Marzena BOGDANIUK[1], Grażyna DEMBSKA,
Grażyna SAPOTA, Agnieszka FLASIŃSKA,
Stanisław WIŚNIEWSKI and Barbara AFTANAS

USE OF MASS SPECTROMETRY FOR OIL SPILL IDENTIFICATION

ZASTOSOWANIE CHROMATOGRAFII GAZOWEJ DO IDENTYFIKACJI ROZLEWÓW OLEJOWYCH

Abstract: A quick and simple method of separating oil products into the aliphatic and aromatic fractions are presented. The aliphatic fraction was analysed, using the GC/MS technique.

Results of analyses of the predominant in oil group of biomarkers, ie the *n*-alkanes and two compounds from the isoprenoid group: pristane and phytane, are presented. Ratios of the content of these compounds (Pr/F), Pr/n-C$_{17}$ and F/n-C$_{18}$ are characteristic for a given oil, and this is used to identify the oil products.

Keywords: oil spills, GC/MS, biomarkers

Oil pollution of sea areas is caused mainly by oil spilled in result of damages of tankers, operation of drilling rigs and of leakage from tanks in oil terminals. As a rule these are megaspills, resulting in significant ecological damage. The large environmental danger connected with oil spills in sea areas, and the global range of their effects, are reflected in numerous publications [1–6]. Special attention is given to the chemical, physical-chemical and biological influence of oil hydrocarbons on the water ecosystem [7–11].

Proper assessment of the level of danger, and selection of appropriate methods of remediation, is possible only if the materials introduced into water and soil are well investigated prior to taking action. Because of this, analysis of oil products is the subject of many investigations, aiming at more effective methods of their determination.

Due to the complex composition and differentiation of properties of the oil products, analysis of environmental pollution by these products is an especially difficult task. Additional difficulties result from changes in composition of the oil products caused by environmental conditions and by matrix properties [12–13].

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[1] Maritime Institute in Gdansk, ul. Długi Targ 41/42, 80–830 Gdańsk, Poland, email: marzena.bog-daniuk@im.gda.pl

Especially useful for oil product analysis is the gas chromatography with mass sensitive detector (GC/MS) technique [14–18]. Identification of hydrocarbons is largely facilitated by the similarity of fragmentation of compounds belonging to the same homologous series. Paraffin hydrocarbons form only a few molecular ions, especially in macromolecular compounds. This group of hydrocarbons is characterised by the series of ions distanced by 14 Da (-CH$_2$-), which occur for values m/z 15, 29, 43, 71, 85, 99 etc. Of the naphthene hydrocarbons, the most easily identified are compounds belonging to alkylcyclohexanes, in which the main ion is m/z 83. In mass spectra of aromatic and alkylaromatic hydrocarbons, the peak of the molecular ion is well visible. Table 1 presents a list of characteristic ions, used for identification of the main groups of hydrocarbons, in that of the specific biomarkers (isoprenoid hydrocarbons: pristane and phytane, triterpanes, steranes) occurring in oil and oil products [14, 15, 17, 19, 20].

Table 1

Characteristic ions (m/z) useful for identifying oil hydrocarbons

Class of compounds	Characteristic ions (m/z)
n-alkanes	113, 183
n-alkenes	57, 71, 85, 99
Isoprenoids (pristane, phytane)	55, 97
Acylcyclohexanes	82, 83
Benzene, alcylbenzene	78, 91, 105, 106, 119, 120
PAH	molecular ions, eg 178 for anthracene and phenanthrene, 202 for pirene, 228 for benzopirenes
Diterpenoids	109, 123, 163, 191
Hopanes	177, 191
Steranes, diasteranes	217, 218, 231, 259

Oil products are multicomponent mixtures of chemical compounds, hydrocarbons mainly, containing also small amounts of heteroorganic or other compounds. A characteristic feature of the composition of oil and oil products is the presence of hydrocarbons belonging to various groups of compounds (paraffin, cycloparaffin, aromatic hydrocarbons, differing by molecular mass, degree of ring condensation and substitution). They can occur in the form of homologous series, eg: *n*-alkanes, alkylcyclohexanes, alkylbenzenes, alkyltoluenes and others.

In non-polar capillary columns, non-polar compounds elute in accordance with the value of temperature of boiling. Chromatograms with characteristic profiles are obtained, the so-called "fingerprints". In turn, selective ion monitoring (SIM) and extraction of selected ions from chromatograms by TIC (*Total Ion Current*) method allow obtaining additional fingerprints, specific for the given oil products.

Analysis of selected fragments of ions, and identification of biomarkers, characteristic to given oils and oil products, is especially useful for identifying sources of pollution and for monitoring the natural environmental degradation of oil pollutants

and/or the effectiveness of adopted methods of remediation. Biodegradation of hydrocarbons depends, among others, on their structure; *n*-alkanes are biodegraded much easier than isoprenoid hydrocarbons, while the least susceptible to biodegradation are hopanes. Therefore, the chromatographic profile of a product differs from the initial chromatographic profile of the pollutant. At least it will have no low-molecular *n*-alkanes [14, 15, 17, 19–21].

The objective of the investigations, carried out by the Department of Protection of Environment of the Maritime Institute, was to evaluate the possibilities of using gas chromatography and mass spectrometry for identifying spilled oil substances and for determining the degree and magnitude of marine environment pollution in result of the spill.

Material and methods

Analysis of selected biomarkers was carried out for:
– diesel oil,
– light heating oil,
– multiseason oil for Diesel engines Elf TURBO 15W40 Diesel,
– heavy heating oil,
– crude oil.

Additionally, for the first four products, the content of biomarkers was determined after three weeks, during which the investigated products were left in open vessels in order to test, in static conditions, for changes in the composition of these products (mainly in effect of evaporation). The diameter of the vessels was 10 cm, thickness of oil layer was 2 cm, mean air humidity – 45 %, mean temperature – 22 $^{\circ}$C. Group separation of hydrocarbons was carried out on silica gel type 100 (70–230 mesh), which, directly before use, was conditioned for 12 hours at 160 $^{\circ}$C.

Determination of asphaltene content

Asphaltene content was determined in samples of crude oil and heavy heating oil. From each sample 0.5 g of oil was taken and dissolved in 10 cm^3 of hexane. Each subsample was filtered through a 0.22 μm teflon filter. The filtrate was collected into a 25 cm^3 measuring flask, leaving it for further analysis. Asphaltenes collected on the filter were washed with dichloromethane into a tared vessel, and weighed after removing the dissolvent. Results are presented in Table 2.

Table 2

Gravimetrically determined asphaltene content in crude oil and heavy heating oil

Samples	Mean asphaltene content in sample [%]	Standard deviation SD
Crude oil	2.22	0.03
Heavy heating oil	6.85	0.06

Group separation of reference mixture

A 1 cm diameter glass column was filled with 2 g of silica gel and conditioned with 20 cm^3 of hexane. Next, 1 cm^3 of the reference mixture was put on the silica gel. The mixture contained 20 aliphatic hydrocarbons (18 *n*-alkanes, pristane and phytane) of 2 µg/cm^3 concentration and 16 polycyclic aromatic hydrocarbons (PAH) of 1 µg/cm^3 concentration, and was eluted using:
 – 10 cm^3 of hexane (fraction 1),
 – 10 cm^3 of hexane – toluen mixture of volumetric ratio 1:1 (fraction 2), and
 – 10 cm^3 of toluene (fraction 3).

The obtained fractions were vaporized in a nitrogen jet to 1 cm^3 and compared with the standard containing *n*-alkanes from C$_8$ to C$_{40}$, pristane, phytane and PAH. In fraction 1 only aliphatic hydrocarbons were found, in fraction 2 – PAH, while in fraction 3 none of the above compounds were present. Determined by these investigations recoveries and standard deviations are shown in Table 3.

Table 3

Values of recoveries of aliphatic hydrocarbons after group separation on silica gel

Compound	Recovery [%]	Standard deviation SD
	Fraction 1	
C-8	95.50	0.42
C-10	96.95	0.35
C-12	96.95	0.21
C14	98.00	0.42
C-16	97.85	0.92
C-17	97.95	0.64
Pristane	98.45	0.64
C-18	99.80	0.42
Phytane	105.5	0.71
C-20	107.2	1.13
C-22	107.6	1.20
C-24	107.4	1.56
C-26	106.0	2.05
C-28	106.1	1.98
C-30	105.0	2.83
C-32	103.9	0.07
C-34	104.5	1.34
C-36	103.5	1.41
C-38	103.1	0.57
C-40	101.9	1.56

Group separation of crude oil and selected oil products

20 mg of the sample, dissolved in hexane, was put on the columns with silica gel. The columns were eluted with 10 cm^3 of hexane to collect aliphatic hydrocarbons

(fraction 1), and next 10 cm^3 of the hexane/toluene mixture – collected in this way fraction 2 contained PAHs. Group separation of crude oil and heavy heating oil was carried out for samples, from which previously were removed asphaltenes. Fraction 1 was tested for the presence of biomarkers (*n*-alkanes, pristane and phytane).

Chromatographic analysis

Biomarker analysis was carried out using a gas chromatograph coupled with a Hewlett-Packard mass spectrometer. The chromatograph was provided with a HP-5 column with dimensions 25 m × 0.25 mm and film thickness 0.25 μm. The separation was performed in the following temperature program: 40 ^{o}C (2 min), 5 ^{o}C/min up to 320 ^{o}C (10 min). Feeder temperature was 300 ^{o}C. The spectra were recorded in Total Ion Current (TIC) mode in the range m/z 30–600, and in Selective Ion Monitoring (SIM) mode for m/z 71 and 85.

Results and discussion

In the tested oil products (except diesel oil), *n*-alkanes were the predominant compounds forming each of the chromatographic profiles. The highest concentration of normal-chained aliphatic hydrocarbons was found in light heating oil, then in crude oil, diesel oil and lowest in heavy heating oil.

The differences in distribution of *n*-alkanes in the tested oil products and in crude oil are shown graphically in Figs. 1a–d and 2.

In oil products, for which tests of environmental influence (mainly evaporation) on the biomarker content were carried out, the loss of mass was:
 – 5.0 % for diesel oil;
 – 7.1 % for light heating oil;
 – 0.5 % for multiseason diesel oil;
 – 4.2 % for heavy heating oil.

The low loss of mass of multiseason diesel oil proves that it is composed mainly of hydrocarbons with higher temperatures of boiling.

Comparison of initial biomarker content with the content after three weeks, during which volatile components were allowed free evaporation, showed that in all products disappeared the three first *n*-alkanes (C_8-C_{10}), concentration of C_{11} decreased by about 50 %, and of C_{12} by about 15 %. There was only a slight change in the concentration of *n*-alkanes with higher numbers of carbon atoms.

The tested products differed by chromatographic profiles. The highest similarity was observed for diesel oil and light heating oil – the range of determined *n*-alkanes was: from C_8 to C_{28}, with a maximum at C_{13}-C_{17}. These products differed visibly only by the size of the non-separated surface (in analytes, which contain a large number of isomers with similar temperatures of boiling, but at very low concentrations, a large part of the compounds is non-separated – the non-separated surface causes a lifting of the basic line of the chromatogram, and in case of heavy products – a characteristic hump in the curve).
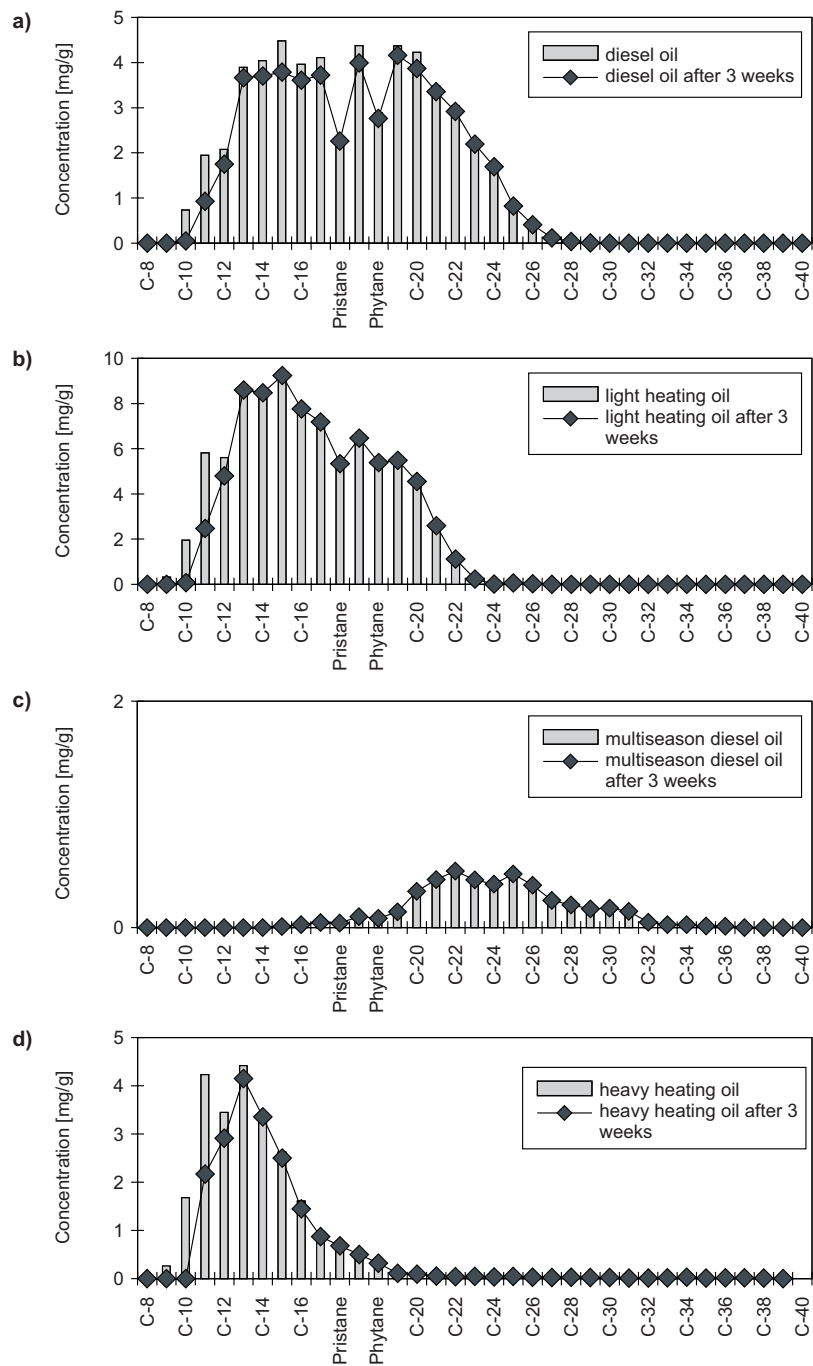
Fig. 1. Concentration of *n*-alkanes in: a) diesel oil, b) light heating oil, c) multiseason diesel oil, d) heavy heating oil
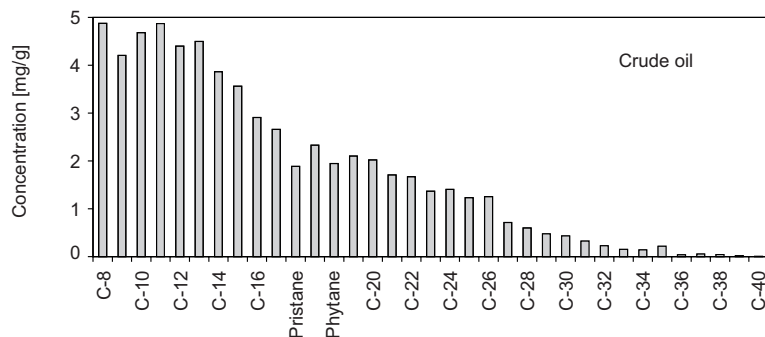
Fig. 2. Concentration of *n*-alkanes in crude oil

Heavy heating oil was characterised by a "wider" composition of hydrocarbons than the two earlier mentioned products (from C_8 to C_{39}), and the point at which the highest concentrations of *n*-alkanes where found was shifted towards lighter hydrocarbons (C_{11}-C_{15}). The non-separated surface was < 50 %.

A characteristic chromatogram was obtained for multiseason diesel oil – over 90 % of non-separated surface (which significantly hindered identification and quantitative determination), resulted in a characteristic hump in the C_{23} to C_{36} range, which, together with the relatively low content of *n*-alkanes, proves that iso- and cycloparaffin hydrocarbons are present in the oil [5, 17]. Since the compounds occur at very low concentrations, they are not recorded in the chromatogram. Besides, none of the first four *n*-alkanes was found in the tested multiseason diesel oil and concentrations of the next seven were below 0.1 mg/g.

The chromatographic profile of crude oil was different from chromatograms obtained for oil products. All determined *n*-alkanes are present, with a maximum at C_8-C_{13} [2].

For distinguishing the investigated oil products, the most often used in oil geochemistry indexes were used [5, 8, 10]:

– Carbon Preference Index (preference of odd *n*-alkanes over even *n*-alkanes):

$$CPI_{(Total)} = \frac{(C_{17} + C_{19} + ... + C_{27} + C_{29}) + (C_{19} + C_{21} + ... + C_{29} + C_{31})}{2(C_{18} + C_{20} + ... + C_{28} + C_{30})},$$

$$C_{(17-23)} = \frac{(C_{17} + C_{19} + C_{21}) + (C_{19} + C_{21} + C_{23})}{2(C_{18} + C_{20} + C_{22})},$$

– pristane/phytane ratio (Pr/F) – sedimentation environment index:
  Pr/F – sedimentation environment,
  < 1 – anaerobic – marine sediments,
  1–3 – aerobic – marine sediments,
  > 3 – land sediments – carbons;

– *n*-heptadecane to pristane ratio (*n*-C_{17}/Pr) and *n*-octadecane to phytane ratio (*n*-C_{18}/F), allows to assess the degree of alteration of the maternal organic substance of the oils and to evaluated the influence of biodegradation.

The distribution of isoprenoids changes with the degree of alteration of organic substance, however not to such a degree as *n*-alkane distribution. Phytane is produced more quickly than pristine, and in effect the Pr/F ratio decreases. Pr/*n*-C_{17} values below 0.5 are typical for marine organic matter, while values over 1.0 are characteristic for the land environment [8, 10]. However, the magnitude of this change is rather small. During generation of hydrocarbons, the concentration of isoprenoids increases much slower than the concentration of *n*-alkanes, therefore the Pr/*n*-C_{17} and F/*n*-C_{18} ratios decrease with growing degree of alteration. Common (comprehensive) interpretation of the *n*-alkane and isoprenoid distributions allows both to evaluate the degree of alteration and the influence of biodegradation.

The described above geochemical indexes were determined for the investigated oil products. Results are shown in Tables 4 and 5.

Table 4

Values of geochemical indexes calculated for the investigated products

Geochemical indexes	Diesel oil	Light heating oil	Multiseason diesel oil	Heavy heating oil	Crude oil
P/F	0.813	0,.977	0.459	2.183	0.967
P/C-17	0.573	0.734	0.867	0.769	0.708
F/C-18	0.661	0.829	0.85	0.635	0.835
CPI total	—	—	0.918	1.003	0.935
CPI 17-23	0.944	0.964	0.845	1.006	0.967

Table 5

Values of geochemical indexes calculated for the investigated oil products
after three weeks of interaction with environment

Geochemical indexes	Diesel oil	Light heating oil	Multiseason diesel oil	Heavy heating oil
P/F	0.819	0.990	0.488	2.125
P/C-17	0.608	0.742	0.889	0.782
F/C-18	0.692	0.834	0.845	0.64
CPI total	—	—	0.955	0.983
CPI 17-23	0.972	0.971	0.868	0.973

It was found that crude oil, diesel oil, light heating oil, multiseason diesel oil and heavy heating oil differ from each other by values of the geochemical indexes. However these indexes can be used for identifying oil spills only to a limited extent – obtaining a chromatographic profile, determination of the *n*-alkane, pristane and phytane concentrations can be only one of the stages of investigations leading to the recognition of spilled oil products.

Values in Tables 3 and 4 differ from each other only slightly for the same oil products (within the margin of error of quantitative determination), which means that they potentially could be used as markers of spilled oil products. However, it should be remembered that in the experimental conditions the factors influencing the tested materials were relatively stable and limited to:

– temperature,
– solar radiation (to a limited extent),
– air humidity.

In natural conditions the number of factors is much larger – movement of air, waves, interaction with water and soil, disintegration by microorganisms and many others.

Conclusion

A quick and simple method of separating oil products into the aliphatic and aromatic fractions is presented. The obtained aliphatic fraction was analysed using the GC/MS technique.

The presented investigations of *n*-alkane, phytane and pristane content and the obtained chromatographic profiles of oil products constitute the first stage of works, which aim at utilising gas chromatography coupled with mass spectrometry for identifying spilled oil products. However, in order to attain unequivocal identification of the origin of oil substances in the environment, it is necessary to extend the investigations to other compounds characteristic to oil substances – PAHs, benzo-thiophenes, and for petrols – to volatile and medium volatile aromatic hydrocarbons.

Characterisation and identification of oil products, which have changed significantly due to the influence of atmospheric factors, will be possible with the use of steranes and hopanes, which, similarly to *n*-alkanes, belong to the biomarker group. An especially important index in this respect is the ratio of hopane C_{29} to C_{30}. This ratio remains practically unchanged for very long time spans.

The laboratory of the Department of Protection of Environment plans a systematic extension of its library of oil product spectra, and of the spectra of products of degradation, in order to facilitate quick identification of oil spills.

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ZASTOSOWANIE CHROMATOGRAFII GAZOWEJ
DO IDENTYFIKACJI ROZLEWÓW OLEJOWYCH

Zakład Ochrony Środowiska
Instytut Morski w Gdańsku

Abstrakt: Przedstawiono szybką i prostą metodę rozdziału produktów naftowych na frakcję alifatyczną i aromatyczną. Otrzymaną frakcję alifatyczną badano przy zastosowaniu techniki GC/MS.

W pracy przedstawiono wyniki analiz dominującej w ropie naftowej grupy biomarkerów – n-alkanów oraz dwóch związków z grupy izoprenoidów: pristanu i fitanu. Stosunki ilości tych związków (Pr/F) oraz Pr/n-C17 i F/n-C18 są charakterystyczne dla określonej ropy, co wykorzystywane jest przy identyfikacji produktów naftowych.

Słowa kluczowe: rozlewy olejowe, GC/MS, biomarkery