

Oil-Spill Identification by Gas Chromatography–Mass Spectrometry

A. Pavlova and D. Papazova

Refining and Petrochemistry Institute, Analytical Department, LUKOIL-NEFTOCHIM-BOURGAS JSC, 8104 Bourgas, Bulgaria

Abstract

Two approaches are proposed for the identification of a contaminant caused by the spilling of oil or oil products in water. A capillary gas chromatography (CGC)–mass spectrometry (MS) method for oil spill identification is applied. The presented approaches describe the use of MS data of 18 selective ions of spilled product and the probable pollutant. The spill identification is accomplished on the bases of a quantitative comparison between the ion chromatograms of the samples taken from the probable pollutant and from the spill itself. The other approach is made by chemometric treatment of complete CGC–MS data.

Introduction

Crude oil and its waste pollutions in developed industrial countries are widely distributed. They form up to 30–40% of common water pollution. The scale of the oil problems ranks highly along with those of nitrogen, sulphur, chlorine, and phosphorous (1).

The pollution of soil and bodies of water by emergency oil spills is another substantial problem. The quantitative and qualitative evaluation of the available components of spilled oil (such as polycyclic aromatic hydrocarbons, *n*-alkanes, isoprenoids, etc.) could be useful in establishing probable ways of loss and transformation of oil hydrocarbons in various sites of the environment. An adequate comparison between the chemical composition and the compound concentrations in the spilled oil and the compound concentrations in the potential source can be used for identification goals.

The modern oil spill identification methods include gas chromatography (GC) (2–4), GC–mass spectrometry (MS) (3,5–12), infrared spectroscopy (13,14), and fluorescent spectroscopy (15). Of these methods, capillary GC (CGC) with flame ionization detection is the most wide spread (4,16,17). This method is fast, intelligent, and in most cases provides enough information for the elimination of many of the potential pollution sources.

However, when the GC information is not sufficient for an unambiguous conclusion about the identity between the spill and the potential source, it is necessary to give more proof using an additional analytical method.

The task of the present study is to suggest two approaches for

oil spill identification in seawater by means of complete GC–MS analysis and chemometric treatment of data. The spill identification is accomplished on the basis of a comparison between the mass chromatograms of samples taken from the probable pollutant and from the spill itself.

Experimental

Crude oil samples

Six different crude oil samples (from three different Russian oils: Novorosijski, Bozachinski, and Iranian heavy oil) have been analyzed with regard to the distribution of *n*-alkanes, isoprenoids, polycyclic aromatic hydrocarbons and their alkyl-homologues, and biomarker compounds (hopanes and steranes). The sampling

Table I. Selective Ions

| Compounds | Group | <i>m/z</i> | <i>C_n</i> interval |
|----------------------------------|-------|------------|-------------------------------|
| Norhopanes | A | 177 | 13–36 |
| Hopanes | A | 191 | 13–36 |
| Methylhopanes | A | 205 | 13–36 |
| 14 α (H)steranes | A | 217 | 16–32 |
| 14 β (H)steranes | A | 218 | 14–32 |
| Alkanes | B | 113 | 13–36 |
| Alkanes and acyclic isoprenoids | B | 183 | 13–36 |
| Hopanes | B | 191 | 13–36 |
| C ₂ -Naphthalenes | B | 156 | 13–15 |
| C ₃ -Naphthalenes | B | 170 | 14–16 |
| C ₄ -Naphthalenes | B | 184 | 15–17 |
| Hopanes | C | 191 | 16–36 |
| Phenanthrene, anthracene | C | 178 | 16–20 |
| C ₁ -Phenanthrenes | C | 192 | 17–19 |
| C ₂ -Phenanthrenes | C | 206 | 19–21 |
| C ₃ -Phenanthrenes | C | 220 | 19–22 |
| Hopanes | D | 191 | 16–36 |
| Dibenzothiopene | D | 184 | 16–18 |
| C ₁ -Dibenzothiopenes | D | 198 | 17–19 |
| C ₂ -Dibenzothiopenes | D | 212 | 17–20 |
| C ₃ -Dibenzothiopenes | D | 226 | 19–22 |

of different oil-spill samples has been made according to the Nordtest Method NT CHEM 001 (16) and ASTM D 4489-85 (17).

CGC-MS

CGC-MS has been carried out by means of an HP 5890-II series GC connected to a mass selective detector (MSD) 5970 (Hewlett-Packard, Palo Alto, CA). The system control and the data acquisition have been executed by an HP 59970 ChemStation (Hewlett-Packard). The MSD was operated in selected ion monitoring (SIM) mode, which allowed for the study of the ions that were selective for the previously mentioned compounds with respect to the identification goals.

A quartz capillary column (25-m \times 0.32-mm \times 0.52- μ m film Ultra-2) was used. The GC operation conditions were as follow: carrier gas, helium (1.4 mL/min); and injector and detector temperature, 300°C. The temperature program was 0 min at 90°C, then ramped to 270°C at 6°C/min, and held for 30 min at 270°C. The injected quantity was 1 μ L of 2% volume solution in tetrachloromethane of the spill sample. The selective ions that are characteristic of the different compound types were chosen. Four groups of compounds (namely, A, B, C, and D) were created. Additionally, the ions were distributed into 14 C_n intervals (Table I). For example, the interval C_n 13–15 indicates that the peaks eluted between n - $C_{13}H_{28}$ to n - $C_{15}H_{32}$ (i.e., the retention times of the respective n -alkanes in the mass spectrograms were used as bench marks for certain C_n interval fixation.

Results and Discussion

Method validation

The validity of the analytical method by laboratory studies using standards and samples has been verified. The standards contain target compounds like n -alkanes and isoprenoids, naphthalenes, phenanthrenes, and dibenzothiophenes in the range of 0.1 up to 30% in n -hexane. It has been proven that the intensity of the ions is linearly related to the standard concentrations. The ions intensity used in the calculations was a result of four consecutive sample analyses that provided data about the quantitative presence of different types of compounds. The quantitative determination of each ion in the obtained mass spectrograms was made by normalization. The spilled sample was Russian crude oil. Parameters of CGC-MS method validation have been shown in Table II.

Oil-spill identification

Quantitative comparisons of the groups

The highest repeatability of 1.9% was accepted to be the maximum admissible difference in parallel determinations of all ions. In case the absolute differences in the concentrations comparing the spill sample and the probable pollutant were higher than $\pm 1.9\%$, then the compared samples were nonidentical. The identity of the compared samples spill-probable pollutant are illustrated in Figure 1. In this case, the difference in concentrations was less than $\pm 1.9\%$.

Chemometric treatment of GC-MS data

This approach allowed for comparison against five summarized characteristic parameters. These parameters were carriers of valuable information for oil spill identification and extremely powerful tools for oil differentiation. These were the area ratio of n - C_{17} /pristane, n - C_{18} /phytane, pristane/phytane, Σn -alkanes/ Σi -alkanes, and Σ odd n -alkanes/ Σ even n -alkanes. Table III shows that the data of these are ratios for the analyzed crude oil on the basis of detection m/z 113 and 183 and their repeatabilities. It has been established that crude oils differ against two or more parameters. The most different is the Bozachinski crude oil,

Table II. Method Validation Parameters of the Ion Contents by CGC-MS Analysis

| Parameter | Ion m/z | | | | | | | | |
|----------------------|-----------|------|------|------|-----|------|------|------|------|
| | 113 | 183 | 156 | 170 | 205 | 177 | 218 | 217 | 191 |
| SD of amounts (%) | 0.1 | 0.2 | 0.1 | 0.2 | 0.2 | 0.7 | 0.6 | 0.7 | 0.6 |
| %RSD | 2.0 | 4.1 | 1.0 | 2.6 | 4.1 | 5.7 | 7.8 | 9.2 | 12.0 |
| Calculated range (%) | 3–8 | 3–16 | 3–25 | 2–20 | 2–7 | 8–32 | 3–18 | 6–21 | 2–15 |
| LOQ | 0.3 | 0.6 | 0.3 | 0.6 | 0.6 | 2.1 | 1.8 | 2.1 | 1.8 |
| Repeatability (%) | 0.3 | 0.6 | 0.3 | 0.6 | 0.6 | 1.9 | 1.7 | 1.9 | 1.7 |

* Abbreviations: SD, standard deviation; LOQ, limit of quantitation (LOQ = 3 \times SD).

Table III. Summary for Comparison of Different Crude Oil Samples on the Basis Detection of m/z 113 and 183

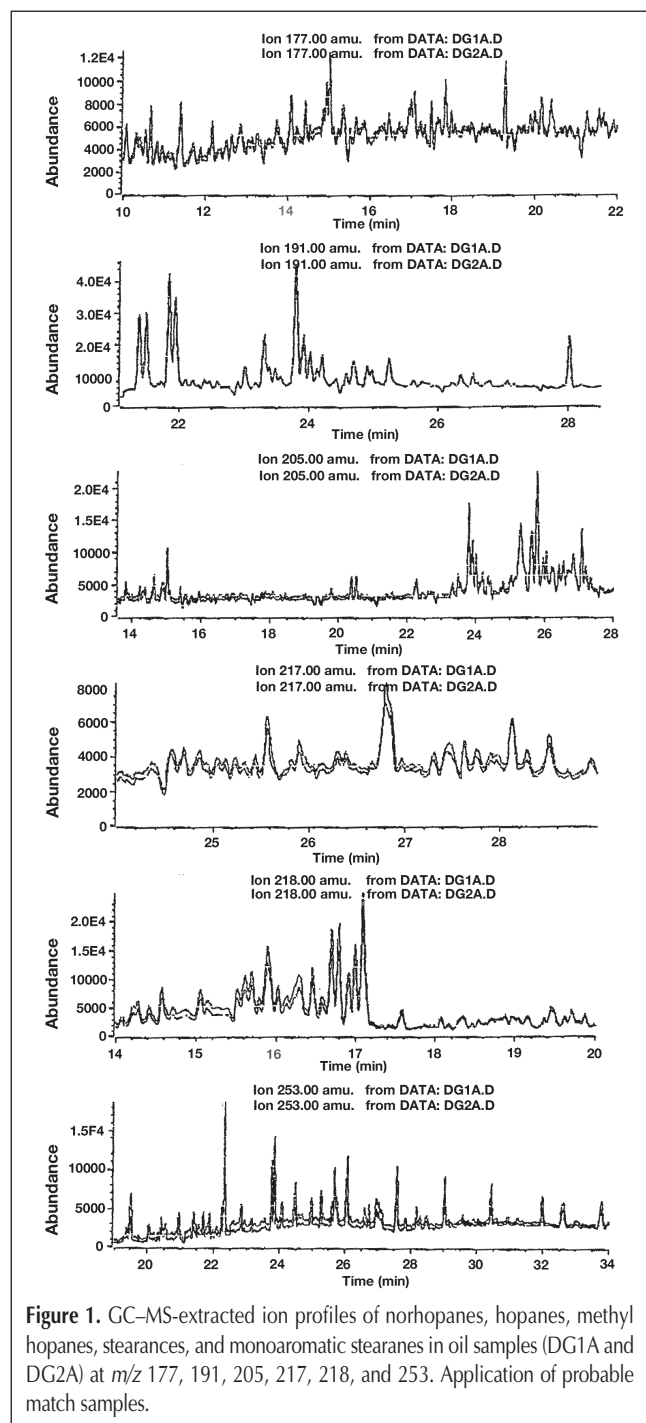
| Parameter | Repeatability* | | Iranian crude oil-1 | | Russian crude oil-1 | | Russian crude oil-2 | | Russian crude oil-3 | | Novorossjiski crude oil | | Bozachinski crude oil | |
|----------------------------|----------------|-------|---------------------|-------|---------------------|-------|---------------------|-------|---------------------|-------|-------------------------|-------|-----------------------|-------|
| | m/z | m/z | m/z | m/z | m/z | m/z | m/z | m/z | m/z | m/z | m/z | m/z | m/z | m/z |
| | 113 | 183 | 113 | 183 | 113 | 183 | 113 | 183 | 113 | 183 | 113 | 183 | 113 | 183 |
| Σn -alkanes | | | | | | | | | | | | | | |
| Σi -alkanes | 0.08 | 0.06 | 2.60 | 0.93 | 2.60 | 0.85 | 2.40 | 0.99 | 2.50 | 0.99 | 2.50 | 0.94 | 1.30 | 0.56 |
| n - C_{17} /pristane | 0.06 | 0.03 | 0.87 | 0.41 | 0.92 | 0.44 | 0.84 | 0.43 | 0.80 | 0.39 | 0.81 | 0.45 | 0.41 | 0.33 |
| pristane/phytane | 0.03 | 0.06 | 1.08 | 1.95 | 0.96 | 1.75 | 1.08 | 1.76 | 1.31 | 2.33 | 1.12 | 1.73 | 1.22 | 2.43 |
| n - C_{18} /phytane | 0.03 | 0.06 | 0.93 | 0.65 | 0.87 | 0.64 | 0.83 | 0.67 | 1.02 | 0.78 | 0.92 | 0.73 | 0.50 | 0.49 |
| Σ odd n -alkanes | | | | | | | | | | | | | | |
| Σ even n -alkanes | 0.03 | 0.03 | 0.90 | 1.22 | 0.88 | 0.96 | 0.88 | 1.22 | 0.90 | 1.20 | 0.88 | 0.95 | 0.89 | 1.37 |

* $n = 4$.

which shows a difference in four of the characteristic parameters for m/z 113 and in all five for m/z 183.

The GC-MS data present the difference of the Bozachinski crude oil to the rest of the analyzed crude oils with regard to the content of isoprenoids $i\text{-C}_{16}\text{H}_{34}$, $i\text{-C}_{18}\text{H}_{38}$ (norpristane), $i\text{-C}_{19}\text{H}_{40}$ (pristane) and $i\text{-C}_{20}\text{H}_{42}$ (phytane) (m/z 113 and 183), C_2 -naphthalenes (m/z 156), dibenzothiophene (m/z 184), C_1 -dibenzothiophenes (m/z 198), and C_3 -phenanthrenes (m/z 220).

The present work demonstrates that efficient oil-spill identification can be accomplished with the use of characteristic parameters capable of providing high specificity within the oil samples.



Conclusion

The proposed GC-MS approaches, when applied to crude oil-spill identification, possess good demarcating ability and high strength of identification, and they provide sufficient and important information regarding the structure of different compound types that belong to the spill and the probable pollutant.

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