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Luminescence Measurements of Selected Refined Petroleum Products and Fish Oil with a Comparison to Crude Oil Luminescence

by

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CONTENTS

ILLUSTRATIONS

TABLES

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ABSTRACT

Laboratory luminescence measurements were made on 13 commercially available petroleum related refinery products, one fish oil sample, 19 pure organic compounds, at four Fraunhofer lines: 396.8 nm, 486.1 nm, 589.0 nm and 656.3 nm. Measured luminescence values of the refined petroleum products were generally highest at the 396.8 nm Fraunhofer line while the fish oil sample was highest at the 656.3 nm Fraunhofer line. There is no compound or class of compounds in the 19 pure organic samples which correlates with refined petroleum luminescence intensity as a function of wavelength. A comparison of multispectral luminescence data, between refined products and previously studied crude oils, suggests that a general classification can be constructed based on these data. Identification of an oil slick material would be of great benefit in a petroleum prospecting or pollution monitoring remote sensing program.

INTRODUCTION

Due to differences in chemical and physical properties between oil and water, remote sensing methods are well suited in their application to detection and identification of oil and other slicks in the marine environment. Of the several systems used by investigators, the ones which measure luminescence properties of the target show great promise in slick detection and may be the only systems, currently developed, which have the potential for material identification. It is important to petroleum explorationists and pollution monitoring groups alike to be able to distinguish between slicks composed of crude oil or a refined petroleum product. The identification of a slick-forming material as a crude oil would not prove the existence of a commercial petroleum deposit but the identification of a slick-forming substance which had been refined would indicate a man-made source.

THE PROBLEM

Detection and identification of oil or other pollutant slicks in the marine environment are distinct yet closely related processes. This paper describes laboratory luminescence measurements of selected refined petroleum products and a fish oil sample to determine if these measurements, made at particular Fraunhofer lines, would permit the distinction between these materials and crude oils. If this distinction can be made in the laboratory, similar measurements in the field may allow broad classification of the material comprising marine slicks.

MATERIALS AND METHODS

Thirteen commercially available refined petroleum products and one fish oil sample (table 1) were analyzed in the laboratory with a Perkin-Elmer* model MPF-3 luminescence spectrometer. A suite of 19 pure organic compounds (table 2) was also selected for measurements identical to those performed on the refined products in table 1. These compounds with the exceptions of samples 57, 58, and 59 are likely to occur in crude oils and refined products in significant quantities (Price, 1976). They were included in this study to determined if any particular compound or family of compounds displayed high luminescence at any of the four Fraunhofer lines used. Laboratory procedures are outline in detail in Henry and Donovan (1984).

The Fraunhofer lines 486.1 nm, 589.0 nm, and 656.3 nm were selected because another phase of this study was to determine the utility of an existing remote-sensing device, the Fraunhofer Line Discriminator (FLD) for slick detection and identification. The 396.8 nm Fraunhofer line was selected because of its potential for incorporation in a future instrument and because of its potential value in petroleum-related work.

RESULTS AND DISCUSSION

Rhodamine WT equivalences in parts per billion (ppb) are shown for the 13 refined petroleum samples in table 3. Nine of the refined petroleum products display the highest luminescence intensity at the 396.8 nm Fraunhofer line. The highest luminescence intensity recorded for the remaining four samples occurs at the 486.1 nm Fraunhofer line. Eight of these samples are lowest in luminescence intensity at the 656.3 nm Fraunhofer lines, three are lowest at the 589.0 nm Fraunhofer line, and one sample is lowest at the 396.8 nm Fraunhofer line. The fish oil sample was highest at the 656.3 nm Fraunhofer line and it displayed the highest luminescence recorded of all samples analyzed at this line. Relative luminescence intensity, as a function of wavelength, is shown in decreasing order in table 4.

Results of luminescence measurements of the pure organic compounds are given in table 5. Of the compounds which are likely to be volumetrically important in crude oil, all but one show low luminescence values (less than 10 ppb rhodamine WT equivalence) at the four wavelengths measured. The exception is cyclopentane which shows a rhodamine WT equivalence of 16.4 ppb at the 396.8 nm Fraunhofer line. The refined products show a general shift toward higher luminescence values at shorter wavelengths as compared to previously studied crude oils (Henry and Donovan 1984) shown in tables 3 and 6. The presence of various additives and dyes in the refined products may be, in part responsible for this shift. The range of hydrocarbon numbers found in gasoline, solvent,

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* Any use of trade names and trademarks in this publication is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

kerosene, and diesel fuel (table 7) shows considerable overlap and would not be expected to give rise to the large differences in luminescence intensity seen among these products. The refining process itself may also affect the differences noted in luminescence intensities between crude oils and refined products. Removal of the dark colored material (NSO, polynuclear, aromatics and asphaltene) from crude oil yields a more transparent liquid which may be less opaque to the excitation energy. This conclusion is in agreement with luminescence data gathered from crude oils (table 6). Crude oils with higher API gravity (more mature) show a general trend toward higher luminescence than the heavier (less mature) oils. Luminescence intensity of the selected crude oils, as a function of wavelength, is shown in decreasing order (table 8).

The data from table 3 and 6 are shown in figures 1 and 2. Figure 1 is a scatter diagram of natural log of the luminescence intensity of the crude oils and refined products plotted for the 486.1 nm and the 656.3 nm Fraunhofer lines. Figure 2 is a similar scatter diagram using data from the 396.8 nm and the 656.3 nm Fraunhofer lines. Both diagrams show that the crude oils and refined products tend to cluster into two fields. It is possible that a more distinct separation could be made between these two groups based on luminescence data collected from other Fraunhofer lines not used in this study. These two figures also demonstrate the usefulness of multispectral data in a classification scheme of this type. More work in this area would lead to a library of multispectral signatures of various pollutants which could be used for material classification, at least in gross categories.

References Cited

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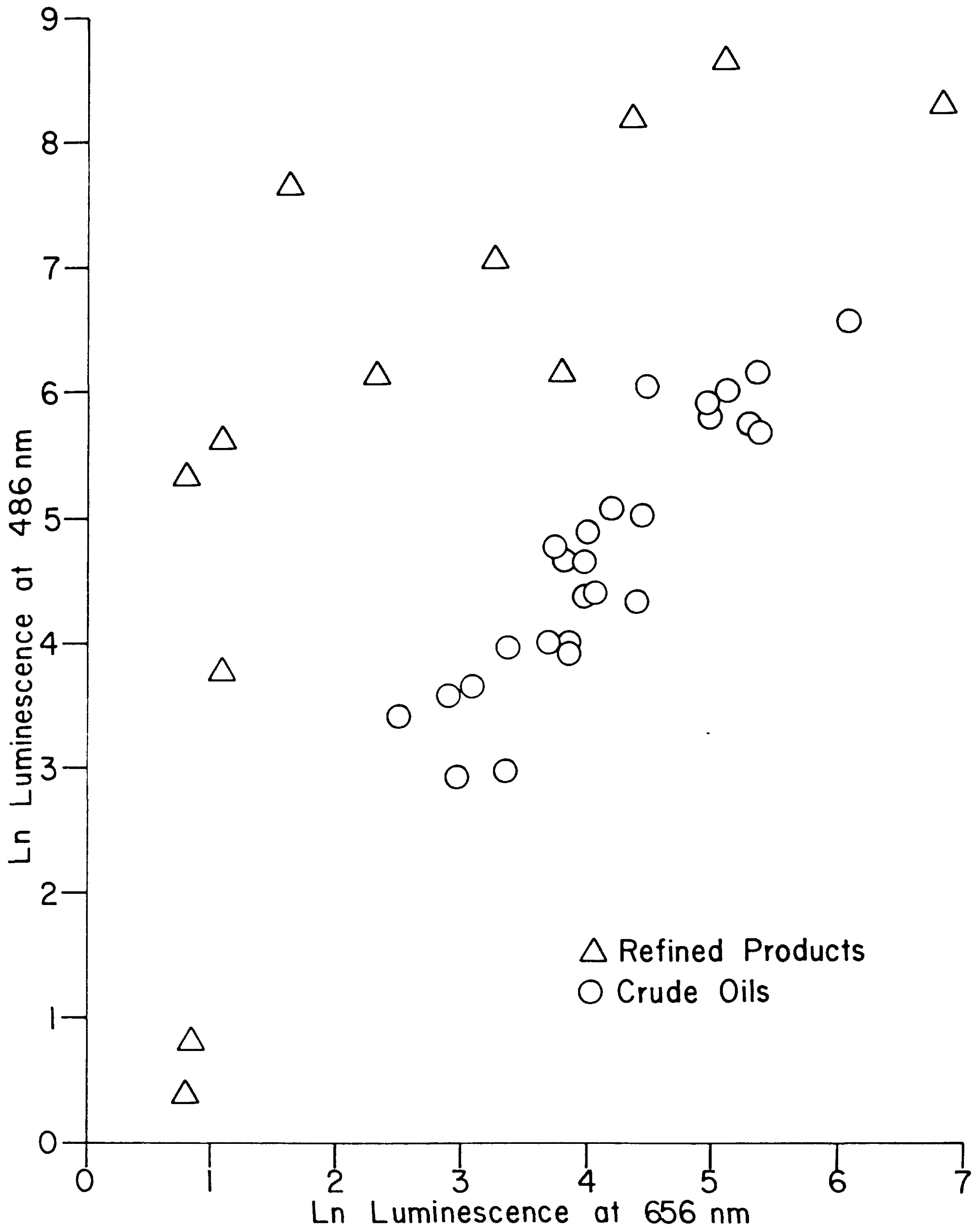

Figure 1. Ln of luminescence intensity measured at the 486.1 nm Fraunhofer line plotted against ln of luminescence intensity measured at the 656.2 nm Fraunhofer line.

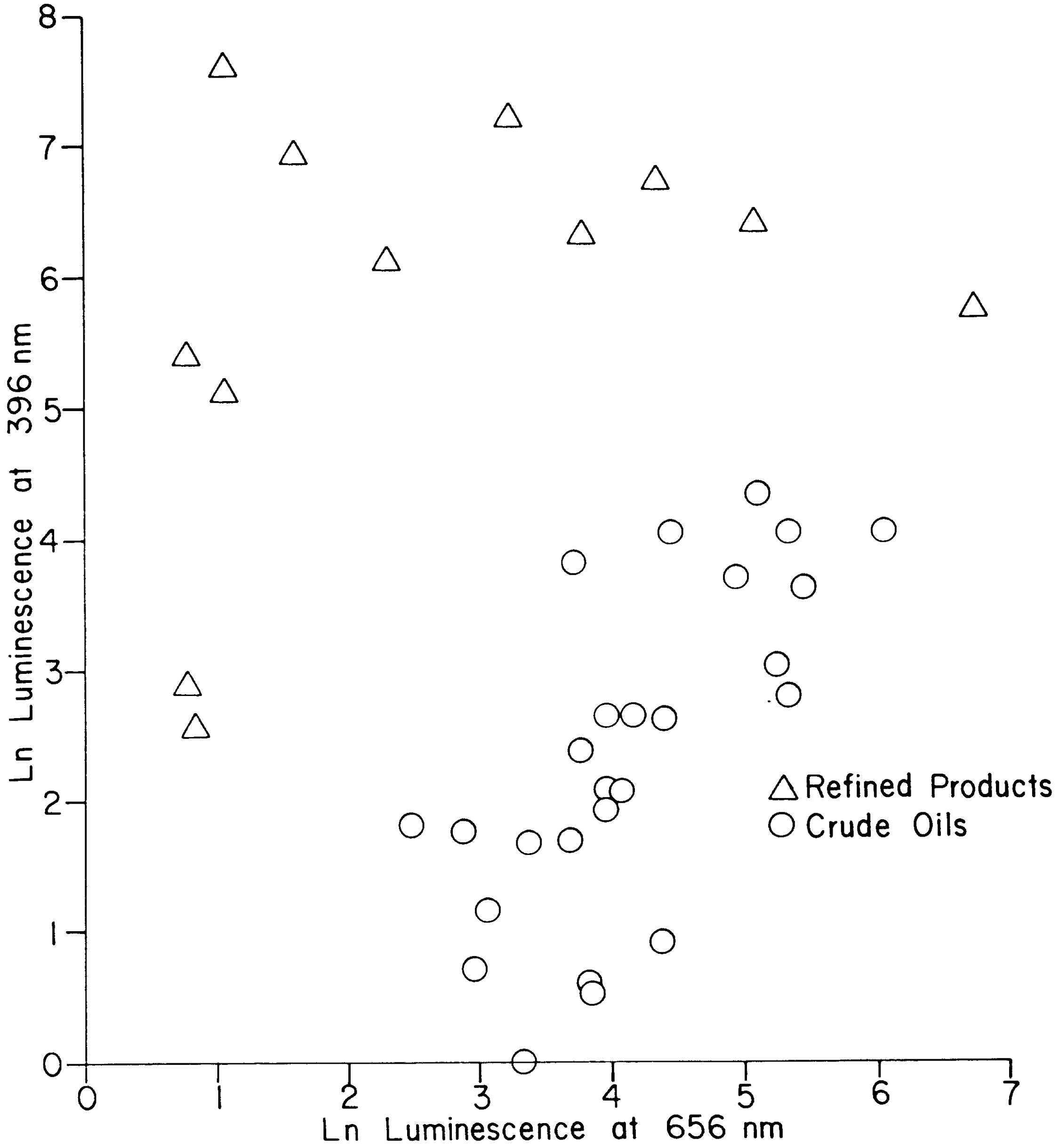

Figure 2. Ln of luminescence intensity measured at the 396.8 nm Fraunhofer line plotted against the ln of luminescence intensity measured at the 656.3 nm Fraunhofer line.

Table 1. Refined Petroleum Products

Sample No.	Product	Supplier
31	Air conditioner pump oil	Everco Industries
32	Power steering fluid	Sta-Lube Inc.
33	Hydraulic jack oil	Sta-Lube Inc.
34	Brake fluid	Raybestos/Manhattan
35	Pennzoil motor oil 30 wt.	Pennzoil Co.
36	Aero-Shell aviation oil 50 wt.	Union Oil Co.
37	Regular gasoline	Union Oil Co.
38	Supreme gasoline	Union Oil Co.
39	Unleaded gasoline	Union Oil Co.
40	Chevron solvent	Union Oil Co.
41	Kerosene	Union Oil Co.
42	Diesel fuel	Union Oil Co.
43	Heating oil	Union Oil Co.
44	Menhaden oil	Zapata Haynie Corp.

Table 2. Pure Organic Compounds[1]

Sample No.	Product	Grade
45	Pentane	PHOTREX
46	Hexanes	BAKER ANALYZED
47	Heptane	PHOTREX
48	2,4-Dimethylpentane	PHOTREX
49	2, 2, 4-Trimethylpentane	PHOTREX
50	Nonane	BAKER
51	Decane	PRATICAL
52	Cyclopentane	BAKER
53	Cyclohexane	PHOTREX
54	Methylcyclohexane	PHOTREX
55	1-Propanol	BAKER ANALYZED
56	2-Propanol	PHOTREX
57	Isobutyl Alcohol	PHOTREX
58	Ethylene Glycol	BAKER ANALYZED
59	Oleic Acid	FOOD CHEMICALS CODEX
60	Benzene	PHOTREX
61	Toluene	PHOTREX
62	O-Xylene	PHOTREX
63	1, 2, 4-Trimethylbenzene	BAKER

[1]J. T. Baker Chemical Company

Table 3. Integrated Excitation Intensity of Refined Products[1]

	Sample	396.8	486.1	589.0	656.3	486.1/589.0	486.1/656.3	589.0/656.3	486.1/396.8	589.0/396.8	656.3/396.8	(396.8+486.1)/656.3
31	Air Cond. Pump Oil	1074.0	2211.9	91.5	5.0	24.2	442.4	18.3	0.1	0.1	<.1	657.2
32	Power Steering Fluid	1367.3	1216.7	81.3	25.5	15.0	47.7	3.2	0.9	0.1	<.1	101.3
33	Jack Oil	828.3	3638.6	503.5	76.5	7.2	47.6	6.6	4.4	0.6	0.1	0.4
34	Brake Fluid	2074.7	293.3	18.2	2.9	16.1	101.1	6.3	0.1	<.1	<.1	816.6
35	Pennzoil 30 wt	313.5	4154.0	2880.4	687.6	1.4	6.0	4.2	13.3	9.2	2.2	6.5
36	Aviation Oil - Aeroshell 50 wt	630.8	5039.7	1033.3	163.5	4.9	30.8	6.3	8.0	1.6	0.3	34.7
37	Regular Gasoline	469.8	412.6	29.3	10.5	14.1	39.3	2.8	0.9	0.1	<.1	84.0
38	Supreme Gasoline	229.8	212.5	126.1	2.2	1.7	96.6	57.3	1.0	0.6	<.1	201.0
39	Unleaded Gasoline	549.1	479.6	17.2	44.4	27.9	10.8	0.4	0.9	<.1	0.1	23.2
40	Chevron Solvent	18.0	1.5	0	2.2	∞	0.5	0	0.1	0	0.1	0.9
41	Kerosene	12.9	2.3	0	2.3	∞	1.00	0	0.2	0	0.2	6.6
42	Diesel Fuel	972.7	709.6	29.8	0	23.8	∞	∞	0.7	<.1	0	∞
43	Heating Oil	173.3	45.2	3.0	3.0	15.0	15.0	1.00	0.3	<.1	<.1	72.8
44	Menhaden Oil	29.2	10.0	47.0	2245.0	0.2	<.1	<.1	0.3	1.6	76.8	<.1

Emission Wavelength (nm)

[1]Values shown are corrected for non-linearity of the excitation lamp, detector response and solar intensity as a function of wavelength, and given in parts per billion (ppb) rhodamine WT equivalence.

Table 4. Refined Petroleum Product Luminescence

Sample No.	Product	Relative Order of Luminescence Intensity from Highest to Lowest[1]
31	Air conditioner pump oil	4 > 3 > 5 > 6
32	Power steering fluid	3 > 4 > 5 > 6
33	Hydraulic jack oil	4 > 3 > 5 > 6
34	Brake fluid	3 > 4 > 5 > 6
35	Pennzoil motor oil, 30 wt.	4 > 5 > 6 > 3
36	Aero-Shell aviation oil, 50 wt.	4 > 5 > 3 > 6
37	Regular gasoline	3 > 4 > 5 > 6
38	Supreme gasoline	3 > 4 > 5 > 6
39	Unleaded gasoline	3 > 4 > 6 > 5
40	Chevron solvent	3 > 6 > 4 > 5
41	Kerosene	3 > 4 = 6 > 5
42	Diesel fuel	3 > 4 > 5 > 6
43	Heating oil	3 > 4 > 5 = 6
44	Menhaden oil	6 > 5 > 3 > 4

[1] 3 Refers to luminescence measured at the 396.8 Fraunhofer line.
4 Refers to luminescence measured at the 486.1 Fraunhofer line.
5 Refers to luminescence measured at the 589.0 Fraunhofer line.
6 Refers to luminescence measured at the 656.3 Fraunhofer line.

Table 5. Integrated Excitation Intensity of Pure Organic Compounds[1]

Sample		Emission Wavelength (nm) 396.8	486.1	589.0	656.3
45	Pentane	2.7	3.7	3.2	1.8
46	Hexanes	2.7	2.3	5.7	1.6
47	Heptane	3.4	1.3	1.2	2.4
48	2, 4 Dimethylpentane	3.8	2.8	2.1	1.6
49	2, 2, 4, Trimenthylpentane	2.3	.95	1.4	1.7
50	Nonane	1.7	1.7	.7	2.1
51	Decane	1.4	.3	.96	2.3
52	Cyclopentane	16.4	.4	1.1	2.2
53	Cyclohexane	6.0	1.2	.5	3.7
54	Methylcyclohexane	2.5	1.1	.3	2.9
55	1-Propanol	5.9	1.0	.7	2.8
56	2-Propanol	3.5	2.1	1.7	2.1
57	Isobutyl Alcohol	8.8	1.1	.07	2.3
58	Ethylene Glycol	1.4	.6	.5	2.4
59	Oleic Acid	98.8	60.6	12.3	5.1
60	Benzene	4.1	.6	.3	2.0
61	Toluene	4.1	.7	.0	2.4
62	O-Xylene	6.0	1.2	.8	1.6
63	1, 2, 4 Trimethylbenzene	4.8	.97	.1	1.8

[1]Values shown are corrected for non-linearity of the excitation lamp, detector response and solar intensity as a function of wavelength, and given in parts per billion (ppb) rhodamine WT equivalence.

Table 6. Integrated Excitation Intensity of Crude Oils[1]

Sample	Oil Type	396.8	486.1	589.0	656.3	486.1/656.3	589.0/656.3	486.1/396.8	589.0/396.8	656.3/396.8	(396.8 + 486.1)/656.3
		Emission Wavelength (nm)									
1	Aliphatic	59.1	749.3	709.3	428.2	1.8	1.7	12.7	12.0	7.3	1.9
2	Aliphatic	37.6	316.9	287.5	139.7	2.3	2.1	8.4	7.7	3.7	2.5
3	Aromatic	59.4	498.4	443.9	206.0	2.4	2.2	8.4	7.5	3.5	2.7
4	Aromatic	12.6	311.7	406.9	208.3	1.5	2.0	24.7	32.3	16.5	1.6
5	Aromatic	2.5	78.9	128.9	78.8	1.0	1.6	31.6	51.6	31.5	1.0
6	Aliphatic	20.8	325.5	352.6	193.3	1.7	1.8	15.7	17.0	9.3	1.8
7	Aliphatic	78.9	425.4	329.7	164.2	2.6	2.0	5.4	4.2	2.1	3.1
8	Aliphatic	40.9	385.6	279.3	140.1	2.8	2.0	9.4	6.8	3.4	3.0
9	Aromatic	6.9	92.0	101.3	52.1	1.8	2.0	13.3	14.7	7.6	2.0
10	Aliphatic	14.2	137.8	104.8	52.8	2.6	2.0	9.7	7.4	3.7	2.9
11	Aliphatic	14.2	164.1	136.3	64.0	2.6	2.1	11.6	9.6	4.5	2.8
12	Aliphatic	13.6	157.2	149.1	81.9	1.9	1.8	11.6	11.0	6.0	2.0
13	Aliphatic	58.0	445.5	263.1	85.6	5.2	3.1	7.7	4.5	1.5	5.9
14	Aliphatic	11.0	110.9	94.4	44.1	2.5	2.1	10.1	8.6	4.0	2.8
15	Aliphatic	1.7	51.8	69.4	46.2	1.1	1.5	30.5	40.8	27.2	1.2
16	Aliphatic	1.9	57.1	81.0	45.8	1.3	1.8	30.1	42.6	24.1	1.3
17	N.D.**	3.9	81.6	125.8	88.0	1.0	1.4	20.9	32.3	22.6	1.0
18	Aromatic	29.3	123.8	85.4	41.0	3.0	2.1	4.2	2.9	1.4	3.7
19	Aromatic	8.1	84.1	88.2	56.6	1.5	1.6	10.4	10.9	7.0	1.6

** N.D. = Not determined.

[1]Values shown are corrected for non-linearity of the excitation lamp, detector response and solar intensity as a function of wavelength, and given in parts per billion (ppb) rhodamine WT equivalence.

Table 6. Continued[1]

		Emission Wavelength (nm)									
Sample	Oil Type	396.8	486.1	589.0	656.3	$\frac{486.1}{656.3}$	$\frac{589.0}{656.3}$	$\frac{486.1}{396.8}$	$\frac{589.0}{396.8}$	$\frac{656.3}{396.8}$	$\frac{396.8 + 486.1}{656.3}$
20	Aromatic	5.5	56.7	66.0	39.0	1.5	1.7	10.3	12.0	7.1	1.6
21	Aromatic	8.1	81.9	88.4	52.8	1.6	1.7	10.1	10.9	6.5	1.7
22	Aromatic	1.0	20.2	36.6	27.4	0.7	1.3	20.2	36.6	27.4	0.8
23	Aromatic	5.4	54.4	58.3	28.4	1.9	2.1	10.1	10.8	5.3	2.1
24	N.D.**	5.6	46.2	48.5	30.4	1.5	1.6	8.3	8.7	5.4	1.7
25	Aromatic	3.3	40.4	40.9	21.2	1.9	1.9	12.2	12.4	6.4	2.1
26	Aromatic	6.0	36.7	32.3	17.6	2.1	1.8	6.1	5.4	2.9	2.4
27	Aromatic	6.2	32.4	28.3	11.7	2.8	2.4	5.2	4.6	1.9	3.3
28	Aromatic	2.0	19.4	26.2	19.1	1.0	1.4	9.7	13.1	9.6	1.1

** N.D. = Not determined.

[1]Values shown are corrected for non-linearity of the excitation lamp, detector response and solar intensity as a function of wavelength, and given in parts per billion (ppb) rhodamine WT equivalence.

Table 7. Range of Carbon Numbers in Common Refined Petroleum Products

Product	Carbon Number
Gasoline	C_4 - C_{12}*
Solvent	C_5 - C_8*
Kerosene	C_9 - C_{17}**
Diesel Fuel	C_9 - C_{17}**
Aviation turbine fuel	C_9 - C_{16}**
Fuel oil	C_{12} - $>C_{20}$**
Lubricating oil	$>C_{20}$**
Asphalt	$>C_{20}$**

* Data from Hobson and Pohl [eds.], 1973.

** Data from A.S.T.M., Manual on Hydrocarbon Analysis, Am. Soc. Testing and Materials, Philadelphia, 1968.

Table 8. Crude Oil Luminescence

Sample No.	Order of Luminescence Intensity from Highest to Lowest*
1	4 > 5 > 6 > 3
2	4 > 5 > 6 > 3
3	4 > 5 > 6 > 3
4	5 > 4 > 6 > 3
5	5 > 4 > 6 > 3
6	5 > 4 > 6 > 3
7	4 > 5 > 6 > 3
8	4 > 5 > 6 > 3
9	5 > 4 > 6 > 3
10	4 > 5 > 6 > 3
11	4 > 5 > 6 > 3
12	4 > 5 > 6 > 3
13	4 > 5 > 6 > 3
14	4 > 5 > 6 > 3
15	5 > 4 > 6 > 3
16	5 > 4 > 6 > 3
17	5 > 4 > 6 > 3
18	4 > 5 > 6 > 3
19	5 > 4 > 6 > 3
20	5 > 4 > 6 > 3
21	5 > 4 > 6 > 3
22	5 > 4 > 6 > 3
23	5 > 4 > 6 > 3
25	5 > 4 > 6 > 3
26	4 > 5 > 6 > 3
27	4 > 5 > 6 > 3
28	5 > 4 > 6 > 3

[1]3 Refers to luminescence measured at the 396.8 Fraunhofer line.
4 Refers to luminescence measured at the 486.1 Fraunhofer line.
5 Refers to luminescence measured at the 589.0 Fraunhofer line.
6 Refers to luminescence measured at the 656.3 Fraunhofer line.