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Analysis and Survey of Marine Fuels and Pollution Samples

The types of oil spills generally encountered in the harbors of British Columbia have consisted of oil mixtures from the ships' bilges. These mixtures are generally bunker fuels, intermediate diesel fuels, and lubricating oils. Such spilled petroleum mixtures have been collected from the surface of the water or from beaches, log booms, and piers [*1*]. Collected samples may range in volume from one litre to microlitre quantities.

The petroleum oil analytical procedure, the results of analysis, some of the techniques devised for the handling of samples of limited size, and the data from a survey analysis of bunker fuels and intermediate fuels from Vancouver, B.C. oil refineries will be considered. These fuel oils currently supply heating installations and industrial boilers throughout southern and central British Columbia, Canada.

A number of papers have been published concerning the identification of pollutants—slop oil [*1*], beach pollutants (crude oil and bunker fuels) [*2,3*] in Great Britain, and deposits from petroleum oils [*4,5*] in Canada. The analytical methods used by the authors of the respective articles consisted of various combinations involving gas chromatography [*1–3,6*] atomic absorption [*4,7*], infrared analyses [*1,8,9*], neutron activation analysis [*10*], or thin-layer chromatography [*11,12*] in conjunction with various physical tests [*13*], fractionation profile analyses [*6*], and constituents determination [*13*]. The procedure used by us differs somewhat from the above methods and has been found to be successful.

Sampling of Oil Spill

Contributors were asked to collect at least five millilitres of oil, not including material such as seawater. Some samples were collected by scooping floating petroleum product from the surface of the water, the intention being to trap as high a ratio of oil to water as possible. Samples were usually submitted in widemouthed mason jars or polyethylene or polypropylene bottles. These containers were airtight and were impervious to petroleum products. Ideally, the pollution sample was collected as soon as possible after discovery and the time and date, as well as the exact location and any unusual circumstances, were noted. Any outfall pipes or fuel lines which discharged into the polluted area were sampled. All ships in the vicinity of the oil spill had representative samples taken from all

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conceivable sources of similar petroleum products. This included bilges, settling tanks, separators, and fuel tanks aboard the vessels.

The difficulties of sampling light oil slicks were overcome with the assistance of a material known as Polycloth®. Polycloth® is a fine woven polypropylon cloth which is hydrophobic and, consequently, the material has an affinity for petroleum slicks. Investigators were advised to sweep the polluted water surface gently with the cloth for maximum coverage of the slick. If a corner of a 1-ft^2 section of polycloth was swept back and forth in contact with an oil slick, sufficient sample could frequently be accumulated in the cloth for analysis. The oil-saturated cloth was placed in an airtight container and submitted as a pollution sample.

Extraction of Oil from Pollution Sample

The methods used consisted mainly of the physical removal of water from the oil sample or solvent extraction of the oil from media such as sea vegetation, dead sea life, or sand. Extraction of the petroleum product was accomplished by one or combinations of the following methods.

1. *Centrifugation*—This sometimes broke the oil-water emulsion that frequently formed.
2. *Solvent extraction*—Methylene chloride was found to be suitable for the extraction of bunker fuels from water.
3. *Vacuum distillation*—The use of liquid nitrogen traps on a high-vacuum line would, if the sample were continuously stirred, remove residual water. This step was used only with samples which were going to be ashed for analysis.

Comparative samples were each treated in the same manner [*6*].

Oil Analysis

Measured aliquots of extracted petroleum samples were diluted with methylene chloride in a ratio of ten parts by volume of solvent to one part by volume of oil. The diluted sample was analyzed by gas chromatography. Instrumental parameters found to be suitable were as follows:

(1) dual flame ionization detectors;
(2) column—¼ in. by 6 ft. 3 percent OV-101, on Chromosorb W (for heavy fuels and crude oils), and ¼ in. by 6 ft. 3 percent OV-1 (for light fractions such as gasoline);
(3) attenuation 8–16;
(4) range 100, 12°C/min program rate;
(5) injection port temperature 225°C;
(6) detector block temperature 350°C;
(7) oven temperature range from 45 to 275°C, with hold at upper limit; and
(8) chart speed 10 mm/min.

The gas chromatograph used for the analysis of petroleum products was the Perkin-Elmer Model 900.

The gas chromatographic analysis characterized the types of petroleum products present giving a paraffin profile (see Figs. 1–4), and allowed a comparison of similar types of petroleum fractions (see Figs. 2 and 3). This analysis facilitated the elimination of grossly different suspect samples. It also revealed mixtures of petroleum fractions and enabled the analyst to estimate approximate composition of these mixtures (see Fig. 4).

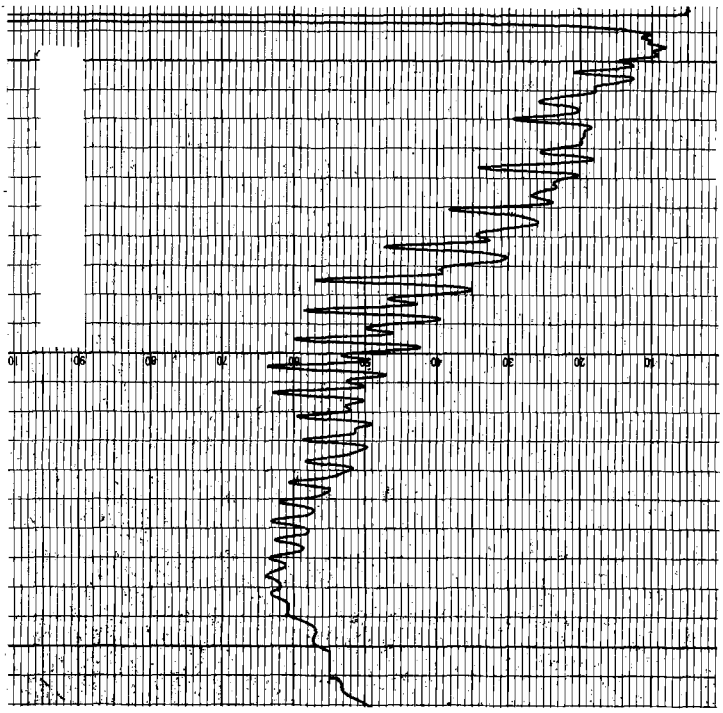

FIG. 2—*Heavy bunker fuel.*

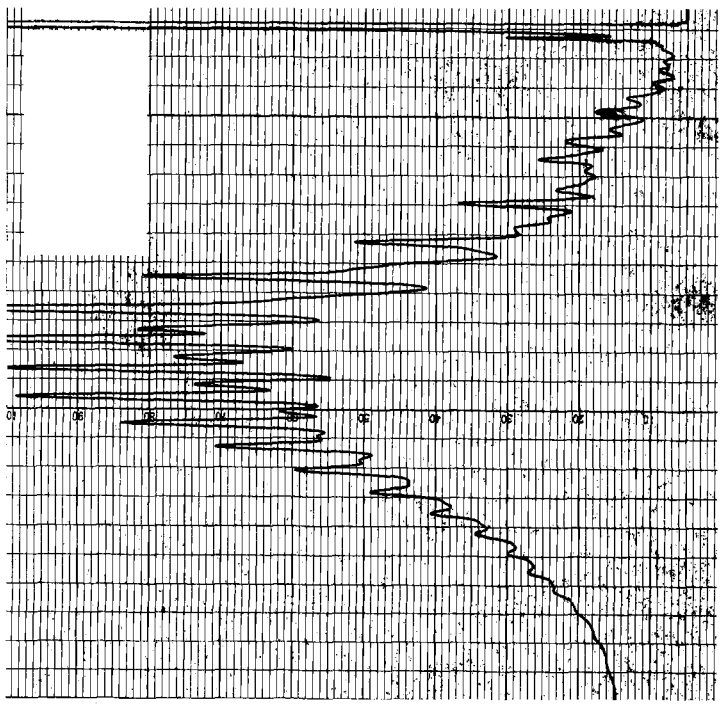

FIG. 1—*Black intermediate diesel fuel.*

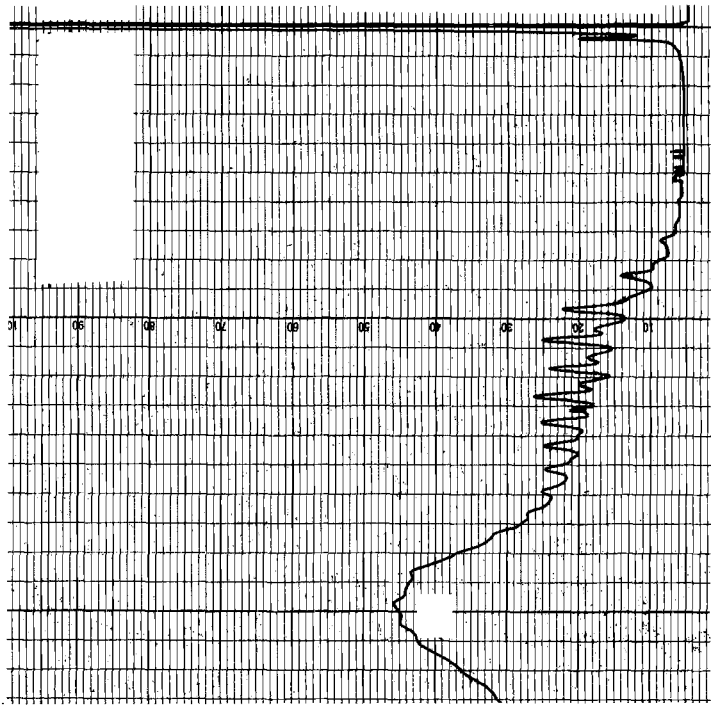

FIG. 4—*Engine room bilges mixture of Bunker C and lubricating oil.*

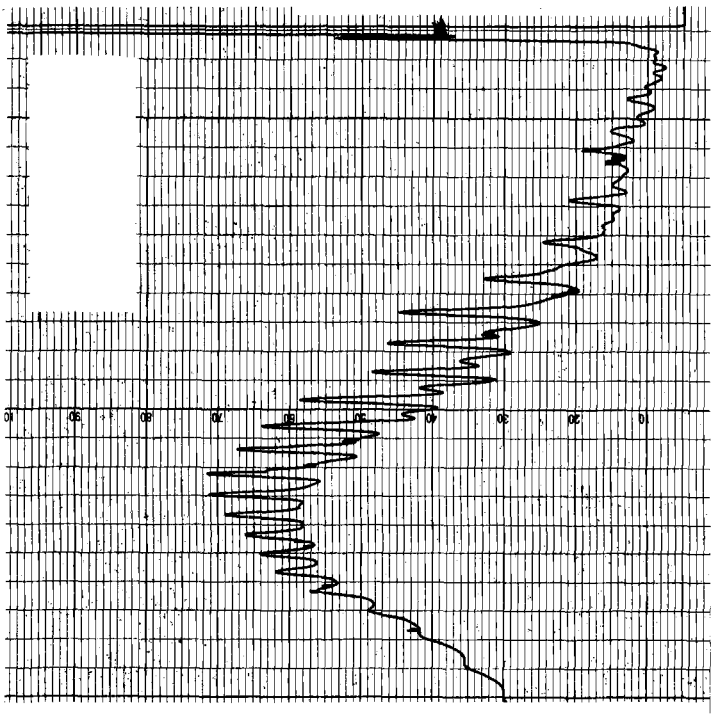

FIG. 3—*Heavy bunker fuel.*

Figures 1 to 4 illustrate gas-liquid chromatography strip chart recordings of some fuel oils using an OV-101 column, with temperatures programming from 45 to 275°C at 12°C/min.

An example of the application of gas chromatography is demonstrated in the following case submission. Three freighters were berthed in the immediate area of an oil spill and all of the freighters were suspect. Consequently, samples were collected from all possible sources on each vessel. These samples were submitted for analysis.

The gas chromatographic analysis revealed the following compositions of the respective exhibits.

Sample 1—Bunker C fuel oil from water alongside Freighter A.

Sample 2—Intermediate black diesel from day tank of Freighter B (see Fig. 1).

Sample 3—Bunker fuel from settling tank of Freighter B (see Fig. 3).

Sample 4—Lubricating oil with a small proportion of bunker fuel from bilges of Freighter B (see Fig. 4).

Sample 5—Bunker C fuel oil from port bilge of engine room of Freighter A.

Sample 6—Bunker C fuel oil from settling tank of Freighter A (see Fig. 2).

Sample 7—Intermediate black diesel from diesel fuel tank of Freighter A.

Sample 8—Intermediate black diesel from bilges of Freighter C.

Sample 9—Intermediate black diesel from fuel oil service tank of Freighter C.

Sample 10—Lubricating oil and partially evaporated intermediate black diesel fuel from previous spill in water.

Sample 13—Intermediate black diesel from engine room bilge of Freighter A.

Sample 14—Bunker C fuel oil from engine bilge of Freighter A.

Sample 15—Bunker C fuel oil and lubricating oil from engine room bilge of Freighter A.

As a result of gas chromatographic analysis, it was determined that residue analysis should be conducted on Samples 1, 3, 5, 6, and 13.

All extracted, undiluted samples of petroleum product were examined by infrared spectrophotometry. Figures 5 and 6 show the absorption patterns of an intermediate black diesel fuel and of a mixture of a lubricating oil and partially evaporated intermediate black diesel fuel, respectively. Differences discernible in these patterns were slight and could not be relied upon to eliminate pollution samples, contrary to the results indicated in Refs *8* and *9*.

Refractive indices of all undiluted, extracted oil samples were measured with the Abbe refractometer. Extracted samples of heavy fuel oils which could not be eliminated by gas chromatographic procedures were prepared for ashing and residue analysis. The samples were vacuum dried and the moisture-free samples of approximately 5-ml volume were placed in tared porcelain crucibles and weighed to the nearest 0.1 mg. The temperature of the crucibles and contents was slowly elevated to 150°C using an electric hot plate, extreme caution being exercised in order to avoid "bumping." The oil samples were then heated on the hot plate to 300°C over a 3-h period and subsequently allowed to stand at this temperature overnight. In the morning the samples were placed in a muffle furnace and the temperature was raised to 450°C [*14*], after which time the samples were fully ashed and ready for spectrographic analysis. The specimens were removed from the muffle furnace, cooled to ambient temperature, and reweighed with note being made of the color of ash. The ash was then loaded in small spectrograph electrodes and burned in the d-c arc of a 3.4-m Jarrell-Ash spectrograph using a step sector and optical wedge. The emission spectra of each exhibit were compared qualitatively (see Tables 1 and 2).

TABLE 1—*Samples from Vancouver oil refineries.*

Source	Ba	B	Al	Si	P	Mn	Pb	Cr	Sb	Mg	Cu	Ni	V	Ca	Ti	Zn	Na	Sn	Fe	Mo	Sr	K
											1968											
Imperial[a] Fuel 46 (Bunker B)	tr	...	wk	m	tr	m	str	wk	wk	m	wk	m	m	m	wk	tr	tr	...	m	...	...	...
Shell Thin Fuel (Bunker B)	tr	...	wk	m	tr	m	wk	wk	...	m	m	m	m	wk	m	tr	wk	...	m	...	...	...
B.A.[b] (Bunker B)	...	tr	wk	m	...	tr	...	tr	...	m	wk	m	m	wk	...	...	...	tr	m	...	...	...
Standard (Bunker B)	tr	tr	tr	m	...	tr	tr	wk	...	m	wk	m	m	m	...	...	tr	...	m	...	...	...
Imperial Fuel (Bunker C)	tr	...	wk	m	tr	m	wk	wk	...	m	wk	m	m	wk	m	tr	wk	...	m	...	...	...
Shell (Bunker C)	tr	...	wk	m	tr	m	wk	wk	...	m	wk	m	m	wk	m	...	wk	...	m	...	...	...
B.A. (Bunker C)	wk	tr	m	str	tr	wk	tr	tr	...	m	wk	str	m	wk	m	...	wk	tr	m	...	...	...
Standard (Bunker C)	tr	...	m	str	tr	tr	tr	tr	...	m	wk	str	m	wk	...	...	wk	...	m	...	...	...
											1970											
Imperial Intermediate 46	tr	...	wk	tr	...	tr	...	tr	...	m	wk	m	str	m	tr	...	tr	...	wk	tr	...	...
Shell Intermediate 45	tr	...	wk	...	...	tr	tr	tr	...	m	wk	m	str	m	tr	...	tr	...	wk	...	...	...
Standard (Bunker B)	...	...	wk	tr	...	...	...	...	...	m	tr	m	m	str	tr	...	tr	...	wk	...	...	...
Chevron (Bunker 10)	...	...	wk	tr	...	...	...	...	...	m	tr	wk	m	str	tr	...	tr	...	wk	...	...	...
Gulf 5	...	tr	m	m	...	tr	...	tr	...	m	tr	m	str	m	tr	...	tr	...	m	...	...	...
Imperial (Bunker C)	...	...	m	m	...	tr	tr	tr	...	m	wk	m	str	m	tr	...	tr	...	wk	tr	...	...
Shell 6 (Bunker C)	...	...	m	tr	...	tr	...	tr	...	m	tr	tr	str	m	tr	...	tr	...	wk	...	...	...
Gulf 6 (Bunker C)	...	tr	...	m	m	tr	...	tr	...	m	wk	m	str	m	tr	...	tr	...	m	...	...	...

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Esso 46	tr	...	m	m	...	tr	tr	tr	...	m	wk	m	str	m	tr	...	tr	...	m	...	...	...
Esso 10–15 Fuel	tr	...	m	m	...	tr	tr	tr	...	m	wk	m	str	m	tr	...	tr	...	m	...	...	...
Shell 15 (Bunker B)	wk	...	m	m	tr	tr	tr	wk	...	m	wk	m	str	str	wk	...	tr	wk	m	...	...	...
Shell 1500 (thin)	tr	...	m	m	...	tr	tr	wk	...	m	m	m	m	str	m	...	wk	...	m	...	m	...
Standard 15	tr	...	m	m	tr	tr	...	tr	...	m	wk	m	m	str	wk	...	tr	...	m	...	m	...
Standard Intermediate and 10	tr	...	m	m	tr	m	tr	tr	...	m	wk	m	m	str	tr	...	tr	...	m	...	m	...
Gulf 5	...	...	str	m	...	tr	...	tr	...	m	wk	m	str	m	wk	...	tr	...	m	...	...	...
Gulf MF 1500	...	...	str	m	tr	tr	tr	tr	...	m	wk	m	str	m	wk	...	tr	...	wk	...	...	...
Esso Naval Fuel (Bunker C)	...	...	m	wk	...	tr	wk	tr	...	m	m	m	m	str	wk	tr	tr	...	wk	...	...	...
Esso (Fuel C)	tr	...	m	m	...	wk	tr	tr	...	m	wk	m	str	str	wk	...	tr	...	m	...	...	...
Standard (Bunker C)	tr	...	m	m	tr	tr	...	tr	...	m	wk	m	m	str	wk	...	tr	...	m	...	m	...
Shell 6	tr	...	m	m	tr	m	tr	wk	...	m	wk	m	str	str	m	...	tr	...	m	...	...	...
Gulf 6	...	...	str	m	...	tr	...	tr	...	m	wk	m	str	str	m	...	tr	...	m	...	...	...

tr = trace intensity
wk = weak line intensity
m = medium line intensity
str = strong line intensity

Line intensity refers to the relative density of line spectra exposure on glass Kodak Spectrum Type III Photographic plates.

[a] Imperial changed its company distribution name to Esso.
[b] Note B.A. oil samples no longer available in Vancouver area.

TABLE 2—*Case samples from bilges, pumps, and filters.*

Type of Oil Sample	Ba	B	Al	Si	P	Mn	Pb	Cr	Sb	Mg	Cu	Ni	V	Ca	Ti	Zn	Ha	Sn	Fe	Mo	Sr	K
Mixture of Diesel and Bunkers	wk	tr	tr	m	...	tr	tr	tr	...	m	wk	wk	m	m	wk	tr	tr	...	wk	...	...	...
Bunker Fuel	...	tr	tr	m	...	tr	tr	tr	...	m	wk	tr	m	str	tr	tr	tr	tr	m	tr	...	...
Intermediate Fuel	wk	...	m	m	tr	m	wk	wk	...	m	wk	tr	m	str	m	tr	tr	tr	wk	tr	tr	...
Diesel and Bunker	tr	...	wk	wk	...	tr	tr	tr	...	m	wk	tr	m	str	tr	tr	tr	tr	m	tr	...	...
Bunker C	...	...	wk	tr	...	tr	m	...	...	m	wk	tr	wk	wk	...	m	m	m	wk	...	...	...
Intermediate	tr	tr	wk	m	tr	wk	m	tr	tr	m	m	...	tr	wk	wk	m	str	m	wk	...	...	...
Bunker C	...	...	wk	wk	...	tr	tr	...	...	m	m	...	m	wk	...	m	...	...	tr	...	...	...
Heavy Fuel and Diesel	...	tr	wk	m	...	wk	m	tr	...	m	wk	...	...	str	...	wk	wk	tr	m	...	...	...
Heavy Bunker	tr	...	wk	m	...	wk	m	tr	...	m	wk	...	...	str	tr	wk	tr	wk	m	...	...	...
Heavy Bunker	...	...	wk	tr	...	tr	tr	tr	...	m	wk	wk	wk	str	tr	...	...	...	wk	...	tr	...
Heavy Bunker	...	...	wk	tr	...	tr	tr	tr	...	m	wk	m	m	str	tr	tr	tr	...	wk	...	tr	...
Bunker C	...	...	m	wk	...	tr	...	tr	...	m	wk	m	m	m	tr	...	tr	...	m	...	tr	...
Bunker C	...	...	str	tr	...	tr	...	tr	...	str	tr	tr	str	str	tr	...	tr	...	wk	...	tr	...
Bunker C	...	...	wk	wk	...	tr	...	tr	...	str	wk	m	m	m	wk	...	tr	...	m	tr	...	...
Lubricating Oil and Bunker C	tr	tr	m	tr	...	tr	...	m	...	m	wk	m	tr	str	tr	tr	tr	...	wk	...	wk	...
Heavy Bunker Fuel	tr	...	wk	tr	...	wk	...	tr	...	str	wk	str	str	str	tr	wk	tr	...	str	tr	...	...
Heavy Bunker Fuel	...	...	tr	...	...	tr	...	...	...	m	tr	tr	m	wk	tr	...	tr	...	tr	...	...	...
Heavy Bunker Fuel	...	...	m	str	...	tr	...	tr	...	str	wk	wk	m	str	wk	tr	wk	...	m	...	...	...
Bunker C Fuel	...	tr	wk	m	...	wk	...	...	...	str	wk	wk	str	str	tr	tr	str	...	wk	...	tr	...
Bunker C Fuel	tr	...	m	wk	...	wk	tr	m	...	str	tr	tr	m	str	tr	tr	tr	...	m	...	...	...
Bunker C Fuel	...	tr	...	...	...	wk	tr	m	...	str	m	m	m	str	wk	tr	tr	...	...	...	...	...
Bunker Fuel and Lubricating Oil	...	...	str	tr	...	tr	...	tr	...	m	wk	wk	m	str	tr	tr	...	...	m	...	...	...
Bunker Fuel and Lubricating Oil	...	...	wk	wk	...	tr	tr	tr	...	str	str	tr	...	str	tr	tr	...	...	m	...	m	...
Bunker Fuel and Lubricating Oil	tr	...	m	m	...	wk	tr	tr	...	str	wk	m	m	str	m	tr	tr	...	m	wk	...	...
Bunker Fuel and Lubricating Oil	...	...	str	wk	...	tr	...	tr	...	str	tr	wk	m	str	wk	tr	wk	...	m	tr	...	...
Intermediate Black Diesel	...	...	tr	...	...	tr	...	...	...	...	tr	tr	m	m	...	...	...	...	wk	...	...	...
Bunker Fuel and Lubricating Oil	...	tr	wk	m	...	m	wk	tr	...	str	wk	tr	m	str	wk	wk	str	wk	m	tr	...	...
Bunker C Fuel	...	tr	m	m	...	m	tr	m	...	str	wk	...	m	str	wk	...	str	...	m	...	...	wk
Float Coat Tank Cleaner	...	...	tr	...	...	...	...	...	...	...	tr	tr	tr	str	tr	...	tr	...	...	...	...	...

tr = trace intensity
wk = weak line intensity
m = medium line intensity
str = strong line intensity

Line intensity refers to the relative density of line spectra exposure on glass Kodak Spectrum Type III photographic plates.

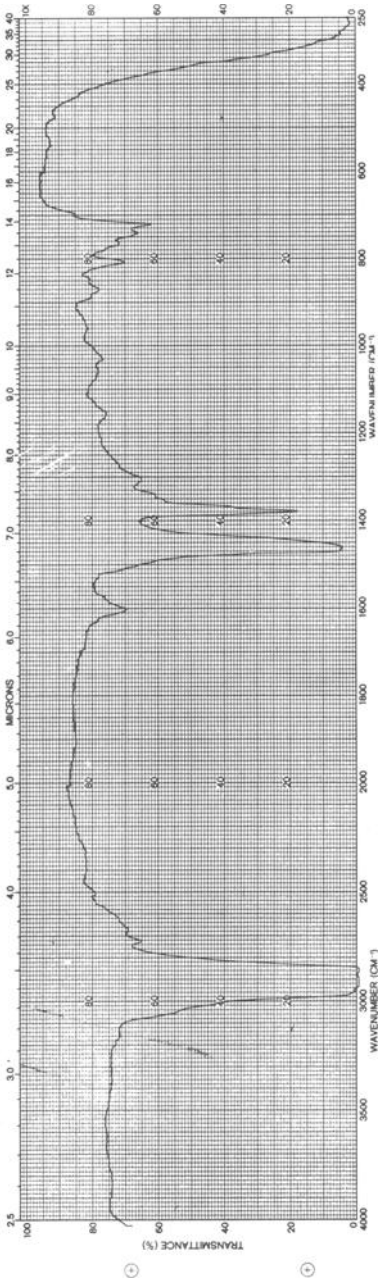

FIG. 5—*Infrared absorption spectrum of an intermediate black diesel fuel.*

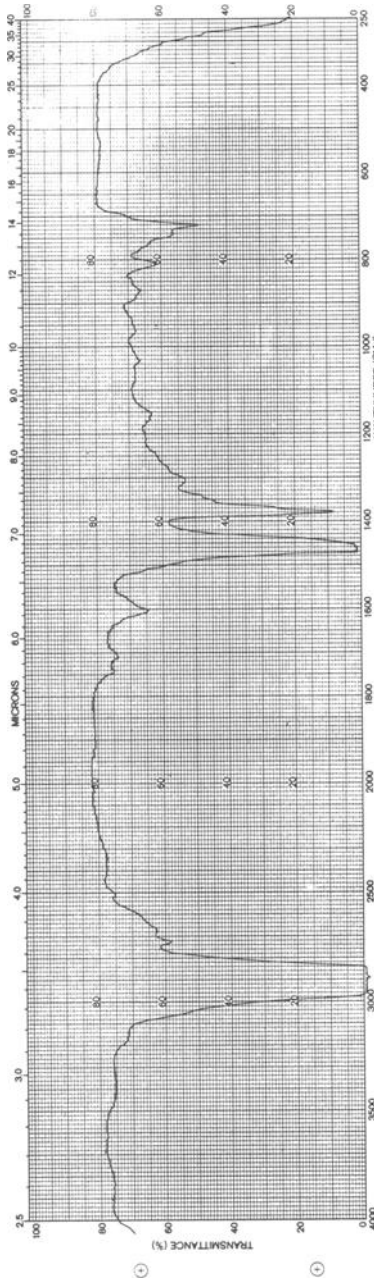

FIG. 6—*Infrared absorption spectrum of lubricating oil and partially evaporated intermediate black diesel fuel.*

Interpretation of Data

Infrared analysis was found to be of little value in characterizing oil samples. A combination of techniques including gas chromatographic analysis, refractive index measurements, ash residues, percentage ash composition, and emission spectrographic analysis of the ashed residues was found to be sufficient in localizing the source of oil spills. A monitoring program of petroleum oils from Vancouver oil refineries (1968 to 1972) has revealed ash residue compositions as tabulated in Table 1.

Table 2 is a listing of elemental compositions of oil samples received in oil pollution cases. These cases occurred over a period of four years and were submitted for analysis in connection with prosecutions under the Migratory Birds Convention Act, The Fisheries Act, and the Canada Shipping Act—Oil Pollution Regulations.

The information contained in Table 1 allows the analyst to evaluate analytical data from case samples as to possible origin. If the elemental composition of the ashed residues is grossly different, the suspect sample can be eliminated as having originated from a British Columbia based refinery.

Elemental compositions as determined from actual case samples illustrate the variation of composition of pollution samples submitted for analysis in a number of pollution offenses.

Acknowledgments

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