UNITED STATES DEPARTMENT OF THE INTERIOR

GEOLOGICAL SURVEY

# Luminescence Properties and Chemical Composition of Crude Oils

by

Mitchell E. Henry and Terrence J. Donovan[1]

Open-File Report 84-385

This report is preliminary and has not been reviewed for conformity with U.S. Geological Survey editorial standards and stratigraphic nomenclature.

---

[1] Flagstaff Field Center
Flagstaff, Arizona

# CONTENTS

# ILLUSTRATIONS

## TABLES

Page

# Luminescence Properties and Chemical Composition of Crude Oils

## Abstract

Luminescence intensity of a suite of 27 crude oils was measured at four Fraunhofer lines: 396.8 nm, 486.1 nm, 589.0 nm, and 656.3 nm. Measured values for the crude oils were generally higher at the 486.1 nm and 589.0 nm Fraunhofer lines. Oils with higher API gravities (lower density) display a shift toward higher luminescence intensity at shorter wavelength Fraunhofer lines. A positive correlation exists between luminescence intensity and percent aliphatic compounds, a crude negative correlation exists between luminescence intensity and percent aromatic compounds present and little or no correlation was found between luminescence intensity and percent polar compounds or asphaltenes present. The closest correlation exists between luminescence intensity and API gravity of the crude oils.

## Introduction

The association between natural petroleum seeps and the discovery of commercial petroleum deposits is well known (Link, 1952). This association, plus the fact that many crude oils have a lower density than sea water and float on the sea surface, has led to research into remote methods for detecting oil films. Methods developed include airborne reconnaissance using conventional photographic equipment (Vizy, 1974), multispectral scanning devices (Munday and others, 1971), video systems (Millard and others, 1975), both active and passive fluorosensors (Measures and Bristow, 1971; Watson and others, 1978), and spaceborne scanners (Deutsch and others, 1977).

Of these methods, the ones which offer the most promise for detecting and identifying petroleum seeps are those which involve some type of luminescence measurements made at selected wavelengths. This report contains laboratory luminescence measurements and gross chemical compositional data from a suite of 27 crude oils from various geologic ages and geographic locations.

## The Problem

There are many methods for the detection of an oil film on water. Most of these are dependent upon subtle differences in color and reflectance between clear water and oil-covered water. Within the visible portion of the electromagnetic spectrum, about 400 nm to 700 nm wavelength, there is little difference in reflectance between oil and water (fig. 1); however, significant differences exist in the luminescence properties of crude oils and water. It has been shown that oil slicks can be detected by using airborne luminescence measuring devices (Fantasia and Ingrao, 1974; Watson and others, 1978). This

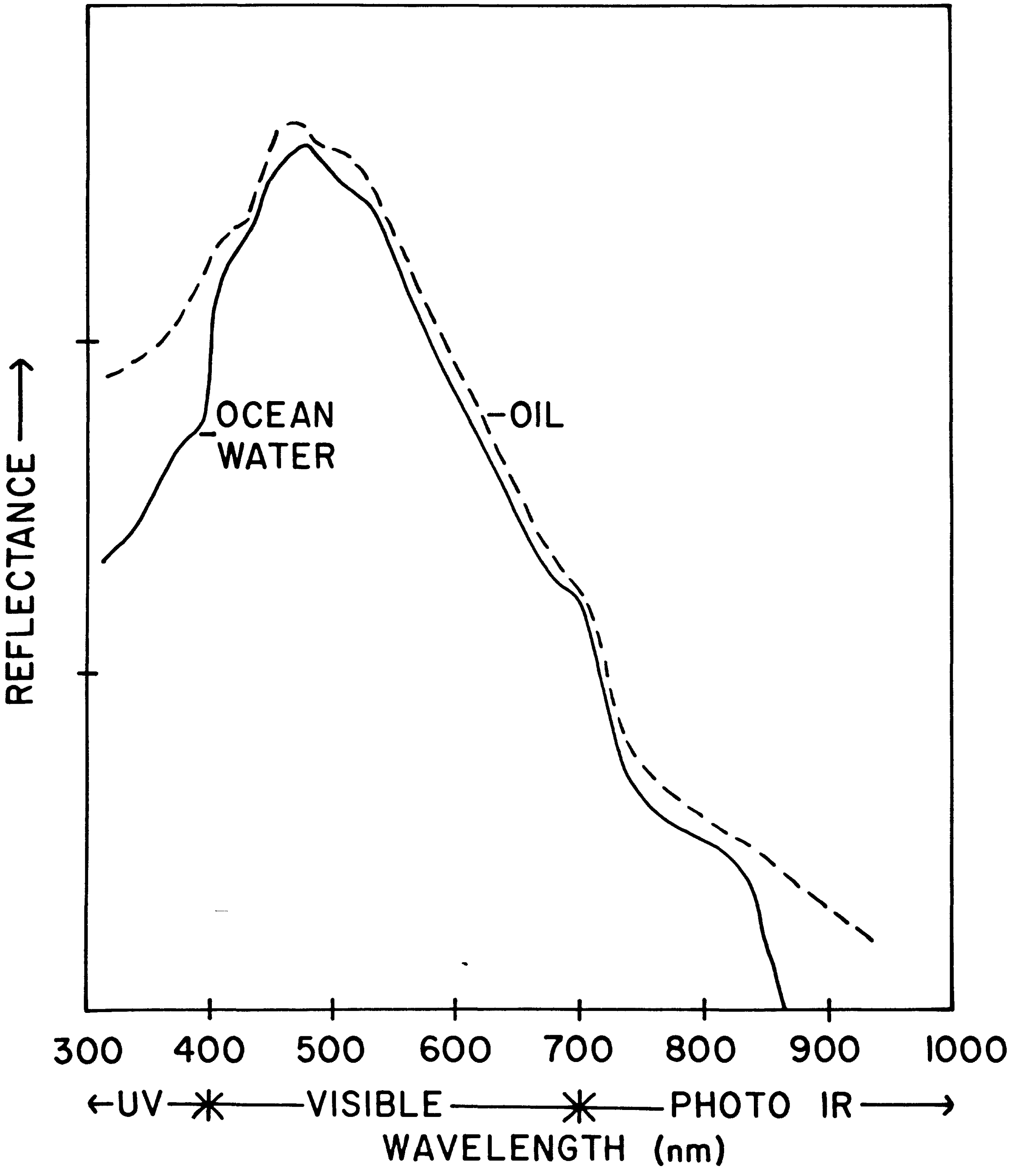

Figure 1. Reflectance of ocean water and oil as a function of wavelength (from Vizy, 1974).

work was undertaken to detemine if different types of crude oils could be identified on the basis of luminescence data alone.

## Materials and Methods

### Crude Oil Separation

A suite of 27 oils supplied by Chevron Oil Field Research Company of California was used in the study (Table 1). An aliquot of each crude oil was separated into four basic classes of organic compounds to determine oil type. Each sample was treated with pentane to precipitate the asphaltene fraction. The asphaltene-free sample was then treated with copper filings to remove sulfur. Saturated hydrocarbons, aromatic hydrocarbons and polar non-hydrocarbons were separated from the deasphaltened samples by column chromatography. The column used was 1.0 cm inside diameter x 25.0 cm long fitted with a teflon stop cock. The column was packed with 18.0 cm of 80-120 mesh chromatographic grade silica previously dried at 120°C. The silica adsorbent was supported either on a coarse frit fused to the column or a pad of glass wool. All solvents used were of pesticide grade.

A 0.5 mg aliquot of the deasphaltened crude oil was injected onto the column. Hexane was used to elute the saturated fraction. The first 5 ml of eluate were rejected. The next 13 ml were collected, evaporated to a small volume in a rotary evaporator, rinsed into a vial, evaporated under nitrogen and weighed. The aromatic fraction was then eluted with a 60:40 mixture of hexane:benzene. The first 7 ml of eluate were rejected. The following 25 ml were collected and concentrated in the same manner as the saturate fraction. The polar fraction (containing functional groups with nitrogen, sulfur, or oxygen) was eluted with a 60:40 mixture of benzene:methanol. The first 25 ml

Table 1. Crude Oils Used

| Sample No. | Chevron ID No. | Reservoir Age | Producing Horizon | Location | Specific Gravity | °API Gravity |
|---|---|---|---|---|---|---|
| 1 | 19327 | Devonian | Dundee | Michigan | 0.8327 | 38.4 |
| 2 | 17394 | Upper Cretaceous | Parkman sand | Wyoming | 0.7866 | 48.4 |
| 3 | 31473 | Cretaceous | Muddy sand | Wyoming | 0.8098 | 43.2 |
| 4 | 24294 | Miocene | Ala 1 | Nigeria | 0.8163 | 41.8 |
| 5 | 24563 | Lower Cretaceous | Lakota | Colorado | 0.8172 | 41.7 |
| 6 | 17636 | Middle Miocene | 8700' sand | Louisana | 0.8834 | 28.7 |
| 7 | 29350-5 | Eocene | Zone IV | Denmark | 0.7790 | 50.1 |
| 8 | 24461 | Upper Cretaceous | Stevens | Mississippi | 0.7932 | 46.9 |
| 9 | 31316 | Miocene | 1st Carneros | California | 0.8532 | 34.3 |
| 10 | 28212 | Upper Cretaceous | Padgett sand | Mississippi | 0.8455 | 35.9 |
| 11 | 31317 | Miocene | 3rd Carneros | California | 0.8377 | 37.4 |
| 12 | 26241 | Middle Miocene | Cruse | Trinidad | 0.8318 | 38.5 |
| 13 | 30534-1 | Jurassic | N.A. | N.A. | 0.7317 | 61.9 |

Table 1. Continued

| Sample No. | Chevron ID No. | Reservoir Age | Producing Horizon | Location | Specific Gravity | °API Gravity |
|---|---|---|---|---|---|---|
| 14 | 32219 | Oligocene | Vaqueros | California | 0.7713 | 52.0 |
| 15 | 24569 | Pennsylvanian | Weber | Colorado | 0.8574 | 33.5 |
| 16 | 27358 | Paleocene | Harash | Libya | 0.8350 | 38.0 |
| 18 | 27458-2 | Mississippian | Pekisko | Canada | 0.7735 | 51.4 |
| 19 | 31851 | Cretaceous | N.A. | Bahrain | 0.8695 | 31.2 |
| 20 | 30229-1 | Jurassic | N.A. | Alaska | 0.8654 | 32.0 |
| 21 | 13588 | Permian | Phosphoria | Wyoming | 0.9110 | 23.8 |
| 22 | 25968-2 | Permian-Pennsylvanian | Minnelusa | Wyoming | 0.8430 | 36.4 |
| 23 | 25179 | Miocene | Asamari | Iran | 0.8854 | 37.6 |
| 25 | 29619 | Pliocene | Repetto | California | 0.8639 | 32.3 |
| 26 | 27360 | Precambrian | N.A. | Libya | 0.8481 | 35.3 |
| 27 | 14525 | Eocene | N.A. | Venezuela | 0.8752 | 30.2 |
| 28 | 17112 | Ordovician | Sparkyzone | Canada | 0.9677 | 14.7 |

were rejected. The next 100 ml were collected and concentrated in the manner described for the saturated hydrocarbon fraction. Each fraction was placed in a glass vial with a teflon-lined cap and refrigerated.

## Laboratory Luminescence Measurements

Each crude oil was analyzed in the laboratory as a neat liquid with a Perkin-Elmer* model MPF-3 fluorescence spectrometer to determine the luminescence intensity emitted by each at the four Fraunhofer lines selected. The front-surface (fig. 2) mode was used to analyze all samples as this mode most closely resembles solar illumination striking an oil slick floating on water and because many crude oils are opaque to the excitation beam in bulk (1 cm thick) samples.

All laboratory luminescence measurements of the crude oils were referenced to a rhodamine WT dye standard at a concentration of 1200 parts per billion (ppb). This standard was analyzed before and after each sample analysis. In order to simulate in the laboratory, the conditions under which these measurements would be made in the field, the emission monochromator was set to a particular Fraunhofer line with the emission band width set to 1 nm and the excitation band width set to 20 nm resulting in broad band excitation and narrow band emission monitoring.

In the field a passive luminescence detector measures luminescence from the target resulting from excitation by the entire solar continuum simultaneously. During laboratory analysis intensity measurements were made at 20 nm intervals beginning with the interval containing 320 nm and ending

---

*Use of trade names in this paper is for descriptive purposes only and does not constitute an endorsement of the product by the U.S. Geological Survey.

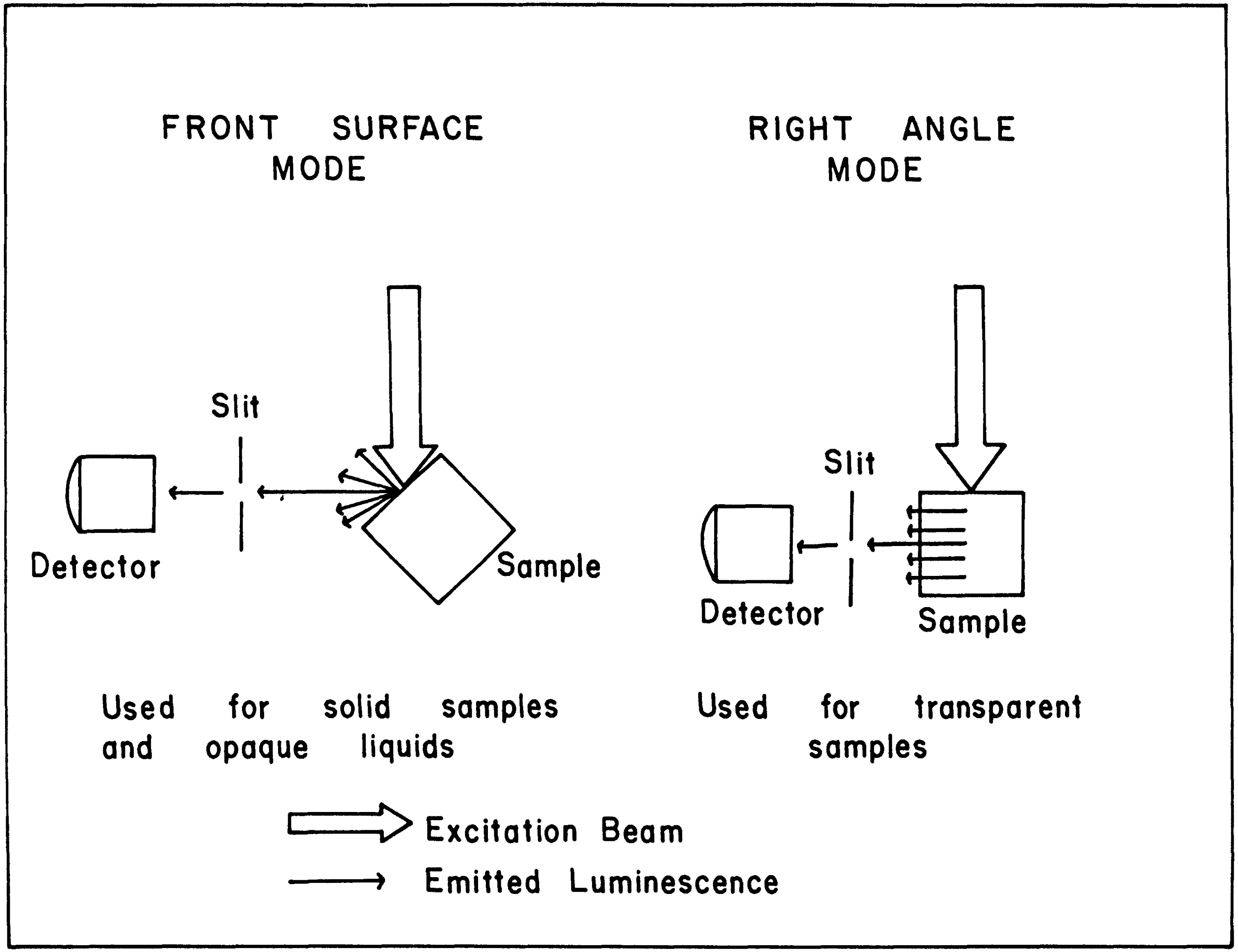

Figure 2. Geometry of sample holder in MPF-3 spectrometer for the two modes of operation.

with the interval prior to the interval containing the Rayleigh scattering peak (Table 2). These values were then multiplied by a correction factor which accounted for non-uniformity of solar radiation, photo multiplier sensitivity, and xenon lamp output as a function of wavelength (R. D. Watson, personal communication, 1980). This yielded a solar-corrected spectrum of the sample under analysis. The correction factors applied to each measurement are given in Table 3. This convolution of the solar spectrum with that generated by the MPF-3 was carried out with the aid of a mini-computer in line with the MPF-3. The luminescence intensity of the sample in terms of rhodamine WT equivalence is given by (modified from Watson and others, 1973):

$$\begin{array}{l}\text{rhodamine WT}\\ \text{equivalence}\end{array} = \frac{\text{Spl}\ \Sigma_{320\ \text{nm}}^{\text{RSP}}}{\text{rh}\ \Sigma_{320\ \text{nm}}^{560\ \text{nm}}} \times 1200$$

where rh $\Sigma_{320\ \text{nm}}^{560\ \text{nm}}$ is the integrated excitation intensity between 320 nm and 560 nm of the rhodamine WT standard measured at the 589.0 nm Fraunhofer line, Spl $\Sigma_{320\ \text{nm}}^{\text{RSP}}$ is the integrated excitation intensity between 320 nm and the interval prior to the interval containing the Rayleigh scattering peak for that particular Fraunhofer line, and 1200 is the concentration of rhodamine WT in the standard. This equation is valid in the range of about 15 to 1200 ppb rhodamine dye.

## Results and Discussion

### Crude Oil Characterization

The results of asphaltene removal procedures and column separations are shown in Table 4. The crude oils analyzed are divided into two broad classes (fig. 3) based on the line separating those oils with greater than 50 percent aliphatic hydrocarbons (termed aliphatic oils in this report) from those with

Table 2. Excitation Intervals Measured for Determination of Luminescence Intensity of Samples

| Faunhofer Line | Interval Containing Rayleigh Scattering Peak |
|---|---|
| 396.8 nm | 390-410 nm |
| 486.1 nm | 470-490 nm |
| 589.0 nm | 570-590 nm |
| 656.3 nm | 650-670 nm |

Table 3. Correction Factors Applied to Raw Laboratory Luminescence Values

| Wavelength | Correction Factor |
|---|---|
| 320 nm | 0.039 |
| 340 nm | 0.102 |
| 360 nm | 0.148 |
| 380 nm | 0.242 |
| 400 nm | 0.313 |
| 420 nm | 0.523 |
| 440 nm | 0.758 |
| 460 nm | 0.828 |
| 480 nm | 0.890 |
| 500 nm | 1.109 |
| 520 nm | 1.242 |
| 540 nm | 1.227 |
| 560 nm | 1.422 |
| 580 nm | 1.414 |
| 600 nm | 1.547 |
| 620 nm | 1.992 |
| 640 nm | 1.992 |
| 660 nm | 1.000 |

Table 4. Results of Asphaltene Removal and Chromatographic Separation of Crude Oils

| Sample No. | Sample Weight (mg) | Aliphatic Hydrocarbons (mg) | Aromatic Hydrocarbons (mg) | N-S-O Compounds (mg) | Asphaltene (mg)* |
|---|---|---|---|---|---|
| 1 | 25.7 | 13.7 | 5.7 | 2.9 | 3.4 |
| 2 | 29.2 | 15.5 | 3.5 | 1.5 | 8.7 |
| 3 | 28.5 | 10.9 | 3.8 | 3.3 | 10.5 |
| 4 | 29.9 | 13.5 | 3.8 | 2.2 | 10.4 |
| 5 | 29.3 | 14.2 | 4.6 | 5.2 | 5.3 |
| 6 | 37.0 | 22.8 | 8.0 | 5.1 | 1.1 |
| 7 | 22.1 | 13.2 | 2.4 | 0.5 | 6.0 |
| 8 | 29.5 | 20.9 | 4.2 | 4.0 | 0.4 |
| 9 | 27.3 | 9.9 | 3.9 | 0.9 | 12.6 |
| 10 | 35.0 | 21.7 | 7.2 | 3.3 | 2.8 |

*The weight of asphaltene was determined by difference as that material was discarded before weighing.

Table 4. Continued

| Sample No. Asphaltene | Sample Weight (mg) (mg)* | Aliphatics Hydrocarbons | Aromatics Hydrocarbons (mg) | N-S-O Compounds (mg) | Polar (mg) |
|---|---|---|---|---|---|
| 11 | 27.8 | 14.3 | 7.0 | 2.8 | 3.7 |
| 12 | 28.5 | 15.7 | 6.7 | 3.6 | 2.5 |
| 13 | 25.1 | 15.4 | 2.1 | 0.2 | 7.4 |
| 14 | 22.4 | 11.6 | 6.4 | 3.5 | 0.9 |
| 15 | 31.3 | 18.6 | 10.1 | 1.5 | 1.1 |
| 16 | 25.3 | 17.5 | 5.6 | 1.6 | 0.6 |
| 18 | 13.9 | 2.8 | 3.7 | 0.7 | 6.7 |
| 19 | 35.0 | 12.8 | 15.3 | 4.5 | 2.4 |
| 20 | 33.0 | 9.6 | 11.3 | 10.2 | 1.9 |
| 21 | 35.0 | 14.7 | 17.0 | 2.4 | 0.9 |
| 22 | 28.9 | 12.8 | 9.3 | 2.7 | 4.1 |

*The weight of asphaltene was determined by difference as that material was discarded before weighing.

Table 4. Continued

| Sample No. | Sample Weight (mg) | Aliphatics (mg) | Aromatics (mg) | Polar (mg) | Asphaltene (mg)* |
|---|---|---|---|---|---|
| 23 | 29.0 | 12.4 | 10.4 | 4.3 | 1.9 |
| 25 | 30.3 | 11.4 | 10.2 | 7.3 | 1.4 |
| 26 | 30.5 | 13.9 | 6.5 | 2.8 | 7.3 |
| 27 | 28.2 | 9.0 | 6.8 | 1.7 | 10.7 |
| 28 | 26.3 | 6.9 | 10.0 | 2.6 | 6.8 |

*The weight of asphaltene was determined by difference as that material was discarded before weighing.

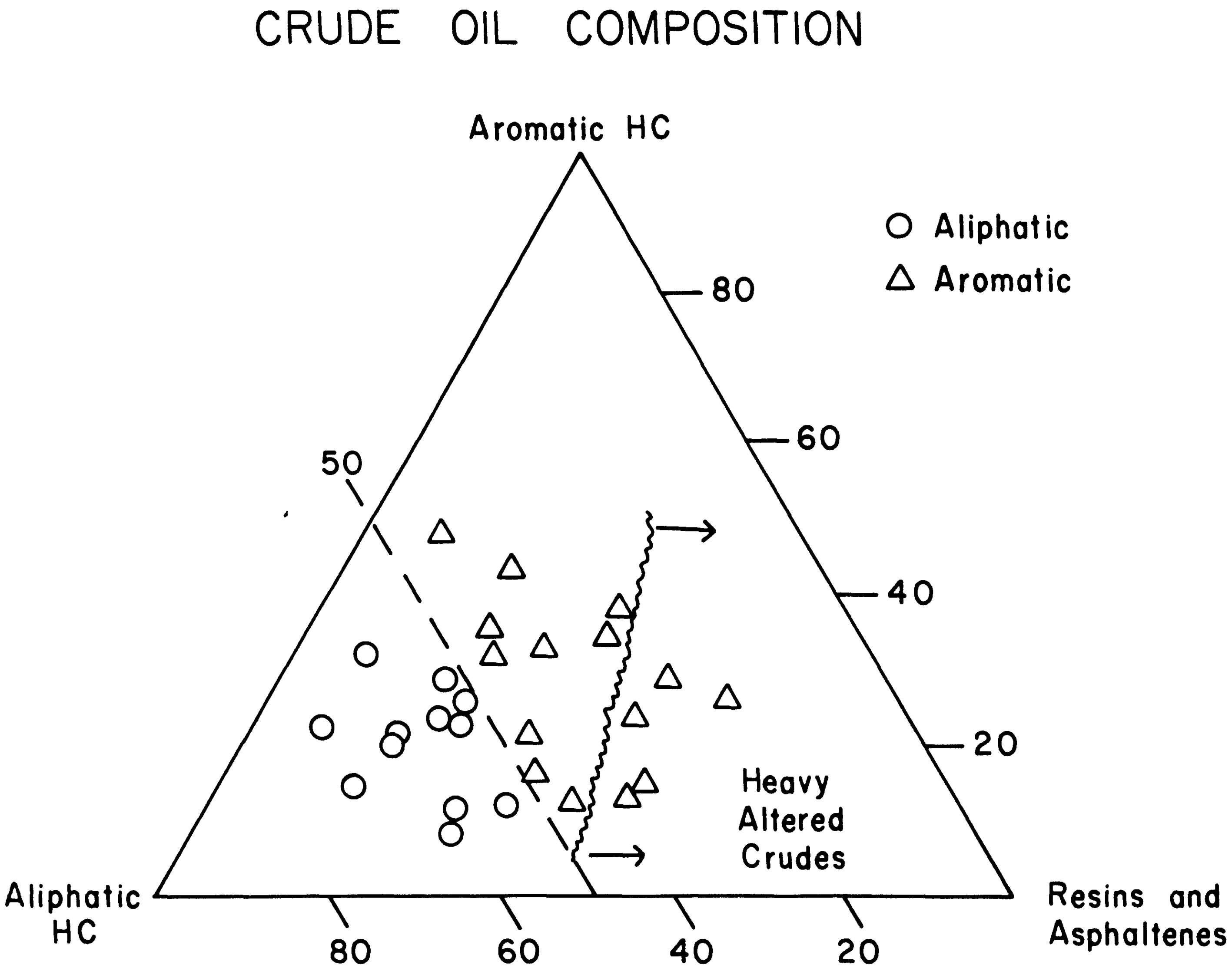

Figure 3. Triangular diagram showing the composition of the crude oils used in this study.

less than 50 percent aliphatic hydrocarbons (termed aromatic oils in this report). The term aromatic oil as defined may apply to some oils which have a higher weight percent of aliphatic hydrocarbons than aromatic hydrocarbons, however, the sum of aromatic by hydrocarbons plus the N-S-O compounds will be greater than 50 percent for these samples. The fraction termed aliphatic or saturated in this report includes all hexane soluble material in the crude oil. The range of API gravity for the aliphatic oils (as defined in fig. 3) is from 28.7 to 61.9 °API with a mean value of 42.4 °API; the range observed for the aromatic-based oils (as defined in fig. 3) is from 14.7 to 51.4 °API with a mean value of 34.0 °API.

## Laboratory Luminescence Measurements

Data gathered from crude oils with the laboratory fluorescence spectrometer are shown in Table 5. The emission and excitation spectra of crude oils and some refined products are normally broad and featureless in the visible portion of the spectrum because these substances are complex mixtures of hydrocarbon and non-hydrocarbon molecules, each of which may have its own characteristic excitation and emission spectrum. The emission and/or excitation spectrum generated from a particular oil sample is therefore the combined result of many narrow but overlapping spectra. Although these spectra are rather featureless, the values listed in Table 16 suggest that there are significant differences in the luminescence intensity of the various samples at the wavelengths measured. Most (~75%) of the aliphatic-based crude oils show the strongest luminescence at the 486.1 nm Fraunhofer line with slightly lower values at the 589.0 nm line. The aromatic-based oils generally show high values of luminescence at the 486.1 nm line also, but most of the values (~71%) are higher at the 589.0 nm line. The

Table 5. Integrated Excitation Intensity of Crude Oils*

| | | Emission Wavelength (nm) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | Oil Type | 396.8 | 486.1 | 589.0 | 656.3 | $\frac{486.1}{656.3}$ | $\frac{589.0}{656.3}$ | $\frac{486.1}{396.8}$ | $\frac{589.0}{396.8}$ | $\frac{656.3}{396.8}$ | $\frac{396.8 + 486.1}{656.3}$ |
| 1 | Aliphatic | 59.1 | 749.3 | 709.3 | 428.2 | 1.75 | 1.66 | 12.68 | 12.00 | 7.25 | 1.89 |
| 2 | Aliphatic | 37.6 | 316.9 | 287.5 | 139.7 | 2.27 | 2.06 | 8.43 | 7.65 | 3.72 | 2.54 |
| 3 | Aromatic | 59.4 | 498.4 | 443.9 | 206.0 | 2.42 | 2.15 | 8.39 | 7.47 | 3.47 | 2.71 |
| 4 | Aromatic | 12.6 | 311.7 | 406.9 | 208.3 | 1.50 | 1.95 | 24.74 | 32.29 | 16.53 | 1.56 |
| 5 | Aromatic | 2.5 | 78.9 | 128.9 | 78.8 | 1.00 | 1.64 | 31.56 | 51.56 | 31.52 | 1.03 |
| 6 | Aliphatic | 20.8 | 325.5 | 352.6 | 193.3 | 1.68 | 1.82 | 15.65 | 16.95 | 9.29 | 1.79 |
| 7 | Aliphatic | 78.9 | 425.4 | 329.7 | 164.2 | 2.59 | 2.01 | 5.39 | 4.18 | 2.08 | 3.07 |
| 8 | Aliphatic | 40.9 | 385.6 | 279.3 | 140.1 | 2.75 | 1.99 | 9.43 | 6.83 | 3.43 | 3.04 |
| 9 | Aromatic | 6.9 | 92.0 | 101.3 | 52.1 | 1.77 | 1.94 | 13.33 | 14.68 | 7.55 | 1.90 |
| 10 | Aliphatic | 14.2 | 137.8 | 104.8 | 52.8 | 2.61 | 1.98 | 9.70 | 7.38 | 3.72 | 2.88 |

*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 5. Continued*

|  |  | Emission Wavelength (nm) |  |  |  |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Sample | Oil Type | 396.8 | 486.1 | 589.0 | 656.3 | $\frac{486.1}{656.3}$ | $\frac{589.0}{656.3}$ | $\frac{486.1}{396.8}$ | $\frac{589.0}{396.8}$ | $\frac{656.3}{396.8}$ | $\frac{396.8 + 486.1}{656.3}$ |
| 11 | Aliphatic | 14.2 | 164.1 | 136.3 | 64.0 | 2.56 | 2.13 | 11.56 | 9.60 | 4.51 | 2.79 |
| 12 | Aliphatic | 13.6 | 157.2 | 149.1 | 81.9 | 1.92 | 1.82 | 11.56 | 10.96 | 6.02 | 2.09 |
| 13 | Aliphatic | 58.0 | 445.5 | 263.1 | 85.6 | 5.20 | 3.07 | 7.68 | 4.54 | 1.48 | 5.88 |
| 14 | Aliphatic | 11.0 | 110.9 | 94.4 | 44.1 | 2.51 | 2.14 | 10.08 | 8.58 | 4.01 | 2.76 |
| 15 | Aliphatic | 1.7 | 51.8 | 69.4 | 46.2 | 1.12 | 1.50 | 30.47 | 40.82 | 27.18 | 1.16 |
| 16 | Aliphatic | 1.9 | 57.1 | 81.0 | 45.8 | 1.25 | 1.77 | 30.05 | 42.63 | 24.11 | 1.29 |
| 17 | N.D.** | 3.9 | 81.6 | 125.8 | 88.0 | 0.93 | 1.43 | 20.92 | 32.26 | 22.56 | 0.97 |
| 18 | Aromatic | 29.3 | 123.8 | 85.4 | 41.0 | 3.02 | 2.08 | 4.23 | 2.91 | 1.40 | 3.73 |
| 19 | Aromatic | 8.1 | 84.1 | 88.2 | 56.6 | 1.49 | 1.56 | 10.38 | 10.89 | 6.99 | 1.63 |

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

**N.D. = Not determined.

Table 5. Continued*

| | | 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 | 1.45 | 1.69 | 10.31 | 12.00 | 7.09 | 1.59 |
| 21 | Aromatic | 8.1 | 81.9 | 88.4 | 52.8 | 1.55 | 1.67 | 10.11 | 10.91 | 6.52 | 1.70 |
| 22 | Aromatic | 1.0 | 20.2 | 36.6 | 27.4 | 0.74 | 1.34 | 20.20 | 36.60 | 27.40 | 0.77 |
| 23 | Aromatic | 5.4 | 54.4 | 58.3 | 28.4 | 1.92 | 2.05 | 10.07 | 10.80 | 5.26 | 2.11 |
| 24 | N.D.** | 5.6 | 46.2 | 48.5 | 30.4 | 1.52 | 1.60 | 8.25 | 8.66 | 5.43 | 1.70 |
| 25 | Aromatic | 3.3 | 40.4 | 40.9 | 21.2 | 1.91 | 1.93 | 12.24 | 12.39 | 6.42 | 2.06 |
| 26 | Aromatic | 6.0 | 36.7 | 32.3 | 17.6 | 2.09 | 1.84 | 6.12 | 5.38 | 2.93 | 2.43 |
| 27 | Aromatic | 6.2 | 32.4 | 28.3 | 11.7 | 2.77 | 2.42 | 5.23 | 4.56 | 1.89 | 3.30 |
| 28 | Aromatic | 2.0 | 19.4 | 26.2 | 19.1 | 1.02 | 1.37 | 9.7 | 13.10 | 9.55 | 1.12 |

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

**N.D. = Not determined.

luminescence of the crude oils at the 396.8 nm line is lowest in all cases. Recorded values of luminescence at the 656.3 nm line are generally lower than those measured at 486.1 nm or 589.0 nm lines with one exception: sample 22. The low levels of luminescence emission at short wavelength (396.8 nm) are due to a factor introduced by the method of data handling. At the 398.6 nm line, the solar correction used to simulate field conditions greatly reduces the luminescence intensity actually emitted from the sample, further, petroleum strongly absorbs energy in the near UV portion of the spectrum (Fantasia and Ingrao, 1974).

Least squares regression lines were calculated to determine whether a functional relationship exists between luminescence intensity and aromatic content of the crude oils (fig. 4). The correlation was not high (r = -0.63 to -0.53). These data indicate that the amount of aromatic compounds present is not the most important factor influencing crude-oil luminescence intensity.

The relationship between luminescence intensity and the percentage of polar compounds present is likewise not straight forward (fig. 5). The negative slope of the calculated regression line is not suprising in view of the known quenching effects of many of the N-S-O compounds (Table 6). However, the wide scatter of these points indicates no consistant relationship.

Asphaltene content and luminescence intensity display a weak positive relationship at the four Fraunhofer lines studied (fig. 6). The slopes of the regression lines decrease with increasing emission wavelength, the opposite of the result expected based upon previous work by Riecker (1962). It is evident that the percentage of asphaltenes present does not vary systematically with luminescence quality or quantity.

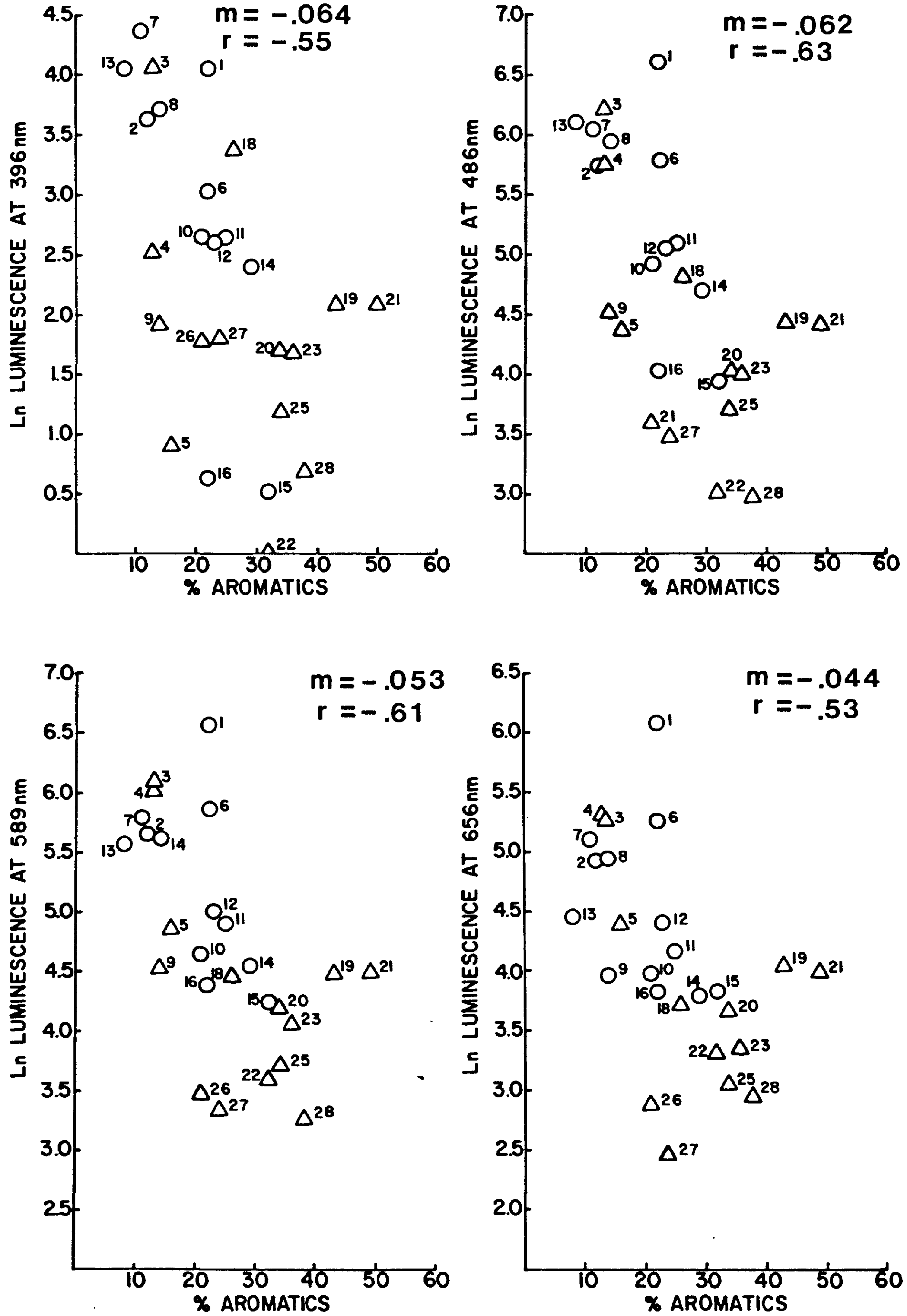

Figure 4. Ln of luminescence intensity measured at the four Fraunhofer lines selected and plotted against percent aromatics present in the crude oils. Open circles indicate aliphatic oils and triangles indicate aromatic oils.

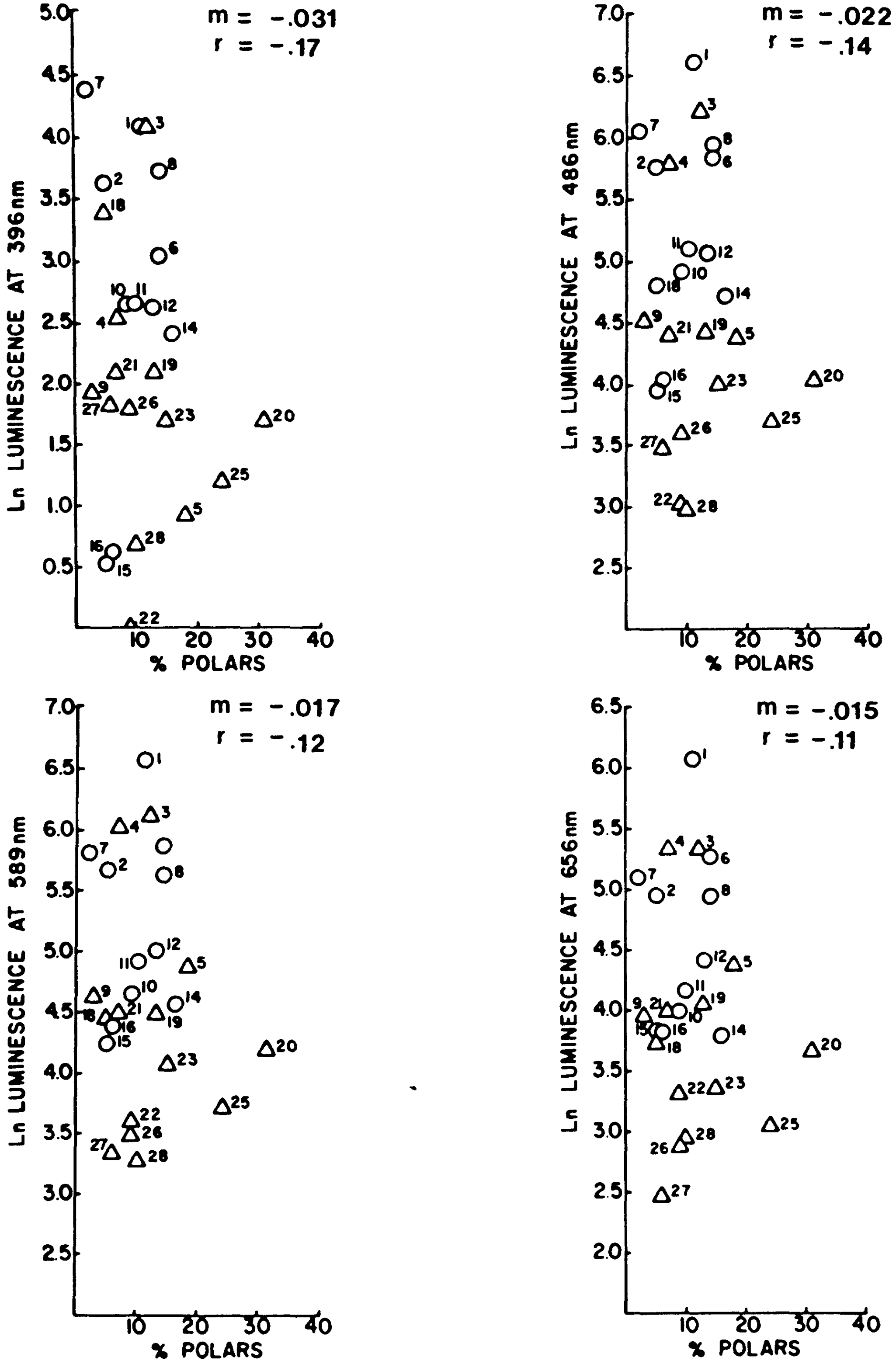

Figure 5. Ln of luminescence intensity measured at the four Fraunhofer lines selected and plotted against percent polar compounds present in the crude oils. Open circles indiate aliphatic oils and triangles indicate aromatic oils.

Table 6. Substituent Effects on Fluorescence of Aromatic Compounds*

| Substituent | Effect on Emission Frequency | Effect on Intensity |
|---|---|---|
| Alkyl | None | Slight increase or decrease |
| OH, $OCH_3$, $OC_2H_5$ | Decrease | Increase |
| $CO_2H$ | Decrease | Large Decrease |
| $NH_2$, NHR, $NR_2$ | Decrease | Increase |
| $NO_2$, NO | -- | Total Quenching |
| CN | None | Increase |
| SH | Decrease | Decrease |
| F<br>Cl<br>Br<br>I | Decrease | Decrease |
| $SO_3H$ | None | None |

*Data from Berlman, 1971

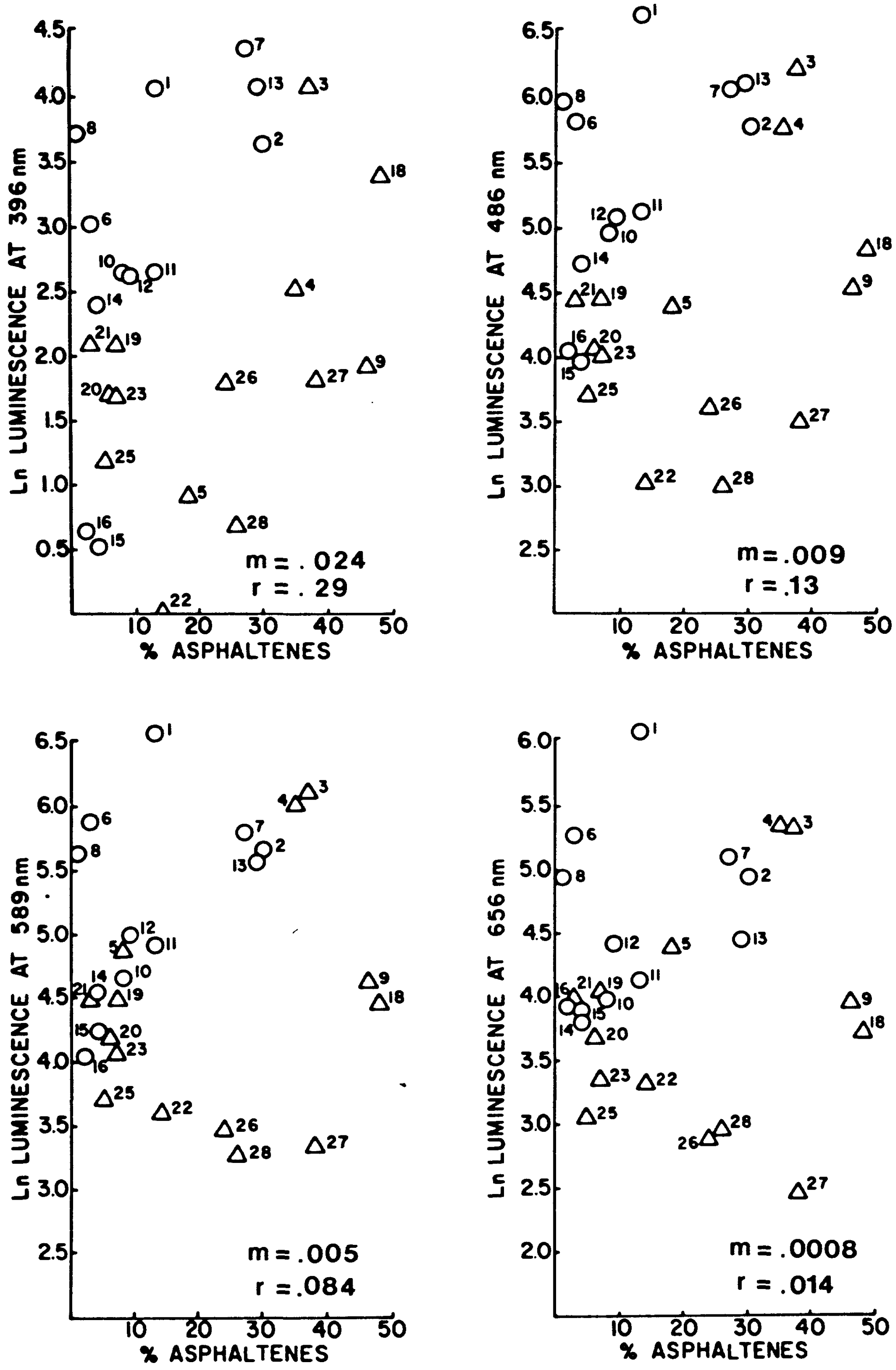

Figure 6. Ln of luminescence intensity measured at the four Fraunhofer lines selected and plotted against percent asphaltene present in the crude oils. Open circles indicate aliphatic oils and triangles indicate aromatic oils.

A positive relationship exists between the aliphatic content and luminescence intensity (fig. 7); however, there is little evidence that this is in fact a cause and effect relationship as aliphatic hydrocarbons are inefficient producers of luminescence (Hirayama and Lipsky, 1969). The origin of this relationship is believed to be from the same set of circumstances which give rise to the relationship between API gravity and luminescence (figs. 8, 9, 10, and 11). There is no clear reason for luminescence to vary as a function of the density or the percentage of aliphatic compounds in the crude oil. This apparent relationship exists because the API gravity and the aliphatic composition are reflections of the overall chemical composition which effects the intensity and hue of the emitted energy. At all four emission wavelengths studied, emission intensity increased with an increase in API gravity.

The correlation coefficients calculated for the data shown in figures 8, 9, 10, and 11 are not high. The vertical position of the regression line shows that the overall intensity for the crude oils is lowest at the 396.8 nm Fraunhofer line, intermediate at the 656.3 nm Fraunhofer line and highest at the 486.1 nm and 589.0 nm Fraunhofer lines. The slope of the regression lines changes from 0.073 at the 396.8 nm line, to 0.061 at the 486.1 nm line, to 0.048 at the 589.0 nm line and to 0.037 at the 656.3 nm line. This change in slope is the result of a shift in luminescence intensity between aromatic and aliphatic crude oils as a function of emission wavelength. The denser oils (generally the aromatic based ones) tend to emit a larger proportion of energy at the longer wavelengths compared to the shorter wavelengths while the opposite is true for the less-dense (generally more aliphatic) crudes.

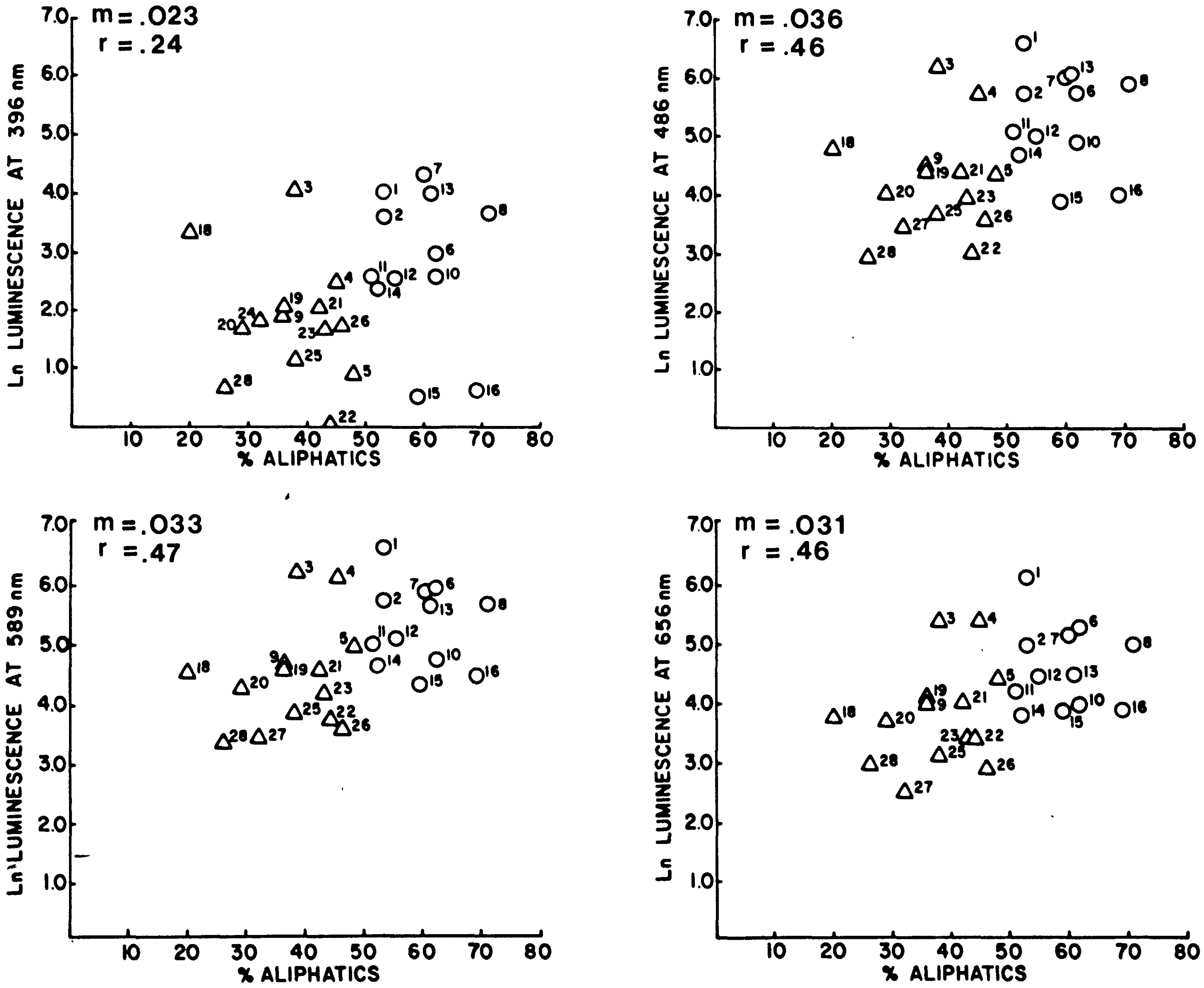

Figure 7. Ln of luminescence intensity measured at the four Fraunhofer lines selected and plotted against percent aliphatic compounds present in the crude oils. Open circles indicate aliphatic oils and triangles indicate aromatic oils.

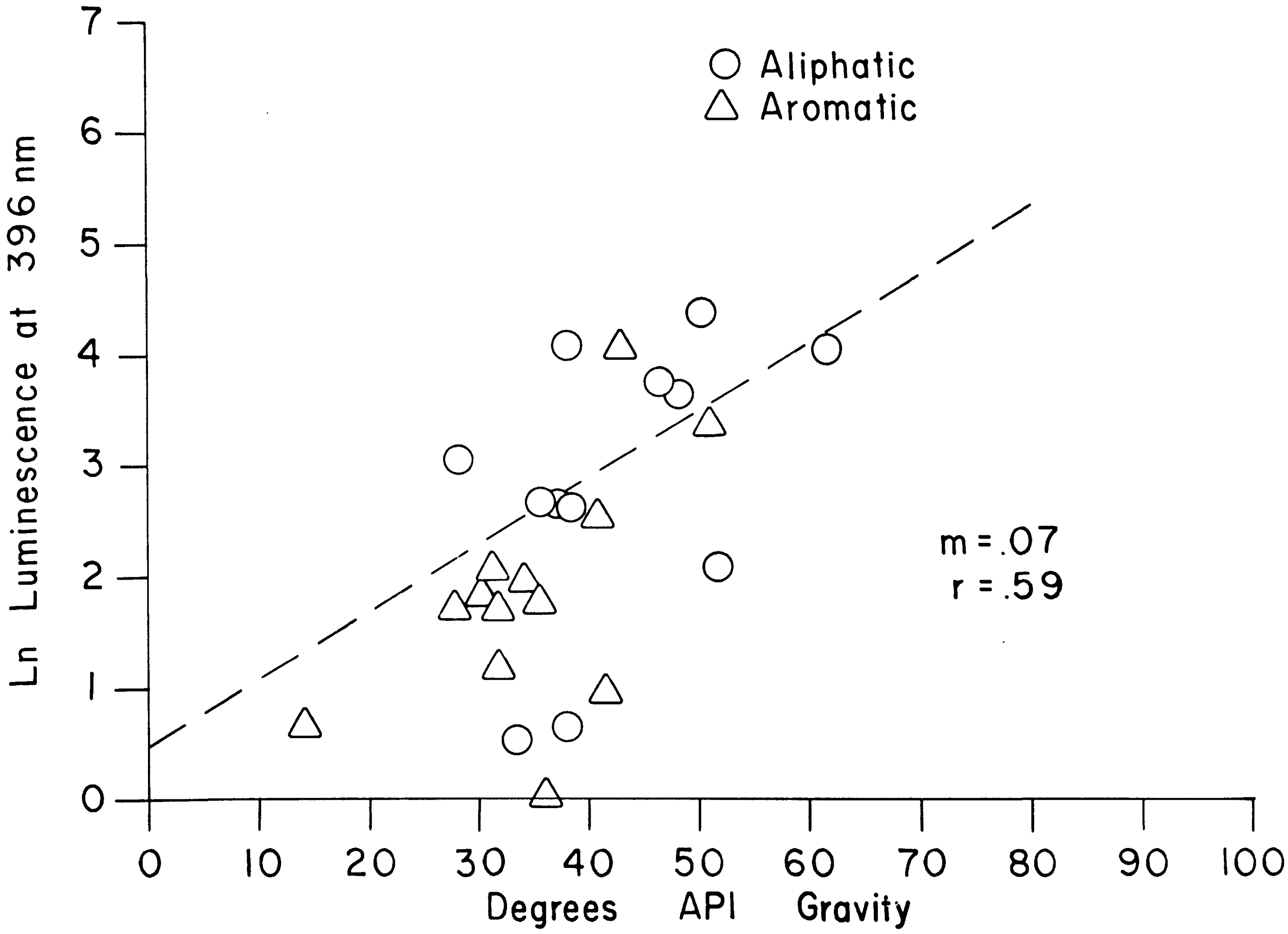

Figure 8. Ln of luminescence intensity measured at the 396.8 nm Fraunhofer line plotted against API gravity of the crude oils.

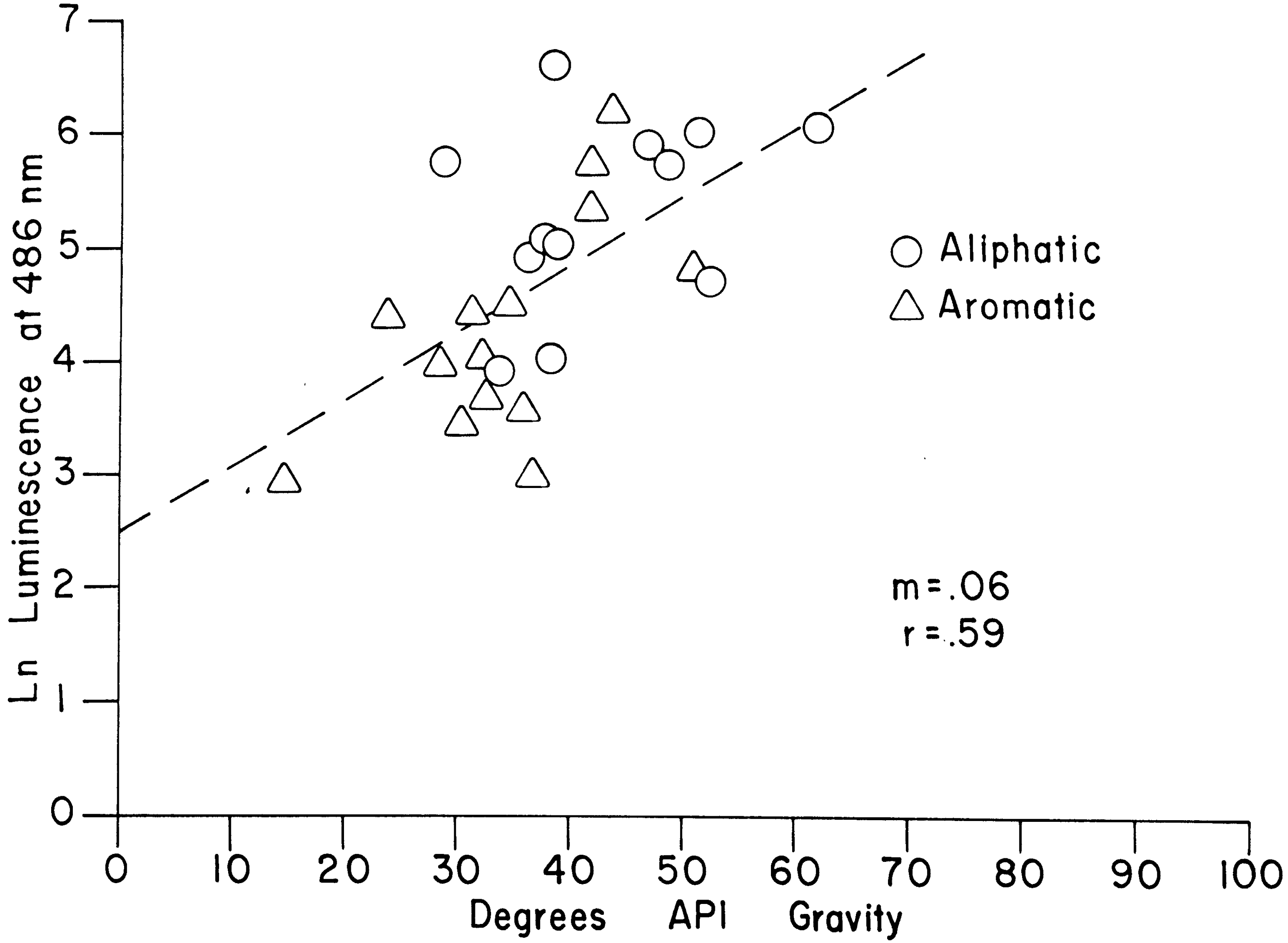

Figure 9. Ln of luminescence intensity measured at the 486.1 nm Fraunhofer line plotted against API gravity of the crude oils.

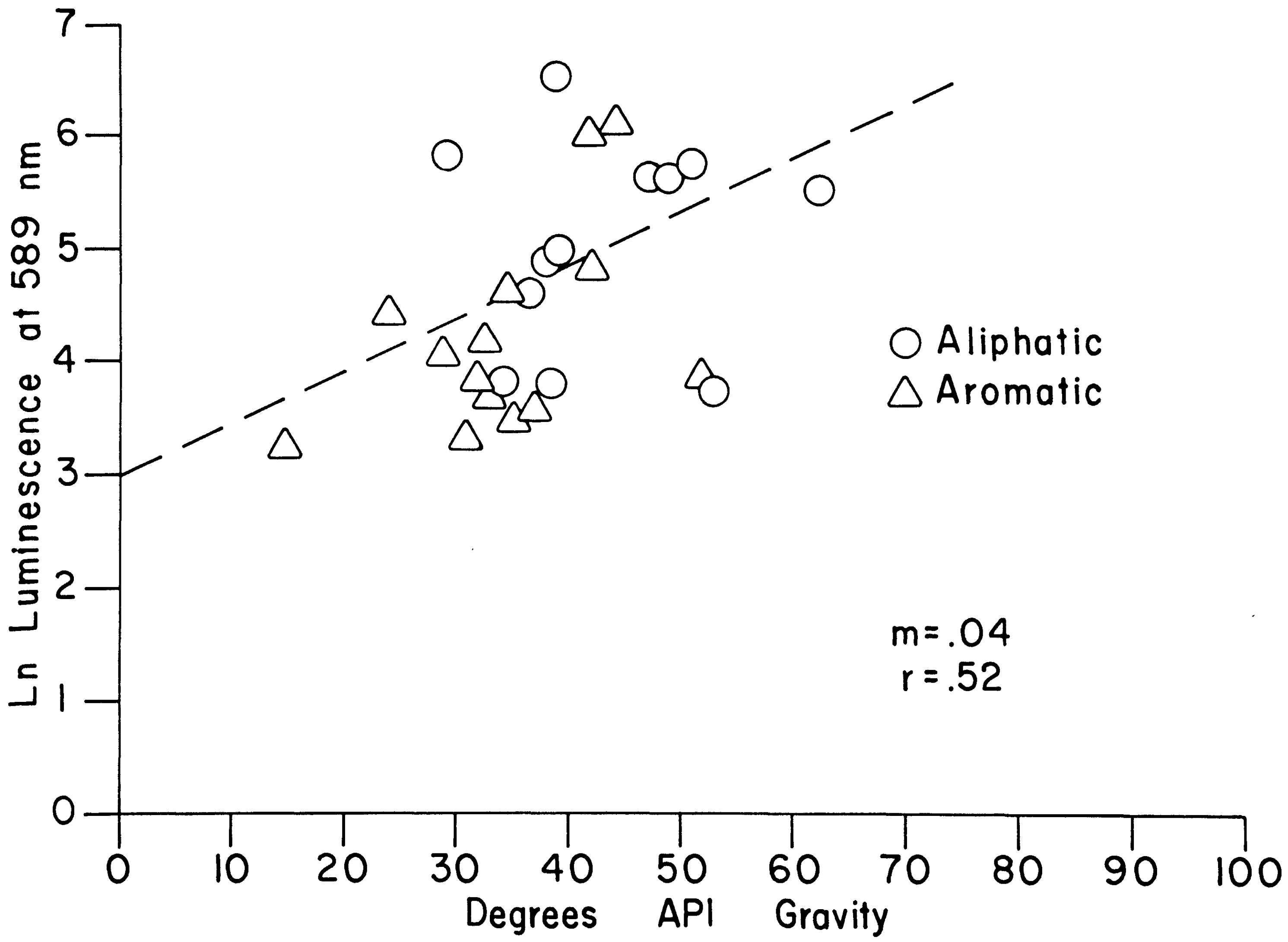

Figure 10. Ln of luminescence intensity measured at the 589.0 nm Fraunhofer line plotted against API gravity of the crude oils.

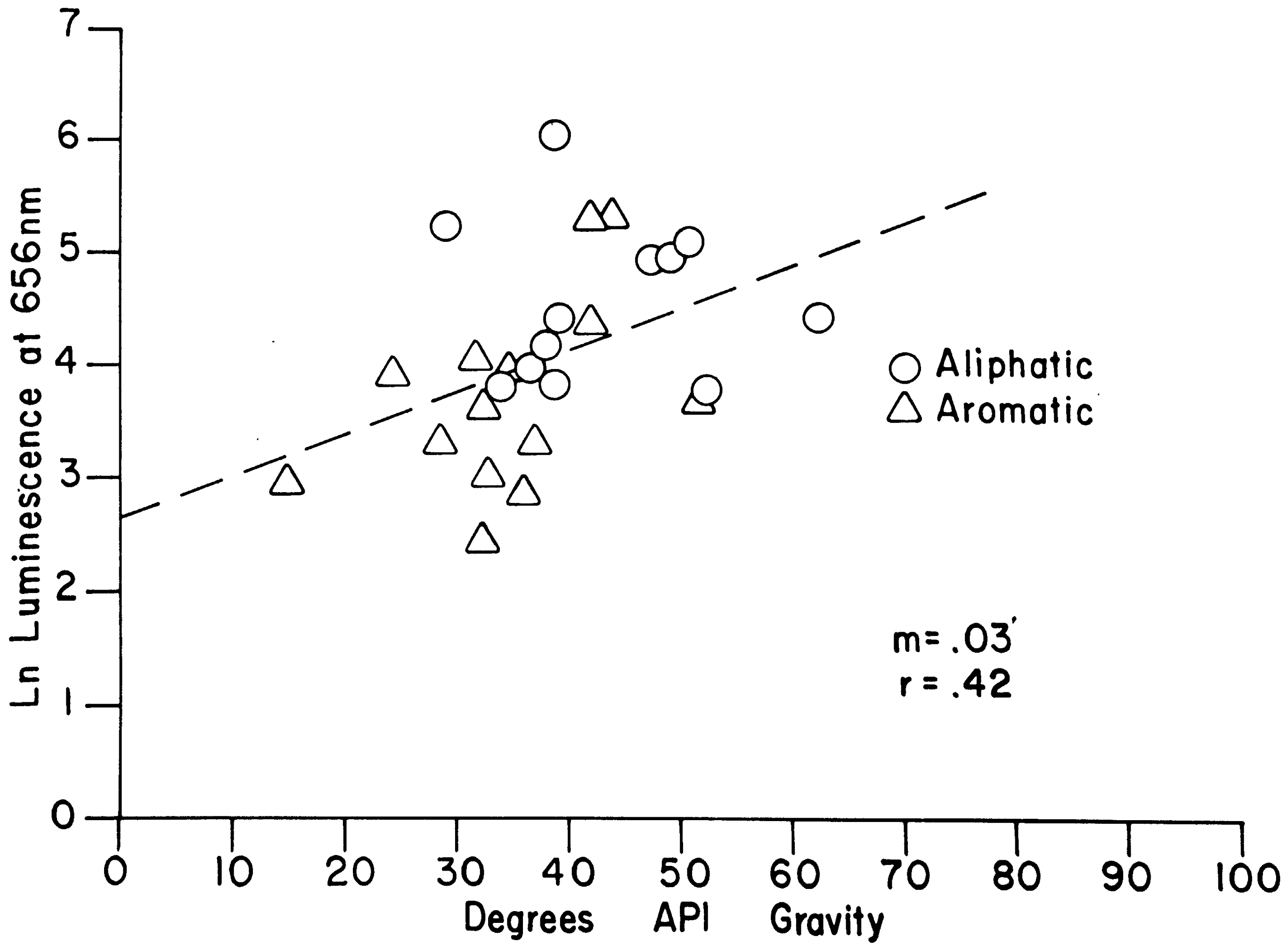

Figure 11. Ln of luminescence intensity measured at the 656.3 nm Fraunhofer line plotted against API gravity of the crude oils.

## Summary and Conclusions

Luminescence properties vary considerably among the crude oils studied in terms of relative intensity at a particular wavelength and as a function of wavelength when a single sample is considered. With few exceptions, crude oils exhibit lower luminescence intensity in the violet and red portions of the spectrum than in the blue and yellow portion.

In some cases there is a shift in wavelength of maximum luminescence intensity toward the red portion of the spectrum for the aromatic oils as compared to the aliphatic oils. The exact cause of this shift was not determined from this study but may be due in part to the relative opacity of the dark aromatic crudes to shorter wavelength energy compared to lighter aliphatic (more transparent) crudes. In addition, larger more complicated and highly-substituted aromatic molecules give rise to long-wave luminescence.

The chromatographic separations do not show a clear relationship between luminescence intensity and general crude oil composition. It is well known that aromatic molecules exhibit luminescence and it is thought (Reicker, 1962) that these molecules are a major contributor to crude oil luminescence; however, the data presented here suggest an inverse relationship between luminescence intensity and the percentage of aromatic components present. These results indicate that the quantity of aromatic molecules present is not the controlling factor in petroleum luminescence intensity.

The values of the ratio formed by summing the luminescence intensity measured at the two shortest Fraunhofer lines and dividing by the luminescence intensity measured at the longest Fraunhofer line used show a narrow range of values considering the range of chemical composition and geologic age of the oils. The values recorded for this ratio do not allow identification of the type of crude oil present, that is, aliphatic crude or aromatic crude as defined in this report. This use of multispectral luminescence signatures to identify a film-forming material on water as a crude oil could have petroleum prospecting or pollution monitoring application.

# References Cited

Berlman, I.B., 1971, Handbook of fluorescence spectra of aromatic molecules (2d ed.): New York, Academic Press, 473 p.

Deutsch, Morris, and J.E. Estes, 1980, Landsat detection of oil from natural seeps: Photogramm. Eng. Remote Sensing, v. 46, p. 1313-1322.

Fantasia, J.F., and H.C. Ingrao, 1974, Development of an experimental airborne laser remote sensing system for the detection and classificatin of oil spills, _in_ Proc. 9th Int. Symp. Remote Sensing of Environment: Univ. Michigan, Ann Arbor, p. 1711-1745.

Hirayama, Fumio, and Sanford Lipsky, 1969, Fluorescence of saturated hydrocarbons: Jour. Chem. Physics, v. 51, p. 3616-3617.

Link, W.K., 1952, Significance of oil and gas seeps in world exploration: AAPG Bull., v. 36, p. 1505-1540.

Measures, R.M., and Mike Bristow, 1971, The development of a laser fluorosensor for remote environmental probing: Joint Conference of Sensing of Environmental Pollutants, Palo Alto, California, AIAA Paper 71-1121, 7 p.

Munday, J.C., W.G. MacIntyre, M.E. Penney, and J.D. Oberholtzer, 1971, Oil slick studies using photographic and multispectral scanner data, _in_ Proc. 7th Int. Symp. Remote Sensing of Environment: Univ. Michigan, Ann Arbor, p. 1027-1043.

Riecker, R.E., 1962, Hydrocarbon fluorescence and migration of petroleum: AAPG Bull., v. 46, p. 60-75.

Tissot, B.P., and D.H. Welte, 1978, Petroleum formation and occurrence: New York, Springer-Verlag, 538 p.

Vizy, K.N., 1974, Detecting and monitoring oil slicks with aerial photographs: Photogramm. Eng., v. XL, p. 697-708.

Watson, R.D., W.R. Hemphill, and T.D. Hessin, 1973, Quantification of the luminescence intensity of natural materials: Symposium for the Management and Utilization of Remote Sensing Data, Sioux Falls, South Dakota, Proc., p. 364-376.

Watson, R.D., M.E. Henry, A.F. Theisen, T.J. Donovan, and W.R. Hemphill, 1978, Marine monitoring of natural oil slicks and man-made wastes utilizing an airborne Fraunhofer line discriminator: Proc. 4th Joint Conference on Sensing of Environmental Pollutants, p. 667-671.