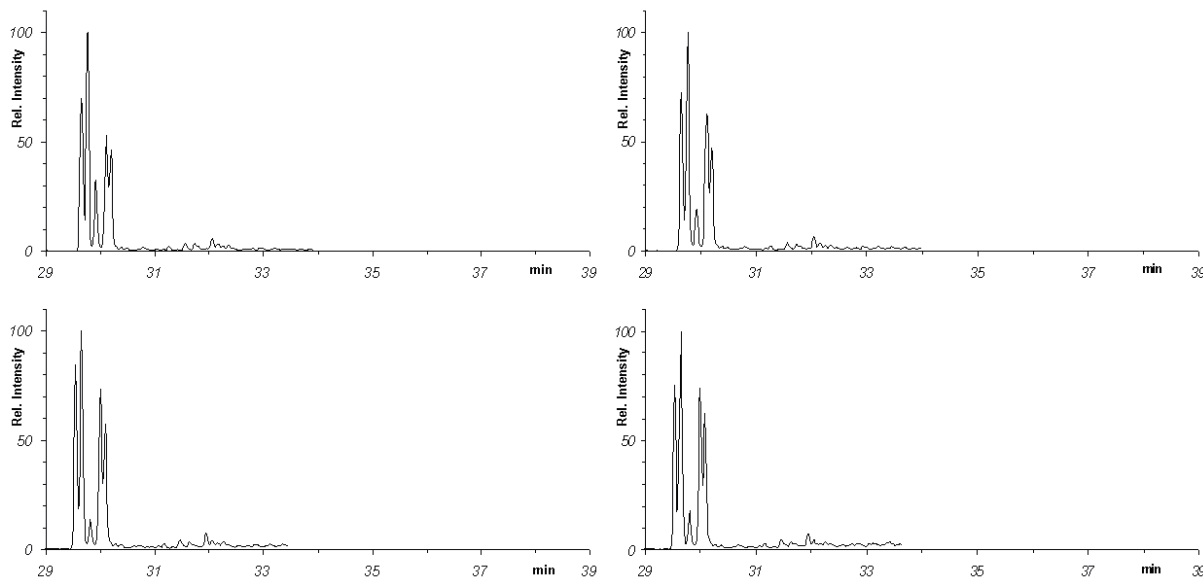


Fig. 19: Mass-chromatograms of mass 192 (M-phenanthrenes, M-anthracene) of HFOs (same samples as in Fig. 15).

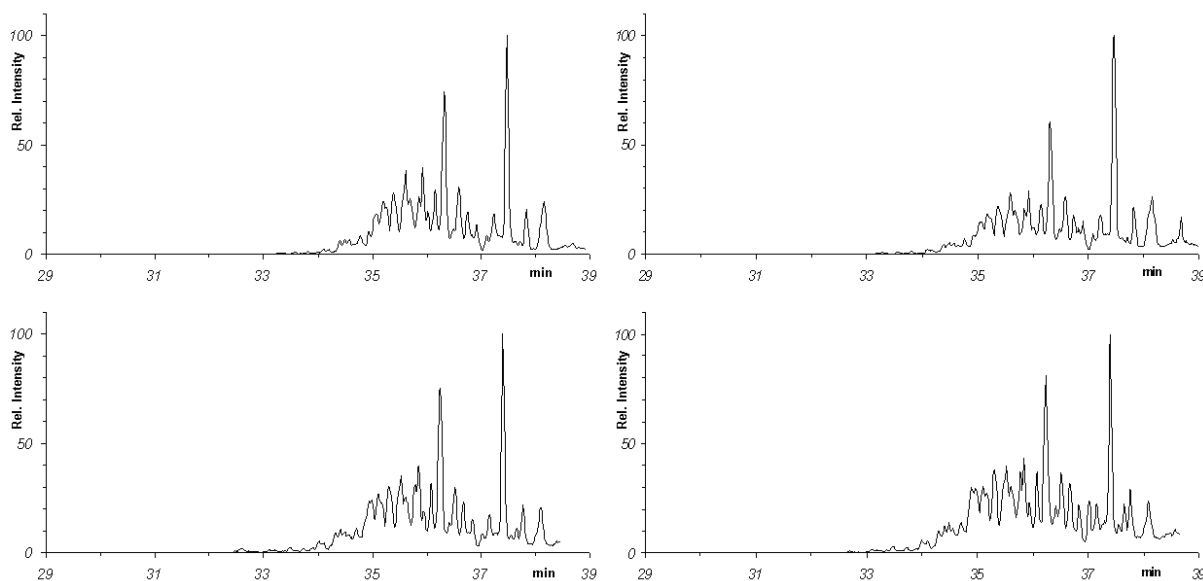


Fig. 20: Mass-chromatograms of mass 234 (tetra-M-phenanthrenes, M- benzo-naphtho-thiophenes) of HFOs (same samples as in Fig. 15).

Figures 19 and 20 show that the characteristic clusters of aromatics from cracking residues can be used for an unequivocal identification of HFOs in cases where aromatics are not readily discernible by GC screening (Figure 15 samples on the right side).

Thus, despite the highly different composition of the HFOs shown in Figures 14 and 15 and their different aromatic contents, these 8 oils are hardly discernible by their aromatic clusters.

The ratio of 2-M-phenanthrene to 1-M-phenanthrene, for example, expressed as $100 \cdot (2\text{-M-phen}/(2\text{M-phen}+1\text{M-phen}))$ of these 8 samples is $66 \pm (\text{max.}) 1\%$.



Aromatics are not suitable for the discrimination among HFO samples because identical or at least very similar clusters of aromatic hydrocarbons are found in most commonly used HFOs.

There are few HFOs which do not contain cracking products (HFOs produced in refineries without cracking units). Consequently, their aromatic clusters are different: although the GCs of the two oils given in Figure 21 look similar, the two samples can be readily differentiated by their aromatic patterns: the typical clusters of aromatics from cracking processes are only found in the right-hand sample.

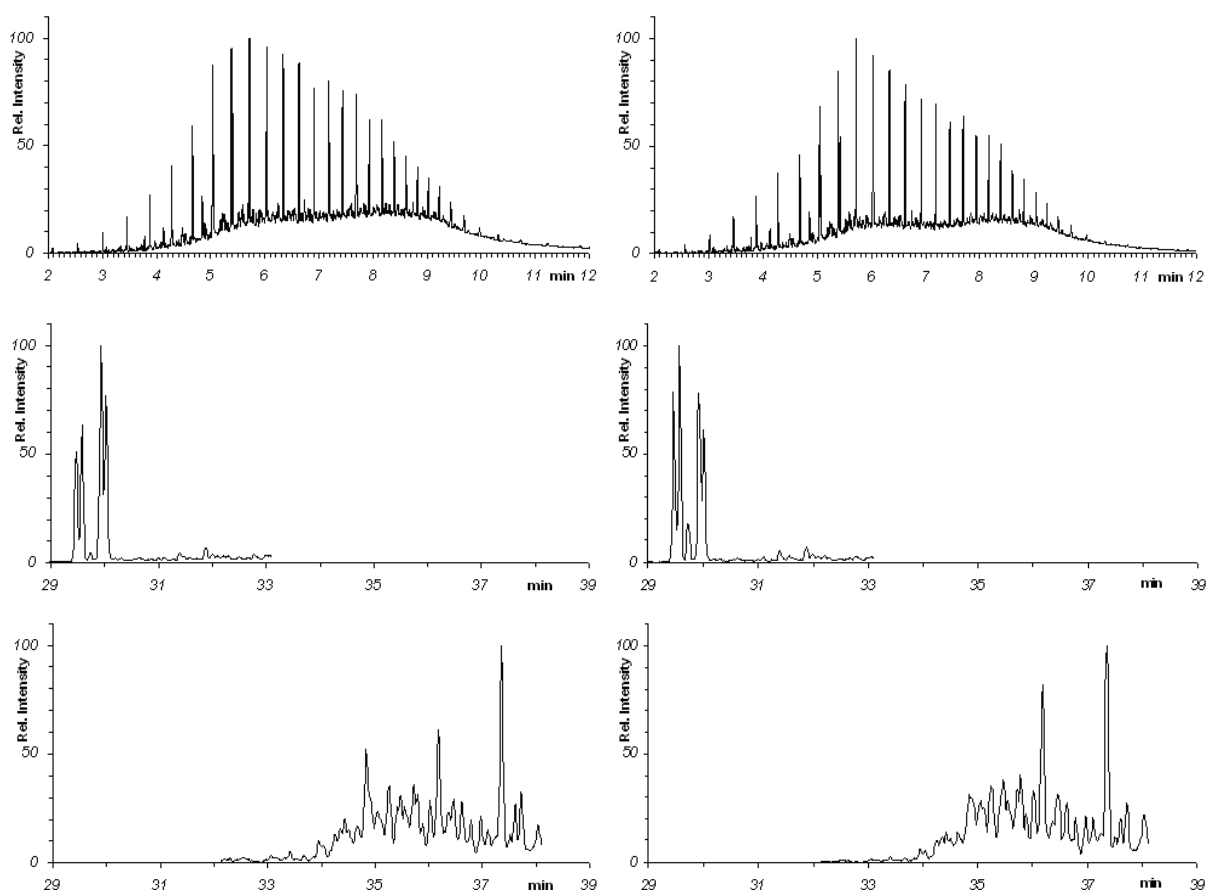


Fig. 21: GCs and mass chromatograms of masses 192 and 234 of two different HFOs.

These two samples were taken from the cargoes of different tankers (transport of HFO) but have been produced from the same type of crude oil (Russian export blend). Consequently, they are hardly discriminable by their biomarker patterns (Fig. 22).

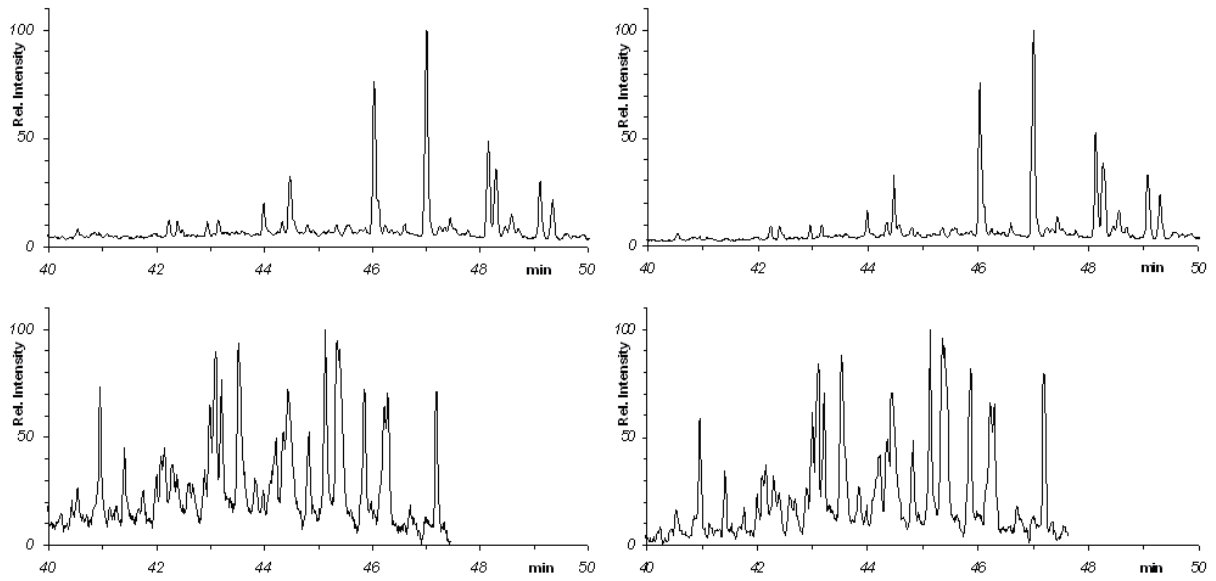


Fig. 22: Mass chromatograms of masses 191 and 217 of two different HFOs (same samples as in Fig. 21).

Crude oils subjected to weathering may, therefore, show a similar composition as HFOs which do not contain any cracking residues. It may be hardly possible, therefore, to differentiate between a HFO which does not contain such cracking residues and a weathered crude oil. The HFO sample shown in Figure 21 on the left side can be easily mistaken for a weathered Russian crude oil (Fig. 23).

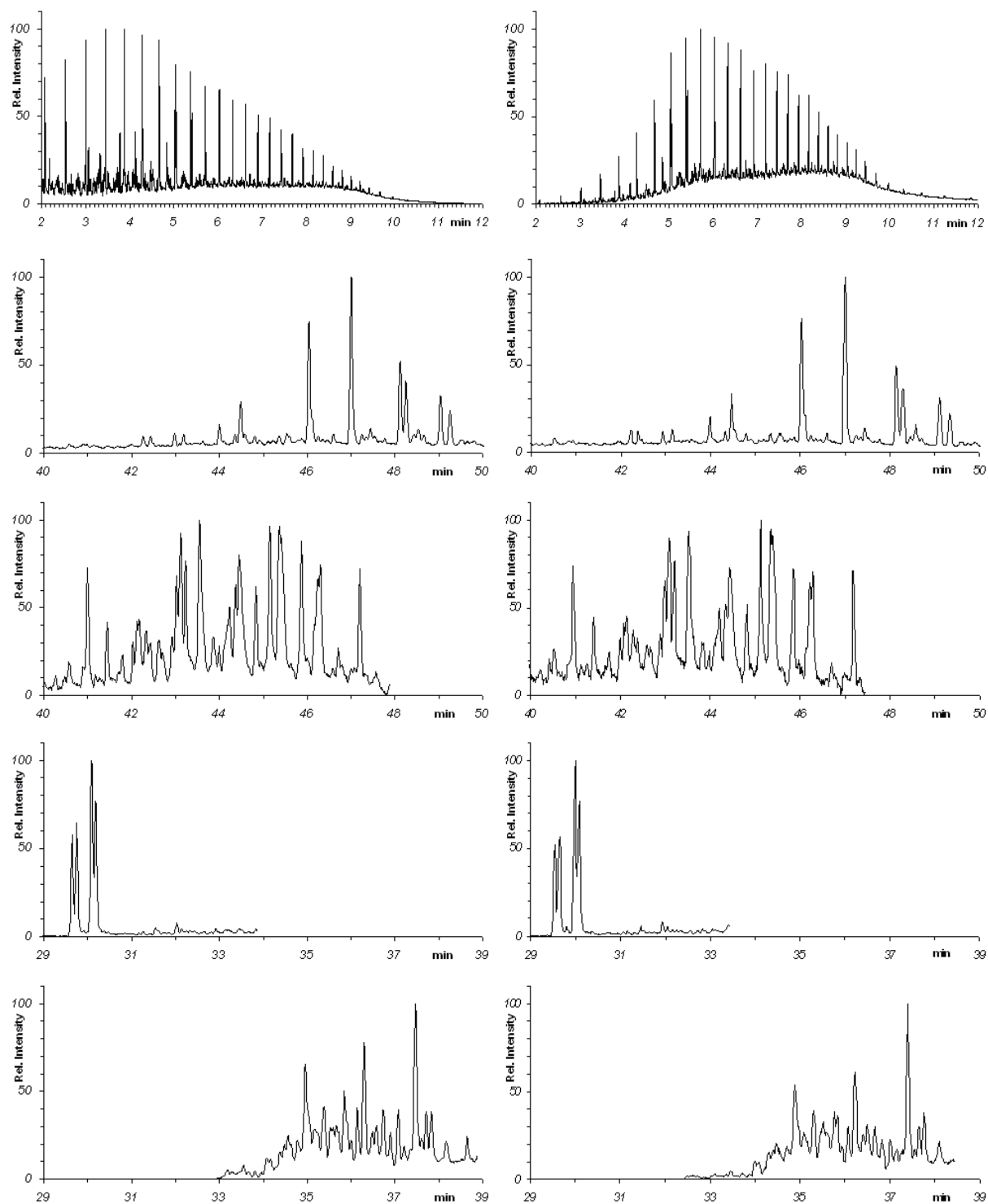


Fig. 23: GCs and mass-chromatograms 191, 217, 192 and 234 of a Russian crude oil (left side) and a HFO (right side, same sample as in Figures 21 and 22 left side).

2.4 Waste oil (bilge oil, sludge, slops)

Illegal discharges of oil from the machinery rooms of ships (waste oil) have been found to be the major source of oil pollution in all areas of intensive shipping traffic, such as the southern North Sea (G. Dahlmann et. al, Oiled Seabirds – Comparative Investigations on Oiled Seabirds and Oiled Beaches in the Netherlands, Denmark and Germany (1990-93), Marine Pollution Bulletin, Vol.28, pp. 305-310, 1994).

If waste oil is involved in an oil spill, the “uniqueness” of the spill is greatly increased: for example, oil from small engine leakages collects in the ship’s bilge. Therefore, bilge oil consists mainly of a mixture of bunker oil and lubricating oil. Bilge oil spills involve different amounts of different products. But the final composition of bilge oil is not only determined by the condition of the ship’s engine but also by the history of this type of oil on board a particular ship: the temperature, amount of water, and ship movements all contribute to alterations in the composition of bilge oil.

An example is shown in Figure 24, where the GCs of bilge samples taken from 8 ships of identical size (fishing vessels) are shown. These samples were taken in connection with an oil spill incident which occurred in a fishing harbour.

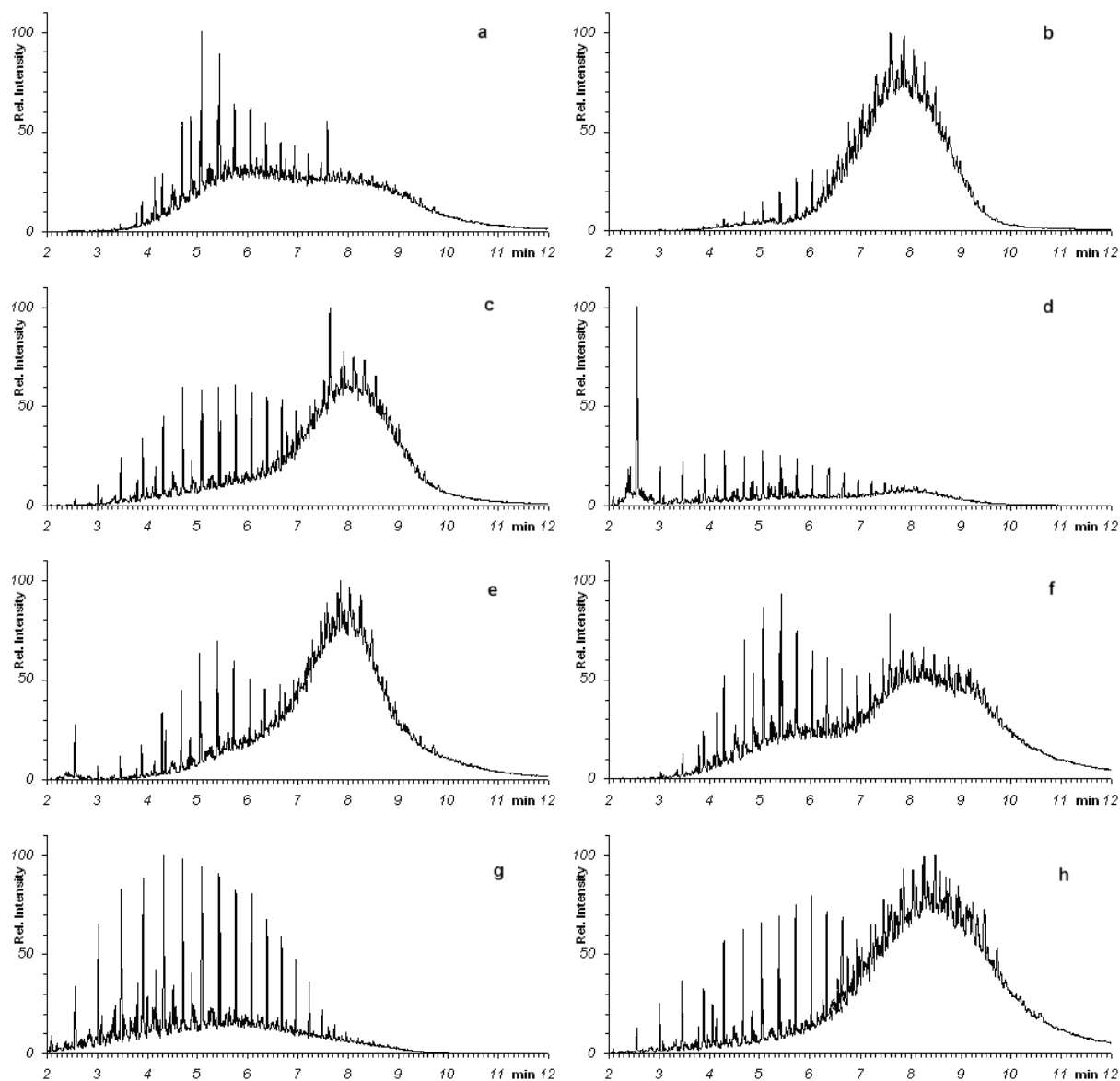


Fig. 24: GCs of bilge samples taken from 8 fishing vessels in connection with an oil spill case in a fishing harbour.

Figure 24 demonstrates the great variability in the composition of bilge oil even in vessels of the same size and type: different amounts of light fuel oil and lubricating oils are obviously involved but also different kinds of products. The light fuel oil part is differently evaporated. In a) high bacterial degradation has already taken place in the ship's bilge. In e) and especially in d) additional very low-boiling hydrocarbons can be detected which very likely originate from cleaning agents commonly used in the machinery spaces of ships.

2.4.1 Analysis

2.4.1.1 GC screening

According to the boiling ranges of the products involved, different regions overlap, and thus different overlays are produced when bunker oils and lubricating oils are mixed. In Figure 25, GCs of a light fuel oil (above) and a heavy fuel oil (below) are given together with the GCs of 3 different grades of lubricating oils (90 cSt, 150 cSt, 600 cSt).

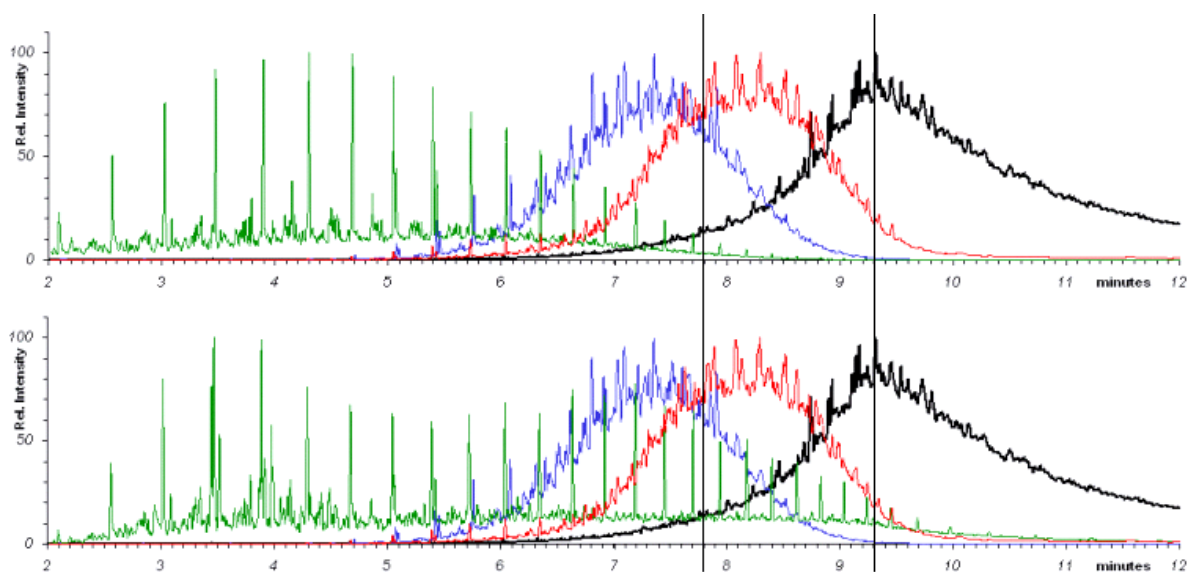


Fig. 25: GCs of a typical light fuel oil (upper) and a typical heavy fuel oil shown together with the GCs of 3 different lubricating oils. The main boiling range of the biomarkers is indicated by the two lines.

Mixtures of light fuel oil and lubricating oil are normally easily detected because of the different boiling ranges of the two products involved (Figure 24).

2.3.1.2 GC-MS analysis

As can be seen in Figure 25, the resulting compound patterns of the biomarkers of bunker oil/lubricating oil mixtures are influenced differently by the corresponding patterns of the individual pure products. Because of the limited boiling range of light fuel oil, biomarkers in light fuel-/lubricating oil mixtures originate nearly completely from the lubricating oil part. Therefore, even the presence of small amounts of lubricating oil can be detected in a light fuel-/lube oil mixture. Figure 26 shows the hopanes and aromatic steranes of the last 4 oils given in Figure 24. While the relatively small amount of lubricating oil is hardly detected in Figure 24 g), for example, the biomarker patterns of this sample are strong evidence of the

presence of lubricating oil. The finding that aromatic steranes are not present in lubricating oils is particularly useful in this case.

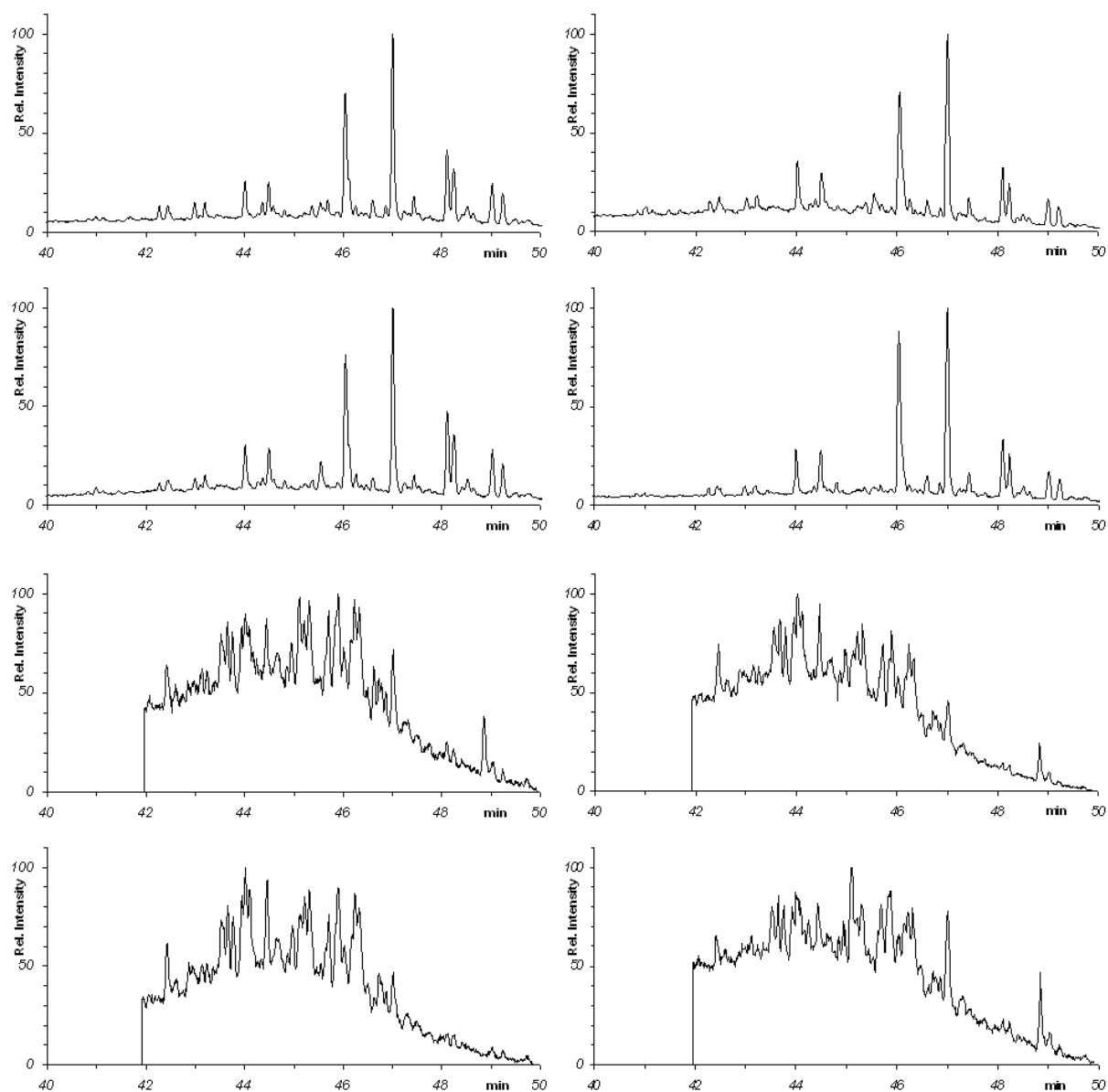


Fig. 26: Mass chromatograms of fragments 191 (upper 4) and 231 of samples e to h in Figure 24.

Because quite different kinds of products are involved, differences in the relative proportions of light fuel-/lubricating oil mixtures may occur, when a spill sample is compared with a corresponding ship sample. These may be caused by weathering (evaporation and/or biological degradation), i.e. processes, which effect only the light fuel oil part of the mixture. In addition, there is the risk of inhomogeneous distributions of waste oil of this kind, caused by incomplete mixing of the two products involved.

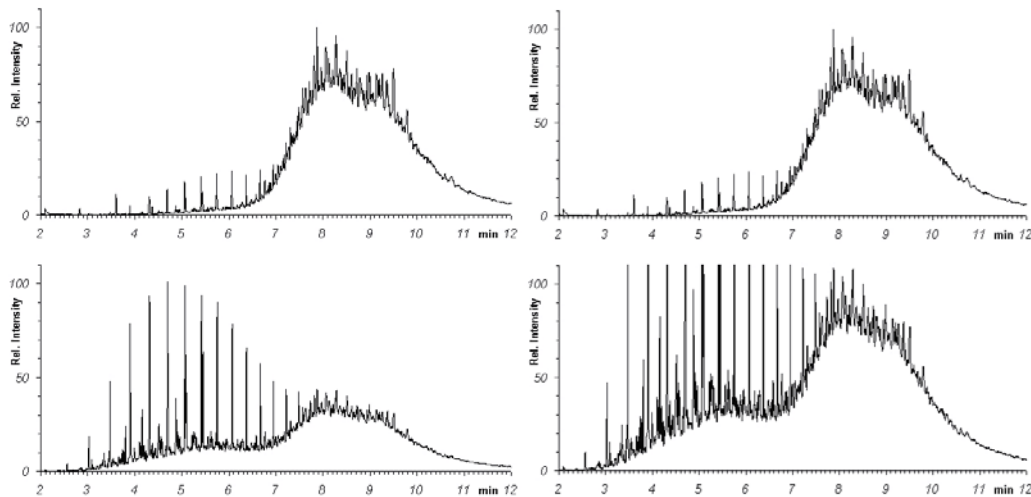


Fig. 27: GCs of a spill sample (upper chromatograms) and the corresponding bilge sample. For better comparability, intensities are normalized on the lubricating oil part in the lower right chromatogram.

An example is given in Figure 27, where a spill sample is compared with a sample taken from the bilge of the suspected polluter. Obviously there is hardly any possibility to compare the light fuel oil part of the samples in detail, whereas high similarities in the lubricating oil part (Figure 28) can already be expected (additional and identical second “hump” in the higher boiling region, which indicates the same mixture of two different lubricating oils).



In order to cope with the problem of inhomogeneous distributions of oil, prosecuting authorities should be advised to take more than one sample from the sampling locations especially when there is the suspicion that waste oil is involved in an oil spill.

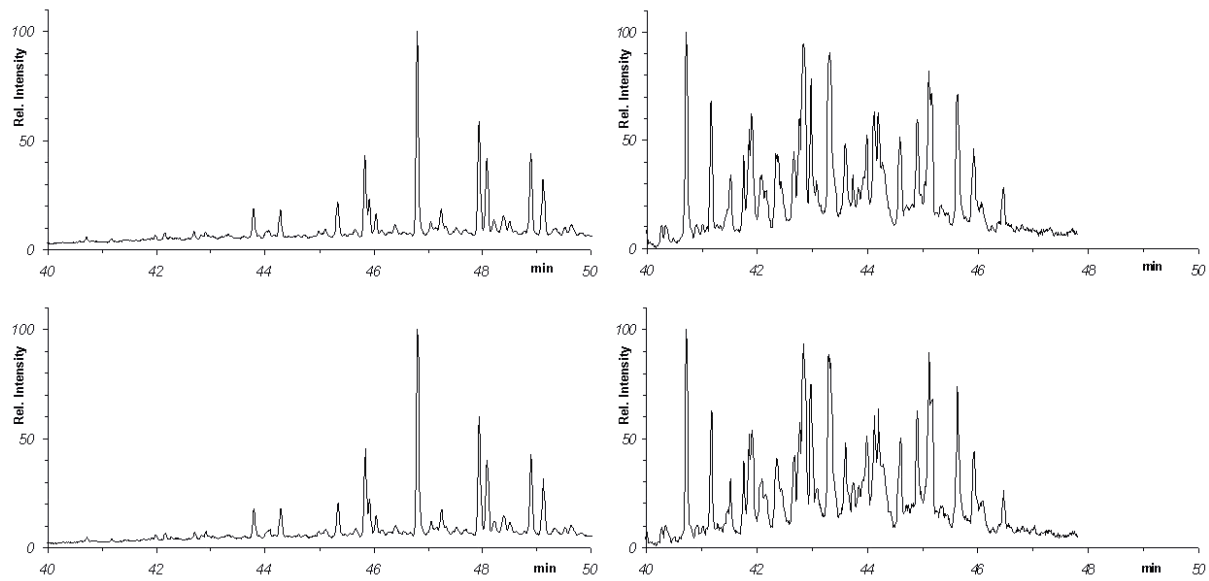


Fig. 28: Hopanes and steranes of a spill sample (upper chromatograms) compared with the bilge sample of the suspected polluter (same samples as in Fig. 27).

Since heavy fuel oils and lubricating oils normally overlap completely in the higher-boiling region, the detection even of smaller amounts of lubricating oil in HFO is more difficult. In most cases, the typical unresolved “hump” of the lubricating oil can be detected by GC-screening in bilge oil or sludge samples also of ships, which use HFO (Figure 29).

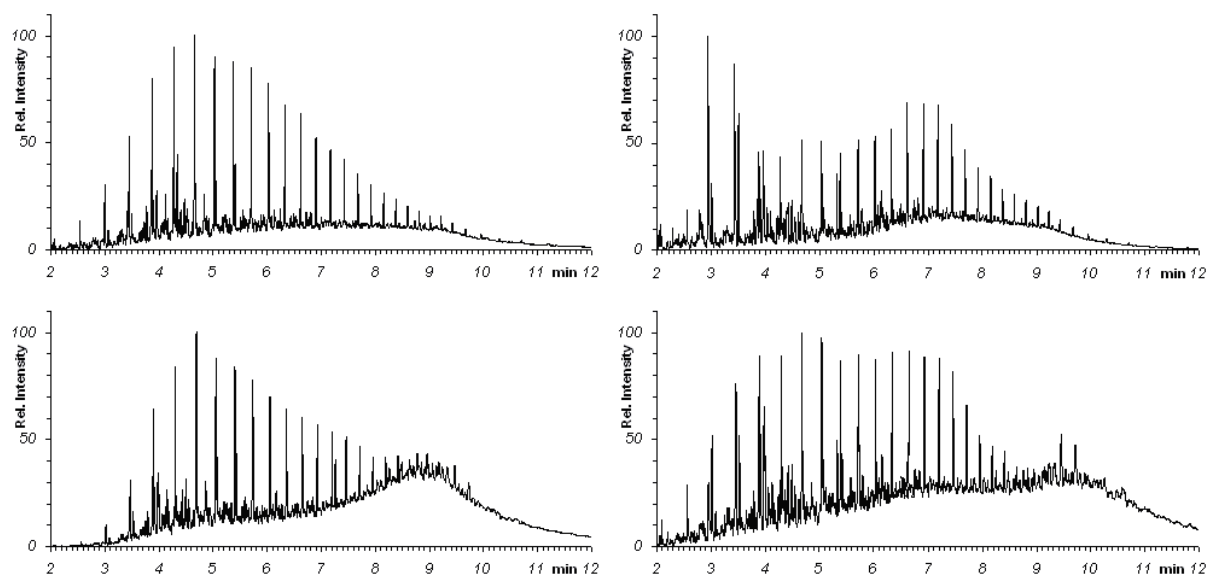


Fig. 29: Gas-chromatograms of HFO-samples from two different ships (above) and sludge-samples taken from these ships (below).

Again, mass-fragment 231 may be of great help here in doubtful cases (see Paragraph 2.2.1.2): whereas hopanes and steranes may show arbitrary mixtures of the clusters of the individual products, the aromatic steranes are much more interesting. Because they solely originate from the HFO in HFO-/lubricating oil mixtures they appear on top of the 4-alpha-steranes, which originate mainly from the lubricating oil (Figure 30 lower chromatograms).

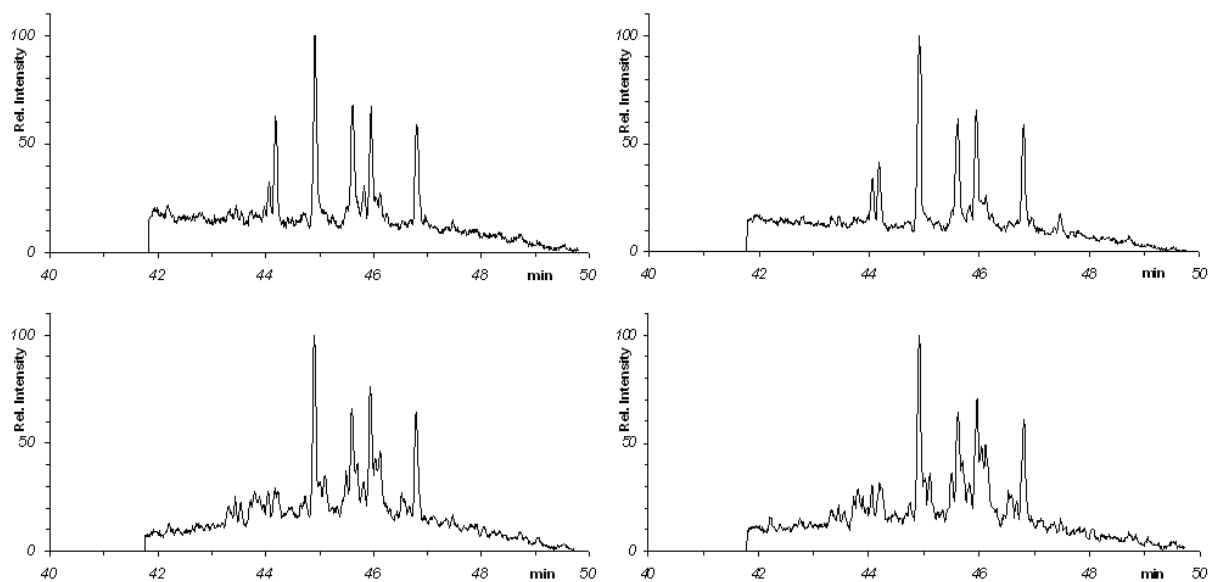


Fig. 30: Mass-chromatograms of mass-fragment 231 of the bunker- and sludge-samples of Figure 26.

2.5 Crude oil

The pollutant must be crude oil if all other product types have been excluded by analysis. Crude oil spills may be caused by crude oil tankers or may originate directly from crude oil production, where feasible.

For example, the finding that crude oil is involved in an oil spill in the congested shipping area of the German Bight means that all ships except tankers can be excluded as possible sources. Crude oil from tank washings of tankers often can be identified by the presence of additional higher-boiling n-alkanes (wax): these compounds adhere to the tank walls after unloading. They are washed out by means of, or together with, residues from the original cargo (“crude oil washing”). But direct input from oil production can be definitely excluded if a non-North Sea crude oil is found. Moreover, experience has shown that even rough further classification by crude oil types may narrow down considerably the number of possible sources, even to a single ship. The classification of crude oils by their main production areas by means of a database of crude oils thus is the first step toward identifying the source of an unknown crude oil pollution. Crude oils are transported mainly in the form of mixed oils or blends (Brent mix, Flotta mix) in which the geochemical differences characterizing single platforms are levelled out. Nigerian light, Russian export blend, Arabian or Iranian light or heavy, are each produced from numerous single wells. Their broader characteristics reflect their general production area.

On the other hand, environmental controlling or monitoring of platforms is an entirely different task. Of course, broader characteristics are only of very rare value when an oil spill in a distinct production area is suspected to have emanated from one of the surrounding platforms. Oil spills from oil production primarily emanate from offshore tanker loading (where the oil is not carried ashore by pipeline), pipeline leaks or wellhead leaks. Pipelines may carry crude from a single or multiple oil fields (blends).

2.5.1 Analysis

Crude oils contain characteristic compounds or compound relations which are typical of their origin in the world's main production areas, such as the Middle East or North Sea, in a particular oil field or even a single platform.



The following findings are based on a collection of 260 samples from crude oils transported or produced in Europe. This collection allows some general conclusions regarding the different crude oil types, although exceptions are, of course, possible.

2.5.1.1 GC screening

Crude oil washing residues from tankers often can be identified by an additional hump of the n-alkanes in the higher boiling region of the GC (“bimodal distribution”, Figure 29 upper samples). Here, high boiling residues sticking to the tank walls after unloading have been washed out by means of or together with residual loading.

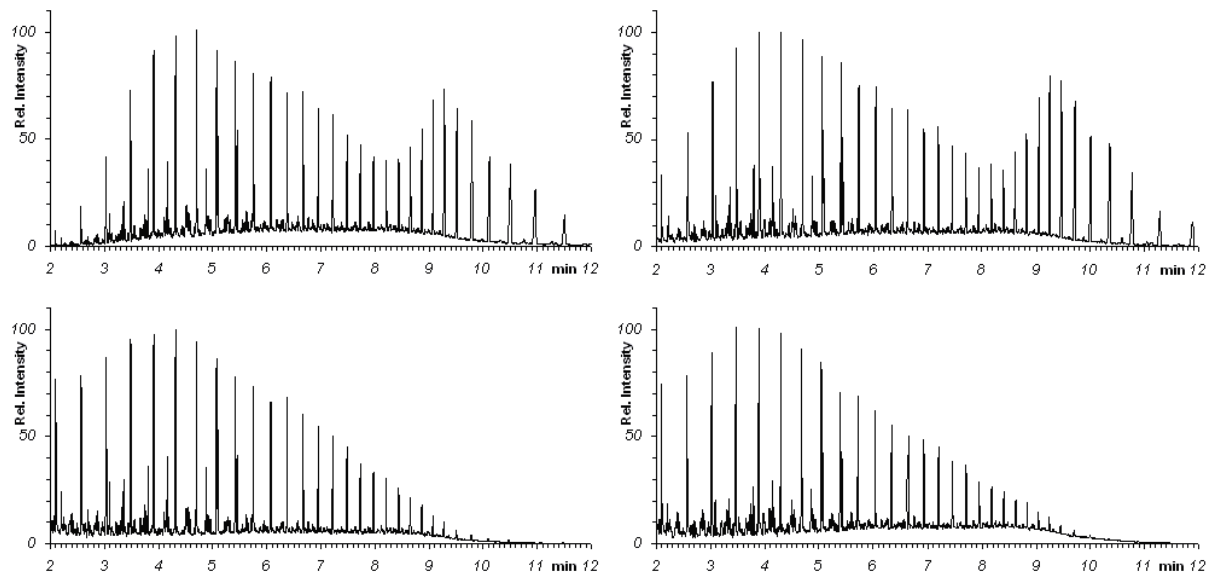


Fig. 29: GCs of two samples from massive oil pollution taken from German and Dutch beaches (above) and possible sources (below).

Crude oils are generally roughly categorised into n-paraffin (wax) based and naphthene based crudes and mixtures of these (Figure 30).

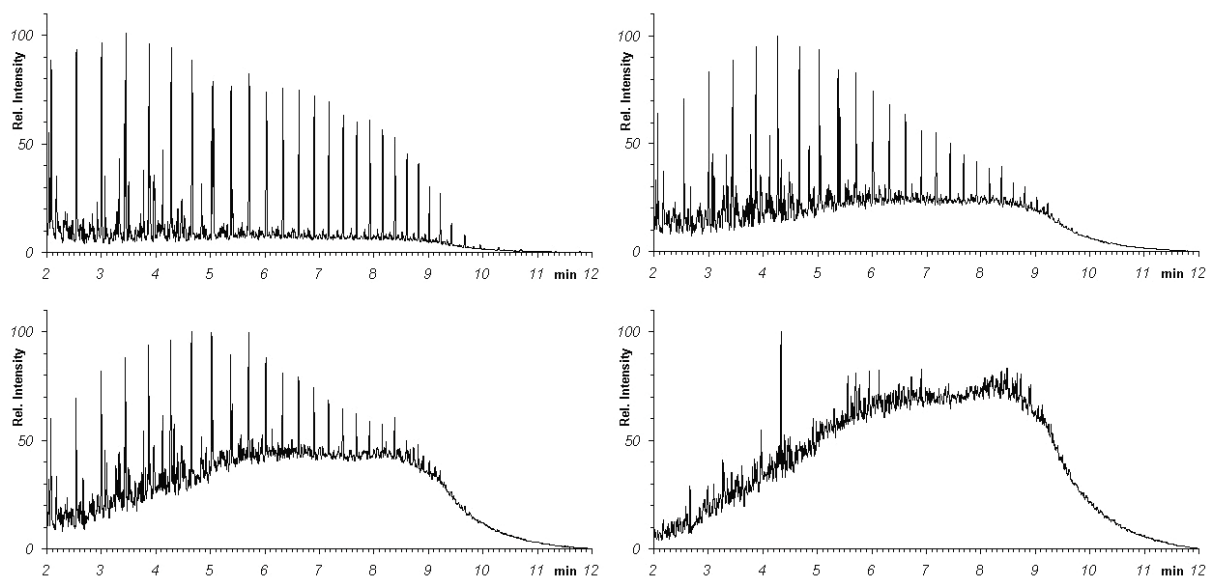


Fig. 30: GCs of four Venezuelan crude oils showing the general variation from n-paraffin (upper left) to naphthene based crudes (lower right).

2.5.1.2 GC-MS analysis

Biomarkers and their relations generally represent source and maturity of crude oils. While source parameters are derived from the specific biomass from which an oil has been formed, maturity parameters represent chemical changes occurring during oil maturation.

Some of them can be highly characteristic, i.e. specific of a particular production area, or even of an oil field. But others may have only a very low meaning, when an oil spill sample is compared with samples from suspected sources.

The relation of the C₃₁+ enantiomers in the hopane series, for example, indicates maturity of organic matter in samples of potential source rocks. With increasing maturity this value reaches about 60:40 although it may slightly vary depending on the carbon number of the homologues being measured. The value of the second pair, expressed as $100 \cdot 32abS/32abR$ (%32abS), of all 260 samples of the collection of crude oils from all over the world has found to be 58 with a standard deviation of only 2.2% (Figure 31).

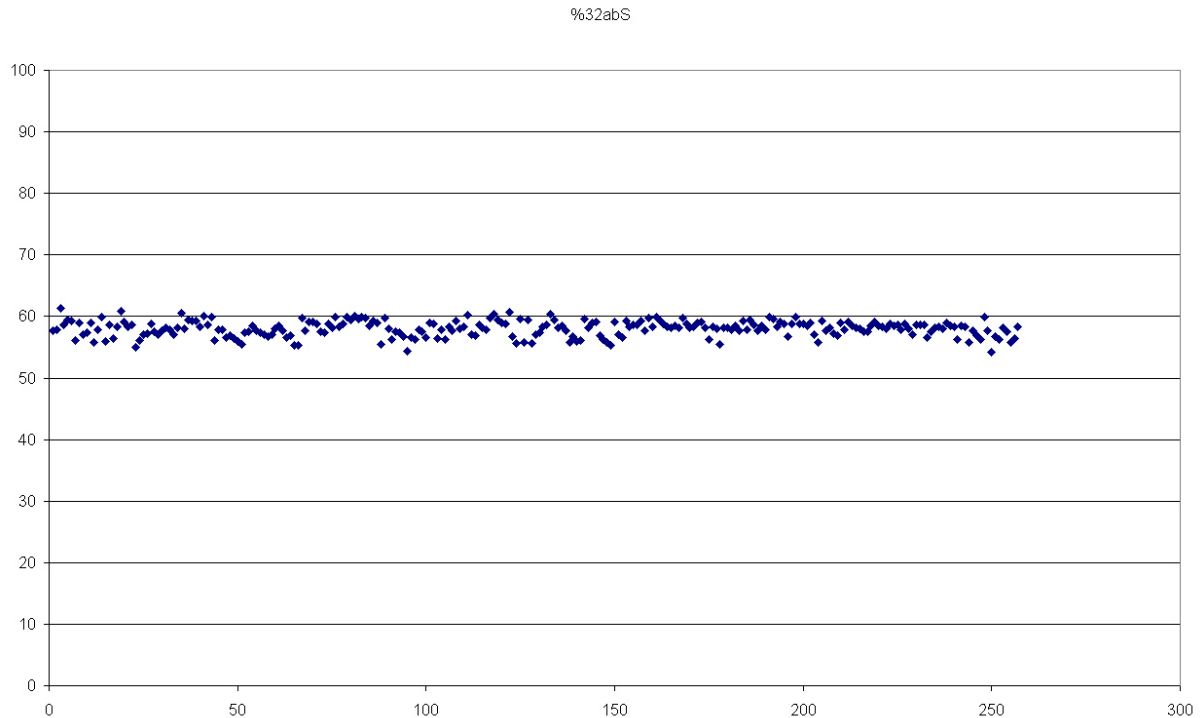


Fig. 31: %32abS of 260 crude oil samples (x-axis: sample number)

%32abS thus cannot be used for result verification in Oil Spill Identification because this parameter must be regarded as a constant here. There is definitely no reason to determine a constant.



Since oil spill identification means in fact oil discrimination, those compounds or compound ratios should preferably be used for result verification, which show the biggest differences between oils. Although these may vary from case to case, some of them can be regarded as “key”-parameters, which require special consideration.

When we move from all oils to a distinct production area, additional parameters may become less and other parameters may become more important.

The rare 25-norhopane, for example, is found in a small amount in crude oil from the central platform of the Norwegian Oseberg field (about 7 % in relation to hopane), whereas this compound is near the detection limit in samples from other platforms of this area (about 1 % in relation to hopane). If this parameter is handled in the same way as all other parameters, only a small difference is demonstrated (Figure 32). This difference is about the same as the difference in the amount of 28-bisnorhopane (peak on the left of 25-norhopane).

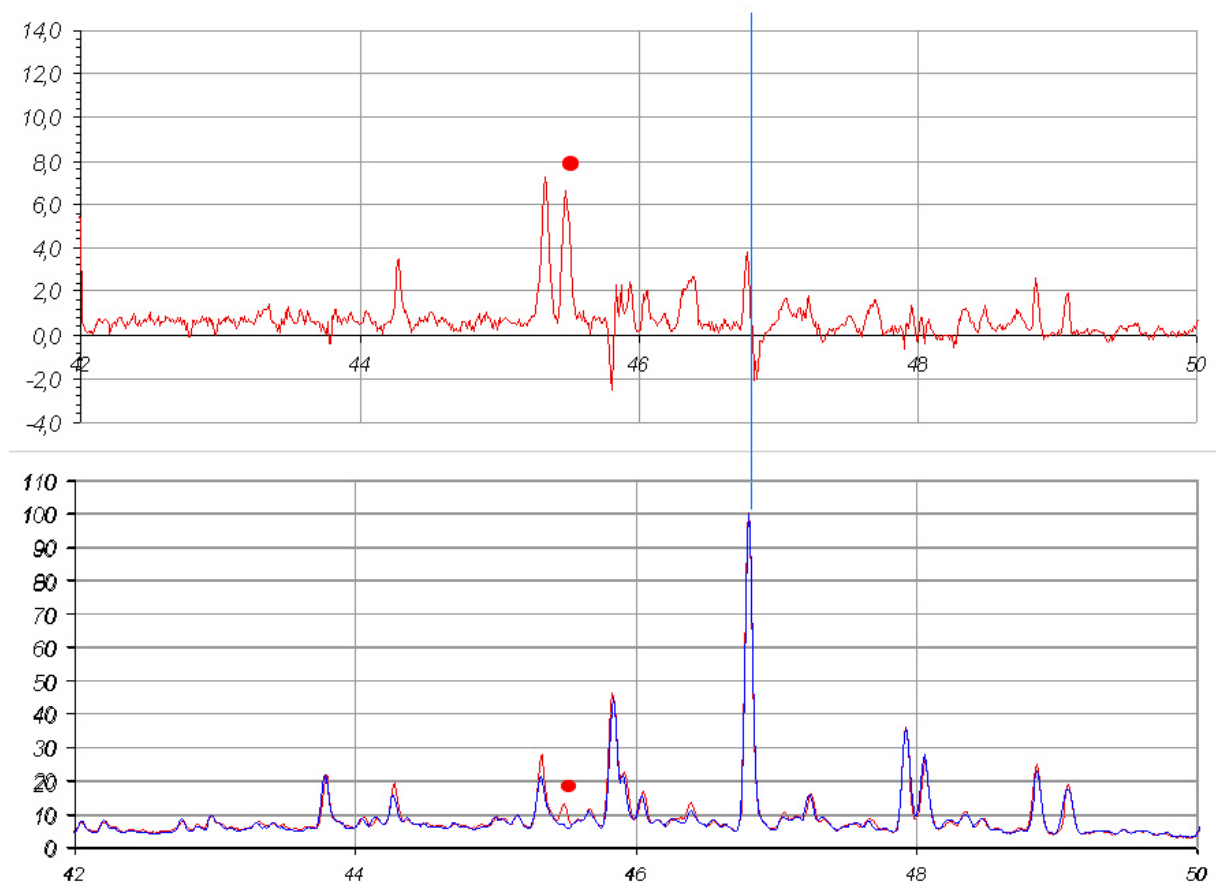


Fig. 32: Overlay of the hopanes of Oseberg C – and Oseberg S crude oil (below), subtracted mass-chromatograms (above). 25-norhopane indicated.

If the high value of this compound for discriminating between oil samples is known, the responsible analyst must come to the conclusion “non-match” already by the visual inspection of the mass-chromatograms.



In order to demonstrate and pronounce differences properly it might be much more convenient in Oil Spill Identification to calculate the (absolute) difference of compound relations between the samples and express this difference in form of percentages of the corresponding compound relations of the sample, which has to be identified, i.e. the spill sample. In the example given in Figure 32 this would lead to differences of about 28% (28-bisnorhopane) and about 85% (25-norhopane), if the higher values of these components were found in the spill sample. Especially the latter value is by far out of the range of analytical errors. Of course, these percentages may become very high or even infinite, in case a compound is not found in the spill sample but present in a comparison sample. But these cases have to be explained in any way: the responsible analyst must have come to the conclusion “non-match” already by the visual inspection of the mass-chromatograms in these cases.

What a difference, in case Oseberg crude oil would be involved in a mystery oil spill in the southern North Sea!

In a first step, it has to be found out here that the oil type “crude oil” is actually involved (Para 2.1 to 2.5). The crude oil type “Oseberg” then may be identified by means of the crude oil database. Here, stored values of crude oil parameters are compared with the corresponding values of the unknown crude oil sample. Statistical calculations are performed in order to find out “best matches” with the spill sample. Even without the characteristic 25-norhopane in this case already the five parameters of the hopane-series given in Table 2 are sufficient, not only to indicate the general area where this oil originated (i.e. between the Shetland Islands and Norway) but also to find out the correct crude oil type (“Oseberg”, Table 1) among the 260 crude oils of the database.

Crude oil	Sampling date	Correlation Coefficient
Oseberg	01.07.1993	0.9997
Oseberg	14.02.2002	0.9988
Oseberg	19.01.2002	0.9974
Statfjord	01.07.1993	0.9971
Gullfacs	01.07.1993	0.9969
Oseberg C (Sintef)	07.05.2001	0.9951
Statfjord	07.01.2002	0.9950
Gullfacs	22.12.2001	0.9931

Tab. 1: “Best matches” of crude oils, when Oseberg C crude oil (spill No 2, sample taken by Sintef) is correlated by using the five parameters given in Table 2 (database: 260 crude oils from all over the world).

Parameter	Spill sample	Best match (Tab.1)	% Difference
Ts/Hopane	0.160	0.155	3
Tm/Hopane	0.121	0.120	1
28-Bisnorh./Hopane	0.230	0.230	0
Norhopane/Hopane	0.394	0.401	2
C31S/Hopane	0.347	0.355	2

Tab. 2: Parameters used, single values and percentage difference of the spill sample versus the “best match” (samples given in Table 1).

If a tanker having transported Oseberg crude oil in this scenario is found, the frequency of transports of this oil type plays the dominant role. A strong connection between the oil spill and a tanker may possibly be achieved by coupling the drift of the oil with the course of the ship. But since the oil does not contain a “fingerprint” of the ship, it might hardly be possible to exclude a second tanker by chemical analysis, if a second tanker would have been under suspicion, too.

These two quite different scenarios show that chemical analysis might play quite different roles in tracing back the sources of oil pollution. But, accordingly, different parameters may have a quite different meaning in Oil Spill Identification. Whereas the 25-norhopane, for example, turns out to be of greatest importance, when an oil spill in the Oseberg area has to be associated with a single platform in the vicinity, this compound might play only a very minor role when crude oil residues from tanker loadings have to be identified. An example is given in Figure 33 where Oseberg C crude is compared with an Arabian heavy crude oil.

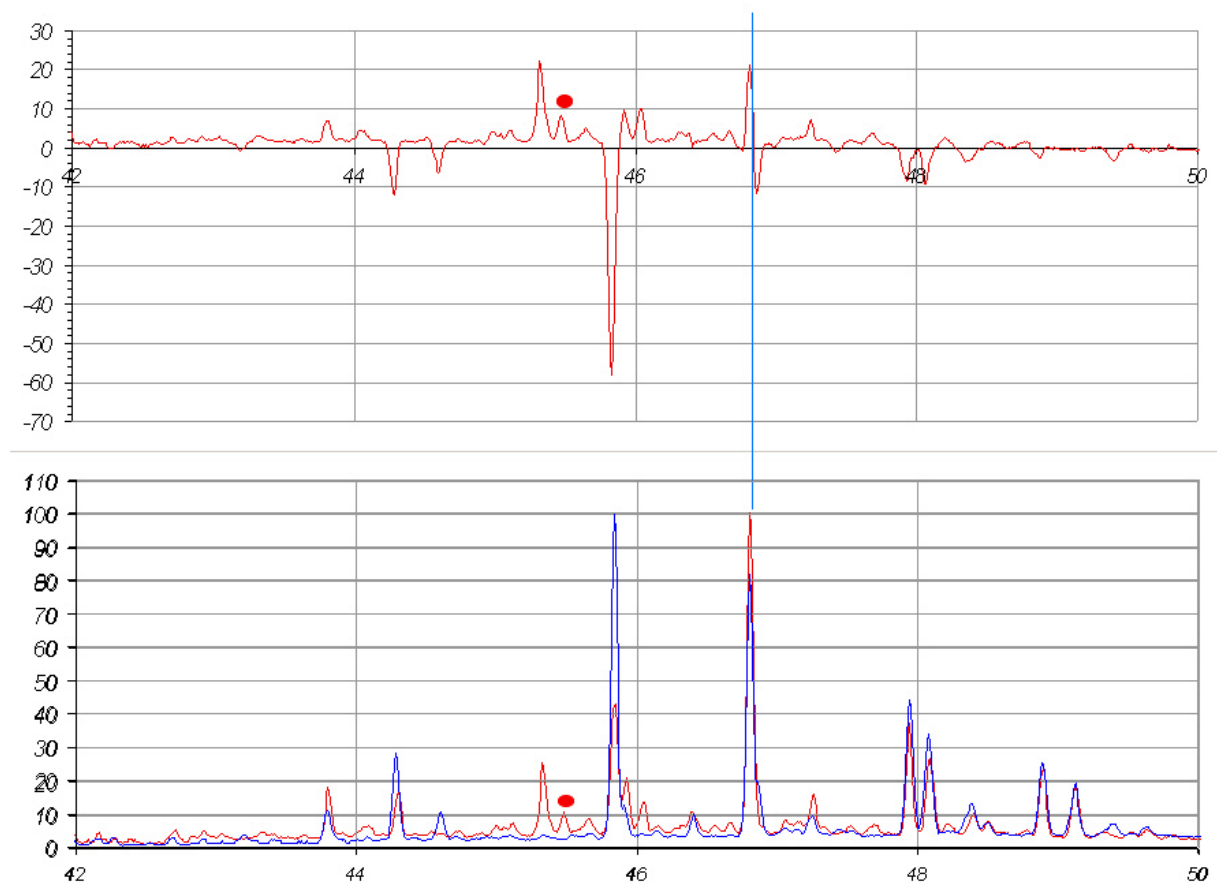


Fig. 33: Overlay of the hopanes of Oseberg C – and Arabian heavy crude oil (below), subtracted mass-chromatograms (above). 25-norhopane indicated.



Generally, the determination of very small peaks, such as the 25-norhopane peak in Figures 32 and 33, should be avoided, if their role is unclear. The determination of very small peaks is not only associated with a bigger analytical error. There is also the high risk that the wrong peaks are chosen from the chromatograms: some crude oils may show such complex hopane-patterns that even the identification of the major peaks of the hopane-series may become difficult (Figure 34). The determination of 25-norhopane in these cases, for example, would require structure determination of a small peak among clusters of overlapping peaks of similar compounds, which is beyond the scope of Oil Spill Identification and simply not practicable in acute cases.

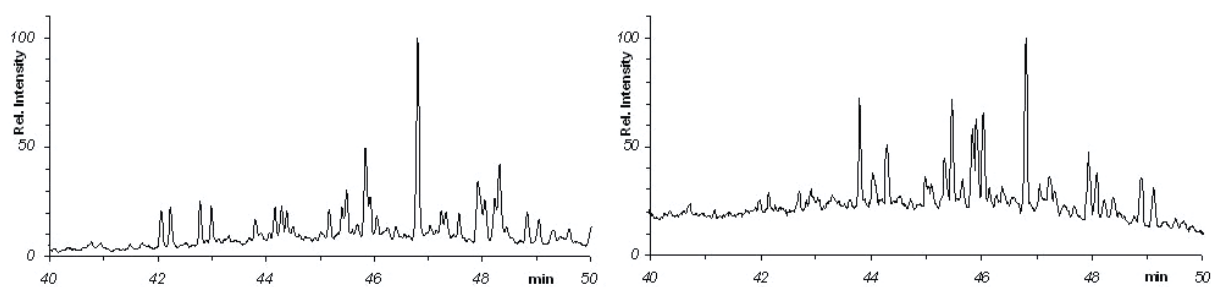


Fig. 34: Examples of more complex hopane-clusters (Angola Quinguila crude, left, Leadon crude, North Sea, right).

The broader platform area of the northern North Sea, including Statfjord, Gullfacs, Brent, Oseberg, Troll etc., seems to be especially characterized by relatively high concentrations of **C28-bisnorhopane**, a compound, which is not a member of the regular hopane series. Its formation from a C30 or C35 biological precursor would have required cleavage of two carbon-carbon bonds in the side chain, which is very improbable. 28-bisnorhopane thus can be regarded as a specific source parameter. Beside in North Sea crudes it is found only in selective crude oils in other areas of the world.

There is roughly a general decline of the C28-bisnorhopane concentrations to the south, up to the Ekofisk-area and the Danish platforms (Figure 35). But this trend is interrupted by the platforms of the Flotta catchment area (Piper, Claymore etc.), where the highest concentrations of C28-bisnorhopane are found (up to about 50% in relation to hopane).

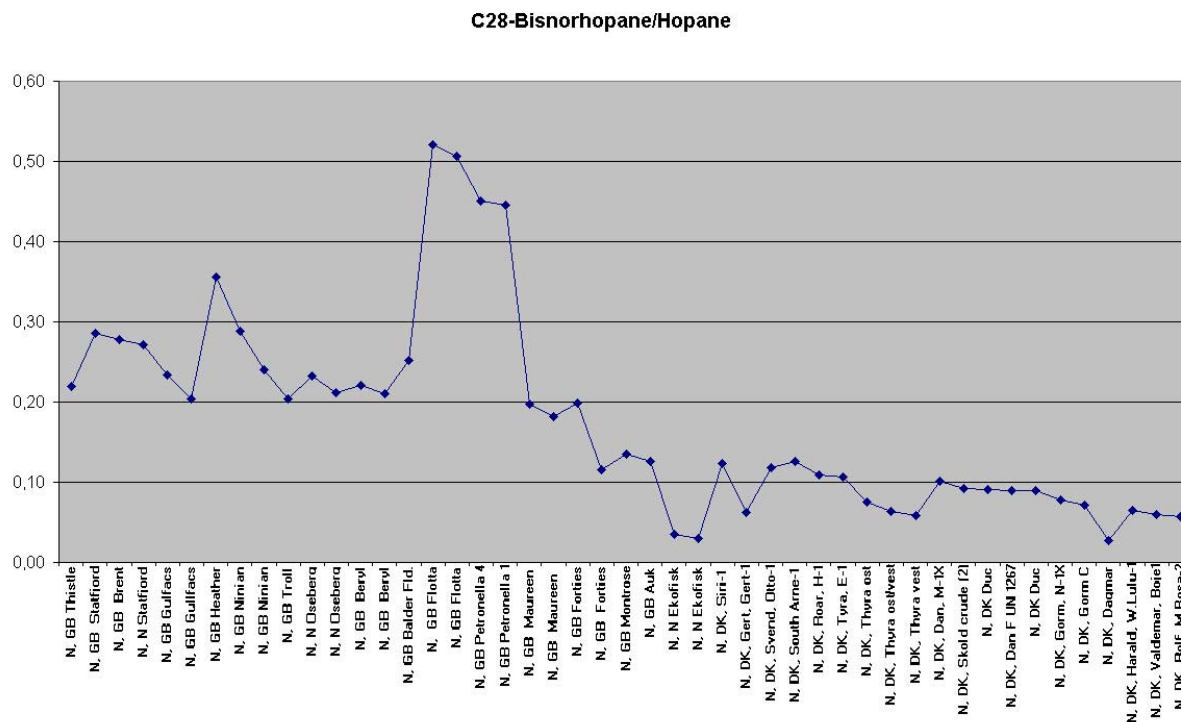


Fig. 35: C28-bisnorhopane (in relation to hopane) in North Sea crudes. Crude oils roughly sorted from north to south (left to right).

But, in addition, all North Sea crudes are generally characterized by parameters which are mainly connected with crude oil maturity. Figures 36 and 37 show that already nearly a full separation of all North Sea crude oils from all Middle East crude oils, for example, is achieved by each of the chosen parameters (Tm/Hopane and Norhopane/Hopane) separately.

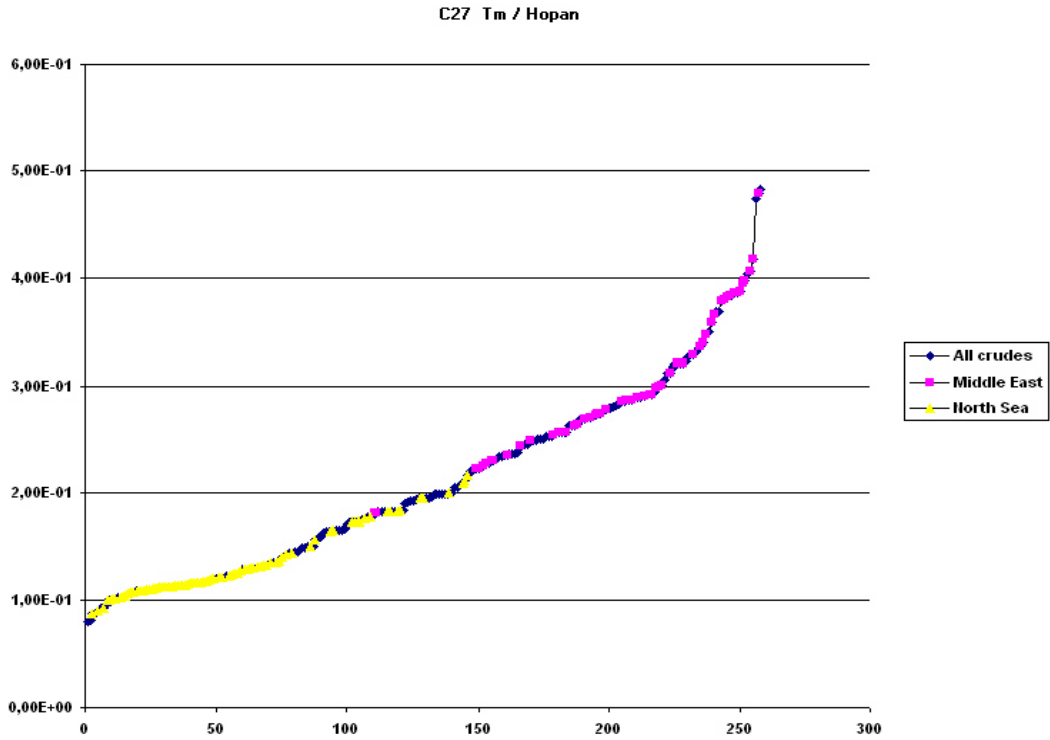


Fig. 36: Ratios of Tm(C27) to hopane sorted in ascending order. Middle East crudes (53 samples) are marked with violet squares, whereas North Sea crudes (85 samples) are shown by a yellow triangle.

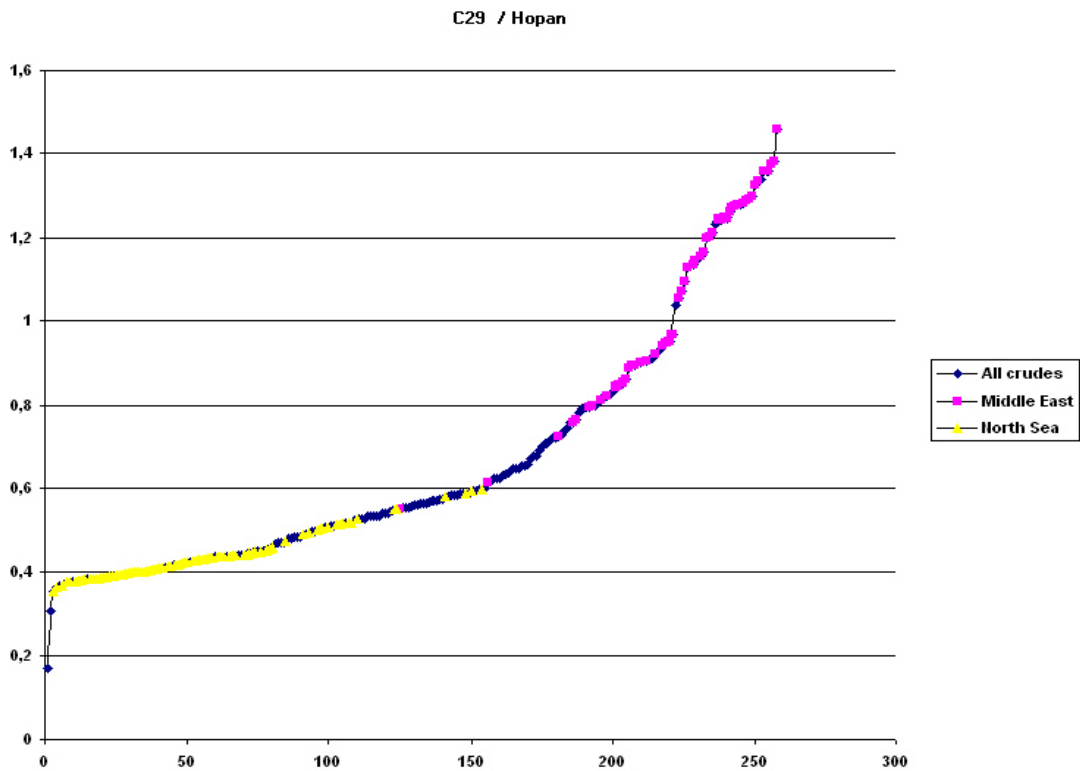


Fig. 37: Ratios of norhopane(C29) to hopane sorted in ascending order. Middle East crudes (53 samples) are marked with violet squares, whereas North Sea crudes (85 samples) are shown by a yellow triangle.

Figures 36 and 37 show, vice versa, that Middle East crudes generally contain higher amounts of Tm and norhopane (C29) than North Sea crudes. This might be connected with a higher maturity of these oils. Especially Arabian crude oils are characterized by a C29/hopane ratio greater than 1. The lower values of 0.7 to 1 are contributed by Iranian - and Emirate crudes, whereas the lowest values of the Middle East crudes belong to two Syrian light crude oils, thus originating from oil fields which are not directly connected with the main Gulf-area (i.e. the Arabian-Iranian Basin).

Oils from the Niger Delta (Nigeria) are characterized by the presence of **Oleanane** in relatively high concentrations. Oleanane is a triterpenoid which presumably originates from terrestrial plants (Figure 38).

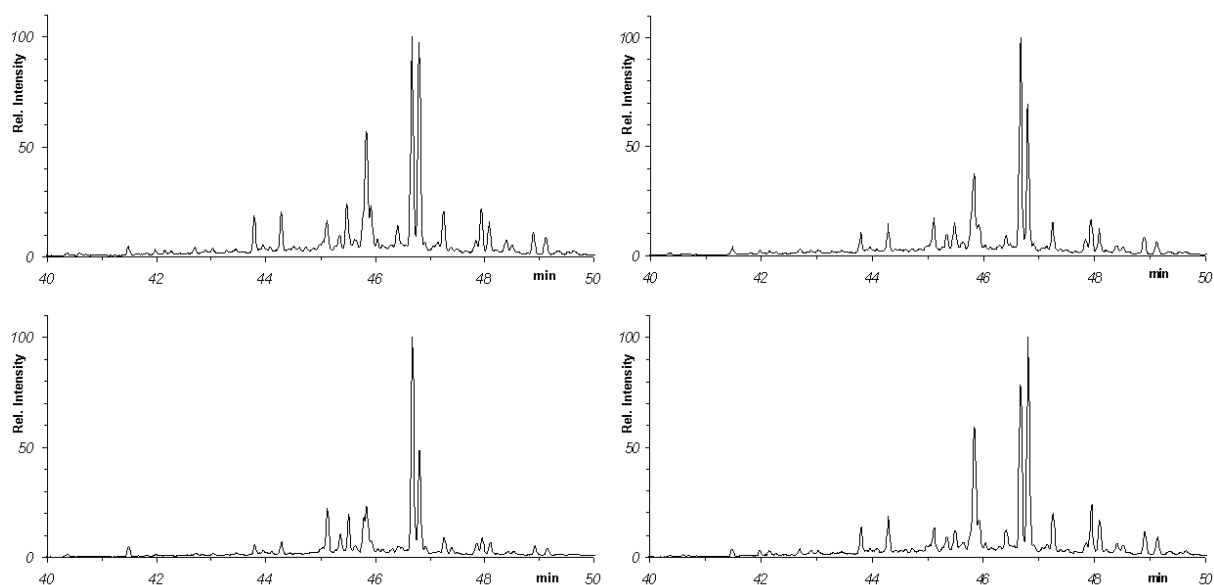


Fig. 38: Hopanes of 4 Nigerian crude oils (Forcados, Oso, Odudu, Bonny Light), showing relatively high concentrations of Oleanane (peak left of hopane at 46.6 minutes).

Oleanane seems to be highly specific for Nigerian crude oils. But, in addition, this characteristic feature is accompanied by relatively high concentrations of pristane in these oils (Figure 39). The source of pristane is presumably phytol, which is derived from the side chain of chlorophyll. The high concentrations of pristane thus additionally point to land plant sources.

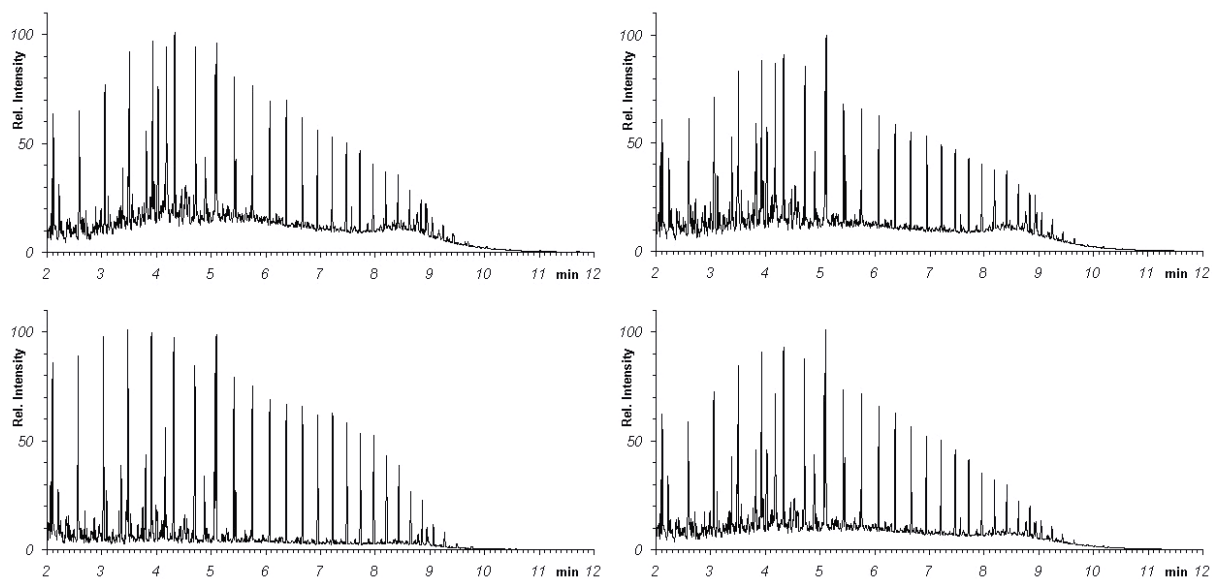


Fig. 39: Gas-chromatograms of 4 Nigerian crude oils (same as in Figure 36), showing relatively high concentrations of pristane (peak at 5.1 minutes).

As with Oleanane, **Gammacerane**, contains a hexacyclic E-ring and can be observed in the 191-mass-chromatogram, following the same fragmentation pattern as the hopanes. This compound indicates mainly marine sources of crude oils. It is found in higher concentrations (up to about 50% in relation to hopane) in the African Angola Cabinda - and Nemba crudes, and in Kongo - and Gabon crude oils (Figure 40).

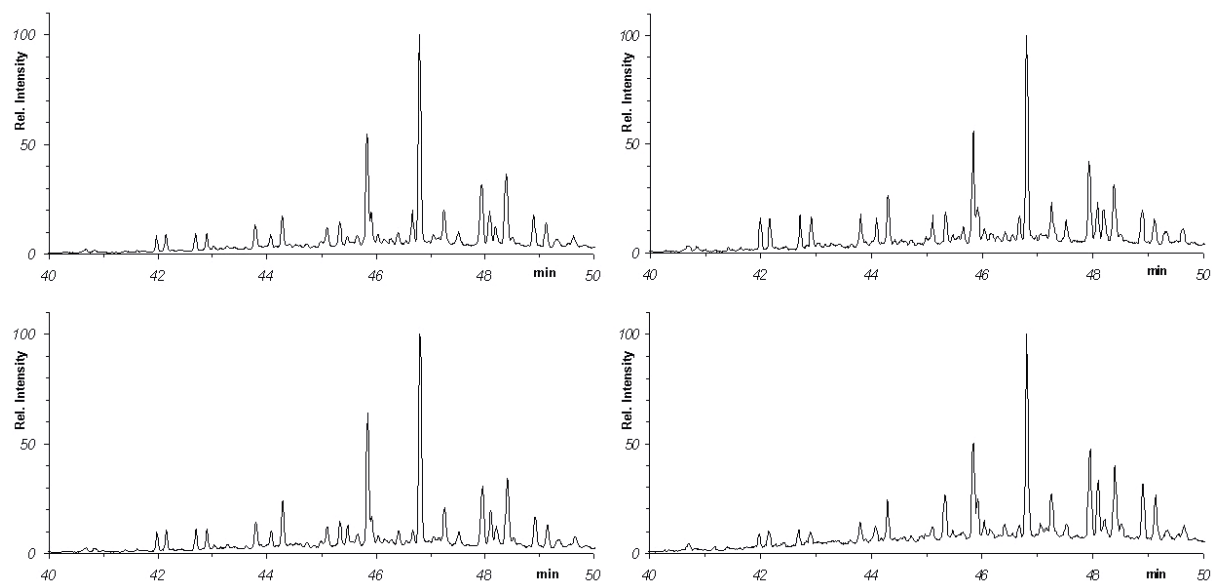


Fig. 40: Hopanes of Angola Cabinda - and Nemba crude (above), Kongo Djeno - and Gabon Mandji crude (below). Gammacerane: peak at 48.4 minutes.

The examples given above are mainly presented in order to show the presence and the position of peaks of compounds, which may have a “special” meaning in distinct oil spill cases. Generally, their rapid recognition may save resources, in case they are present in the spill sample but not in the comparison sample. On the other hand, their presence in both samples may indicate a much stronger connection between these samples than other compounds.

A more detailed geochemical interpretation of the biomarker patterns of the world’s crude oils is beyond the scope of this contribution and beyond the scope of Oil Spill Identification.

A substantial database of crude oils from all over the world is the prerequisite for the further classification of crude oils by their main production areas for Oil Spill Identification.

3 Conclusion

The meaning of compounds (or compound ratios) in oil samples is different from case to case, and a parameter set generally suitable for the verification of results in all oil spill cases might rarely exist. Whereas one single parameter may already be the decisive factor in a distinct case, other cases may require much more detailed investigations.

However, some general rules exist with regard to different oil types and their occurrence and behaviour in the aquatic environment.

The vast majority of oil spills in European waters originates from “normal” shipping operations. But when oil products or product mixtures, such as waste oils, are considered, the original meaning and the specificity of the pristine biomarker relations in crude oils are lost totally. The production (and or mixing) process plays the dominant role here. Care must thus be taken in order to avoid misinterpretation, when oil products are compared. Parameters may be similar or even identical simply because of the same production process.

Therefore, a step-by-step procedure is provided for identifying the oil type, even in (highly) weathered samples, and guidance is given on how to handle oil parameters with respect to the different characteristics of oil types.

It has finally been shown that monitoring of platforms and identifying crude oil pollution caused by tankers are quite different tasks. Different parameters may thus have a highly different meaning when crude oil pollution has to be identified.

It must be kept in mind, generally, that Oil Spill Identification by chemical analysis is an important –sometimes the most important- instrument for providing evidence in criminal proceedings. Not knowing the type of oil, which was analyzed, does not only show

insufficient knowledge and experience. There is even the high risk that erroneous conclusions are drawn.

REFERENCES:

- Dahlmann, G.: Eine neue sichere Methode zur Identifizierung der Verursacher von Ölverschmutzungen (Dt. hydrogr. Z. 37(5), 1984, 217-220)
- Dahlmann, G: Identification of oil pollution. In: Seminar on Oil Pollution Questions, Norrköping, (Baltic Sea Environment Proceedings No. 22, Baltic Marine Environment Protection Commission - Helsinki Commission, 1987, 149-160)
- Dahlmann G., Timm D., Averbeck Chr., Camphuysen C., Skov H., Durinck J.: Oiled Seabirds- Comparative Investigations on Oiled Seabirds and Oiled Beaches in the Netherlands, Denmark and Germany (1990-93)(Mar. Poll. Bull., Vol. 28, No. 5, 305-310, 1994)
- Dahlmann, G. Müller-Navarra, S.: The Source of Oil Pollution on the East Frisian islands in October 1989 – an Exemplary case (Dt. Hydrogr. Z. 49, 35-43, 1997)

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