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Improved and standardized methodology for oil spill fingerprinting

P.S. Daling, L.-G. Faksness [1], A. B. Hansen [2] & S. A. Stout [3]
[1] *SINTEF Applied Chemistry, NORWAY,*
[2] *NERI, Dept. Environmental Chemistry & Microbiology, Denmark*
[3] *Battelle Memorial Institute, USA*

Abstract

The existing Nordtest Methodology for Oil Spill Identification has over the past 10 years formed an important "platform" for solving oil spill identification cases both in the Scandinavian countries as well as other countries in Europe, the USA and Canada. *"Revision of the Nordtest Methodology for Oil Spill Identification"* is a co-operative project between the National Oil Spill Identification laboratories in Norway, Sweden, Finland, Denmark and Battelle Memorial Institute (Duxbury) in the USA. The goals of the project are: (1) to refine the existing Nordtest methodology into a technically more robust and defensible oil spill identification methodology with focus on determination of quantitative diagnostic indices (ratios) and (2) to adjust the revised Nordtest methodology into guidelines for the European Committee for Standardization (CEN).

This paper presents the recommended methodology for defensible oil spill identification and assessment when a single oil source is involved and there are no confounding effects of pre-spill background hydrocarbons. The sampling techniques and handling of oil samples prior to their arrival at the environmental forensic laboratory is not covered in this paper. The recommended methodology approach is a result of documented analytical improvements and a more quantitative treatment of analytical data from gas chromatographic-flame ionization detector (GC/FID) and gas chromatographic-mass spectrometer methods (GC/MS-SIM) and the operational experiences over past few years among the participating forensic laboratories. The

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experience and literature in the field of oil exploration and production geochemistry have also played an important role for the recommended methodology. The results from a recent Round Robin test carried out among 12 laboratories using this new methodology is presented in a separate paper at this conference (Faksness et al. [6]).

1 Introduction

1.1 Revision of the existing methodology for oil spill identification

The existing Nordtest Methodology for Oil Spill Identification developed in 1991 (NT CHEM 001, [12]) has been used for chemical fingerprinting of samples from oil spills and suspected sources at environmental forensic laboratories in Scandinavia as well as at laboratories in e.g. the USA, Canada, the Netherlands, the UK, and Ireland.

Advances in both interpretive and analytical methods over the past ten years indicated that there was a need for further improvements to the existing Nordtest methodology. It is anticipated that various technical refinements would lead to a more quantifiable, objective and defensible means to differentiate among qualitatively similar oils from a spill and any available candidate sources.

Nordtest (*Internet:* http://www.nordtest.org/) is an institution under the Nordic Council of Ministers, and it acts as a joint Nordic body in the field of conformity assessment. In 2000, Nordtest initiated the still ongoing project called *"Revision of the Nordtest Methodology for Oil Spill Identification"*. The project is organized into a project team from the National Forensic Oil Spill Identification laboratories in Finland, Denmark, Norway, Sweden and Battelle Laboratories in USA. The main objectives of this project are to:

- Refine the existing Nordtest methodology into a technically more robust and defensible oil spill identification methodology. The primary refinements focus on the use of:
  - Semi-quantitative analysis of petroleum biomarkers and an extended suite of parent and alkylated polycyclic aromatic hydrocarbons (PAHs)
  - Determination of quantitative diagnostic ratios and statistical data treatment.
- Adjust the revised Nordtest methodology into guidelines for the European Committee for Standardization (CEN)

During Phase 1 of the project (2000-2001), the following tasks / activities were carried out:

1. Review of recently published oil spill (e.g., Wang et al.[20]; Stout et al. [16]) and the petroleum geochemistry (e.g., Peters and Moldowan [14] and ref. therein) literature.
2. Development of improved analytical techniques in the laboratory (sample preparation, clean up, and analysis focused on defining relevant diagnostic ratios),

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3. A preliminary Round Robin test (hereafter referred to as Series A): For this test, oil samples were collected during the *"Deep Spill field experiment"* (conducted in the Norwegian Sea, June 2000). The samples were analyzed according to the existing standard (Nordtest or other) practice at the participating laboratories. This Round Robin Test Series A demonstrated the potential to improve and harmonize the existing Nordtest methodology by more use of (semi-) quantitative approach for parent and alkylated PAH, and in the use of diagnostic ratios of selected PAHs and petroleum biomarker components as a means of identifying the source of an oil. (Faksness et. al [5]).

1.2 Towards an improved methodology for oil spill identification

In Phase 2 of the project (2001-2002), a second Round Robin test (Series B) took place. In all, twelve laboratories from ten different countries participated in this Series. The Round Robin test was organized by SINTEF, in co-operation with the Norwegian General Standardizing Body (NAS). The technical protocols for this Round Robin test were based on the revised /improved methodology that had been developed during Phase 1 and consensus based on the experiences among the Nordtest project team. *Conclusions from Round Robin Test Series B:*

Considering that this was the first time the methodology was applied in many laboratories, and that only a very short time had been available for adoption of the new methodology, this Round Robin test demonstrates the potential of this methodology as a strong technically defensible tool in oil spill identification. The results are reported in Faksness *et al.* [7] and are also presented separately at this proceedings (Faksness *et al.* [9])

1.3 Harmonization of oil spill identification methodology

[1] In parallel to this ongoing Nordtest project, the Technical Board (BT) of the European Committee for Standardisation (CEN), in 2000 established a Task Force (working group) called: *"CEN/BT/Task Force 120 Oil Spill Identification"*. The Norwegian General Standardizing Body (NAS) has the secretariat and SINTEF is convenor for the working group.

The scope of the *CEN/BT/TF 120 Oil Spill Identification* is to establish guidelines for a technically robust and defensible methodology for identification of waterborne oil spills and their correlation to suspected sources which encompasses:

- oil sampling
- handling of samples
- preparation of samples
- chemical analysis and data processing
- data interpretation and reporting

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The CEN-guidelines are presently under development, and will cover the following issues:

- Issue 1: Guidelines on the methodology for identification of waterborne oils.
- Issue 2: Guidelines for sampling of waterborne oils for oil spill identification.
- Issue 3: Analytical methodology and data processing specifications for oil spill identification.

It is also the intention of the CEN working group that the establishment of these CEN guidelines can form the common basis of the national oil spill identification protocol in each of the European countries, as well as being the norms for further international use.

The methodology is restricted to oil samples of petrogenic origin containing significant proportion of hydrocarbons with boiling points above 200 °C. Examples are: Crude oils, diesel fuel oils, residual or bunker oils, lubricants, and mixtures of bilge and sludge samples. Thus, the methodology is not intended for application to automotive gasolines or other light petroleum products. When suspected sources are not available, the methodology is still useful in that it can be used to thoroughly characterize the spill hydrocarbons by product type (e.g. crude, refined product, residual), and identify potential candidate sources on this basis. The methodoloty is further restricted to situations involving single source spills and where pre-spill petrogenic hydrocarbons form either natural or anthropogenic sources are absent.

2 Summary of the revised methodology for oil spill identification

2.1 Protocol / decision chart of analytical and data treatment levels

The new methodology is based on a revision of the Nordtest method NT CHEM 001 "Oil Spill Identification" [12]. A protocol / decision-chart of the new recommended methodology is shown in Figure 1 below includes the following tiered "levels" of analyses and data treatment:

Level 1:

After sample preparation, the chemical fingerprinting analysis in the laboratory starts with a whole oil gas chromatography (GC/FID) screening analysis of all samples (i.e., both spilled oils and suspected sources). Results of this screening level analysis on each sample forms the basis for:

- Characterizing the sample by obtaining the overall boiling (carbon) range of the spilled oil (i.e. total distribution of hydrocarbons including n-alkanes C_{10}-C_{40}),
- Establishing selected acyclic isoprenoid indices/ratios readily determined using GC/FID, and

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- Establishing a "weathering check" (self-normalizing to a non-weathered or weathering resistant compound).

At this level of the investigation, the spill samples can be qualitatively and quantitatively compared to the suspected sources, and obviously "non-matched" samples can be ruled out and eliminated from additional levels of analysis.

Level 2:

The next analytical "level" is analysis of spill and candidate source samples using gas chromatography combined with mass spectrometry operated in the selected ion monitoring mode (GC/MS-SIM). This analysis is useful for determining the content and distributions of a suite of petroleum biomarkers and polycyclic aromatic hydrocarbons (PAH) target analytes. These semi-quantitative data form the basis for:

- Generating a suite of calculated diagnostic ratios based on selected PAH for degree of weathering estimates and source identifications.
- Generating a suite of calculated diagnostic ratios for selected biomarkers (hopanes and other triterpanes, regular steranes and diasteranes, and triaromatic steroids) for source identification.
- Establishing a "weathering check" from a suite of selected PAH groups.

Level 3:

- Assess the impact of weathering (based on weathering check data of n-alkanes from level 1 and eventual semi-quantitative distribution of the PAH groups from level 2)
- Evaluate and eliminate those diagnostic ratios exhibiting considerable variability due to analytical variance and sample heterogeneity.
- Correlation studies: Results from triplicate analyses are used to calculate the analytical relative standard deviation followed by the selection of the more robust (i.e., precisely measured and weathering resistant) diagnostic ratios using the "Student's t" statistical tool. The results comparing the spill sample and suspected source(s) are presented in simple x-y plots, linear regressions are performed, and conclusions based on the "fit" between spill and source samples for the selected suite of robust diagnostic ratios can be made.

The results and the overall conclusions should be reported for the combined qualitative and quantitative results of the test methodology. The total assessment can be concluded by the following four operational and defensible identification terms (as in ASTM D3328-00 [1]): Positive match, probable match, inconclusive or non-match, which are defined in the conclusions of this paper.

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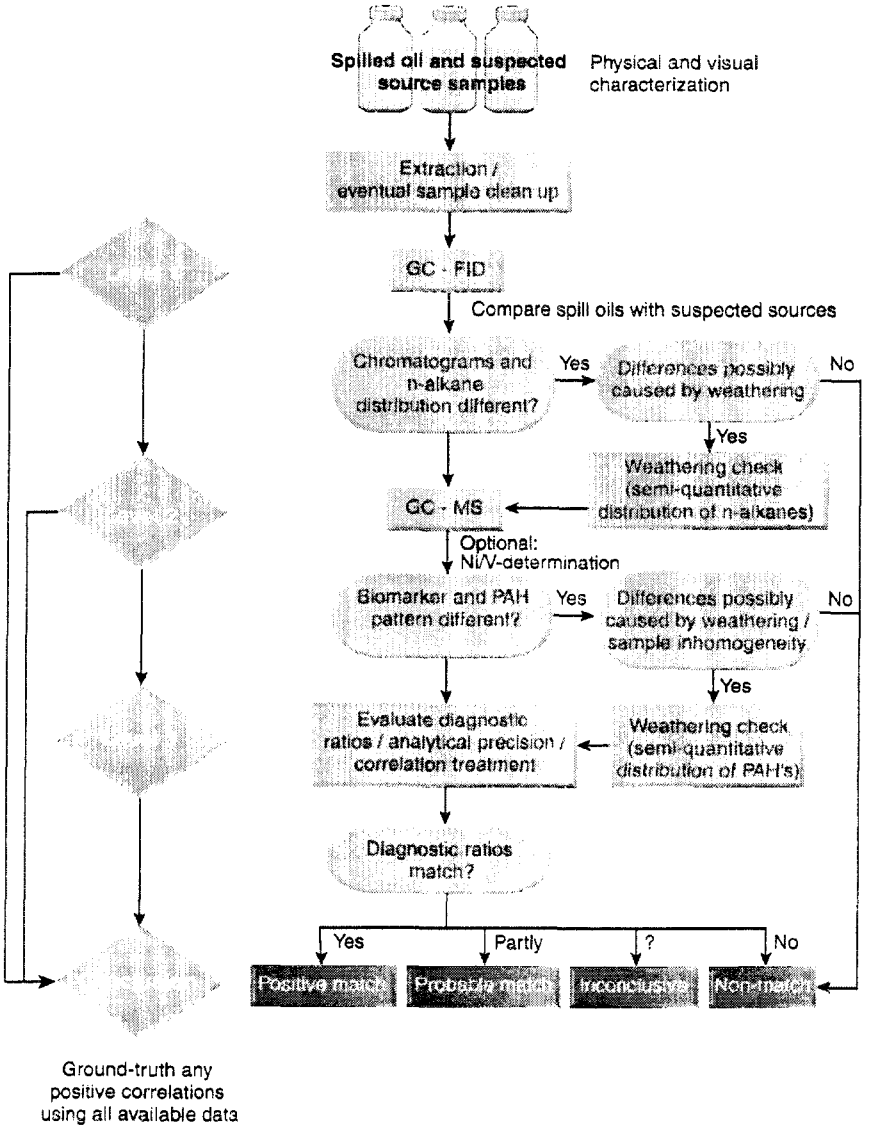

Figure 1 Protocol / decision chart for the oil spill identification methodology.

2.2 Visual and physical examination of samples

The visual appearance and physical characteristics of the oil / emulsion samples, such as their color, density (*e.g.* ASTM- D4052-81), viscosity (McDonagh *et al* [11]), emulsified water (*e.g.* Karl Fisher Titration) are parameters that optionally

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might be determined for characterization – particularly in cases connected to a response operation. Eventual content of free water and debris are noted visually and reported. It is also recommended that each sample be photographed to document its "as-received" condition.. Wood, fabric, feathers and other debris should be removed from the sample with a pair of tweezers and noted in the report.

2.3 Sample preparation

The same sample preparation procedure is followed for both GC/FID and GC/MS analysis (*i.e.* the same extracts are analyzed for both analysis). If a sample clean-up must be performed, eventual recovery internal standards are added after the clean up, if required (Daling and Faksness [2]).

If a sample cannot be prepared immediately after arrival at the laboratory, it should be stored in a secure refrigerator (5±2°C). Sample preparation should not be delayed more than three days, particularly in cases concerning emulsions or samples containing visible amounts of water.

Specific procedures for preparation of: water-free oils sample, emulsified oil samples, oily water samples, Teflon net used for thin oil films, samples from oily birds, animals and debris on shore are given in Faksness *et al.* [6] and [8].

2.4 Recommended sample clean up methodology

Matrix interference may be caused by contaminants that are co-extracted from the sample. Since biogenic materials may cause interference, an alumina column clean-up is recommended to remove lipids and polar compounds prior to chemical analysis. If the purpose of the clean-up is to remove polar and heavy naturally occurring compounds from the extract (*e.g.* for oils containing high content of asphaltenes), a pre-packed silica column should be sufficient. Recommended clean-up procedures are given in Faksness *et al.* [6] and [8].

2.5 Analytical instrumental parameters

All analytical instrumental conditions / procedures for the GC/FID and the GC/MS-SIM analysis are given in detail in Daling and Faksness [2] and summarized in this proceeding (Faksness et al., [9]).

3 Total evaluation of analytical data

When evaluating the analytical data, it is important to have a good understanding of how the variety of weathering processes i.e. evaporation, dissolution, photo-chemical oxidation, microbial degradation etc. may influence on the analytical results. Within a term of hours to days after an oil spill, evaporation may cause considerable changes in chemical composition and physical properties of the spilled oil that have to be taken into account in the interpretation of the defensive oil spill identification analysis (Wang and Fingas [21]). Also "re-distribution" of

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chemical components in the oil (*i.e.* wax- enrichment /-depletion) can be observed as a result of oil being exposed to the turbulence at sea and in the surf-zone (Strøm-Kristiansen *et al.* [19]).

3.1 GC - FID screening

The GC/FID approach is used as a quick screening characterization of the oil samples. The GC/FID chromatogram (Level 1 in the Decision Chart) gives a descriptive "picture" of the distribution of the dominating hydrocarbons in a sample (*e.g.* individual resolved n-alkanes and major isoprenoids, as illustrated in Fig. 2.). They also provide good information on the weathering extent of the spilled oil, and also if any "characteristic features" or possible "contaminating" components are present. For biodegraded oil, the n-alkanes are normally the predominating /characteristic peaks distributed regularly over the whole retention interval.

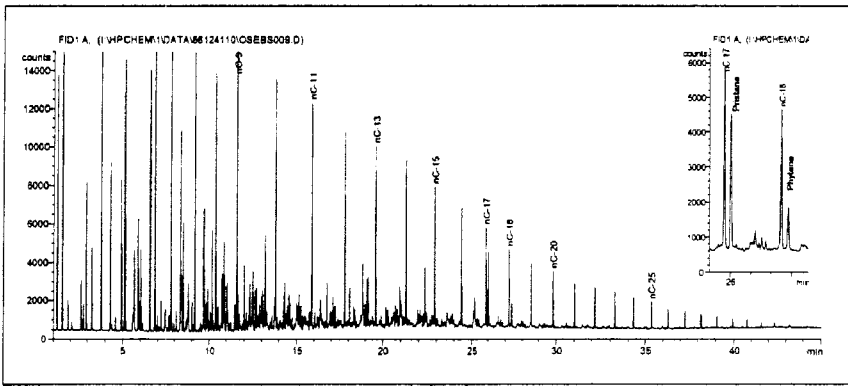

Figure 2 Whole oil GC/FID chromatogram of a non-weathered Oseberg crude oil (North Sea province).

The ratios between or among normal alkanes and acyclic isoprenoids, e.g., n-C_{17}/Pristane, n-C_{18} /Phytane and Pristane/ Phytane are important diagnostic indices assessable in the GC/FID chromatograms (these ratios should be based on peak heights, Daling and Faksness, [2]).

It is important to note that, if the analysis reveals differences not caused by analytical inaccuracy or by weathering, the analysis may be concluded at this point, since non-match has been established. However, if there is any doubt, the identification process should be continued.

3.1.1 Weathering check of n-alkanes

GC analyses alone may give limited oil diagnostic characteristics when the petroleum sample has been highly weathered (*e.g.* samples taken from thin oil films at sea) or when the oil type in the samples are very similar (*e.g.* diesel oils and mineral oils of similar boiling ranges and alkane composition).

To get an illustrative picture of the degree of weathering, a simple "weathering check" can be obtained by integrating (or measuring peak heights)

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of the n-alkanes in the GC/FID chromatogram and display the sample comparison in bar-charts normalized to non-weathered compounds. Figure 3 gives an example of such a bar-chart, where the n-alkanes have been normalized to n-C_{25}. Such presentation of the n-alkane distribution in the samples will also reflect information on potential wax/paraffin redistribution as a part of the weathering process (Strøm-Kristiansen *et al.* [19], see Figure 4).

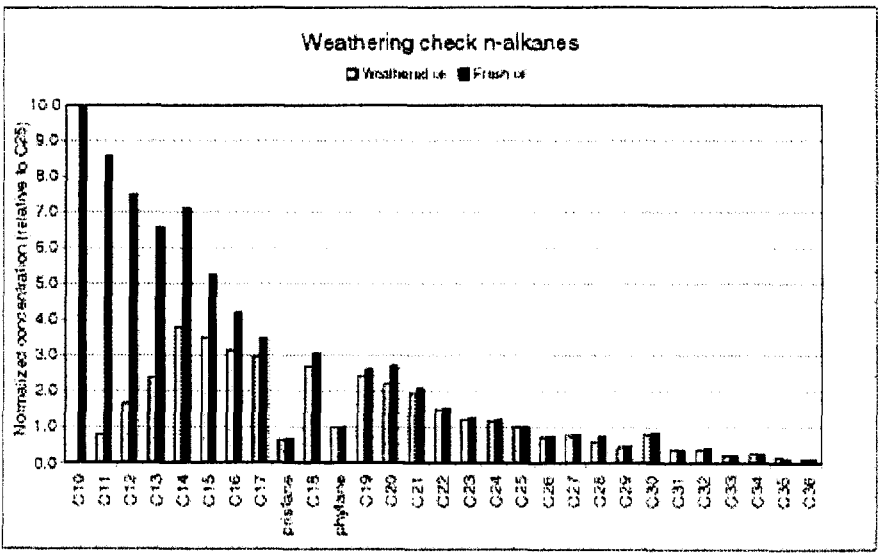

Figure 3 "Weathering Check" of a Spilled Oil Sample Versus a Suspected Non-weathered Source Oil by Comparing Alkane Peak Areas Normalized Relative to n-C_{25} (Aquila crude oil).

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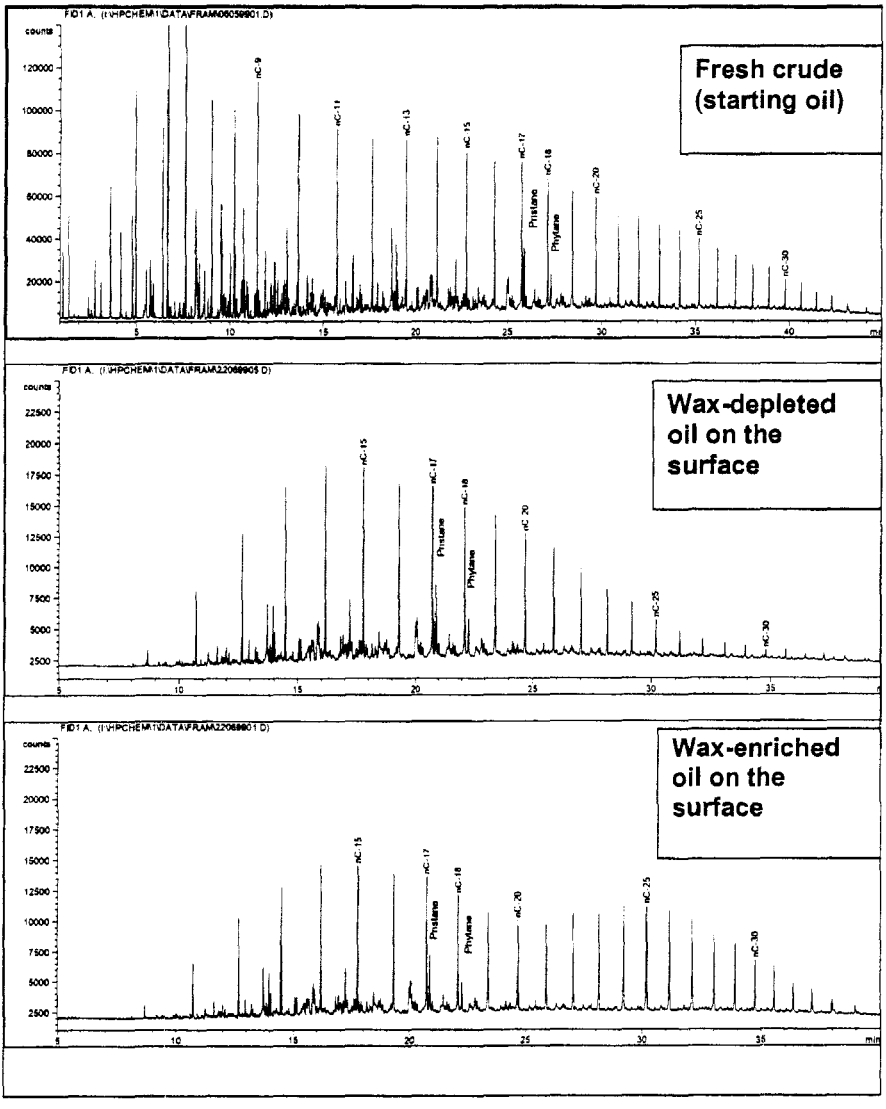

Figure 4. Example of re-distribution of chemical composition (wax-enrichment/-depletion) of oil spilled at sea. (from a weathering study of Fram - a paraffinic North Sea crude)

3.2 GC/MS analyses data of biomarkers and PAHs

The recommended GC/MS method provides the significant advantage of being applicable for determination of biomarker compounds and the PAH including the alkylated homologues (Table 1), during the same analytical run.

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Table 1 List of PAHs and Biomarkers Analyzed by GC/MS-SIM (analyzed in one run)

Target PAH/PAH group	Abbrev	Qion (m/z)	Target biomarkers	Abbrev	Qion (m/z)
PAH/PAH groups			**Pentacyclic triterpanes (hopanes)**		
Naphthalene	N	128	18α(H)-22,29,30-trisnorhopane	27Ts	191
C1-naphthalenes	N1	142	17α(H)-22,29,30-trisnorhopane	27Tm	191
C2-naphthalenes	N2	156	17α(H),21β(H)-28,30-bisnorhopane	28ab	191
C3-naphthalenes	N3	170	17α(H),21β(H)-25-norhopane	25nor30ab	191
C4-naphthalenes	N4	184	17α(H),21β(H)-30-norhopane	29ab	191
Biphenyl	B	154	18α(H)-30-norneohopane	29Ts	191
Acenaphthylene	ANY	152	15α-methyl-17α(H)-27-norhopane (diahopane)	30d	191
Acenaphthene	ANA	154	17β(H)-21α(H)-30-norhopane (normoretane)	29ba	191
Dibenzofuran	DBF	168	18α(H)-oleanane	30O	191
Fluorene	F	166	17α(H),21β(H)- hopane	30ab	191
C1-fluorenes	F1	180	17β(H)-21α-(H)-hopane (moretane)	30ba	191
C2-fluorenes	F2	194	17α(H),21β(H), 22S-homohopane	31abS	191
C3-fluorenes	F3	208	17α(H),21β(H), 22R-homohopane	31abR	191
Phenanthrene	P	178	*Gammacerane*	30G	191
Anthracene	A	178	17α(H),21β(H), 22S- bishomohopane	32abS	191
C1-phenanthrenes/anthracenes	P1	192	17α(H),21β(H), 22R-bishomohopane	32abR	191
C2-phenanthrenes/anthracenes	P2	206	17α(H).21β(H), 22S- trishomohopane	33abS	191
C3-phenanthrenes/anthracenes	P3	220	17α(H),21β(H), 22R-trishomohopane	33abR	191
C4-phenanthrenes/anthracenes	P4	234	17α(H),21β(H), 22S- tetrakishomohopane	34abS	191
Dibenzothiophene	D	184	17α(H),21β(H), 22R-tetrakishomohopane	34abR	191
C1-dibenzothiophenes	D1	198	17α(H),21β(H), 22S- pentakishomohopane	35abS	191
C2-dibenzothiophenes	D2	212	17α(H),21β(H), 22R-pentakishomohopane	35abR	191
C3-dibenzothiophenes	D3	226			
C4-dibenzothiophenes	D4	240	**Diasteranes and steranes**		
Fluoranthene	FL	202	13β(H),17α(H),20S-cholestane (diasterane)	27dbS	217
Pyrene	PY	202	13β(H),17α(H),20R-cholestane (diasterane)	27dbS	217
C1-fluoranthrenes/pyrenes	FL1	216	24-methyl-5α(H),14α(H),17α,20R-cholestane	28aaR	217
C2-fluoranthenes/pyrenes	FL2	230	24-ethyl-5α(H),14α(H),17α.20S-cholestane	29aaS	217
C3-fluoranthenes/pyrenes	FL3	244	24-ethyl-5α(H),14β(H),17β,20R-cholestane	29bbR	217
Benz(a)anthracene	BA	228	24-ethyl-5α(H),14β(H),17β,20S-cholestane	29bbS	217
Chrysene	C	228	24-ethyl-5α(H),14α(H),17α,20R-cholestane	29aaR	217
C1-chrysenes	C1	242	5α(H),14β(H),17β(H),20R-cholestane	27bbR	218
C2-chrysenes	C2	256	5α(H),14β(H),17β(H),20S-cholestane	27bbS	218
C3-chrysenes	C3	270	24-methyl-5α(H),14β(H),17β,20R-cholestane	28bbR	218
C4-chrysenes	C4	284	24-methyl-5α(H),14β(H),17β,20S-cholestane	28bbS	218
Benzo(b)fluoranthene	BBF	252	24-ethyl-5α(H),14β(H),17β,20R-cholestane	29bbR	218
Benzo(k)fluoranthene	BKF	252	24-ethyl-5α(H),14β(H),17β,20S-cholestane	29bbS	218
Benzo(e)pyrene	BEP	252			
Benzo(a)pyrene	BAP	252	**Triaromatic steroids**		
Perylene	PER	252	C20-triaromatic steroid hydrocarbon	C20TA	231
Indeno(1,2,3-c,d)pyrene	IN	276	C21-triaromatic steroid hydrocarbon	C21TA	231
Dibenz(a,h)anthracene	DBA	278	C26, 20S-triaromatic steroid hydrocarbon	SC26TA	231
Benzo(g,h,i)perylene	BPE	276	C26,20R-+C27,20S-triaromatic steroid hydrocarbon	RC26TA+SC27TA	231
Decalin (ref.)	DE	138	C28, 20S-triaromatic steroid hydrocarbon	SC28TA	231
C1-decalins (ref.)	DE1	152	C27, 20R-triaromatic steroid hydrocarbon	RC27TA	231
C2-decalins (ref.)	DE2	166	C28, 20R,triaromatic steroid hydrocarbon	RC28TA	231
C3-decalins (ref.)	DE3	180			
C4-decalins (ref.)	DE4	194	**Single PAHs**		
Benzo(b)thiophene	BT	134	2-methyl phenanthrene	2-MP	192
C1-benzo(b)thiophenes	BT1	148	1-methyl phenanthrene	1-MP	192
C2-benzo(b)thiophenes	BT2	162	Retene	Retene	234
C3-benzo(b)thiophenes	BT3	176	4-methyl dibenzothiophene	4-MD	198
C4-benzo(b)thiophenes	BT4	190	1-methyl dibenzothiophene	1-MD	198

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A visual inspection of the extracted ion chromatograms of the biomarker and of selected PAH's for identifying eventual "characteristic features" in the ion-chromatograms is recommended before selecting and calculating the diagnostic ratios. Additionally, a semi-quantitative measurement of the suite of PAH target groups and their alkyl homologues may give supplementary diagnostic information and visualization of those PAHs influenced by weathering.

3.2.1 Weathering check of semi-quantitative PAH homologues (optional)

The major compositional changes of alkyl PAH compounds due to evaporative weathering can be summarized as follows (Wang and Fingas [21]):

- A pronounced decrease in naphthalene and its alkyl homologues relative to other PAH homologues series
- Most homologous groups show the same evaporative loss trend: C0 >C1 >C2 >C3>C4.
- No loss of alkylchrysenes (4-rings) due to evaporation.

An illustrative check on weathering effects on the PAHs can be obtained by normalizing the PAH data relative to C30-hopane (based on peak area, Daling and Faksness, [2]) and presented graphically, as shown in Figure 5. The decalins are in the same boiling point area as the more water soluble naphthalenes, and are therefore useful "reference components" to reveal any loss of PAHs due to dissolution in addition to eventual evaporative loss.

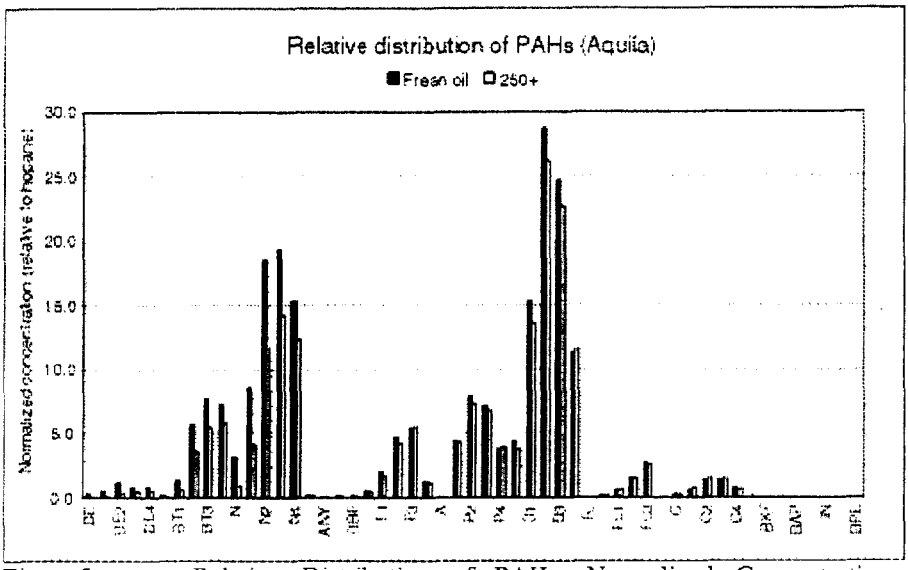

Figure 5 Relative Distribution of PAHs: Normalized Concentration Relative to C_{30}-hopane (Aquila fresh crude and an Aquila 250°C+ weathered residue)

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3.2.2Diagnostic ratios of PAHs

Crude oil from different oil field and provinces can have very different PAH distributions. Several diagnostic ratios are used for oil identification (Radke [15], Douglas [3]. Wang *et al.*, [20] and Stout *et al.* [18]). The most common diagnostic PAH families are the dibenzothiophenes and the phenanthrenes. Methyldibenzothiophenes (C1-dibenzothiophenes, C_{18}-C_{19} boiling range, m/z 198, Figure 6) are usually present in crude oils in easily detectable concentrations. The distribution profiles and ratios among C1-dibenzothiophene isomers are often distinct from oil to oil. The ratios of isomeric C1-dibenzothiophenes are subject to little interference from evaporative weathering of short-term or lightly weathered oils. Among the C1-dibenzothiophenes, the bacteria most preferentially tend to degrade the 2-/3-methyldibenzothiophene isomers (Wang and Fingas [21]). The ratio 4-MD/1-MD is therefore often used as a diagnostic ratio.

Retene, (C_{19}-C_{22} boiling range, m/z 234, Figure 7) is an aromatic diterpane (1-methyl-7-(1-methylethyl)-phenanthrene) derived from plant resins (*e.g.* abietic acid), and is highly resistant to weathering. The diagnostic ratio between retene and total C4-phenanthrenes can be a useful feature in distinguishing among otherwise similar oils (Stout *et al.* [18]).

Methylphenanthrenes (C1-phenanthrenes, C_{18}-C_{19} boiling range, m/z 192, Figures 8a and b) can provide valuable information in forensic investigations, particularly in cases involving middle distillate fuels, in which the C1-phenanthrenes are common constituents. The distribution of C1-phenanthrene isomers in a crude oil is sensitive to both the source rock facies from which the oil was generated as well as its geological thermal maturity. Furthermore, the 2-methylphenanthrene isomer is more sensitive to biodegradation in the reservoir than the other isomers (Radke [15], Wang and Fingas [21]). The ratio 2-MP/1-MP is therefore recommended as a diagnostic ratio.

Methylphenanthrenes have also reportedly been used to differentiate between crude oil and bunker oil (Eurocrude [4]). According to this research, in many crude oils, the first doublet peak (3- and 2-methylphenanthrenes) is smaller than the second doublet (9-/4- and 1-methylphenanthrenes) and the methyl-anthracene (the peak between the two doublet peaks) is very small or insignificant (e.g., see Figure 8a). While, for bunker fuel oils, the first doublet peak is reportedly higher than the second doublet (even for highly weathered fuel oils), and the methyl-anthracene (the peak between the two doublets) is often more pronounced (Eurocrude, [4]; e.g., see Figure 8b). This statement must, however, only be considered as "indicative", and not always be valid (e.g. Faksness *et al.* [6]).

Thus, in total there are six recommended diagnostic ratios derived from the PAHs that are given in Table 2. Following the approach employed by petroleum geochemists (e.g., Weiss et al. [22]), all of these ratios (e.g. between a peak A and a peak B) are calculated as percentages based on the formula (1):

$$100\% \times [A/(A+B)] \quad (1)$$

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Table 2 Suggested Diagnostic Ratios for PAHs

Ratio name	**Definition**
C2-dbt/C2-phe (%)	100 * [C2-dibenzothiophenes/ (C2-dibenzothiophenes + C2-phenanthrenes]
C3-dbt/C3-phe (%)	100 * [C3-dibenzothiophenes/ (C3-dibenzothiophenes + C3-phenanthrenes)]
C3-dbt/C3-chr (%)	100 * [C3-dibenzothiophenes/ (C3-dibenzothiophenes + C3-chrysenes)]
2-MP/1-MP (%)	100 * [2-methyl phenanthrene/ (2-methyl phenanthrene + 1-methyl phenanthrene)]
4-MD/1-MD (%)	100 * [4-methyl dibenzothiophene/(4-methyl dibenzothiophene + 1-methyl dibenzothiophene)]
Retene/C4-phe (%)	100 * [Retene/(retene + C4-phenanhrenes)]

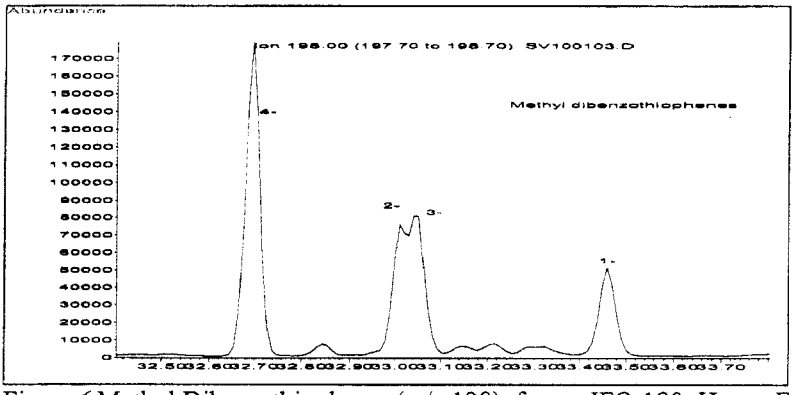

Figure 6 Methyl Dibenzothiophenes (m/z 198), from a IFO-180 Heavy Fuel Oil.

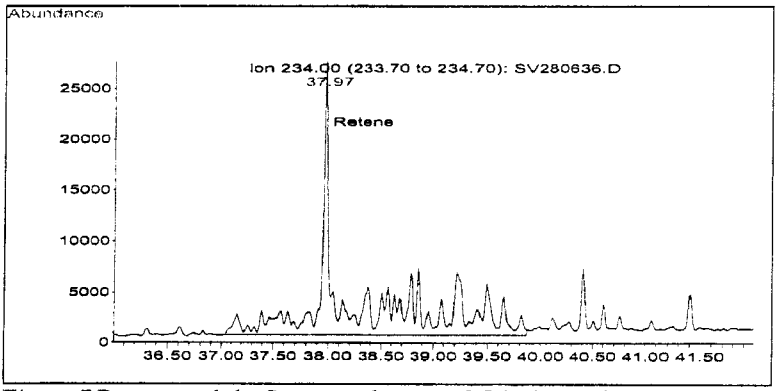

Figure 7 Retene and the Integrated Area of C4-phenanthrenes (m/z 234) from a North Sea Crude Oil (Oseberg crude).

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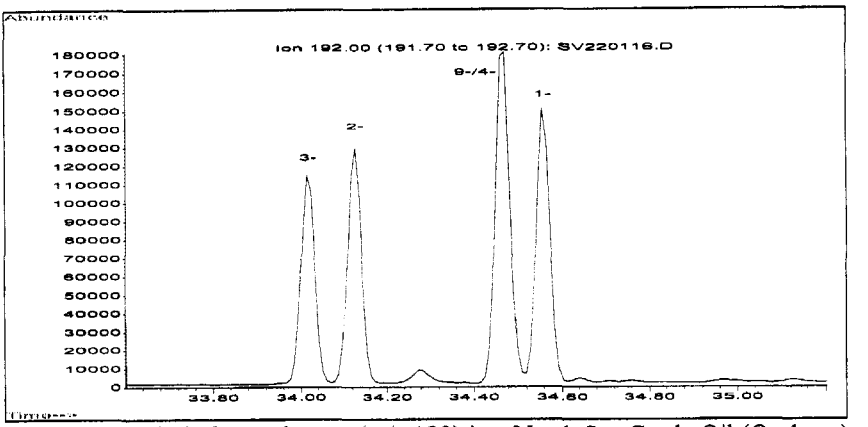

Figure 8a Methyl Phenanthrenes (m/z 192) in a North Sea Crude Oil (Oseberg).

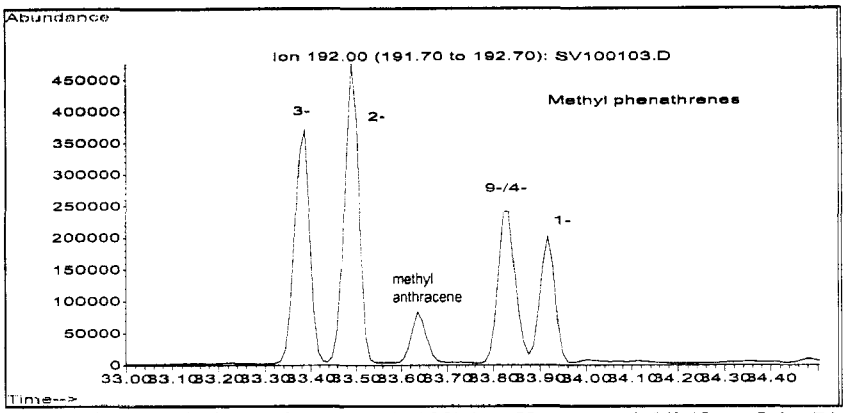

Figure 8b Methyl Phenanthrenes (m/z 192) in a Heavy Fuel Oil (from John R).

3.2.3 Diagnostic ratios of biomarkers

Biomarkers are naturally occurring, ubiquitous and stable hydrocarbons that occur in crude oils and most petroleum products. They are complex molecular fossils derived from once-living organisms. Biomarkers' specificity, diversity, complexity, and relative resistance to weathering therefore make them extremely useful "markers" in the characterization and differentiation of spilled oils and candidate source oils (Stout *et al.* [16]). The most common biomarkers used by organic geochemists include terpanes, steranes and mono- and triaromatic steroids (Peters and Moldowan [13], [14]).

By making use of the experience gained by petroleum exploration and production geochemistry, combined with an extensive analysis of a large number of oils (Faksness *et al.*, [6]), a suite of 18 diagnostic biomarker ratios have been selected as defensible indices to differentiate among qualitative similar oils from spills and available candidate sources. Figure 9 illustrates the span of the values for 23 selected diagnostic ratios (18 biomarkers and 5 PAHs ratios) among 28 different crude oils and refined oil products (Faksness *et al.* [6]).

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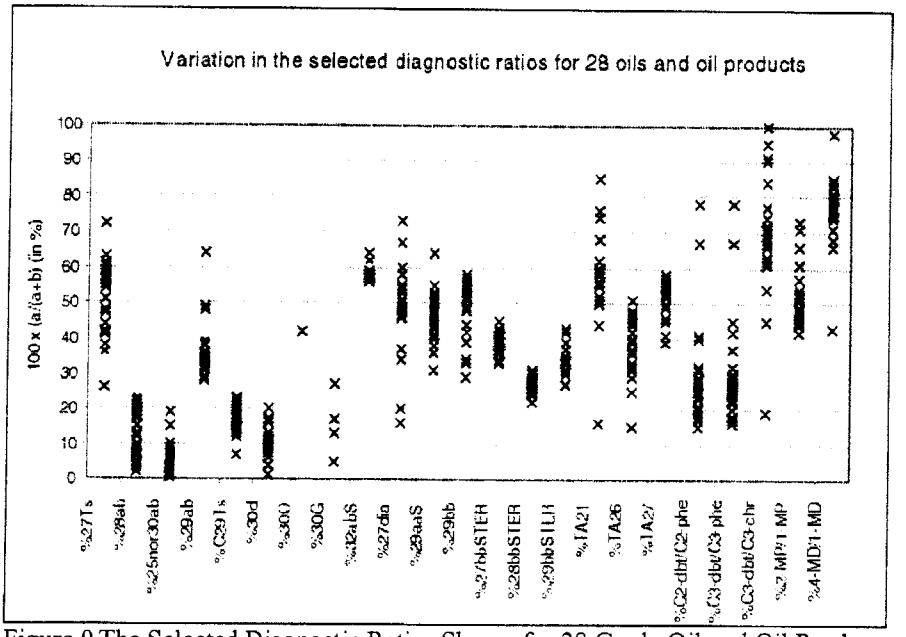

Figure 9 The Selected Diagnostic Ratios Shown for 28 Crude Oil and Oil Products.

The criteria used for selection of the diagnostic ratios were:

- Specificity and diversity
- Resistance to weathering
- Analytical precision / complexity (*e.g.* ratios with different m/z not used)

The ion chromatograms with peak identity of the hopanes and other pentacyclic triterpanes (m/z 191), regular steranes, diasteranes and triaromatic steroids are given in Figures 10, 11 and 12 respectively, and the formulas for the selected diagnostic ratios in the Tables 3, 4 and 5.

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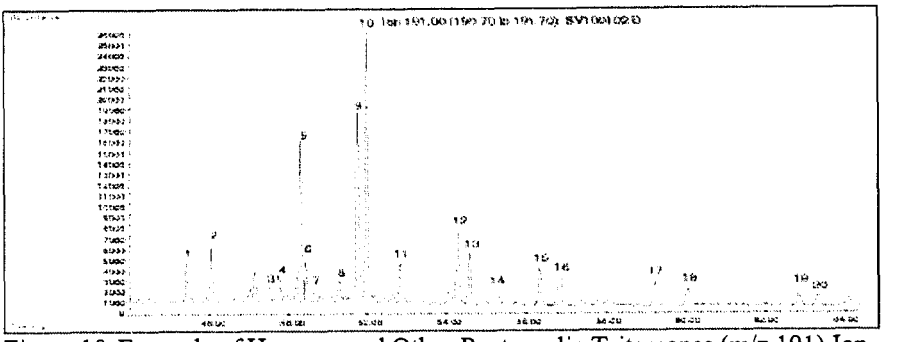

Figure 10 Example of Hopanes and Other Pentacyclic Triterpanes (m/z 191) Ion Chromatogram (IFO-180)

Peak #	Abbreviation	Target analytes name
1	27Ts	18α(H)-22,29,30-trisnorhopane
2	27Tm	17α(H)-22,29,30-trisnorhopane
3	28ab	17α(H),21β(H)-28,30-bisnorhopane
4	25nor30ab	17α(H),21β(H)-25-norhopane
5	29ab	17α(H),21β(H)-30-norhopane
6	29Ts	18α(H)-30-norneohopane
7	30d	15α-methyl-17α(H)-27-norhopane (diahopane)
8	29ba	17β(H)-21α(H)-30-norhopane (normoretane)
9	30O	18α(H)-oleanane (not present in or rare in oil from pre-Cretaceous source rocks)
10	30ab	17α(H),21β(H)- hopane
11	30ba	17β(H)-21α-(H)-hopane (moretane)
12	31abS	17α(H),21β(H), 22S- homohopane
13	31abR	17α(H),21β(H), 22R-homohopane
14	30G	Gammacerane (not abundant in North Sea oils)
15	32abS	17α(H),21β(H), 22S- bishomohopane
16	32abR	17α(H),21β(H), 22R-bishomohopane
17	33abS	17α(H),21β(H), 22S- trishomohopane
18	33abR	17α(H),21β(H), 22R-trishomohopane
19	34abS	17α(H),21β(H), 22S- tetrakishomohopane
20	34abR	17α(H),21β(H), 22R-tetrakishomohopane

Figure 10 cont.: Hopanes (m/z 191) Target Analytes and Abbreviations

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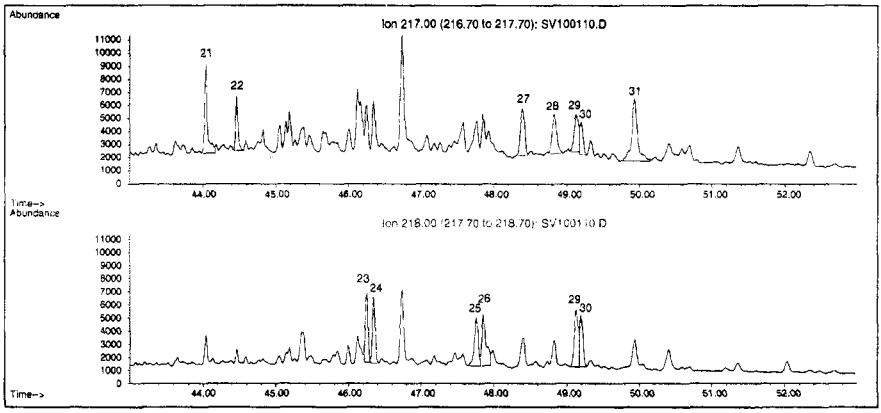

Peak#	Abbreviation	Target analytes name
21	27dbS	13β (H), 17α(H), 20S - cholestane (diasterane)
22	27dbR	13β (H), 17α(H), 20R - cholestane (diasterane)
27	28aaR	24-methyl-5α(H), 14α(H), 17α, 20R- cholestane
28	29aaS	24-ethyl-5α(H), 14α(H), 17α, 20S- cholestane
29	29bbR	24-ethyl-5α(H), 14β (H), 17β, 20R- cholestane
30	29bbS	24-ethyl-5α(H), 14β (H), 17β, 20S- cholestane
31	29aaR	24-ethyl-5α(H), 14α(H), 17α, 20R- cholestane
23	27bbR	5α (H), 14β(H), 17β(H), 20R-cholestane
24	27bbS	5α (H), 14β(H), 17β(H), 20S-cholestane
25	28bbR	24-methyl-5α(H), 14β (H), 17β, 20R- cholestane
26	28bbS	24-methyl-5α(H), 14β (H), 17β, 20S- cholestane
29	29bbR	24-ethyl-5α(H), 14β (H), 17β, 20R- cholestane
30	29bbS	24-ethyl-5α(H), 14β (H), 17β, 20S- cholestane

Figure 11 Regular Steranes and Diasteranes (m/z 217 and 218): Ion Chromatograms, Target Analytes and Abbreviations.

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Table 3 Recommended Diagnostic Ratios for Hopanes (m/z 191)

Ratio name	Definition
%27Ts	100 * [27Ts(191)]) / ([27Ts(191)] + [27Tm(191)])
%28ab	100 * [28ab(191)] / ([28ab(191)] + [30ab(191)])
%25nor30ab	100 * [25nor30ab(191)] / ([25nor30ab(191)] + [30ab(191)])
%29Ts	100 * [29Ts(191)] / ([29Ts(191)] + [30ab(191)])
%30O	100 * [30O(191)] / ([30O(191)] + [30ab(191)])
%30G	100 * [30G(191)] / ([30G(191)] + [30ab(191)])
%29ab	100 * [29ab(191)] / ([29ab(191)] + [30ab(191)])
%30d	100 * [30d(191)] / ([30d(191)] + [30ab(191)])
%32abS	100 * [32abS(191)] / ([32abS(191)] + [32abR(191)])

Table 4 Recommended Diagnostic Ratios for Regular Steranes and Diasteranes (m/z 217 and 218)

Ratio name	Definition
%27dia	100 * ([27dbS(217)]+[27dbR(217)]) / ([27dbS (217)]+ [27dbR(217)] + [27bbR(217)] + [27bbS(217)])
%29aaS	100 * [29aaS(217)] / ([29aaS(217)]+ [29aaR(217)])
%29bb	100 * ([29bbR(217)]+[29bbS(217)]) / ([29bbS(217)]+ [29bbR(217)] + [29aaS(217)] + [29aaR(217)])
%27bbSTER	100 * [27bb(S+R)(218)] / ([27bb(S+R)(218)]+[28bb(S+R)(218)]+[29bb(S+R)(218)]))
%28bbSTER	100 * [28bb(S+R)(218)] / ([27bb(S+R)(218)]+[28bb(S+R)(218)]+[29bb(S+R)(218)]))
%29bbSTER	100 * [29bb(S+R)(218)] / ([27bb(S+R)(218)]+[28bb(S+R)(218)]+[29bb(S+R)(218)]))

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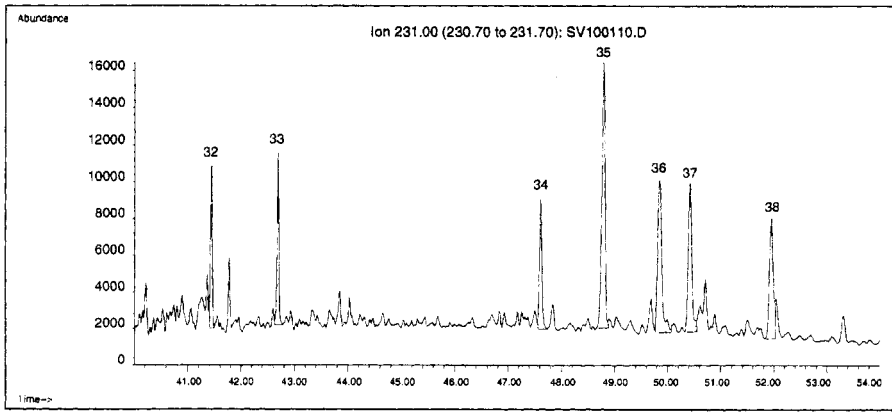

Peak #	Abbreviation	Target analytes name
32	C20TA	C20-triaromatic steroid hydrocarbon
33	C21TA	C21-triaromatic steroid hydrocarbon
34	SC26TA	C26, 20S-triaromatic steroid hydrocarbon
35	RC26TA+SC27TA	C26, 20R- +C27, 20S-triaromatic steroid hydrocarbon
36	SC28TA	C28, 20S-triaromatic steroid hydrocarbon
37	RC27TA	C27, 20R-triaromatic steroid hydrocarbon
38	RC28TA	C28, 20R,triaromatic steroid hydrocarbon

Figure 12 Triaromatic Steroids (m/z 231): Ion Chromatograms, Target Analytes and Abbreviations.

Table 5 Recommended Diagnostic Ratios for Triaromatic Steroids (m/z 231)

Ratio name	Definition
%TA21	100 * [C21TA(231)] / ([C21TA(231)]+ [RC28TA(231)])
%TA26	100 * [SC26TA(231)] / ([SC26TA(231)]+ [SC28TA(231)])
%TA27	100 * [RC27TA(231)] / ([RC27TA(231)]+ [RC28TA(231)])

3.2.4 Metals (optional)

Among the best known metal containing organic moieties in crude oils are nickel (Ni) and vanadium (V) metallo-porphyrins. The concentration of Ni and V is usually so low in petroleum that the detection limit for atomic absorption measurements is not good enough. But with the development and availability of inductively coupled plasma-mass spectrometry (Quadropole ICP-MS or High

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resolution ICP-MS) metal isotope ratio Ni/V may provide unique, weathering resistant fingerprints.

4 Criteria for elimination of diagnostic ratios

It is important to realize that the suite of diagnostic PAH and biomarker ratios (as suggested in Tables 2, 3, 4, and 5) are neither all inclusive nor appropriate for all oil spill identification cases. In some spill cases it may be prudent to include a certain characteristic feature of the spilled oil that is recognized as particularly diagnostic. In other situations, the abundance for some compounds necessary for determining the suggested diagnostic ratios are below analytical measurable limits. Thus, maintaining flexibility in the selection of diagnostic ratios to be used in a specific case study is very important. Acquiring a broad range of target compounds (*i.e.*, ion chromatograms) allows that flexibility.

In order to evaluate statistically the precision of the "quantitative" diagnostic ratios, the use of replicate samples is strongly recommended. A triplicate analysis (preferable for one of the spilled oil samples) is recommended to evaluate the laboratory preparation of sample and instrumental precision for any diagnostic indices/ratios under consideration in an oil spill investigation. Only those indices that can be measured precisely should be evaluated for comparing candidate sources to a spilled oil. This is important because without some means of testing whether or not a given diagnostic ratio is statistically different (or the same) between samples, the ability to defensibly correlate a spilled oil to a candidate source is significantly undermined (e.g. Stout *et al.* [17]).

To accommodate both for the limitation in analytical precision and impact of eventual samples inhomogeneity (*e.g.* spill samples variability due to weathering or e.g. variability within the samples from a suspected source due to inhomogeneities in the storage tank), Stout *et al.* [16] have suggested a protocol by which candidate diagnostic ratios are evaluated in order to identify those that are most useful for further correlation analysis. The flowchart (slightly modified from Stout *et al.* [16]; [17]) describing the suggested protocol is shown in Figure 13. The evaluation of the indices (diagnostic ratios) can be conducted by a simple statistical test (relative standard deviation) to identify those ratios that are unaffected by sample heterogeneity and analytical precision.

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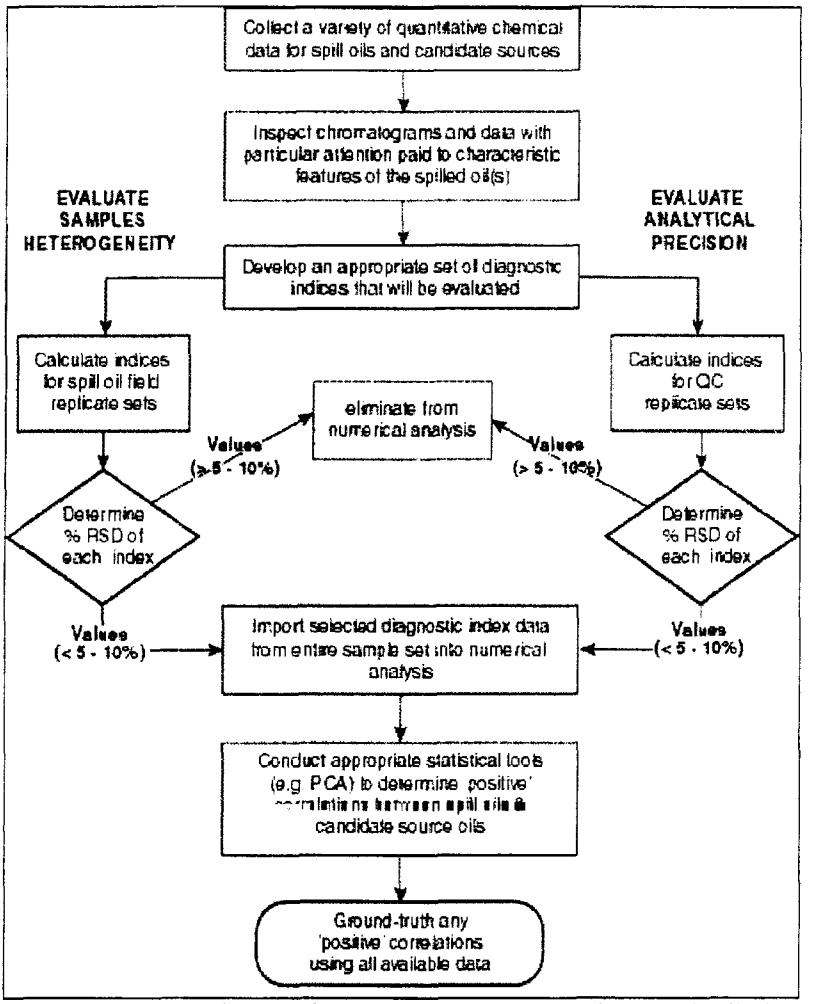

Figure 13 Suggested Flowchart – Protocol for Evaluation / Elimination of Diagnostic Ratios (modified after Stout et al. [16], [17]).

5 Correlation analysis

The recommended method requires triplicate analyses of one of the samples (preferable the spill sample) to calculate the analytical standard deviation of the diagnostic ratios (DR). The accuracy of the instrumental analysis and calculation of diagnostic ratios relies on the measured variability of the triplicate analyses. The values can be calculated as the relative variation at a 95 % confidence interval or confidence limit (CL) in triplicate samples using the "Student's *t*" statistical tool.

The Student's *t* distribution can be described by two parameters: the mean value, $\bar{x}$, which is the center of the distribution, and the standard deviation, *s*, which is the spreading of the individual observations around the mean. Given

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those two parameters, the shape of the distribution further depends of the number of degrees of freedom, *N-1*, where *N* is the number of observations (i.e. analyses). When the number of observations increases towards an infinite number, the Student's *t*-distribution becomes identical to the normal distribution.

The confidence interval is an expression stating that the true mean, μ, is likely to lie within a certain distance from the measured mean, $\bar{x}$. The confidence interval of μ is given by

$$\mu = \bar{x} \pm \frac{t \cdot s}{\sqrt{N}} \tag{2}$$

where s is the measured standard deviation between triplicate samples, N is the number of observations and t is the Student's t, taken from Table 6 (Harris [10]). The degrees of freedom in Table 6 are defined as *N-1*.

Table 6 Values of Student's t (from Harris [10])

	Confidence level (%)		
Degrees of freedom	95	98	99
1	12.706	31.821	63.657
2	4.303	6.965	9.925
3	3.182	4.541	5.841
4	2.776	3.747	4.604
5	2.571	3.365	4.032
∞	1.960	2.236	2.576

The mean value, $\bar{x}$, and the standard deviation, s, are calculated from Excel. If triplicate samples are analyzed (N = 3), the degree of freedom is 2, and a 95% confidence level gives t = 4.303 (from table 6).

Formula (2) can then be simplified to formula (3):

$$\mu = \bar{x} \pm s \cdot 2.484 \tag{3}$$

The results of comparing the spill sample and suspected source(s) are presented in simple *x-y* plots, linear regressions are performed, and conclusions based on the "fit" between spill and source samples for the selected suite of measured diagnostic ratios can be made.

The straight-line (x = y) presents "perfect" match (i.e. all DRs for the spill sample is exactly the same as for the source oil). If the error bars of all diagnostic ratios are overlapping the line, the spill sample displays a positive match to the source oil (i.e. within the analytical variation).

An example of a positive match between the spill and the suspected source sample ("A") is given in Figure 14a, while Figure 14b shows an example of non-

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match between the spill and another potential source sample ("C"). Further examples in using this correlation analysis in oil spill identification cases, are given by Faksness *et al.* ([6] and [9]).

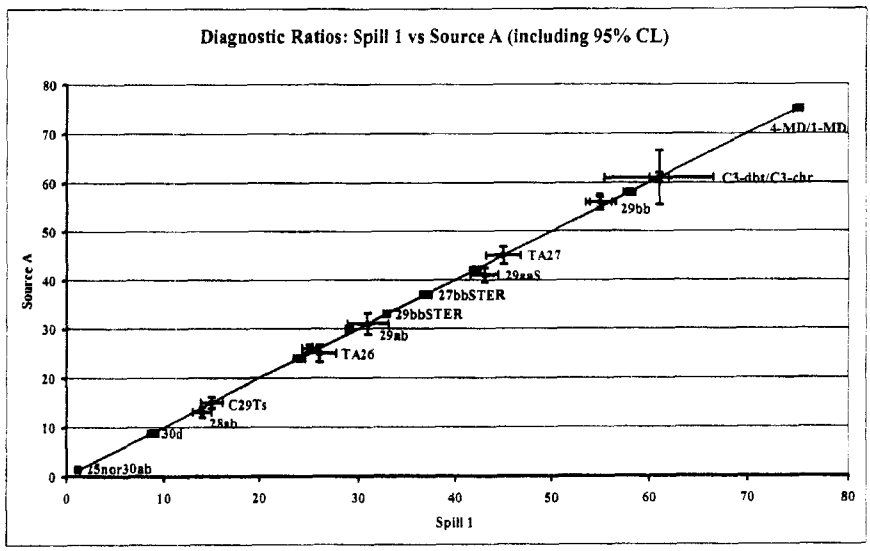

Figure 14a Example of "positive match". Correlation Between Spill and a Suspected Source ("A") Using a 95% Confidence Limit.

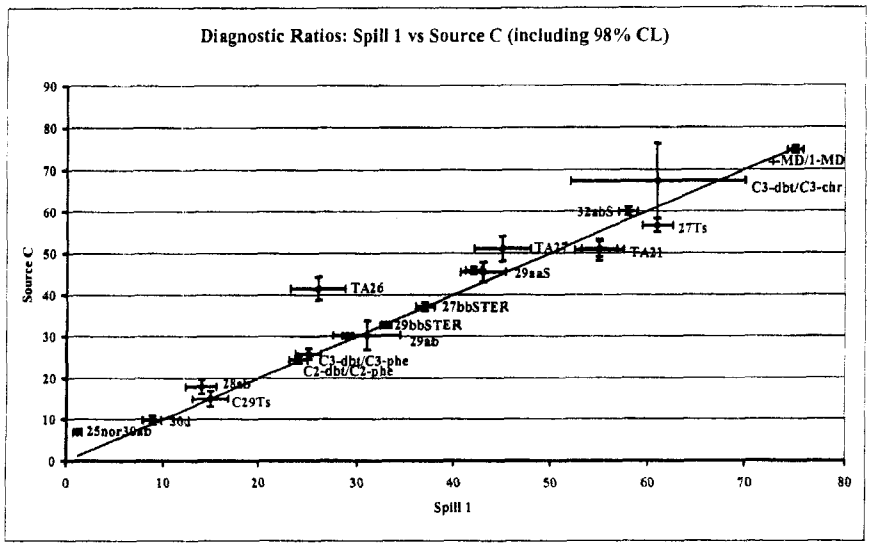

Figure 14.b Example of "Non-match". Correlation Between Spill and a Source "C", Using a 98% Confidence Limit.

Based on the experience from a Round Robin test (Faksness et al.[7] and [9]), it recommended that the correlation analyses of the diagnostic ratios are used to classify samples as described in Table 7.

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Table 7 Suggested Criteria for Classification of Spill Samples from Correlation Studies of Diagnostic Ratios.

Classification	Definition
Positive match	All DR within the CL 95 %
Probable match	All DR within the CL 98 %
Non-match	Any key DR outside of CL 98 %

DR = diagnostic ratio

It is important to visually inspect the chromatograms, and not only the measured ratios, before conclusions are made. In accordance to the decision chart in Figure 1, the final conclusion must be made based on a total evaluation using all available data.

6 Conclusion

The revised Nordtest methodology for oil spill identification presented in this paper is based on a GC/FID screening of all involved samples (Level 1) and a GC/MS fingerprinting of spill and candidate source samples (Level 2), from which 24 diagnostic ratios of selected PAHs and biomarkers are extracted. Diagnostic ratios are evaluated and selected on the basis of their analytical variability and changes due to weathering. Only those diagnostic ratios that can be precisely measured and are resistant to weathering effects are used for correlating spill and candidate oil samples (Level 3). By statistical treatment of the correlations using confidence limits and an overall assessment of results from all analytical levels, the oil spill identification case study using this methodology can be concluded in terms of four operational and technically defensible identification terms (as in ASTM D3328-00 [1]): Positive match, probable match, inconclusive or non-match. These categories represent degrees of differences between the analyses of two oils according to the present criteria:

Positive match: The chromatographic patterns of the samples submitted for comparison are virtual identical and the only observed differences between the spill sample and the suspected source are caused by acceptable analytical variance and/or weathering.

Probable match: The chromatographic patterns of the spill sample is similar to that of the samples submitted for comparison, except: (a) for obvious changes which could be attributed to weathering (e.g. loss of lower-molecular-weight peaks, wax redistribution etc.), or (b) differences attributable to specific contamination.

Inconclusive: The chromatographic patterns of the spill sample is somewhat similar to that of the sample submitted for comparison, except for certain differences that are of such magnitude that is impossible to ascertain whether the unknown is the same oil heavily weathered, or a totally different oil.

Non-match: Unlike the samples submitted for comparison.

In the event of non-match, it is possible to stop the analytical procedure as soon as significant differences (not attributable to weathering) are confirmed. This will save time and resources in cases where the suspected source cannot be

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responsible for the pollution. Otherwise, the further "levels" in the process will provide more extensive, specific and conclusive documentation.

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