

Development of a Simple Gas Chromatographic Method for Differentiation of Spilled Oils

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Abstract

An approach for the fast, preliminary identification and differentiation of fresh oil spills is proposed. Capillary gas chromatography with flame ionization detection for the determination of *n*-alkane and isoprenoid distribution in oil spill samples is applied. An internal standard method is used for the quantitation of the selected compounds. Five characteristic parameters are checked for adequate presentation. *n*-Alkanes and isoprenoids are chosen as the most suitable structures for the identification and differentiation of fresh oil spills. In many cases, this information is sufficient to eliminate most of the oils as potential sources of the pollution.

Introduction

The use of gas chromatographic–mass spectrometric (GC–MS) approaches for the positive identification of oil spills is well established (1–4). In cases where the spill and the suspected source of pollution are different, a less sophisticated method can give adequate results. In such cases, identifying the specific compounds typical for the chemical origin of a given spill is enough for its characterization and comparison with the source.

The present study suggests a simple approach for the differentiation of spilled samples from the source based on the distribution of specific groups of compounds. It has been established that among the different types of compounds in crude oil or corresponding fractions, the *n*-alkanes and isoprenoids are a convenient combination for the identification, characterization, and quantitation of the oil-spill samples (4,6,7). The distribution profiles of these compounds are different among crude oils and the different types of fuels and heavy residues. In fact, the *n*-alkanes and isoprenoids are generally not of toxicological concern, but they are relatively

resistant to chemical and photochemical reactions, their identification is easy without standards, and their quantitative estimation from a chromatogram is more reliable. It is well known that the ratios of *n*-C₁₇ to pristane and *n*-C₁₈ to phytane are convenient biodegradation indicators (2). These ratios relative to the spilled source oil can provide information about the effect of microbial biodegradation on the loss of hydrocarbons in the polluted area.

Capillary GC with flame ionization detection (GC–FID) (3–5) is widely used in oil analyses, especially for the determination of *n*-alkanes and isoprenoids, and its application to the proposed task is quite easy. The data obtained will be used for the selection of suitable characteristic parameters for the comparison of the samples.

Table I. Relative Response Factors

Compound	Relative response factors	RSD* (%)
<i>n</i> -C ₉	0.9585	3.03
<i>n</i> -C ₁₀	0.9898	1.62
<i>n</i> -C ₁₁	0.9221	2.71
<i>n</i> -C ₁₂	0.9481	1.02
<i>n</i> -C ₁₃	0.9550	0.89
Tetradecene-1	1.0000	—
<i>n</i> -C ₁₄	0.9822	0.65
<i>n</i> -C ₁₅	0.9823	0.53
<i>n</i> -C ₁₆	1.0014	2.00
<i>n</i> -C ₁₇	1.0334	0.74
<i>n</i> -C ₁₈	1.0221	1.24
<i>n</i> -C ₂₀	1.1107	3.74
<i>n</i> -C ₂₄	1.4174	2.39
<i>n</i> -C ₂₆	1.8333	5.18
<i>n</i> -C ₃₀	4.0298	6.45

* Relative standard deviation, *n* = 4.

with Na₂SO₄. For a thin layer of oil film, the sampling was made with a Teflon film or sheet. The sheet absorbed the oil and repelled the water. The sampling was made with 8 strips of Teflon (70 mm × 50 mm × 0.4 mm). Each strip was moved on the water's surface to allow better sorption of oil. To increase the efficiency of oil collection, the strips should have five 1.5-mm holes per square centimeter. The quantity of oil and petroleum products was scraped into the glass bottle with a stainless steel spatula.

The samples were closed and labeled with the important characteristics of the sampling. In order to prevent damage, samples should be adequately protected during transport; these samples were put in containers containing oil sorbent material for their protection. The available samples were transported to a laboratory as quickly as possible.

Capillary GC

A Hewlett-Packard (Palo Alto, CA) HP 5890 II series GC with an FID was used. A fused-silica capillary column (25 m × 0.32 mm, 0.52- μ m film thickness, Ultra-2, Hewlett-Packard) was used for the separation of compounds in the analyzed samples. The GC operation conditions were as follows: carrier gas, hydrogen (2.0 mL/min); injector temperature, 290°C; detector temperature, 300°C; temperature program, 90 to 270°C at 6°C/min, held 30 min; injected sample size, 0.6 μ L. The sample was a 5% (v) solution of the spill in CCl₄.

The concentrations of individual *n*-alkanes and selected isoprenoids (pristane and phytane) were determined by the method of internal standard. The instrument was calibrated using standard solutions of C₈ through C₃₀ *n*-alkanes. Tetradecene-1 (Merck, Schuchardt, Germany) was used as an internal standard. The response factors for each hydrocarbon compound were calculated, and the relative

Table II. Parameters of Method Validation

Component	Concentration (μ g/mL)	Method accuracy (% recovery)	Method precision		
			SD (μ g/mL)	RSD (%)	Repeatability (μ g/mL)
<i>n</i> -C ₉	980	99.3	12	1.3	34
<i>n</i> -C ₁₀	730	98.9	14	1.4	39
<i>n</i> -C ₁₁	740	98.2	45	4.8	125
<i>n</i> -C ₁₂	680	98.4	15	1.6	42
<i>n</i> -C ₁₃	980	99.7	16	1.6	44
<i>n</i> -C ₁₄	1000	99.4	15	1.5	42
<i>n</i> -C ₁₅	740	98.0	18	1.8	50
<i>n</i> -C ₁₆	680	97.6	25	2.4	69
<i>n</i> -C ₁₇	620	97.6	34	3.2	94
<i>n</i> -C ₁₈	1000	98.2	34	3.3	94
<i>n</i> -C ₂₀	730	99.2	63	5.8	175
<i>n</i> -C ₂₄	810	99.9	22	1.4	61
<i>n</i> -C ₂₆	760	93.6	42	2.2	116
<i>n</i> -C ₃₀	740	98.2	56	1.7	155

Table III. Variance of Characteristic Parameters for Differentiation of Oils

Parameter	Value (<i>n</i> = 4)	SD	RSD (%)	Repeatability
Pristane/phytane	1.13	0.05	4.40	0.14
<i>n</i> -C ₁₇ /pristane	2.12	0.05	2.40	0.14
<i>n</i> -C ₁₈ /phytane	1.97	0.07	3.60	0.19
$\Sigma(n\text{-C}_8 + n\text{-C}_{10} + n\text{-C}_{12} + n\text{-C}_{14}) / \Sigma(n\text{-C}_{22} + n\text{-C}_{24} + n\text{-C}_{26} + n\text{-C}_{28})$	6.60	0.20	3.00	0.53
$\Sigma(\text{odd } n\text{-alkanes}) / \Sigma(\text{even } n\text{-alkanes})$	1.02	0.05	4.90	0.14

Table IV. Characteristic Parameters for Different Grades of Crude Oil and Diesel Fuels

Parameter	Russian 1	Russian 2	Russian 3	Iranian heavy	Iranian light	Iraqian	Azeri light	Boza- chinski	Diesel fuel 1	Diesel fuel 2	Diesel fuel 3	Diesel fuel 4
Pristane/phytane	0.93	1.29	1.05	1.05	1.20	0.84	1.47	1.07	1.02	1.23	1.03	1.13
<i>n</i> -C ₁₇ /pristane	1.81	1.58	1.65	1.65	1.73	2.92	1.14	0.84	2.07	1.99	2.22	2.13
<i>n</i> -C ₁₈ /phytane	1.42	1.78	1.52	1.51	1.72	2.22	1.46	0.85	1.89	1.94	1.90	1.96
$\Sigma(n\text{-C}_8 + n\text{-C}_{10} + n\text{-C}_{12} + n\text{-C}_{14}) / \Sigma(n\text{-C}_{22} + n\text{-C}_{24} + n\text{-C}_{26} + n\text{-C}_{28})$	3.86	2.19	1.10	0.98	2.55	2.36	3.45	0.57	2.85	4.87	3.70	4.87
$\Sigma(\text{odd } n\text{-alkanes}) / \Sigma(\text{even } n\text{-alkanes})$	0.82	0.93	1.04	0.89	1.05	1.06	0.81	0.92	1.02	1.00	1.02	1.00

response factors of compounds are presented in Table I. The response factor of pristane (i-C₁₉H₄₀) has been accepted as being equal to n-C₁₇H₃₆, and that of phytane (i-C₂₀H₄₂) is equal to n-C₁₈H₃₈ (4,6,7).

Results and Discussion

The identification of n-alkanes was carried out using standards, and literary data (6,7) have been used for the identification of isoprenoids. Information about the distribution of n-alkanes, pristane, and phytane was obtained from the GC-FID analysis of different types of crude oil and diesel fuels. Figures 1 and 2 show chromatograms of Russian oil and Azeri Light oil. The chromatograms of these samples show very typical profiles of n-alkanes and isoprenoids; thus, they are suitable for the differentiation of the compared samples.

The method was validated using standard solutions and diesel fuel samples, following the guiding principles of Good Laboratory Practice (8,9). The parameters of the GC-FID method validation are shown in Table II. The standard solutions contain C₈ through C₃₀ n-alkanes in the range 600–1200 µg/mL in n-hexane. The linearity was validated by a series of injections of standard solutions containing hydrocarbons in the concentration range 400–20000 µg/mL. The limit of quantitation (LOQ), which is equal to three times the standard deviation (SD), varied from 36 to 190 µg/mL.

Five characteristic parameters, specifically n-C₁₇/pristane, n-C₁₈/phytane, pristane/phytane, $\Sigma(n-C_8 + n-C_{10} + n-C_{12} + n-C_{14})/\Sigma(n-C_{22} + n-C_{24} + n-C_{26} + n-C_{28})$, and $\Sigma(\text{odd } n\text{-alkanes})/\Sigma(\text{even } n\text{-alkanes})$, have been calculated and tested for the differentiation of investigated oil spill samples. The variance of parameters expressed by SD, relative standard deviation, and repeatability have been determined from 4 consecutive analyses of diesel fuel and are presented in Table III. The obtained analytical data are summarized in Table IV. Although the most sensitive ratio is $\Sigma(n-C_8 + n-C_{10} + n-C_{12} + n-C_{14})/\Sigma(n-C_{22} + n-C_{24} + n-C_{26} + n-C_{28})$, it is supposed that all studied parameters would be more useful for the fast and reliable identification and differentiation of fresh oil spills. The spill sample and potential source of the pollution must be compared using these characteristic parameters. If a parameter's values do not match within the SD of GC analysis, the conclusion is that the samples are not from the same source.

Conclusion

A fast, simple, and reliable approach for the differentiation of spilled oils is described. Capillary GC-FID was used for the determination of the chosen characteristic compounds. Five characteristic parameters were calculated on the basis of the distribution of n-alkanes and isoprenoids present in oil and spills. The quantitative measurement was made using the internal standard method. In most cases, a simple comparison distinguishes the spill from the source of the pollution. The approach is proposed as a preliminary step. If a confirmation of identity is necessary, a more expensive and time-consuming GC-MS technique must be used for a positive identification of the oil spill.

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