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REPORT NO. DOT- TSC-USCG-71-7

AN INVESTIGATION OF OIL FLUORESCENCE AS A TECHNIQUE FOR THE REMOTE SENSING OF OIL SPILLS

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DEPARTMENT OF TRANSPORTATION ★ UNITED STATES OF AMERICA ★

JUNE 1971

FINAL REPORT

Prepared for
UNITED STATES COAST GUARD
WASHINGTON,D.C. 20591

1. Report No.
TSC-USCG-71-7

2. Government Accession No.

3. Recipient's Catalog No.

4. Title and Subtitle
An Investigation of Oil Fluorescence as a Technique for the Remote Sensing of Oil Spills

5. Report Date

6. Performing Organization Code

7. Author(s)
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8. Performing Organization Report No.

9. Performing Organization Name and Address
DOT/Transportation Systems Center
55 Broadway
Cambridge, Mass. 02142

10. Work Unit No.
71-CG03

11. Contract or Grant No.

12. Sponsoring Agency Name and Address
U.S. Coast Guard
400 Seventh St. S.W./DAT-4
Washington, D.C. 20591

13. Type of Report and Period Covered
Technical Progress Report - July 1,70 to June 30, 1971

14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

The feasibility of remote sensing of oil spills by laser-excited oil fluorescence is investigated. The required parameters are measured in the laboratory; these parameters are fed into a physical model to predict signal and background levels; and the predictions are verified by field experiments. Airborne detection, identification, and quantification of oil spills at sea are shown to be feasible with existing equipment, day or night.

17. Key Words

- Oil Spills
- Oil, Remote Sensing
- Oil Fluorescence
- Laser

18. Distribution Statement
Unlimited

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price
UNCL	UNCL		

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SUMMARY

TSC has conducted a study and an experimental measurement program to determine the feasibility of using laser-excited oil fluorescence as a means of detecting, identifying, and quantifying oil spills at sea.

The results of this program show that: oil films 0.1 micrometers thick are detectable; each oil type has a distinct fluorescent spectral signature and, when correlated with API gravity fluorescent conversion coefficient and fluorescent lifetime, can be positively identified and classified; the areal extent of the oil spill can be accurately measured; and it appears oil film thickness, within certain limits, can be measured with this technique.

The technique of remotely sensing oil spills by laser-excited fluorescence is technically feasible and well within the state-of-the art. Furthermore, the components required to build a fluorescence sensor are available off-shelf.

SECTION 1

INTRODUCTION

This document is the final technical report summarizing an investigation of a laser-excited oil fluorescence technique for the remote sensing of oil spills at sea.

The program began with a search of the literature on existing techniques used for the remote sensing of oil spills at sea. These techniques range from the ultraviolet to the microwave region of the electromagnetic spectrum. They employ such systems as microwave radiometry; radar; aerial photography; ultraviolet, visible, and infrared radiometry; and low light level television. All techniques can detect oil spills under a particular set of conditions suited to each individual system. Some are also capable of mapping the spill. However, all of these systems are unable to adequately identify or quantify the oil spill. It was because of a need to identify the type and amount of oil spilled that oil fluorescence was investigated.

The technical approach consisted of: a study of the nature of oil, a theoretical analysis of the oil fluorescence phenomenon, laboratory measurements of required parameters, and field measurements.

This report concludes with a feasibility determination and recommendations.

SECTION 2

PROPERTIES OF OIL AND OIL SLICKS ON THE SEA SURFACE

2.1 PHYSICAL AND CHEMICAL

Crude petroleum and refined fuels consist of mixtures of hydrocarbons, with traces of nitrogen, oxygen, and sulfur derivatives.[1] The number of distinct molecular compounds in any one oil is large, ranging from dozens in refined fuels to hundreds in crude petroleum.

Most oils are lighter than seawater, and float on its surface in a separate phase*. Wave agitation causes some bulk mixing of the two phases, but their solubility in each other is low. Sea waves are reduced under an oil slick.

In a closed container, any one oil forms a single solution with a uniform specific gravity, viscosity, and optical properties. However, when the same oil spreads on the sea surface, fractionation can occur, because different molecules have different mobilities through the oil, into the atmosphere, and into the water. Generally the smaller molecules move faster in all three ways, but chemical differences among the molecules also govern

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*The API gravity of water varies from 6 (for seawater of 35% salinity) to 10 (for fresh water). Oils with API gravity lower than that of the surface water will sink, unless supported by the surface tension of the water.

their mobilities, especially in water. The above three processes: diffusion, evaporation, and dissolution produce a lateral gradient of mechanical and optical properties within an oil slick, and a change in its overall properties due to loss of its lighter fractions.

Besides these physical changes in the state of the oil, chemical changes occur in the presence of sunlight, air, seawater, wave agitation, and micro-organisms. All of the above aging processes raise doubts of any laboratory measurements that have not been field checked.

Oil slick spreading is accelerated by a class of substances known as surfactants, whose molecules readily align at the interface between oil and water. Surfactants are rare in crude petroleum, but are formed in oil slicks by photochemical and biochemical oxidation of hydrocarbons. A monomolecular surfactant film is enough to accelerate oil spreading.

2.2 OPTICAL

2.2.1 Reflection

The refractive indices of oils in the visible region range from 1.4 to 1.6, which is higher than that of seawater (1.34). Therefore, the reflectivities of oils are also higher than that of seawater. Over calm water, one can find an oil slick thicker than a half-wavelength of light, by its brighter reflection of the sky. Observing a rough sea along a slant path heightens this difference.

The rough open water averages the reflection of a large portion of the sky, while the wave-calming effect of an oil slick causes it to reflect more of the bright sky near the horizon. However, under some local wind conditions, there are numerous false alarms due to varying wave orientation. Patches of waves with ridges parallel to the viewing direction appear to be slicks.

2.2.2 Absorption

Oils have strong ultraviolet absorption extending into the visible region to produce their characteristic yellow, brown, or brownish-black colors. These colors can be seen in oil slicks only with near-vertical viewing, where the sky reflection is weak. Since the oils are liquids composed of many substances, their spectra contain no sharp absorption or transmission features.

Oils also absorb at characteristic hydrocarbon vibration frequencies in the mid-infrared. These frequencies occur in regions where the atmosphere is relatively opaque.

2.2.3 Fluorescence

A portion of the ultraviolet absorption of oils is re-emitted at longer wavelengths. This phenomenon, known as fluorescence, provides a means of remote detection of oil slicks. Moreover, the fluorescent intensities, emission spectra, and emission lifetimes of various oils, differ enough to permit remote identification. After identification, fluorescent intensity enables one , under certain conditions, to measure the thickness of a thin slick, from which the total volume of oil in the slick can be estimated.

SECTION 3

REMOTE FLUOROMETRY OF OIL SPILLS

3.1 INTRODUCTION

Since an oil spill surveillance system should be capable of both day and night operation, and since the fluorescence power conversion coefficient of oil is relatively low, passive systems excited by sunlight or moonlight etc., are not feasible and are not being considered. Instead, we considered an active system, consisting of a transmitter and a receiver aboard a single aircraft. The transmitter is an artificial light source that is aimed at the sea surface and causes oil to fluoresce. The receiver is a light collector feeding a photomultiplier. Using remote fluorometry to detect oil fluorescence signals in the presence of backgrounds is a problem. Some of this background is present in the natural environment, and some of it is generated by the transmitter.

3.2 BASIC SPECTRORADIOMETRIC EQUATIONS

3.2.1 Geometry of the Physical Model

Referring to Figure 3.1, the transmitter sends a beam whose power P_L, is attenuated by transmitter optics with an efficiency ε_L, at a wavelength λ_L, distributed through a solid angle Ω_L. This beam strikes an external medium (atmosphere, oil, or sea-

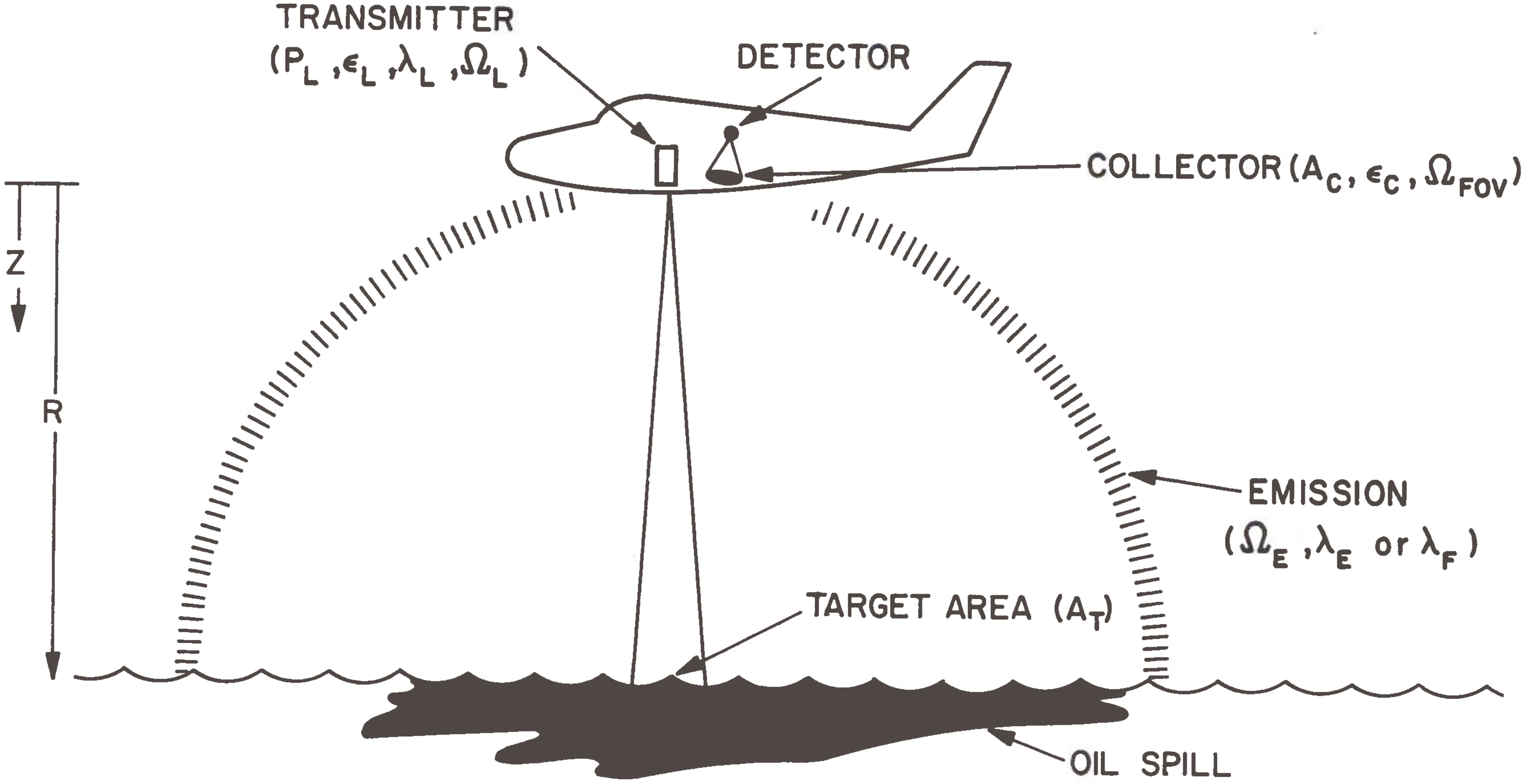


Figure 3.1 - Remote Fluorometry of Oil Spills

water), which then emits some of the energy through a solid angle Ω_E. This emitted energy may be at the same wavelength λ_L (scattering, reflection) or at a longer wavelength λ_F (fluorescence). A portion of the energy is collected by the receiver, with collector area A_c, efficiency ε_c, and field-of-view Ω_{FOV}.

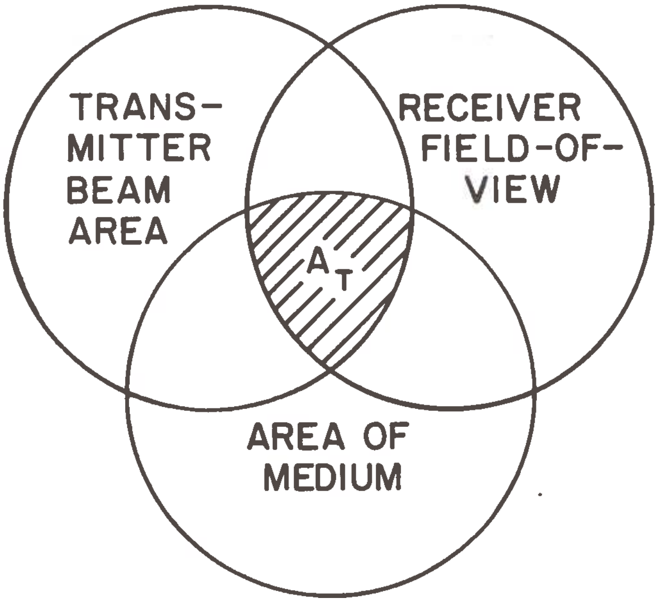
The transmitted and received beams are attenuated passing through atmosphere, oil, and seawater, with exponential attenuation coefficients which depend on the medium and the wave length. Distances are measured from the aircraft along the coordinate Z. For the transmitter-generated signal and background, the target area A_T is that part which is common to both Ω_L and Ω_{FOV} (Figure 3.2).

Similarly, each medium returns light from the sun and sky, which is then collected by the receiver. In this case, A_T lies within Ω_{FOV} (Figure 3.2).

3.2.2 Radiative Transfer Equations

The energy sources seen by the receiver (Figure 3.3) are oil and seawater fluorescence (OF and WF), surface reflection (R), and atmospheric and underwater backscatter (AB and WB). Each of these five emitting media respond to the transmitter (L), direct sunlight (S), and indirect sunlight from the sky and clouds (K). The total detectable power P_D is

TRANSMITTER–GENERATED CASE



NATURAL BACKGROUND CASE

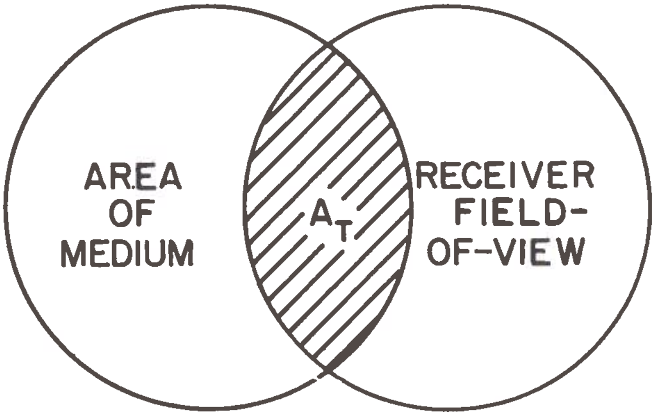


Figure 3.2 - Definition of Target Area A_T

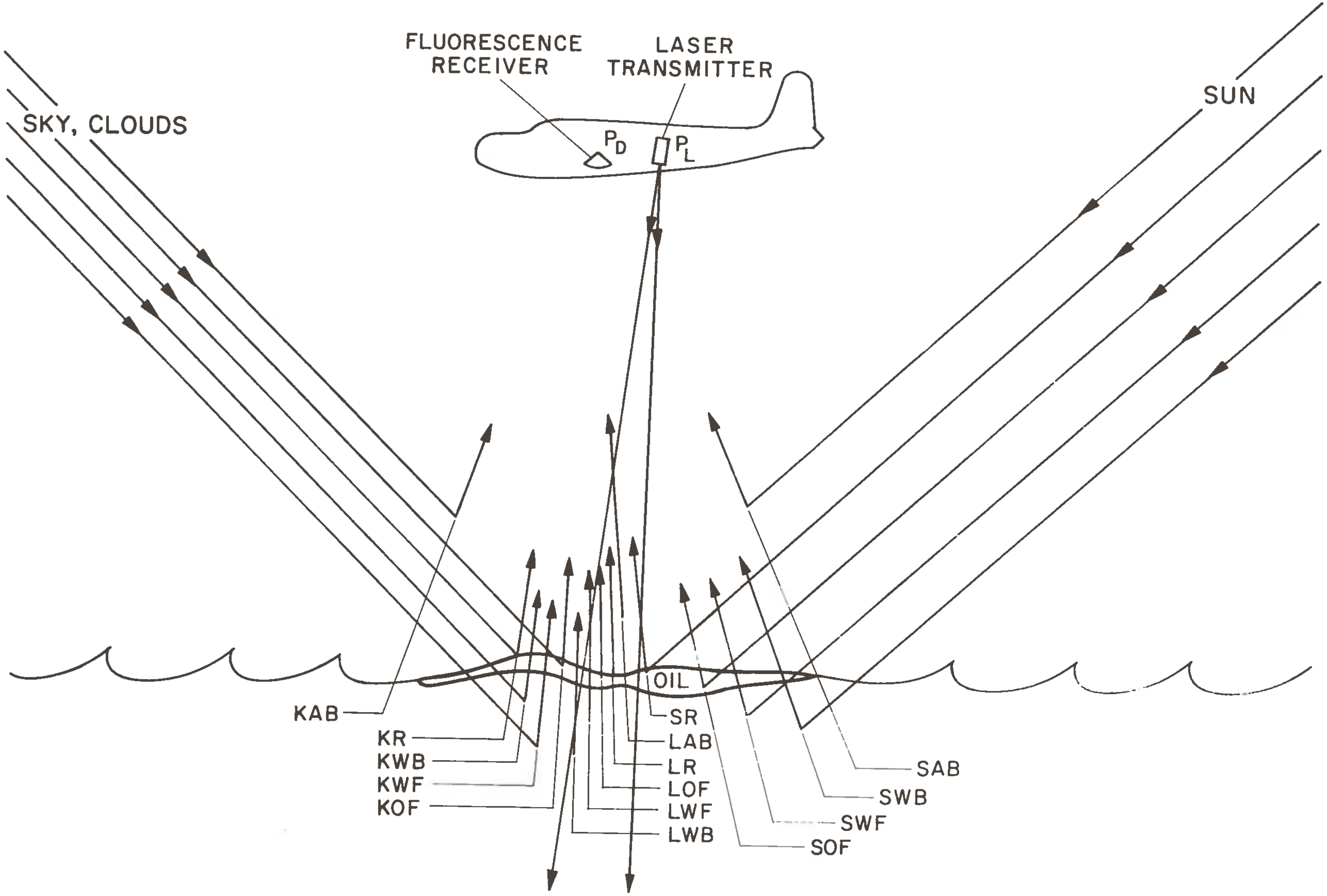


Figure 3.3 - Energy Sources Seen by the Receiver

$$\begin{aligned} P = {} & P_{DLOF} + P_{DLWF} + P_{DLR} + P_{DLAB} + P_{DLWB} \\ & + P_{DSOF} + P_{DSWF} + P_{DSR} + P_{DSAB} + P_{DSWB} \\ & + P_{DKOF} + P_{DKWF} + P_{DKR} + P_{DKAB} + P_{DKWB} \end{aligned} \tag{1}$$

See following table for complete list of symbols.

TABLE 3.1 - SYMBOLS USED IN RADIATIVE TRANSFER EQUATIONS

P_L = transmitter power

A_T = area of target lying within both the laser beam and the receiver's field of view

A_C = area of collector

R = range from aircraft to sea suface

Ω_L = solid angle of the laser beam

Ω_E = solid angle of emission

Ω_{FOV} = solid angle of receiver's field of view

Ω_T = solid angle subtended by target

ϵ_L = efficiency of transmitter optics

ϵ_C = efficiency of receiver optics, including spectral filter

ϵ_O = oil fluorescence coefficient

ϵ_W = seawater fluorescence coefficient

$\gamma^{\text{wavelength}}_{\text{attenuating medium}}$ = attenuation coefficient

wavelengths: laser (L), sun (S), sky (K)

media = atmosphere (ATM), oil (O), water (W)

TABLE 3.1 - SYMBOLS USED IN RADIATIVE TRANSFER EQUATIONS (Cont.)

$$\left.\begin{array}{l}\beta^{S}_{ATM}\\ \beta^{S}_{W}\\ \beta^{L}_{W}\\ \beta^{L}_{ATM}\end{array}\right\}\ \text{Backscatter Coefficient}\qquad \beta^{\text{wavelength}}_{\text{medium}}$$

Z = Distance along range co-ordinate

Z_O = Optical thickness of oil

Z_W = Optical thickness of water

H_{sun} = Irradiance

ρ_{in} = Reflectivity of the surface, to the entering beam

ρ_{out} = Reflectivity of the surface, to the exiting beam

θ = Look angle

ϕ = Solar Zenith angle

N_K = Radiance

SS = Sea State

Pol = Polarization

t_L = active source pulse width, sec

t_g = receiver gate time = $t_1 + t_2$

t_1 = gate time before mean sea level

t_2 = gate time after mean sea level

TABLE 3.1 - SYMBOLS USED IN RADIATIVE TRANSFER EQUATIONS (Cont.)

t_{ss} = transit time through wave profile at a given sea state

t_{of} = oil fluorescence half-life

t_{wf} = sea water fluorescence half-life

r_g = repetition rate of gate (and active source)

$f_{o,w}^{s,k}$ = surface reflectance function, which depends on (θ, ss, ϕ, Ω_{FOV}, P)

Equations have been derived for each of these terms, and are listed in Table 3.2. Three types of remote sensing have been considered: continuous (sine or square wave modulated CW); pulsed with total gated power and pulsed with total gated peak power detection.

TABLE 3.2 - SYSTEM RADIATIVE TRANSFER EQUATIONS - CW CASE

Transmitter-generated oil fluorescence

$$P_{DLOF} = P_L \epsilon_L \epsilon_C A_C \; e^{-\left(\gamma^L_{ATM}+\gamma^O_{ATM}\right)R} \; \frac{\epsilon_O A_T}{R^4 \Omega_L \Omega_E}$$

Transmitter-generated seawater fluorescence

$$P_{DLWF} = P_L \epsilon_L \epsilon_C A_C \; e^{-\left(\gamma^L_{ATM}+\gamma^O_{ATM}\right)R} \; \frac{\epsilon_W \, e^{-\left(\gamma^L_O+\gamma^W_O\right)z_O} \, (1-\rho_{in})(1-\rho_{out})}{4\pi R^2 \left(\gamma^L_W+\gamma^W_W\right)}$$

Transmitter-generated surface reflection

$$P_{DLR} = P_L \epsilon_L \epsilon_C A_C \; e^{-2\gamma^L_{ATM}R} \; \frac{\rho_O A_O f_O(\theta,ss)+\rho_W A_W f_W(\theta,ss)}{R^2 \Omega_E A_T}$$

Transmitter-generated atmospheric backscatter

$$P_{DLAB} = P_L \epsilon_L \epsilon_C A_C \, \beta^L_{ATM} \int_O^R \frac{f(z)}{z^2} \, e^{-2\gamma^L_{ATM}Z} \, dz$$

TABLE 3.2 - SYSTEM RADIATIVE TRANSFER EQUATIONS - CW CASE (Cont.)

Transmitter-generated seawater backscatter

$$P_{DLWB} = P_L \epsilon_L \epsilon_C A_C \frac{\beta^L_W e^{-2\gamma^L_O z_O}}{2R^2 \gamma^L_W \Omega_E}$$

Sun-generated oil fluorescence

$$P_{DSOF} = \frac{\epsilon_C A_C A_T}{R^2 \Omega_E} \iint H^\lambda_S e^{-\left(\gamma^S_{ATM}+\gamma^O_{ATM}\right)R} \epsilon_O(\lambda_S,\lambda_O) d\lambda_S d\lambda_O$$

Sun-generated water fluorescence

$$P_{DS} = \int_0^\infty \iint H^\lambda_S \epsilon_W(\lambda_S,\lambda_W) e^{-\left(\gamma^S+\gamma^W\right) z_W -\left(\gamma^S_{ATM}+\gamma^W_{ATM}\right)R}$$

$$A_C \epsilon_C \Omega_{FOV}(1-\rho_{in})(1-\rho_{out}) e^{-\gamma^W_O z_O} \cdot d\lambda_S d\lambda_W dz$$

Sun glitter

$$P_{DSR} = \frac{H_S A_C \epsilon_C e^{-\gamma^S_{ATM} R}\left[\rho_O A_O f^S_O(\theta,ss,\phi,\Omega_{FOV} Pol)+\rho_W A_W f^S_W(\theta,ss,\phi,\Omega_{FOV},Pol)\right]}{R^2 \Omega_E}$$

TABLE 3.2 - SYSTEM RADIATIVE TRANSFER EQUATIONS - CW CASE (Cont.)

Solar atmospheric backscatter

$$P_{DSAB} = \frac{H_s \beta^s_{ATM} A_C \epsilon_C \Omega_{FOV} \left(1-e^{-\gamma^s_{ATM} R}\right)}{\gamma^s_{ATM}}$$

Solar underwater backscatter

$$P_{DSWB} = \frac{H_s \beta^s_W A_C \epsilon_C \Omega_{FOV} (1-\rho_{in})(1-\rho_{out}) e^{-\gamma^s_{ATM} R}}{\left(1+\frac{\cos\theta}{\cos\phi}\right)\gamma^s_W}$$

Sky-generated oil fluorescence

$$P_{DKOF} = \frac{\epsilon_C A_C A_T}{R^2 \Omega_E} \iint H^\lambda_K \, e^{-\left(\gamma^K_{ATM}+\gamma^o_{ATM}\right)R} \, \epsilon_o(\lambda_K, \lambda_o) \, d\lambda_K d\lambda_o$$

Sky-generated seawater fluorescence

$$P_{DKWF} = A_C \epsilon_C \, \Omega_{FOV} (1-\rho_{in})(1-\rho_{out}) e^{-\gamma^w_o z_o} \int_o^\infty \iint H^\lambda_K$$

$$\cdot \, \epsilon_w(\lambda_K, \lambda_w) \, e^{-\left(\gamma^K_w+\gamma^w_w\right)z_w - \left(\gamma^K_{ATM}+\gamma^w_{ATM}\right)R} \, d\lambda_K d\lambda_w dz$$

TABLE 3.2 - SYSTEM RADIATIVE TRANSFER EQUATIONS - CW CASE (Cont.)

Sky reflection on surface

$$P_{DKR} = H_K A_C \epsilon_C e^{-\gamma^K_{ATM} R} \left[\frac{\rho_o A_o f^k_o(\theta, ss, \phi, \Omega_{FOV} Pol) + \rho_w A_w f^k_w(\theta, ss, \phi, \Omega_{FOV} Pol)}{R^2 \Omega_E} \right]$$

Skylight atmospheric backscatter

$$P_{DKAB} = \frac{H_K \beta^K_{ATM} \; A_C \epsilon_C \, \Omega_{FOV} \left(1 - e^{-\gamma^K_{ATM} R}\right)}{\gamma^K_{ATM}}$$

Skylight underwater backscatter

$$P_{DKWB} = \frac{H_K \beta^K_w \; A_C \epsilon_C \, \Omega_{FOV} (1 - \rho_{in})(1 - \rho_{out}) e^{-\gamma^K_{ATM} R}}{1 + \frac{\cos\theta}{\cos\phi} \gamma^K_w}$$

SYSTEM RADIATIVE TRANSFER EQUATIONS - PULSED CASE

Transmitter-generated peak detectable power

Oil fluorescence

$$P^{PK}_{DLOF} = P^{PK}_L \epsilon_L \epsilon_C A_C \frac{A_T \epsilon_o e^{-\left(\gamma^L_{ATM} + \gamma^o_{ATM}\right) R}}{R^4 \Omega_L \Omega_E \sqrt{t_L^2 + t_{oF}^2 + t_{ss}^2}} \quad t_L$$

TABLE 3.2 - SYSTEM RADIATIVE TRANSFER EQUATIONS - PULSED CASE (Cont.)

Water fluorescence

$$P^{PK}_{DLWF} = P^{PK}_{L}\epsilon_{L}\epsilon_{C}A_{C}\;\frac{e_{w}ct_{L}e^{-\left(\gamma^{L}_{ATM}+\gamma^{w}_{ATM}\right)R\;-\;\left(\gamma^{L}_{o}+\gamma^{w}_{o}\right)z_{o}}}{R^{2}\,\Omega_{E}}$$

Surface reflection

$$P^{PK}_{DLR} = P^{PK}_{L}\epsilon_{L}\epsilon_{C}A_{C}\left(\frac{\rho_{o}A_{o}f_{o}+\rho_{w}A_{w}f_{w}}{R^{2}\Omega_{E}\;A_{T}}\right)e^{-2\gamma^{L}_{ATM}\;R}\;\frac{t_{L}}{\sqrt{t_{L}^{2}+t_{ss}^{2}}}$$

Atmospheric backscatter

$$P^{PK}_{DLAB} = P^{PK}_{L}\epsilon_{L}\epsilon_{C}A_{C}\;\frac{\beta^{L}_{ATM}\;ct_{L}\;e^{-2\gamma^{L}_{ATM}\;R}}{R^{2}}$$

Underwater backscatter

$$P^{PK}_{DLWB} = P^{PK}_{L}\epsilon_{L}\epsilon_{C}A_{C}\;\frac{\beta^{L}_{w}ct_{L}e^{-2\gamma^{L}_{ATM}\;R}}{R^{2}}$$

TABLE 3.2 - SYSTEM RADIATIVE TRANSFER EQUATIONS - PULSED CASE (Cont.)

Natural Background Peak Detectable Power

$$P_{DS}^{PK} = P_{DS} = P_{DSOF} + P_{DSWF} + P_{DSR} + P_{DSAB} + P_{DSWB}$$

$$P_{DK}^{PK} = P_{DK} = P_{DKOF} + P_{DKWF} + P_{DKR} + P_{DKAB} + P_{DKWB}$$

Transmitter-Generated Average Detectable Power

Oil fluorescence

$$P_{DLOF}^{AV} = P_L^{PK} \epsilon_L \epsilon_C A_C r_g \frac{A_T e^{-\left(\gamma_{ATM}^{L} + \gamma_{ATM}^{o}\right)R} t_L}{R^4 \Omega_L \ \Omega_E}$$

Water fluorescence

$$P_{DLWF}^{AV} = P_L^{PK} \epsilon_L \ \epsilon_C A_C r_g \frac{\epsilon_w c t_L e^{-\left(\gamma_{ATM}^{L} + \gamma_{ATM}^{w}\right)R - \left(\gamma_o^L + \gamma_o^w\right) z_o} t_2}{R^2 \Omega_E}$$

Surface reflection

$$P_{DLR}^{AV} = P_L^{PK} \epsilon_L \ \epsilon_C A_C r_g \ e^{-2\gamma_{ATM}^{L} R} t_1 \left(\frac{\rho_o A_\alpha f_o + \rho_w A_w f_w}{A_E \ A_T} \right)$$

TABLE 3.2 - SYSTEM RADIATIVE TRANSFER EQUATIONS - PULSED CASE (Cont.)

Atmospheric backscatter

$$P_{DLAB}^{AV} = P_L^{PK} \epsilon_L \epsilon_C A_C r_g \frac{\beta_{ATM}^L \, c t_L e^{-2\gamma_{ATM}^L R} t_1}{R^2}$$

Underwater backscatter

$$P_{DLWB}^{AV} = P_L^{PK} \epsilon_L \epsilon_C A_C r_g \frac{\beta_w^L c t_1 t_2 e^{-2\gamma_{ATM}^L R}}{R^2}$$

Natural background average detectable power

$$P_{DS}^{AV} = P_{DS} \, t_g r_g$$

$$P_{DK}^{AV} = P_{DK} \, t_g r_g$$

3.2.3 Consequences of the Equations

The first line in Equation (1) contains the desired signal P_{DLOF}, and the four transmitter-generated background channels. The last three of these channels (P_{DLR}, P_{DLAB}, P_{DLWB}) are at the same wavelength as the transmitter, and can be removed by a filter that transmits λ_F and rejects λ_L, mounted at the receiver. This leaves P_{DLWF} as the only transmitter-generated background.

There are four ways to minimize the natural background (the last ten terms in Equation (1):

1. Minimize the receiver field-of-view, since nearly all these terms are proportional to Ω_{FOV}. The minimum field-of-view that can be achieved without losing some of the desired signal is $\Omega_{FOV} = \Omega_L$. Therefore Ω_L should also be minimized. The most practical way to minimize Ω_L, while maintaining high transmitter power, is to use a laser as the transmitter.
2. Choose optimum viewing directions. The P_{DSR} channel can be nearly eliminated by not viewing the sun's glitter pattern on the sea surface. The P_{DKR} channel (sky reflection) can be minimized by viewing the surface at Brewster's angle for seawater (53^o from nadir), with a suitable polarizer at the receiver.
3. Minimize the on-time of the receiver. This can be achieved with a pulsed transmitter and a gated receiver. However, pulsed transmitters generally have lower average power than continuous transmitters.
4. Confine the optical bandwidth of the receiver to spectral regions where the sun is weak. The receiver can be confined to the ultraviolet, but the fluorescent efficiency for crude and bunker-C oils is low; or it can be confined to the near infrared, where the fluorescent efficiency for light oils and diesel fuel

is low; or it can be confined to the Fraunhofer lines [2] in the visible spectrum, requiring very narrow wavelength filters, which at best reduce the natural background by one order of magnitude.

Analyzing the four ways of minimizing the natural background above, 1 and 2 are acceptable without reservation; 3 is acceptable, subject to consideration of the available pulsed or CW transmitter power; 4 is unacceptable, because most of the desired spectral information for identification of oils occurs in the visible region, where sunlight is strong.

SECTION 4

LABORATORY PARAMETER MEASUREMENTS

4.1 FLUORESCENCE SPECTROSCOPY

4.1.1 Theory

If a substance which is strongly illuminated by light absorbs, it may fluoresce. The fluorescent light generally has a longer wavelength than the incident light. Further, each different substance has its own characteristic fluorescence spectrum. Characterization of a fluorescent substance, requires two types of spectra, excitation and emission. The excitation spectrum determines the best wavelength for raising the substance to an activated state. The emission spectrum is a characterization of the light emitted when the activated substance returns to its ground state.

4.1.2 Instrumentation and Measuring Technique

The fluorescence spectra of various oil samples were obtained using a Model 4-8203 Aminco-Bowman Spectrophotofluorometer (SPF), fitted with an oil film sampler of our own design (see Figure 4.1).

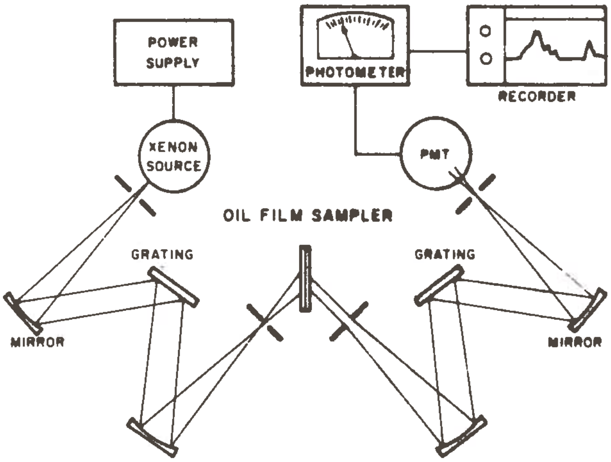


Figure 4.1 - Spectrophotofluorometer Optical Configuration

The oil film sampler consists of two spaced fused silica optical flats mounted in a rotatable U-channel holder. Transmission of the sampler without oil is greater than 90% from 200 to 800 nanometers.

During operation with the oil film sampler, light from the Xenon-lamp is dispersed by the excitation monochromator (grating type) into monochromatic radiation incident on the sample. A similar monochromator disperses the fluorescent light from the sample into monochromatic radiation incident on the photomultiplier tube (RCA type C31025C, see Figure 4.2). The radiation is there transformed into a weak electrical signal and fed to the photometer where it is amplified. The photometer output is indicated on a self-contained meter and transmitted to the Y axis of a Mosely-Autograph X-Y recorder.

The monochromator gratings are rotated by motor-driven cams to which graduated discs are coupled for visual observation and wavelength adjustment.

Transducers, coupled to the gratings, supply wavelength information in the form of a direct-current signal to the X axis of the recorder.

When the scanning emission monochromator's output is connected to the recorder X-input, and when the excitation monochromator is set at a maximum excitation wavelength, a wavelength versus intensity diagram (emission spectrum) is plotted.

Alternately, when the scanning excitation monochromator's output is connected to the recorder X-input and when the emission monochromator is set for a maximum fluorescence wavelength, a wavelength versus intensity diagram (excitation spectrum) is plotted.

Figure 4.3 shows the spectral distribution of a Pen Ray Mercury Discharge tube taken with the SPF emission monochromator. The 3031.5 and 3131.7Å lines are just resolved, indicating a bandwidth of 10-nanometers.

The conventional way of reporting fluorescence spectra for pure substances is to show the emission spectrum for the peak

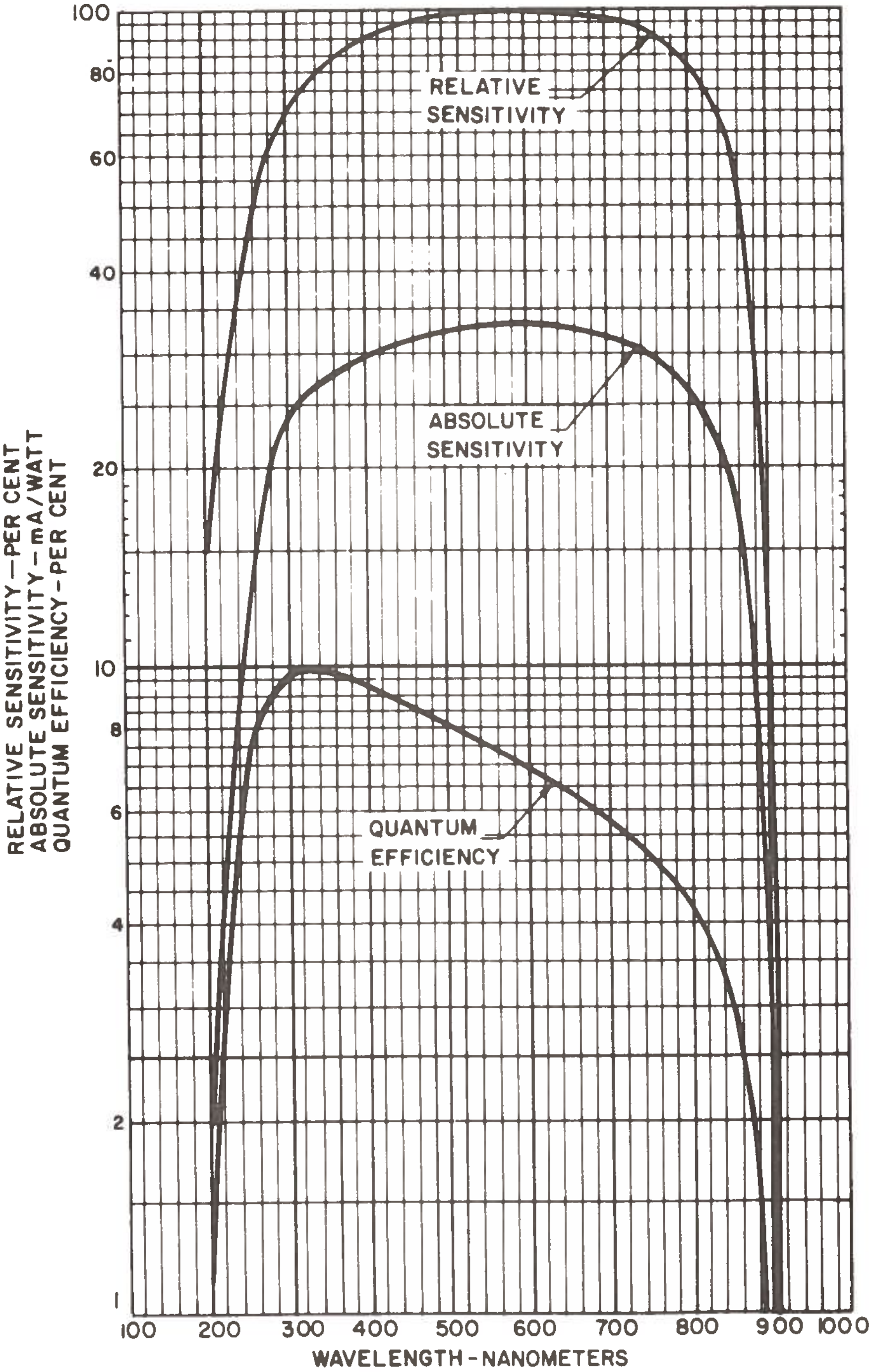


Figure 4.2 - Typical Photocathode Spectral Response Characteristics (RCA C31025C)

excitation wavelength, and the excitation spectrum for the peak emission wavelength.

Figures 4.4 through 4.7 are the excitation and emission spectra of four selected oil samples.

Figure 4.4 shows the fluorescence spectrum of a refined fuel oil designated sample D1, origin Lake Arthur, API gravity 46.3 product of Cities Service Oil Co. The excitation and emission peaks are quite specific and narrow at 306 and 406 nanometers. The other peaks are not a part of the spectra per se but due to direct scattered radiation of the xenon source.

Figure 4.5 shows the excitation and emission spectra of a Light Crude Oil, sample C2, origin West Texas Sour, API gravity 33.9, product of the Getty Oil Co. Two important features are present: the excitation spectrum is broader than D1 and a small peak appears at 470 nm. The broadening of the excitation curve becomes even greater with increasing density of the crude oil. (Also indicated by a decreasing API gravity number). The broadening is probably due to the greater number of oil fractions that combine to form the heavier crudes. Another noticeable indication is that the peak emission is at the longer wavelength 498 nm. The small peak in the excitation spectra at 470 nm is due to a prominence in the xenon source.

Figure 4.6 shows the excitation and emission spectra of a heavy crude, sample B2, origin, southern California, API gravity 12.8, product of the Shell Oil Co. The peak at 470 nm is quite

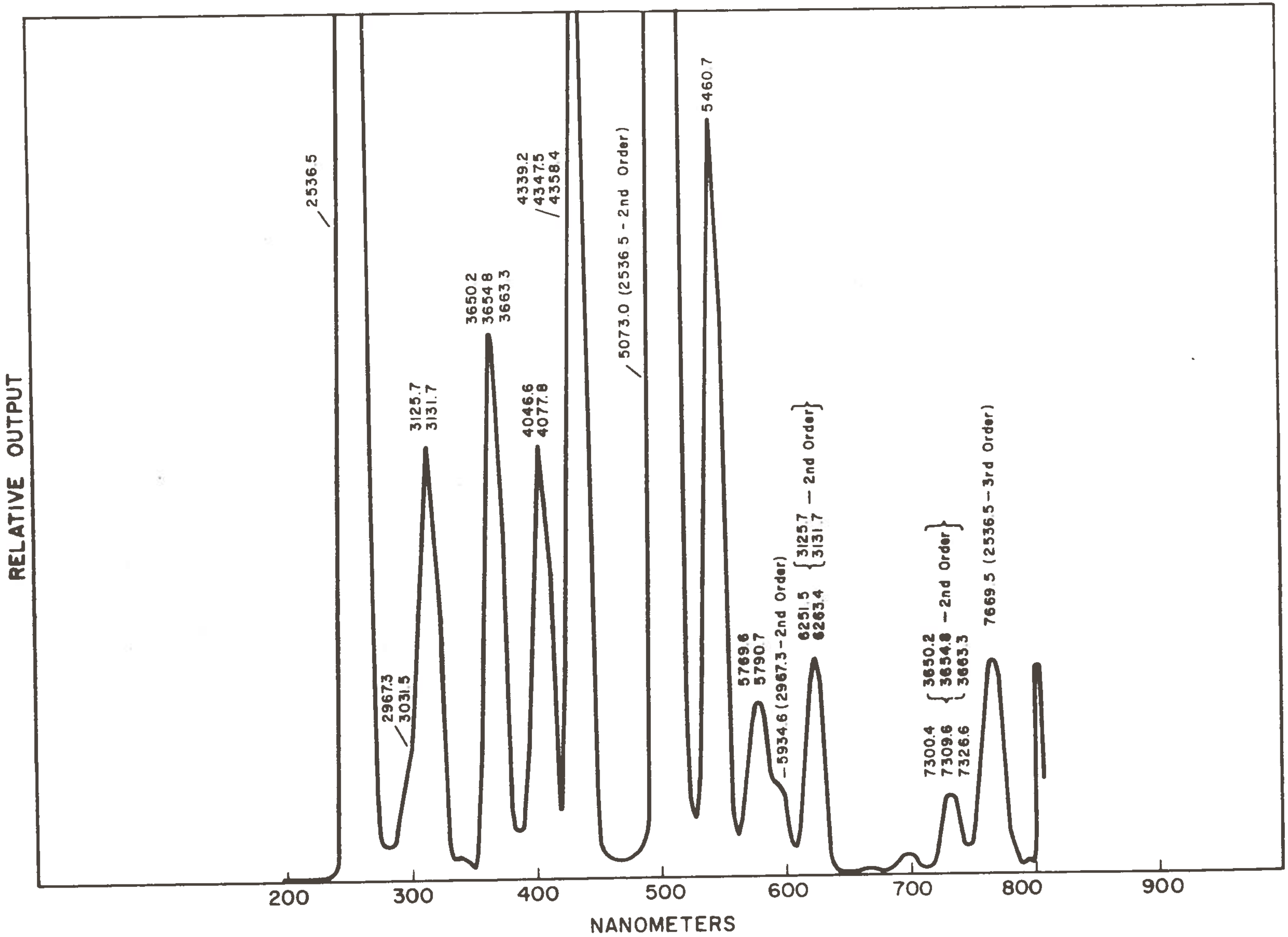


Figure 4.3 - Mercury Calibration Spectra

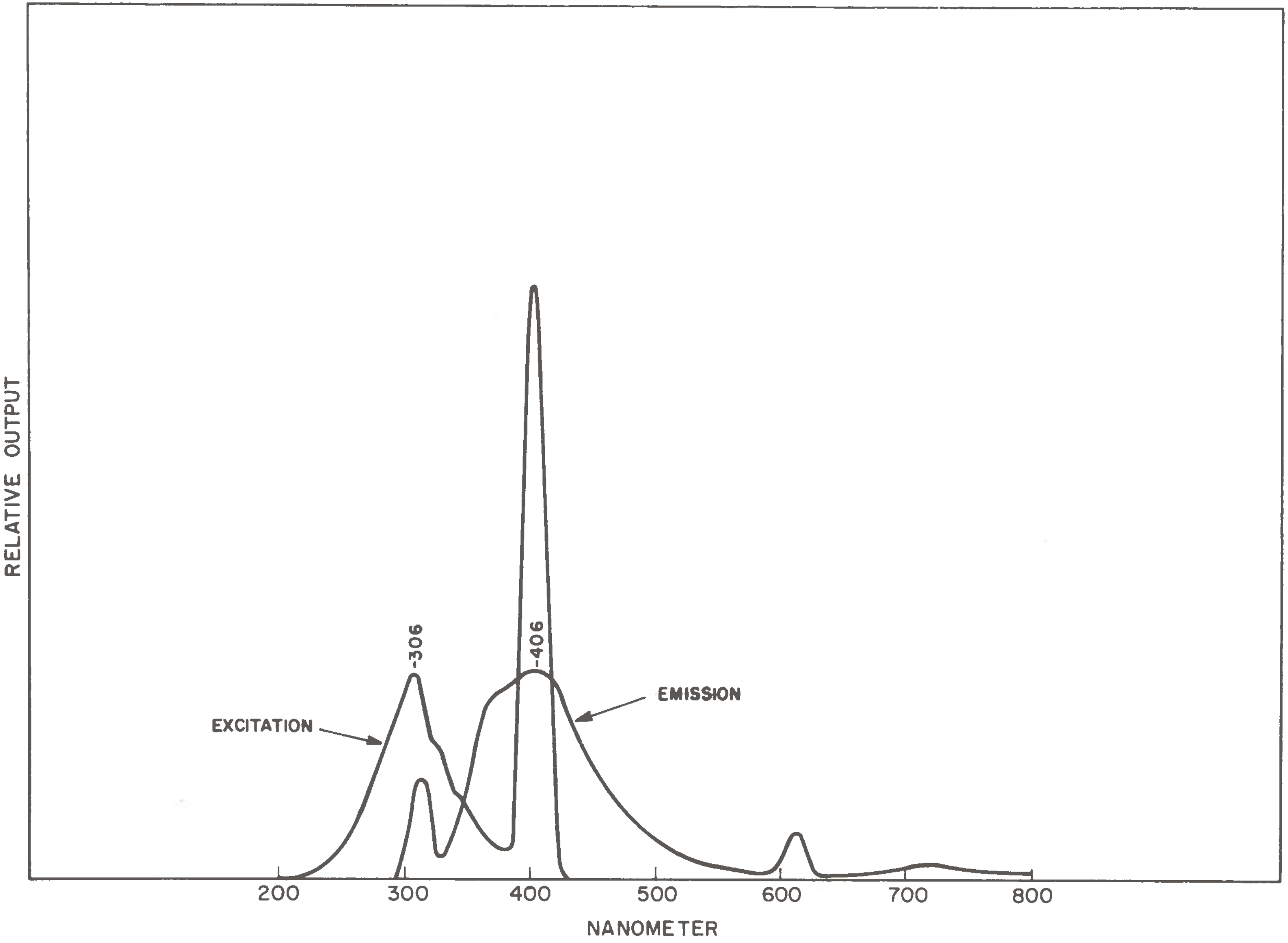


Figure 4.4 - Excitation and Emission Spectra (Sample D1)

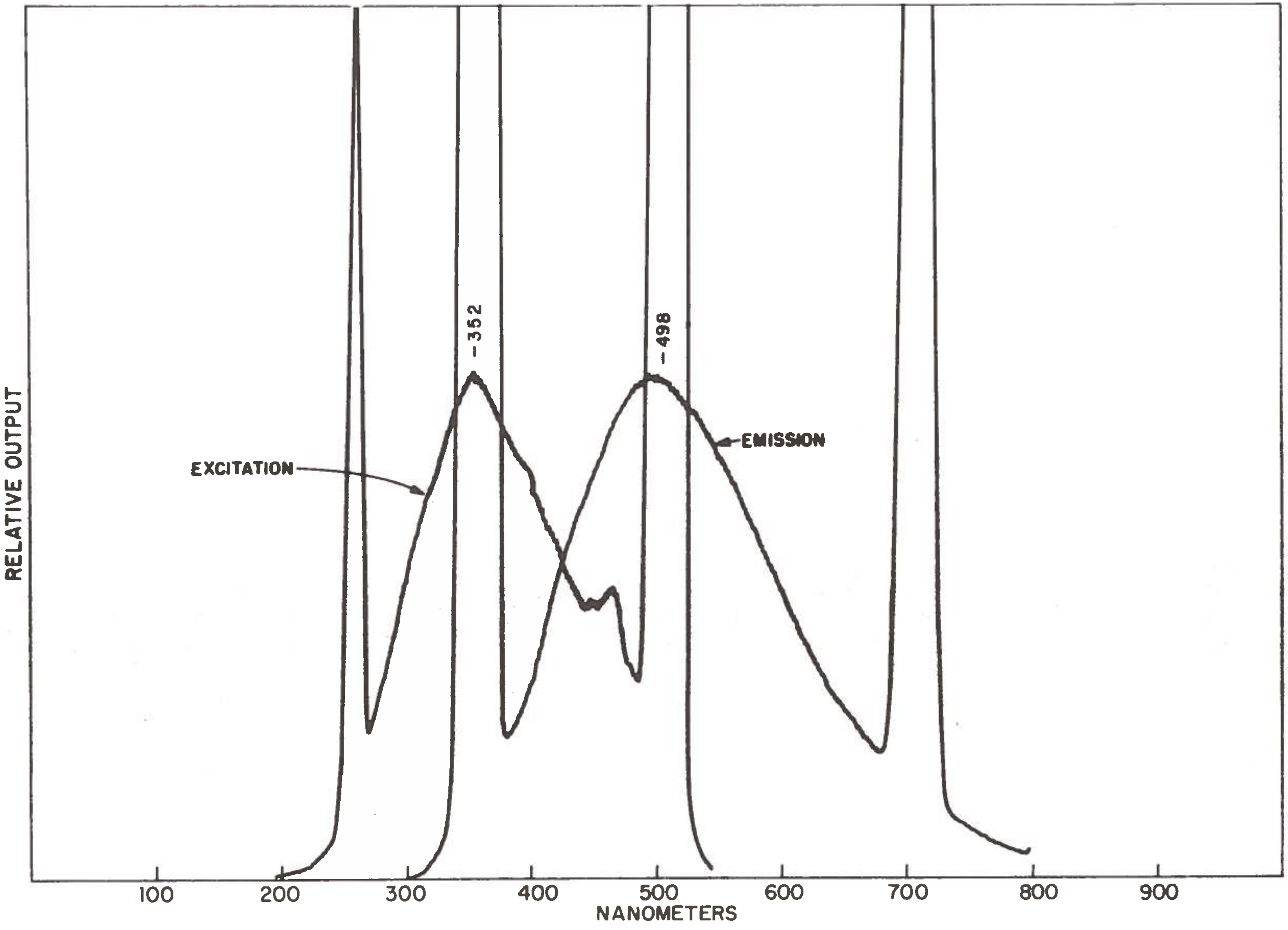


Figure 4.5 - Excitation and Emission Spectra (Sample C2)

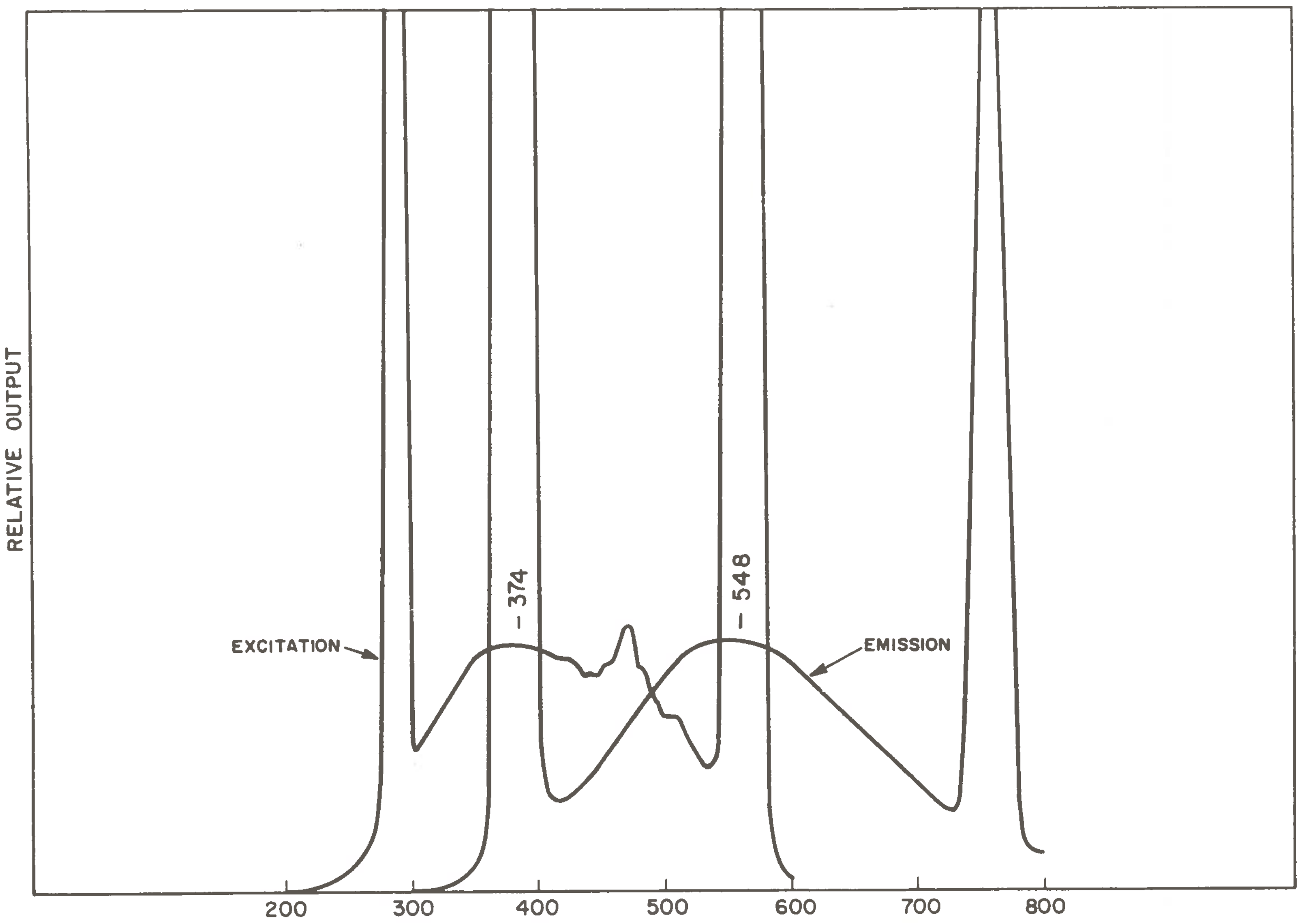


Figure 4.6 - Excitation and Emission Spectra (Sample B2)

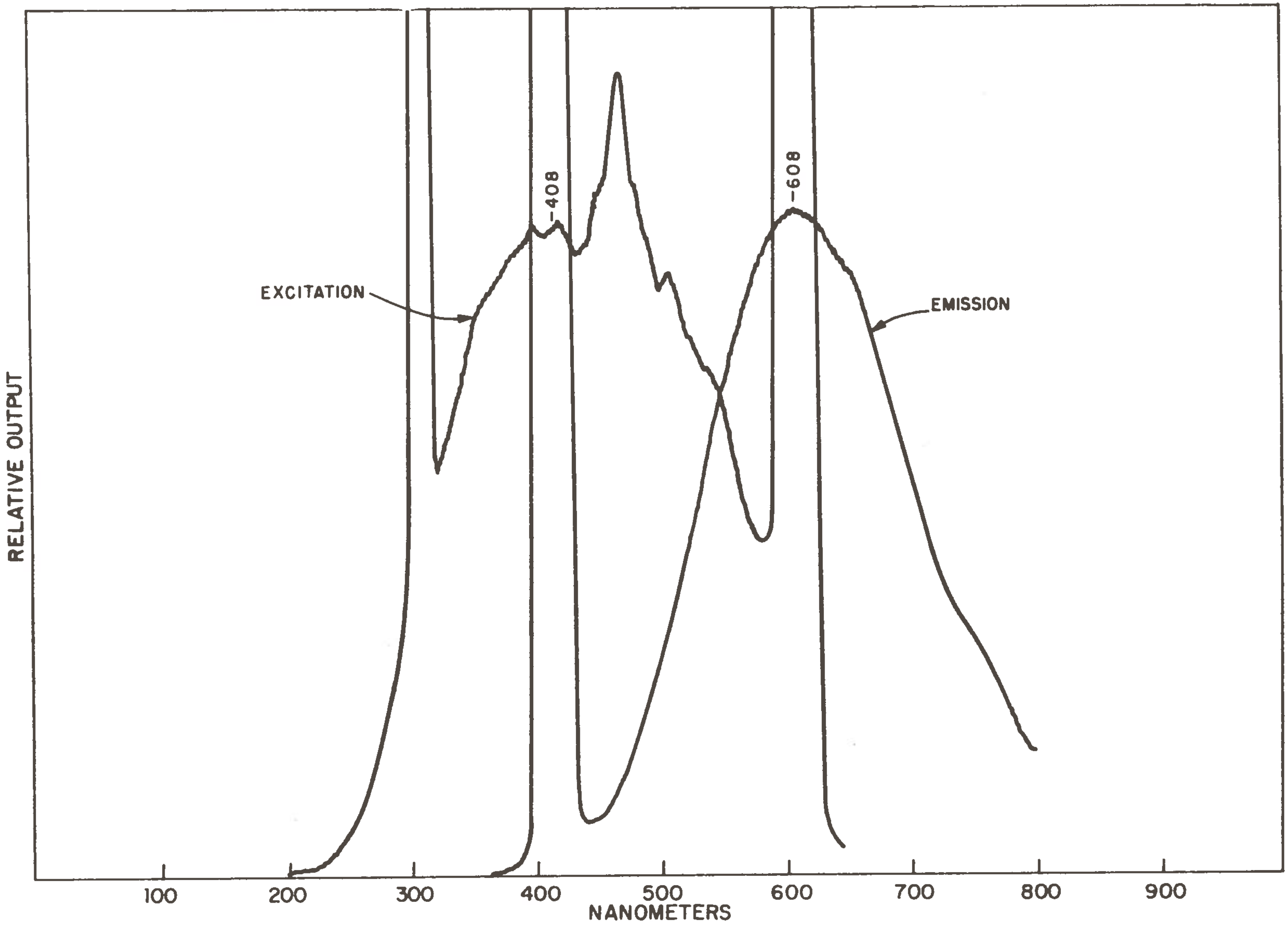


Figure 4.7 - Excitation and Emission Spectra (Sample A3)

pronounced, although unfortunately not characteristic of the oil sample, but due to the xenon source.

Figure 4.7 shows the excitation and emission spectra of a heavy residuum, sample A3, origin Delaware Refinery, API gravity -1.7, a product of the Getty Oil Co. Again the prominence at 470 nm, and a shift of the emission peak toward the red.

4.1.3 Experimental Results

Table 4.1 lists the optimum excitation and emission wavelengths.

4.2 FLUORESCENT COEFFICIENT

4.2.1 Definition

The fluorescent coefficient is defined as the ratio of fluorescent emission power (output at the emission wavelength) to the excitation power (input at the excitation wavelength). The output is taken through the whole solid angle of emission. The output is specified for a narrow wavelength band rather than the total emission spectrum.

4.2.2 Instrumentation and Measuring Technique

The fluorescent coefficient of the various oil samples was measured using the Model 4-8203 Aminco-Bowman Spectrophotofluorometer (SPF), Model 9914 Eppley Labs Thermopile, Model 150B Keithley Microvolt Meter, and two neutral density filters.

TABLE 4.1 OPTIMUM FLUORESCENT EXCITATION AND EMISSION WAVELENGTHS

TSC OIL SAMPLE*	EXCITATION (NANO-METERS)	EMISSION (NANO-METERS)	TSC OIL SAMPLE	EXCITATION (NANO-METERS)	EMISSION (NANO-METERS)
A1	365	565	C4	336	482
A2	418	520	C5	352	484
A3	408	608	C6	348	464
A4	360	560	C7	353	490
B1	352	494	C8	350	482
B2	374	548	C9	313	440
B3	359	542	C10	312	450
B4	350	503	C11	344	486
B5	331	458	C12	354	451
B6	357	508	C13	352	480
B7	353	470	D1	306	406
B8	350	510	D2	353	520
C1	351	495	D3	351	500
C2	352	498	D4	393	579
C3	352	487	Seawater**	361	419

*See Appendix 8.4 for oil sample description

**Seawater sample obtained from the seawater surrounding the USCG station, at Point Allerton, Hull, Mass.

The measuring technique was as follows: (see Figure 4.8): The excitation monochromator was set and fixed at 337 nm to obtain conversion coefficients which are closer to an actual surveillance system which will use a uv laser source for excitation of the oil spill; the emission monochromator was set at the peak emission wavelength λ_M.

The oil sample fluorescent emission S_M at λ_M was measured with the photomultiplier tube (RCA type C31025C).

The excitation monochromator wavelength was changed to λ_M, and a white, non-fluorescing diffusing screen was substituted for the oil sample behind a quartz microscope slide.

The scattered radiation E_M at λ_M was measured with the photomultiplier, while attenuating E_M with neutral density filters, by a factor 1/a to a signal level comparable to S_M.

The ratio S_M/aE_M is independent of emission monochromator efficiency and photomultiplier spectral sensitivity. This ratio must be corrected for different power levels incident upon the sample region.

The diffusing screen was removed and a thermopile was inserted behind the quartz slide to detect the beam from the excitation monochromator. The thermopile signals I_M and I_E were measured with the excitation monochromator set at λ_M and λ_E.

It is assumed that the screen is 100% diffusely reflective, and that both the screen and the fluorescent sample radiate with the same spatial distribution. It was also assumed that the

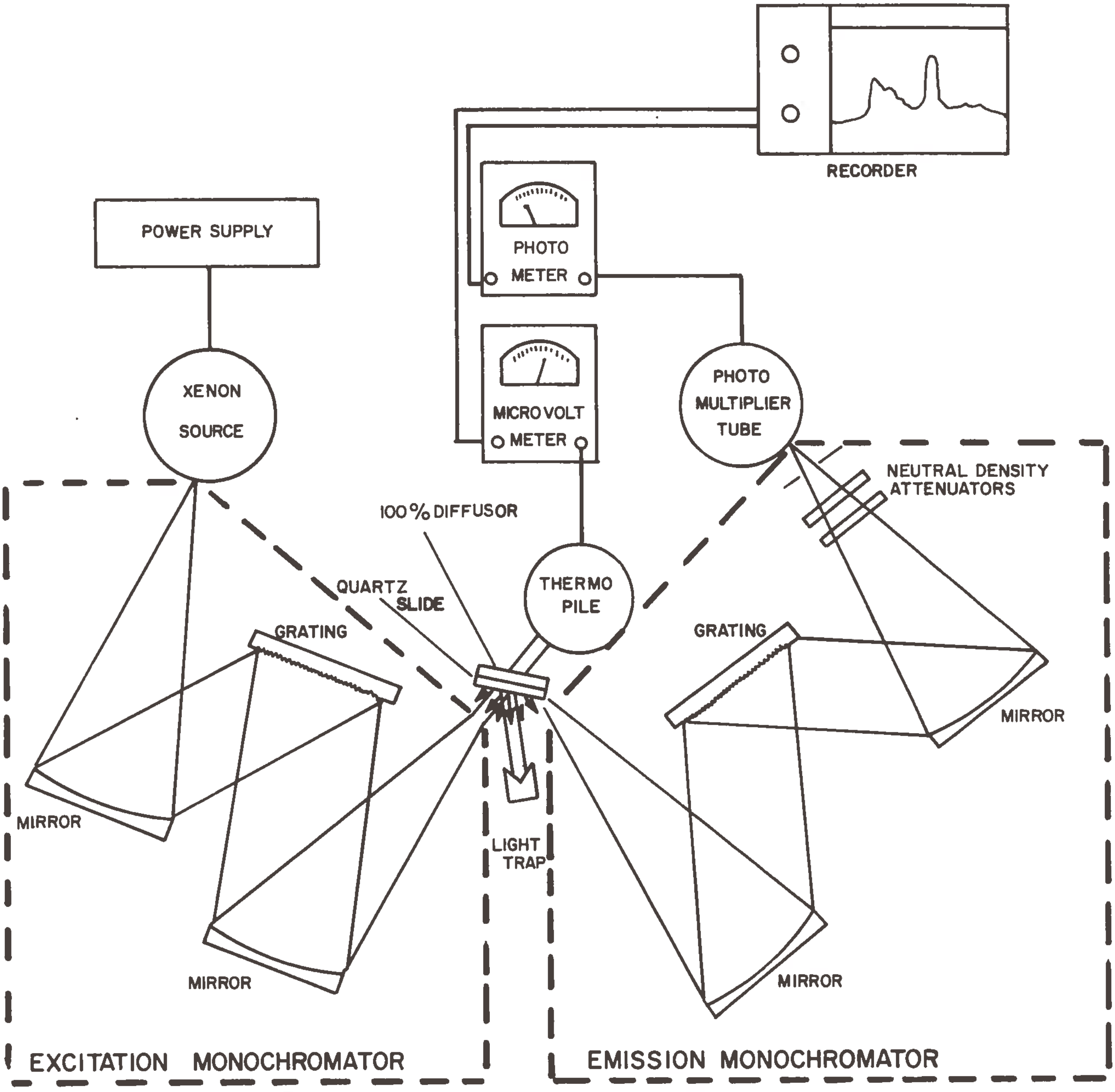


Figure 4.8- Fluorescent Power Conversion Coefficient of Oils Measuring Apparatus

power sensitivity of the thermopile is independent of wavelength. The monochromator slit widths have been kept constant throughout the procedure. The fluorescent conversion coefficient of oil ε_o, within the spectral bandpass of the emission monochromator is given by

$$\varepsilon_o = \frac{S_M}{aE_M} \cdot \frac{I_M}{I_E}$$

4.2.3 Seawater

Seawater samples were obtained from a pier near Revere Beach, Revere, Massachusetts, and from the seawater surrounding the USCG Station, at Point Allerton, Hull, Massachusetts. Fluorescence of seawater, unlike oil, is a volume phenomenon. Because of the very high ultraviolet extinction coefficient of oils, it is possible to approximate the fluorescence by Lambertian emission from a surface.

However, seawater has a much lower extinction coefficient, so this approximation gives an unrealistically low estimate for the expected seawater fluorescence. The experimental method for measuring the fluorescence power conversion efficiency of seawater must take into account the depth through which the pumping radiation passes, and the depth through which the emission is observed. The method is essentially the same as previously described in section 4.2.2 except that a quartz cuvette containing seawater is substituted for an oil film sandwiched between quartz slides. The target volume that lies in the viewing field of both the excitation and the emission monochromators has a thickness (z) of about 5 mm. It is assumed the total extinction over these short paths is negligible. The data were as follows: excitation wavelength (λ_E) 333 nm, emission wavelength (λ_M) 450 nm, fluorescent emission signal (S_M) 0.0135, excitation power $I_M = 14.55$ and $I_E = 13.50$. Diffusor emission (EM) 6.30, neutral density filter attenuation $a=2 \times 10^3$.

$$\text{Fluorescent Conversion Coefficient } \varepsilon_w = \frac{S_M I_M}{a E_M I_E} \; \frac{1}{Z} = 2 \times 10^{-4} m^{-1}$$

(Note that ε_o for the oil samples was dimensionless, whereas for seawater ε_w is given per unit thickness for the above reasons given.)

The emission from a 5 mm sample of seawater is less than the emission from the weakest oil sample (Bl). However, for realistic attenuation lengths (0.1m to 10m), the total seawater fluorescence is greater than the fluorescence of Bl. This agrees with field observations conducted at the Coast Guard Base in Boston Inner Harbor in October 1970.

4.2.4 Experimental Results

For an emission bandpass of 7nm, we obtained ε_{ow} ranging from 10^{-3} to 10^{-6} (see Table 4.2). Reproducibility checks showed these data to be precise only to an order of magnitude.

TABLE 4.2 FLUORESCENCE POWER CONVERSION COEFFICIENT

TSC OIL SAMPLE	EXCITATION WAVELENGTH λ_E (NANOMETERS)	EMISSION WAVELENGTH λ_M (NANOMETER)	FLUORESCENT EMISSION S_M	RELATIVE		DIFFUSOR EMISSION E_M	ε_{OW}
				AT λ_M I_M	AT λ_E I_E		
D1	337	406	0.210	17.9	15.9	0.048	$2.28\text{x}10^{-3}$
B5	337	459	0.186	17.9	15.9	0.081	$1.28\text{x}10^{-3}$
C6	337	459	0.123	17.7	15.9	0.081	$8.40\text{x}10^{-4}$
C9	337	446	0.104	16.6	15.9	0.074	$7.32\text{x}10^{-4}$
B7	337	458	0.098	17.7	15.9	0.080	$6.74\text{x}10^{-4}$
C7	337	480	0.099	17.8	15.9	0.082	$6.72\text{x}10^{-4}$
C3	337	480	0.089	17.8	15.9	0.082	$6.04\text{x}10^{-4}$
C5	337	472	0.086	20.0	15.9	0.094	$5.72\text{x}10^{-4}$
C10	337	456	0.073	17.6	15.9	0.078	$5.14\text{x}10^{-4}$
C12	337	450	0.070	17.1	15.9	0.078	$4.77\text{x}10^{-4}$
C8	337	474	0.068	19.7	15.9	0.090	$4.62\text{x}10^{-4}$
C2	337	490	0.039	16.2	15.9	0.073	$2.67\text{x}10^{-4}$
C13	337	470	0.038	20.0	15.9	0.096	$2.50\text{x}10^{-4}$
A3	337	597	0.031	10.4	15.9	0.043	$2.31\text{x}10^{-4}$
C4	337	482	0.024	17.7	15.9	0.082	$1.62\text{x}10^{-4}$
C11	337	480	0.022	17.8	15.9	0.082	$1.53\text{x}10^{-4}$
B6	337	502	0.014	14.8	15.9	0.069	$9.38\text{x}10^{-5}$
C1	337	481	0.013	17.7	15.9	0.082	$8.97\text{x}10^{-5}$
B2	337	530	0.012	13.5	15.9	0.060	$8.09\text{x}10^{-5}$

TABLE 4.2 FLUORESCENCE POWER CONVERSION COEFFICIENT (Cont.)

TSC OIL SAMPLE	EXCITATION WAVELENGTH λ_E (NANOMETERS)	EMISSION WAVELENGTH λ_M (NANOMETER)	FLUORESCENT EMISSION S_M	RELATIVE		DIFFUSOR EMISSION E_M	ε_{OW}
				AT λ_M I_M	AT λ_E I_E		
D2	337	514	0.010	14.7	15.9	0.068	6.48×10^{-5}
B3	337	530	0.008	13.5	15.9	0.060	5.77×10^{-5}
B8	337	505	0.007	15.0	15.9	0.069	4.76×10^{-5}
B4	337	495	0.006	15.6	15.9	0.070	4.18×10^{-5}
D3	337	490	0.004	16.2	15.9	0.073	2.98×10^{-5}
D4	337	565	0.003	11.8	15.9	0.052	1.84×10^{-5}
A1	337	545	0.002	12.6	15.9	0.057	1.38×10^{-5}
A2	337	505	0.002	15.0	15.9	0.069	1.09×10^{-5}
A4	337	553	0.001	12.2	15.9	0.054	7.77×10^{-6}
B1	337	495	0.001	15.6	15.9	0.070	7.66×10^{-6}
Seawater	337	450	0.014	14.6	13.5	6.30	2.00×10^{-4} M^{-1}

A: Asphalt

B: Heavy Crude

C: Light Crude

D: Refined

4.3 FLUORESCENT LIFETIMES

4.3.1 Introduction and Theory

Fluorescent lifetimes of oils were investigated for the following reasons:

1. Oil lifetime differences can provide signatures for remote classification or identification. These temporal signatures supplement the spectral signatures of Section 4.1.
2. Lifetime representative values are needed to predict the performance of pulsed remote sensors. Excessively long lifetimes would reduce the merits of pulsed, versus continuous, sensors.

When a short pulse of ultraviolet radiation is absorbed by an oil, its fluorescent emission is greatest at the time of absorption, and decays exponentially thereafter. The time required for this emission to drop to half its peak value is called its half-life, whereas the lifetime is the time required for the emission to drop to (1/e) times the peak value. The lifetime is 1.44 times the half-life.

The half-life is also the full-width-at-half-maximum of the emitted pulse that would be observed using a very fast transmitter and receiver. In practice, the transmitter has a finite pulse width and the receiver has a finite impulse response time. The resultant observed pulse width is the square root of sum of squares of the fluorescent half-life, the pulse width of the transmitter, and the impulse response time of the receiver, all measured at half-maximum.

For a given average return power, a shorter pulse width corresponds to a higher peak power. It also corresponds to a better signal-to-background ratio when the receiver is gated, or when the receiver uses pulse-height discrimination.

4.3.2 Instrumentation

A nitrogen laser was constructed* (Figure 4.9) to serve as a fast ultraviolet excitation source for measuring the fluorescent lifetimes of oils. This pulsed laser emits one kilowatt peak power at a wavelength of 337 nanometers. The full-width-at-half-maximum of the pulses is 4 nanoseconds (Figure 4.10), and the repetition rate is variable up to ten pulses per second.

We used the same laser, with minor modifications, as the transmitter in our field experiments in the remote sensing of oil fluorescence (Section 5.3).

The experimental setup for determining fluorescent lifetimes is diagrammed in Figure 4.11. Proceeding to the right from the nitrogen laser, the beamsplitter sends a portion of the laser output to a photodiode, triggering the oscilloscope display. The ultraviolet-pass filter (Corning #7-60) screens out the visible spontaneous emission of the laser. A lens focuses the beam onto the sample, which consists of an oil film pressed between microscope slides. Part of the fluorescence passes through

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* For the basic design of this laser, we are indebted to H. Ceccon and H.W. Furumoto of TSC.

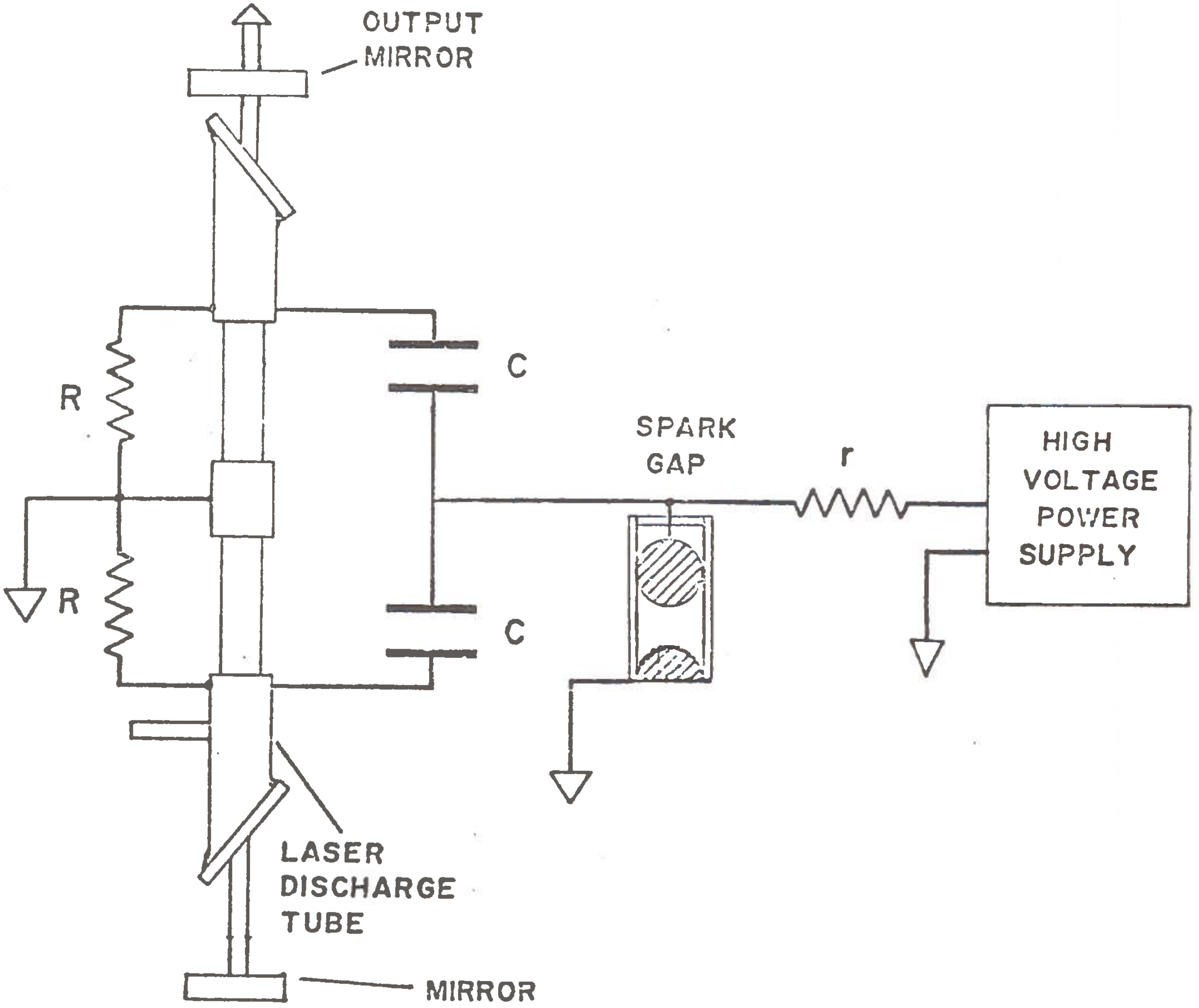


Figure 4.9 - Nitrogen Laser Schematic Diagram. (Laser built at TSC for the remote sensing of oil spills.)

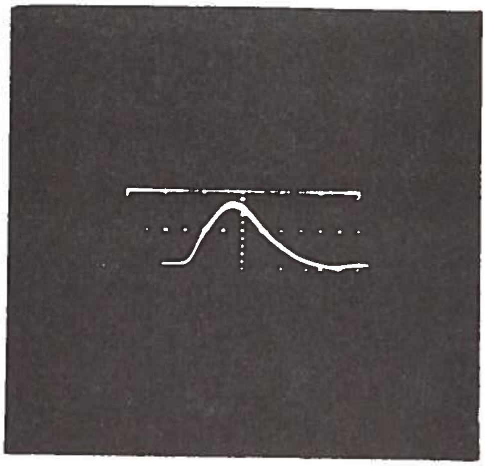


Figure 4.10 - Output of Nitrogen Laser. (ITT 4503 planar diode, Tektronix 519 oscilloscope 2 ns/div.)

a series of neutral-density and wavelength filters, and is focused by a second lens into the photomultiplier. The ultraviolet absorbing filter (Corning #3-74) removes the nonfluorescent laser radiation scattered by the sample. The photomultiplier (RCA 1P28) has a risetime of two nanoseconds. The oil fluorescence pulse is displayed on a Tektronix 556 oscilloscope with 1A1 plug-in, with a system risetime of seven nanoseconds. The neutral density filters are inserted to obtain constant oscilloscope deflection at fixed photomultiplier voltage and amplifier gain, thereby avoiding the effects of non-linearities in the detection system.

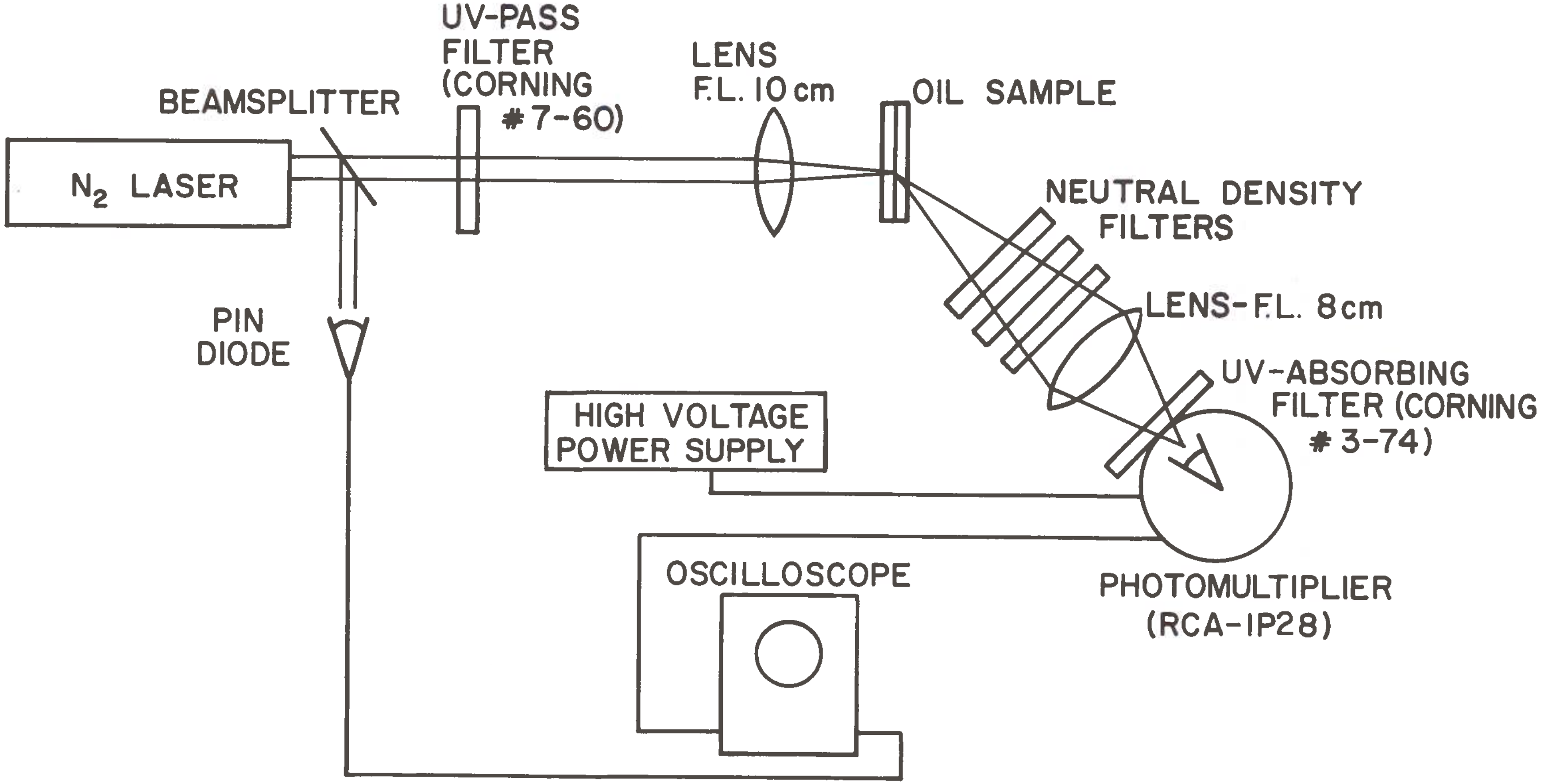


Figure 4.11 - Measurement of Oil Fluorescent Lifetime

4.3.3 Results

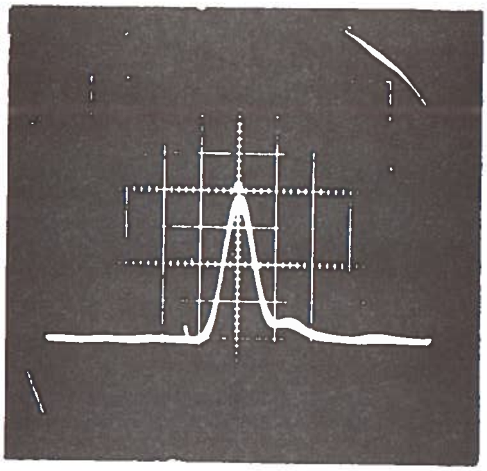
Figure 4.12a shows the fluorescence of a heavy crude oil, whose waveform is less than one nanosecond wider than the system response to reflected light from the laser (3-74 filter removed). A longer lifetime is apparent in Figure 4.12b, which shows the fluorescence of a light crude oil. In this case, the observed pulse width is 13 ± 1 nanoseconds, the calculated half-life is 9.8 nanoseconds, and the lifetime is 14 ± 2 nanoseconds.

Similarly, the fluorescent pulse widths of all 29 oil samples were measured and their lifetimes were calculated as given in Table 4.3.

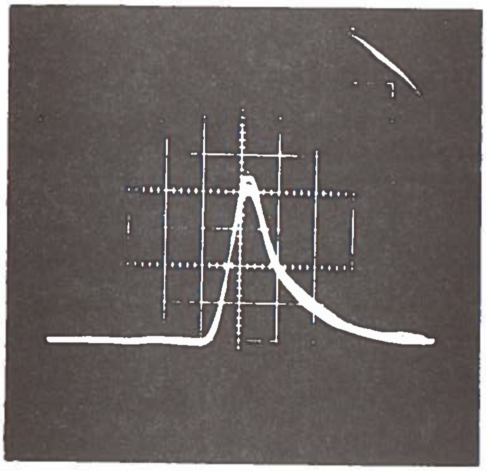
Strong correlations were established between spectral and temporal behavior:

a. Observing the oils through a wideband filter (400-700 nm), we find that oils with peak emission wavelengths in the blue region have longer lifetimes than oils whose peak emission wavelengths lie toward the red (Figure 19).

b. For any one oil, if we observe its emission through each of a set of filters of 20 nm bandpass, we find that its measured lifetimes increase with increasing emission wavelength.



(a)



(b)

Figure 4.12(a&b) - Oil Fluorescence. (Observed with Nitrogen Laser, 1P28 Photomultiplier, and Tektronix 556 Oscilloscope with 1A1 Plug-in, 10 ns per Division.)
(a) Oil sample B1, 9.9° API heavy crude, Chevron
(b) Oil sample C3, 39.0° API light crude, Shell

TABLE 4.3 FLUORESCENT HALF-LIVES AND LIFETIMES OF OILS

TSC OIL SAMPLE	HALF-LIFE (Nanoseconds)	LIFE TIME Nanoseconds	TSC OIL SAMPLE	HALF-LIFE (Nanoseconds)	LIFE TIME Nanoseconds
A1	3	4	C6	10	14
A2	3	4	C7	9	12
A3	5	8	C8	9	12
A4	3	4	C9	12	18
B1	3	4	C10	9	12
B2	5	8	C11	5	8
B3	5	8	C12	15	21
B4	3	4	C13	7	10
B5	17	25	D1	19	28
B6	5	8	D2	5	8
B7	14	20	D3	5	8
B8	3	4	D4	3	4
C1	5	8			
C2	5	8			
C3	10	14			
C4	7	10			
C5	7	10			

These half-lives and lifetimes have an uncertainty of ±2 ns. They were calculated from fluorescent pulse widths measured with a nitrogen laser (4 ns full-width-at-half-maximum) and a receiver whose response to the laser had a full-width-at-half-maximum of 8.4 ns. For oil descriptions see Appendix.

4.4 API GRAVITY: (RELATIVE DENSITY)

API gravity measurements were made of the various crude oil* samples, using the API Standard Method of Test[3]. Correlated with fluorescence, (spectra, lifetime, and conversion coefficients), API gravity will be used to give approximate oil type. The method is based on the principle that the gravity of a liquid varies directly with the depth of immersion of a body floating in it. The floating body, which is graduated in API gravity units in this method, is called an API hydrometer. API gravity is defined and calculated as follows:

API gravity, deg = $(141.5/\text{sp.gr.}\ \frac{60}{60}\ \text{F} - 131.5)$.

The API gravity is read by observing the freely floating API hydrometer and noting the graduation nearest to the apparent intersection of the horizontal plane surface of the liquid with the vertical scale of the hydrometer, after temperature equilibrium has been reached. Table 4.4 lists the API gravity corresponding to our sample identification code.

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*Samples A1 thru A4 are solid asphalts, whose API Gravity values were calculated on the basis of the suppliers' specific gravity measurements.

TABLE 4.4 API GRAVITY OF OIL SAMPLES

TSC OIL SAMPLE	°API	TSC OIL SAMPLE	°API	TSC OIL SAMPLE	°API
A1	8.7	C1	31.3	D1	46.3
A2	10.0	C2	33.9	D2	10.2
A3	-1.7	C3	39.0	D3	19.0
A4	7.2	C4	43.7	D4	5.7
B1	9.9	C5	27.1	Seawater*	6.8
B2	12.8	C6	42.5		
B3	15.5	C7	31.0		
B4	19.2	C8	39.9		
B5	25.0	C9	42.3		
B6	32.6	C10	46.5		
B7	30.3	C11	34.6		
B8	17.4	C12	40.6		
B7	30.3	C13	40.6		

*Seawater sample obtained from a pier near Revere Beach, Revere, Mass.

4.5 REFLECTANCE SPECTROSCOPY

4.5.1 Theory

Oils have higher reflectances than has seawater. The reflectance depends strongly upon angle of viewing, and weakly upon wavelength. The angular dependence is given by the Fresnel equations.

4.5.2 Instrumentation

The wavelength dependence was investigated with a Hitachi EPS-3T UV-VIS-NIR spectrophotometer, which we adapted for measuring the reflectance of liquids at 45° incidence.

4.5.2 Results

The reflectance of seawater is nearly constant from 350 to 700 nm. Oils show a weak minimum at 550 to 600 nm, with the reflectance increasing toward both the infrared and the ultraviolet. Similar results have been reported by Millard and Arvesen (NASA Ames Research Center, to be published) from field measurements, but their minimum contrast ratio (oil/seawater) occurs at 450 to 500 nm. Their measurements included the daylight scattering from seawater, which peaks near 450 nm, and were taken with near vertical viewing, for which the underwater contribution would be at its strongest. Our laboratory samples were 3 mm thick; thus we saw only the surface contribution from seawater. Our spectral result could be used to predict contrast ratios for viewing directions shallower than the critical angle for water (48.5°).

Maximum contrast (oil/seawater) occurs in the ultraviolet from 260 to 320 nm. Atmospheric scattering in this region would offset any advantages for high altitude photography.

SECTION 5

REMOTE SENSING PARAMETER CONSIDERATIONS

5.1 INTRODUCTION

Operational requirements that are imposed on an oil spill surveillance system are derived from many factors. Most important are: the oil-sea-sky-atmosphere environment, the host (surveilling) aircraft, and the time of observation. It is expected that the primary oil spill surveillance will be conducted from an aircraft, based upon the need for very large areal coverage (navigable waters of the United States, adjoining shorelines, or waters of the contiguous zone) and speed of surveillance. Appendix 8.3 lists characteristics of the aircraft types most likely to be used for this purpose. Oil that is spilled onto the sea will remain on the surface and will spread horizontally. The extent and rate of spread is not considered in this report [4,5,6]. However, since the discovery of an oil spill of any size must be reported, the detectable size of a given spill will be determined by the system capability.

The following sections predict the performance of a laser-excited oil fluorescence surveillance system theoretically, and then verify the predictions by means of field measurements.

5.2 ANALYTICAL CONSIDERATIONS

5.2.1 Operational Requirements

Determining the feasibility of the laser-excited fluorometry method for oil spill sensing, it is necessary to evaluate the energy sources seen by the airborne receiver. These sources are diagrammed in Figure 3.3, and radiative transfer equations for them are presented in Table 3.2.

The terms P_{DLR}, P_{DLAB}, and P_{DLWB} are omitted in the following section, since the receiver is equipped with a filter which effectively rejects the laser excitation radiation at 3371 Å.

5.2.2 Signal and Noise Considerations

On the basis of the previously derived equations, Table 3.2, a signal to noise power ratio (S/R) is calculated for a laser-excited oil spill fluorescence surveillance system. Since the mode of operation can be CW, pulsed, or pulsed average, a calculation is made for all three. Table 5.1 lists the system parameters used in these calculations. Certain assumptions and approximations were made in order to complete this work. Where indicated, the assumption or approximation is explained, and if an estimate is used the source is identified.

The following calculations are made for daylight operation with 25-kilometer visibility, aircraft altitude of 1000-feet, and

TABLE 5.1 RELEVANT SYSTEM PARAMETERS

Symbol	Parameter	Value	Reference
ϵ_L	Transmitter Optics Efficiency	0.5	A
ϵ_C	Receiver Optics Efficiency	0.1	A
ϵ_O	Fluorescence Coefficient (3120 Å and 4500 Å)	2.1×10^{-4}	B
ϵ_W	Seawater Fluorescent Coefficient (3330 Å and 4500 Å)	$0.23\ km^{-1}$	B
ϵ_O^{λ}	Fluorescence Coefficient (3000-4000 Å and 4500 Å)	2.1×10^{-4}	B
ϵ_W^{λ}	Seawater Fluorescent Coefficient (3000-4000 Å and 4500 Å)	$0.23\ km^{-1}$	B
γ_{ATM}^{L}	Atmos. attenuation at 3371 Å (Nitrogen Laser)	$0.24\ km^{-1}$	8
$\gamma_{ATM}^{O,S,W}$	Atmos. attenuation at 4500 Å (0.1 Fluorescence)	$0.15\ km^{-1}$	9
γ_W^L	Water attenuation coefficient at (3350 Å)	$210\ km^{-1}$	12
γ_W^W	Water attenuation coefficient at (4500 Å)	$19\ km^{-1}$	13
γ_W^{λ}	Seawater attenuation coefficient at (3000 to 4000 Å)	$175\ km^{-1}$	19
H_S	Sun's irradiance (50 Å band at 4500 Å)	$4.53 \times 10^6\ w/km^2$	10
H_K	Skylight Irradiance (50 Å band at 4500 Å)	$2.16 \times 10^6\ w/km^2$	16
H_S^{λ}	Sun's effective excitation radiation at (3000 to 4000 Å)	$10^8\ w/km^2$	18
H_K^{λ}	Skylight effective excitation radiation at (3000 to 4000 Å)	$5 \times 10^7\ w/km^2$	20
β_{ATM}^{S}	Atmospheric backscatter coefficient at (4500 Å)	$9.43 \times 10^{-3}\ km^{-1}$	11
β_W^S	Water backscatter coefficient at (4500 Å)	$0.8\ km^{-1}\ Sr^{-1}$	17
ρ_W	Reflectance of seawater	0.05	14
ρ_O	Reflectance of oil	0.07	15
Ω_L	Solid angle of the laser transmitter	$4 \times 10^{-6}\ Sr$	A
Ω_E	Solid angle of emission from the illuminated area	π, 2π, 4π	A
Ω_{FOV}	Solid angle of receiver field of view	$4 \times 10^{-6}\ Sr$	A
θ	Look angle	0°	A
ϕ	Solar zenith angle	0°	A
A_C	Area of collecting optic (30 cm diameter)	$7.20 \times 10^{-8}\ km^2$	A
$A_{T,O}$	Area of target ($\Omega_L\ R^2$)	$3.6 \times 10^{-7}\ km^2$	A
R	Range (1000 ft)	0.3 km	A
f_O^K	Skylight, Surface Reflectance Function	1	A
f_O^S	Sunlight, Surface Reflectance Function	10^{-3}	A

Reference
- A. Assumed or estimated by TSC
- B. Measured by TSC

a selected oil sample C5, whose fluorescent coefficient* is typically near the median of the range for oil samples.

The signal-to-noise power ratio is given by[7]:

$$S/N = \eta {P_S}^2/2B\, h\nu\, P_B,$$

where η is the detector quantum efficiency, P_S is the signal power, B is the post-detection bandwidth, $h\nu$ is the energy per photon, and P_B is the background power.

The signal power given refers to the power received at the detector due to the fluorescence of oil excited by laser illumination. The background power consists of two kinds: synchronous, i.e., temporally indistinguishable from the signal power, and a DC component.

CW Mode

$P_S = P_{DLOF}$ = Signal Power due to laser illumination

$P_B^S = P_{DLWF}$ = Synchronous Background Power due to laser illumination

$$P_B = P_{DSAB} + P_{DSR} + P_{DSWB} + P_{DSOF} + P_{DSWF} + P_{DKAB} + P_{DKR} + P_{DKWB} + P_{DKOF} + P_{DKWF}$$

= DC Background Power

Note that P_S and P_B^S are indistinguishable. However, in actual flight surveillance it is expected that the system will be constantly receiving a signal from the seawater fluorescence only,

---

*Value obtained at λ_E = 312 nm.

to establish a reference, prior to receiving a signal from the oil slick. Therefore the signal-to-noise ratio for P_B^S establishes a threshold level for detecting an oil slick. Whereas a SNR for P_B^S is for a clear water condition, the SNR for P_S is calculated for an oil-filled field of view. An oil-filled field of view implies an oil film which effectively extinguishes any light returned to the receiver from the sea surface and below. But the following calculation includes all the contributing background signal as if the oil slick were not there.

P_{DLOF}

$$P_{DLOF} = \frac{\epsilon_O \ \epsilon_L \ \epsilon_C \ A_C \ A_T \ e^{-(\gamma^L_{ATM} + \gamma^0_{ATM})R} \ P_L}{R^4 \ \Omega_L \ \Omega_E}$$

$$= \frac{(2.1x10^{-4})(0.5)(0.1)(7.20x10^{-8})(3.6x10^{-7})e^{-(0.24+0.15)0.3} P_L}{(0.3)^4 \ (4x10^{-6})(3.14)}$$

$$\boxed{P_{DLOF} = 2.3x10^{-12} \ P_L}$$

P_{DLWF}

$$P_{DLWF} = \frac{P_L \ \epsilon_L \ \epsilon_C \ \epsilon_W \ A_C \ e^{-(\gamma^L_{ATM} + \gamma^0_{ATM})R} \ (1-\rho in)(1-\rho out)}{4\pi \ R^2 \ (\gamma^L_W + \gamma^W_W)}$$

$$= \frac{(0.5)(0.1)(.23)(7.2x10^{-8})(e^{-(.24+.15)0.3})(1-0.05)(1-0.05) \ P_L}{4(3.14)(.3)^2 \ (210+19)}$$

$$\boxed{P_{DLWF} = 2.6x10^{-12} \ P_L}$$

P_{DSAB}

$$P_{DSAB} = \frac{H_S \, \beta^S_{ATM} \, A_C \, \epsilon_C \, \Omega_{FOV} \, (1-e^{-\gamma^S_{ATM} R})}{\gamma^S_{ATM}}$$

$$= \frac{(4.53x10^{6})(9.43x10^{-3})(7.20x10^{-8})(0.1)(4x10^{-6})(1-e^{-0.15(0.3)})}{0.15}$$

$$\boxed{P_{DSAB} = 3.6x10^{-10} \text{ watts}}$$

P_{DSR}

$$P_{DSR_{\substack{O\\W}}} = \frac{H_S \, A_C \, \epsilon_C \, e^{-\gamma^S_{ATM} R} \left[\rho_O \, A_O \, f_O \, (\theta,\ SS,\ \phi,\ \Omega_{FOV},\ P) + \rho_W \, A_W \, f_W \, (\theta,\ ....?)\right]}{R^2 \, \Omega_E}$$

The term f^O_W is a function of total reflectance which depends on θ - look angle, SS - sea state, ϕ - zenith angle, Ω_{FOV} - field of view and P - polarization. f^O_W is estimated to be 10^{-3} outside of the glitter pattern of the sun. Since the calculation is for either an oil-filled or a water-filled field of view the term with the greater reflectance is used, which is ρ_O. Rewriting

$$P_{DSR} = \frac{H_S \, A_C \, \epsilon_C \, e^{-\gamma^S_{ATM} R} \, (\rho_O \, A_O \, f_O)}{R^2 \, \Omega_E}$$

$$= \frac{(4.53x10^{6})(7.20x10^{-8})(0.1) \, e^{-0.15(0.3)} \, (0.07)(3.6x10^{-7})(10^{-3})}{(0.3)^2 \, (2\pi)}$$

$$\boxed{P_{DSR} = 1.3x10^{-12} \text{ watts}}$$

P_{DSWB}

$$P_{DSWB} = \frac{H_S\, \beta_W^S\, A_C\, \epsilon_C\, \Omega_{FOV}(1-\rho_W^{in})(1-\rho_W^{out})\,e^{-\gamma_{ATM}^S R}}{(1 + \frac{\cos\theta}{\cos\phi})\gamma_W^S}$$

$$= \frac{(4.53\text{x}10^{6})(0.8)(7.2\text{x}10^{-8})(0.1)(4\text{x}10^{-6})(1-0.05)(1-0.05)\,e^{-0.15(0.3)}}{(1 + 1)(19)}$$

$$\boxed{P_{DSWB} = 6.0\text{x}10^{-10} \text{ watts}}$$

P_{DSOF}

$$P_{DSOF} = \frac{H_S^\lambda\, \epsilon_C\, A_C\, A_T\, \epsilon_o^\lambda\, e^{-\gamma_{ATM}^0 R}}{R^2\, \Omega_E}$$

$$= \frac{(10^{8})(0.1)(7.2\text{x}10^{-8})(3.6\text{x}10^{-7})(2.1\text{x}10^{-4})\,e^{-0.15(0.3)}}{(0.3)^2\;(3.14)}$$

$$\boxed{P_{DSOF} = 1.8\text{x}10^{-10} \text{ watts}}$$

P_{DSWF}

$$P_{DSWF} = \frac{H_S^{\lambda}\ \epsilon_C\ A_C\ \Omega_{FOV}\ \epsilon_W\ (1-\rho in)(1-\rho out)e^{-\gamma^{W}_{ATM}\ R}}{\Omega_E\ (\gamma_W^{\lambda} + \gamma_W^{W})}$$

$$= \frac{(10^{8})(.1)(7.2\text{x}10^{-8})(4\text{x}10^{-6})(.23)(1-0.05)(1-0.05)e^{-0.15(.3)}}{4(3.14)(175 + 19)}$$

$$\boxed{P_{DSWF} = 2.3\text{x}10^{-10} \text{ watts}}$$

P_{DKAB}

$$P_{DKAB} = P_{DSAB} \text{ x } \frac{H_K}{H_S} = 3.6\text{x}10^{-10} \text{ x } \frac{2.16\text{x}10^{-6}}{4.53\text{x}10^{6}}$$

$$\boxed{P_{DKAB} = 1.7\text{x}10^{-10} \text{ watts}}$$

P_{DKR}

$$P_{DKR} = P_{DSR} \text{ x } \frac{H_K}{H_S}\ \frac{f_o^K}{f_o^S} = 1.3\text{x}10^{-12} \text{ x } \frac{2.16\text{x}10^{6}}{4.53\text{x}10^{6}}\ \frac{1}{10^{-3}}$$

$$\boxed{P_{DKR} = 6.2\text{x}10^{-10} \text{ watts}}$$

$\underline{P_{DKWB}}$

$$P_{DKWB} = P_{DSWB} \ x \ \frac{H_K}{H_S} = 6x10^{-10} \ x \ \frac{2.16x10^{6}}{4.53x10^{6}}$$

$$\boxed{P_{DKWB} = 2.9x10^{-10} \ \text{watts}}$$

$\underline{P_{DKOF}}$

$$P_{DKOF} = P_{DSOF} \ x \ \frac{H^{\lambda}_K}{H^{\lambda}_S} = 1.8x10^{-10} \ x \ \frac{0.5x10^{8}}{10^{8}}$$

$$\boxed{P_{DKOF} = 0.9x10^{-10} \ \text{watts}}$$

$\underline{P_{DKWF}}$

$$P_{DKWF} = P_{DSWF} \ x \ \frac{H^{\lambda}_K}{H^{\lambda}_S} = 2.34x10^{-10} \ x \ \frac{0.5x10^{8}}{10^{8}}$$

$$\boxed{P_{DKWF} = 1.2x10^{-10} \ \text{watts}}$$

then the signal power due to laser illumination is:

$$\boxed{P_S = P_{DLOF} = 2.3\text{x}10^{-12}\ P_L}$$

the synchronous background

$$\boxed{P_B^S = P_{DLWF} = 2.6\text{x}10^{-12}\ P_L}$$

and the DC background power is:

$$P_B = P_{DSAB} + P_{DSR} + P_{DSWB} + P_{DSOF} + P_{DSWF} + P_{DKAB} + P_{DKR} + P_{DKWB} + P_{DKOF} + P_{DKWF}$$

$$= (3.6 + 1.3\text{x}10^{-2} + 6.0 + 1.8 + 2.3 + 1.7 + 6.2 + 2.9 + 0.9 + 1.2)\text{x}10^{-10} \text{ watts}$$

$$= 2.8\text{x}10^{-9} \text{ watts}$$

Signal to Noise Power Ratio - CW Mode

$$S/N = \eta P_S^2/2Bh\nu P_B$$

η	Photodetector quantum efficiency	0.16
B	Post detection bandwidth	100.0 Hz
h	Planck's Constant	6.625×10^{-34} watt-$\sec^2$
ν	Optical fluorescent emission frequency (4500 Å)	6.7×10^{14} Hz

$$S/N = 0.16(2.3 \times 10^{-12} P_L)^2/2(10^2)(6.6 \times 10^{-34})(6.7 \times 10^{14})(2.8 \times 10^{-9})$$

$$\boxed{S/N = 3.5\, P_L^2}$$

Peak Pulsed Mode

The signal power as given here is the peak power received at the detector due to the fluorescence of the oil, excited by laser illumination. As in the CW mode the background is composed of a synchronous (pulsed), and a dc background.

$P_S = P^{PK}_{DLOF}$ = Peak signal power due to pulsed laser illumination.

$P^S_B = P^{PK}_{DLWF}$ = Peak synchronous background power due to pulsed laser illumination.

P_B = Same as CW = DC background power.

P^{PK}_{DLOF}

$$P^{PK}_{DLOF} = P_{DLOF} \frac{P^{PK}_{L}}{P_{L}} \frac{t_L}{\sqrt{t_L^2 + t_{OF}^2 + t_{SS}^2}}$$

where t_L - Laser output pulsewidth; t_{OF} - 0.1 fluorescence half-life; and t_{SS} - transit time through wave profile for a given sea state. Assume the following: $t_{OF} = 2\ t_L$ and $t_{SS} = 0$. Then

$$P^{PK}_{DLOF} = \frac{2.3\text{x}10^{-12}\ P^{PK}_{L}}{\sqrt{5}}$$

$$\boxed{P^{PK}_{DLOF} = 1.03\text{x}10^{-12}\ P^{PK}_{L}}$$

P^{PK}_{DLWF}

$$P^{PK}_{DLWF} = P_{DLWF} \frac{P^{PK}_{L}}{P_{L}} (\gamma^{L}_{W} + \gamma^{W}_{W})\ ct_L$$

$$= 2.6\text{x}10^{-12}\ P^{PK}_{L}\ (229)(3\text{x}10^{5})t_L$$

$$\boxed{P^{PK}_{DLWF} = 1.8\text{x}10^{-4}\ P^{PK}_{L}\ t_L}$$

The peak signal power due to laser illumination is:

$$\boxed{P_S = P^{PK}_{DLOF} = 1.03\text{x}10^{-12}\ P^{PK}_L}$$

the synchronous peak background power is:

$$\boxed{P^S_B = P^{PK}_{DLWF} = 1.8\text{x}10^{-4}\ P^{PK}_L\ t_L}$$

and the DC background is the same as the CW mode

$$\boxed{P_B = 2.8\text{x}10^{-9}\ \text{watts}}$$

Signal to Noise Power Ratio - Peak Pulsed Mode

$$S/N = \eta P^2_S / 2Bh\nu P_B$$

η - Photodetector quantum efficiency = 0.16

B - Post-detection bandwidth = $5\text{x}10^{8}$ Hz

h - Planck's Constant = $6.6\text{x}10^{-34}$ watt-sec^2

ν - Optical fluorescent emission frequency (4500 Å) = $6.7\text{x}10^{14}$ Hz

$$S/N = 0.16(1.03\text{x}10^{-12} P_L^{PK})^2 / 2(5\text{x}10^8)(6.6\text{x}10^{-34})(6.7\text{x}10^{14})$$

$$(2.8\text{x}10^{-9})$$

$$\boxed{S/N = 1.4\text{x}10^{-7} (P_L^{PK})^2}$$

Average Pulsed Mode

The signal power given below is the peak power received at the detector at a fixed repetition rate, also due to the fluorescence of the oil slick, excited by the laser transmitter. As in the previous modes the background power is a combination of a synchronous and a dc component.

$P_S = P_{DLOF}^{AV}$ = Average signal power due to continuously pulsed laser illumination

$P_B^S = P_{DLWF}^{AV}$ = Average synchronous background power due to continuously pulsed laser illumination.

P_B = Same as CW = DC background power.

P_{DLOF}^{AV}

$$P_{DLOF}^{AV} = P_{DLOF}^{PK} \cdot r_g \cdot t_L$$

$$\boxed{P^{AV}_{DLOF} = 1.03\text{x}10^{-12}\; P^{PK}_{L}\; r_g\; t_L}$$

$\underline{P^{AV}_{DLWF}}$

$$P^{AV}_{DLWF} = P^{PK}_{DLWF} \sqrt{t_L^2 + t_{OF}^2 + t_U^2 + t_{SS}^2 \;\; r_g}$$

Where t_U - aircraft's altitude uncertainty

Assume $t_{OF} = 2t_L$ and $t_{SS} = t_U = 0$ then

$$= P^{PK}_{DLWF}\; t_L \sqrt{5\; r_g}$$

$$\boxed{P^{AV}_{DLWF} = 4.0\text{x}10^{-4}\; t_L^2\; r_g\; P^{PK}_{L}}$$

The average signal power due to laser illumination is:

$$\boxed{P_S = P^{AV}_{DLOF} = 1.03\text{x}10^{-12}\; t_L\; r_g\; P^{PK}_{L}}$$

the synchronous average background power is:

$$\boxed{P^{S}_{B} = P^{AV}_{DLWF} = 4.0\text{x}10^{-4}\; t_L^2\; r_g\; P^{PK}_{L}}$$

and the dc background is the same as the cw mode.

$$\boxed{P_B = 2.8\text{x}10^{-9} \text{ watts}}$$

Signal to Noise Power Ratio - Average Pulsed Mode

$$S/N = \eta P_S^2/2Bh\nu P_B$$

η - Photodetector quantum efficiency	0.16
B - Post-detection bandwidth	$5\text{x}10^{8}$ Hz
h - Planck's Constant	$6.6\text{x}10^{-34}$ watt-sec^2
ν - Optical fluorescent emission frequency (4500 Å)	$6.7\text{x}10^{14}$ Hz

$$S/N = \frac{0.16(1.03\text{x}10^{-12})^2 t_L^2 r_g^2 (P_L^{PK})^2}{2(5\text{x}10^{8})(6.6\text{x}10^{-34})(6.7\text{x}10^{14})(2.8\text{x}10^{-9})}$$

$$\boxed{S/N = 1.4\text{x}10^{-7} (P_L^{PK})^2 t_L^2 r_g^2}$$

The choice of mode of operation, i.e., cw, pulsed peak or pulsed average will depend on many factors such as weight, size, power input, scan pattern, false alarm rate, availability of off-shelf components, etc., as well as signal to noise ratio. However, on the basis of signal to noise ratio alone, the detection and identification of some crude oils (depending on their individual fluorescent coefficient) can be made with presently available off-the-shelf lasers and receiver components.

Table 5-2 shows the spot size, and signal-to-noise ratio for various altitudes, assuming in all cases a pulsed N_2 laser transmitter - receiver system with a 100 kilowatts peak power output pulse and a collimated beam with 2.0 milliradian divergence. A pulsed nitrogen laser with a peak power output of 100 kilowatts is presently available, off-shelf, from several vendors.

All other parameters are the same as given in Table 5-1.

TABLE 5.2 S/N AND SPOT DIAMETER FOR VARIOUS AIRCRAFT ALTITUDES

ALTITUDE (ft)	SPOT DIAMETER (ft)	S/N (db)
500	1.13	38.3
1,000	2.26	35.5
2,500	5.65	17.7
5,000	11.30	2.3
7,500	16.95	- 7.4
10,000	22.60	-15.3

5.2.3 Eye Safety Considerations

The potential hazard of a laser stems from its inherent brightness. Should the average power density (or, in the case of a pulse, the pulse energy) falling on the eye be excessive, it can cause tissue damage.

The particular concern here is with pulsed nitrogen lasers, with durations of ten nanoseconds. For Q-switched pulses, the value given (Surgeon General's Report) is 10^{-7} Joules/cm^2. The same number appears in the appendix of the recently published regulations of the Massachusetts Department of Public Health.[21] A comprehensive treatment of laser eye hazards is presented in reference 22.

Also, the Air Force has issued a report[23] which differentiates between ruby and Nd laser radiation. The limits quoted therein for Q-switched pulse energy <u>into</u> the eye are $\sim 10^{-6}$(6943Å) and 45×10^{-6}(1.06μ). Taking a fully-opened iris of 8mm, the <u>corneal</u> energy density limits are then 2×10^{-6}J/cm^2(6943Å) and 90×10^{-6}J/cm^2(1.06μ). These numbers are respectively one and two orders of magnitude larger than those of the Surgeon-General report.

The nitrogen laser has unique properties with respect to the eye. The ocular fluid and/or lens absorb its wavelength strongly.

The transmission of the eye[24] to 3371Å is about 1% of the transmission at 6943Å. However, we know of no published safety values for the nitrogen laser.

The numbers which we use in this report for safe energy densities at the cornea are

	Energy Density	Peak Power Density	Pulse-width
Nitrogen(3371Å)	10^{-5} J/cm^2	1000 W/cm^2	10 nsec.

For the oil detection system, the peak laser intensity I_L on the water surface will be: (neglecting atmospheric attenuation)

$$I_L = \frac{P_L}{\Omega_L R^2}$$

where P_L is the laser power (watts), Ω_L is the solid angle divergence of the laser, and R is the distance of the laser from the water (cm). For $I_L = 10^3$ watt/cm^2, R = $3\text{x}10^4$ cm (1000 ft) $\Omega_L = 4\text{x}10^{-6}$ steriadian.

The limiting eye-safe laser power is

$$P_L = 3.6\text{x}10^6 \text{ watts}$$

5.3 FIELD PARAMETER MEASUREMENTS

5.3.1 Introduction

Field experiments were undertaken to:

a. Verify estimates of laser-excited oil fluorescence signal versus background.

b. Verify methods for remote identification and quantification.

c. Field-test components similar to those that would be used in an airborne remote sensing system.

5.3.2 Instrumentation and Field Site

The remote sensor was assembled at TSC and is shown in Figures 5.1 and 5.2. The box at the top of Figure 5.1 contains the pulsed nitrogen laser transmitter designed and built at TSC. Beneath the laser is the telescope receiver, with its photomultiplier detector at left. The top shelf of the accessory cart holds the laser monitor control, the high-voltage supply for the photomultiplier, and an electrometer to measure the total photomultiplier anode current due to daylight background. The lower shelf of the cart holds the nitrogen gas, vacuum pump, and high-voltage supply used to operate the laser. Figure 5.2 shows the interior of the laser, which is also diagrammed in Figure 4-9.

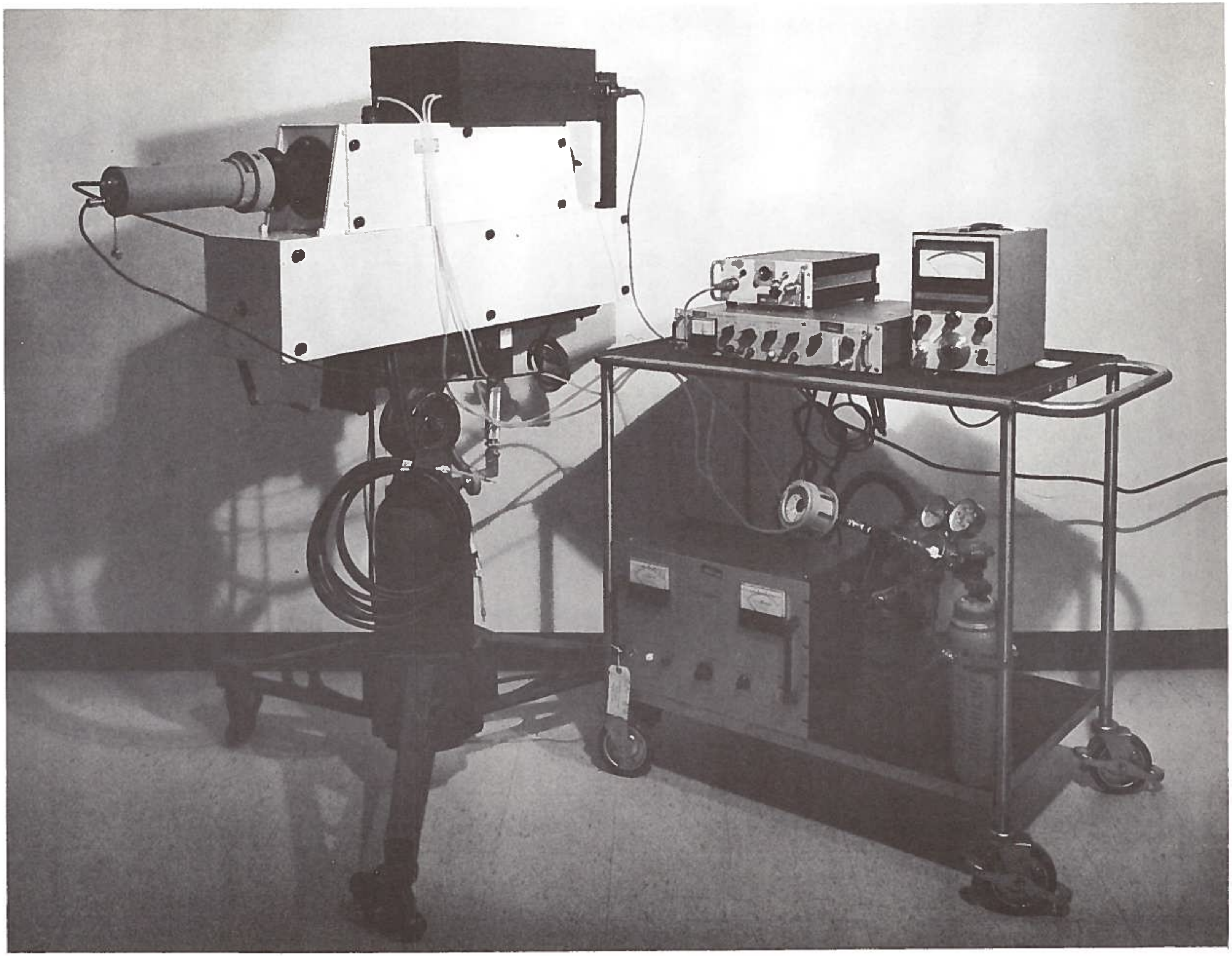

Figure 5.1 - Remote Sensor

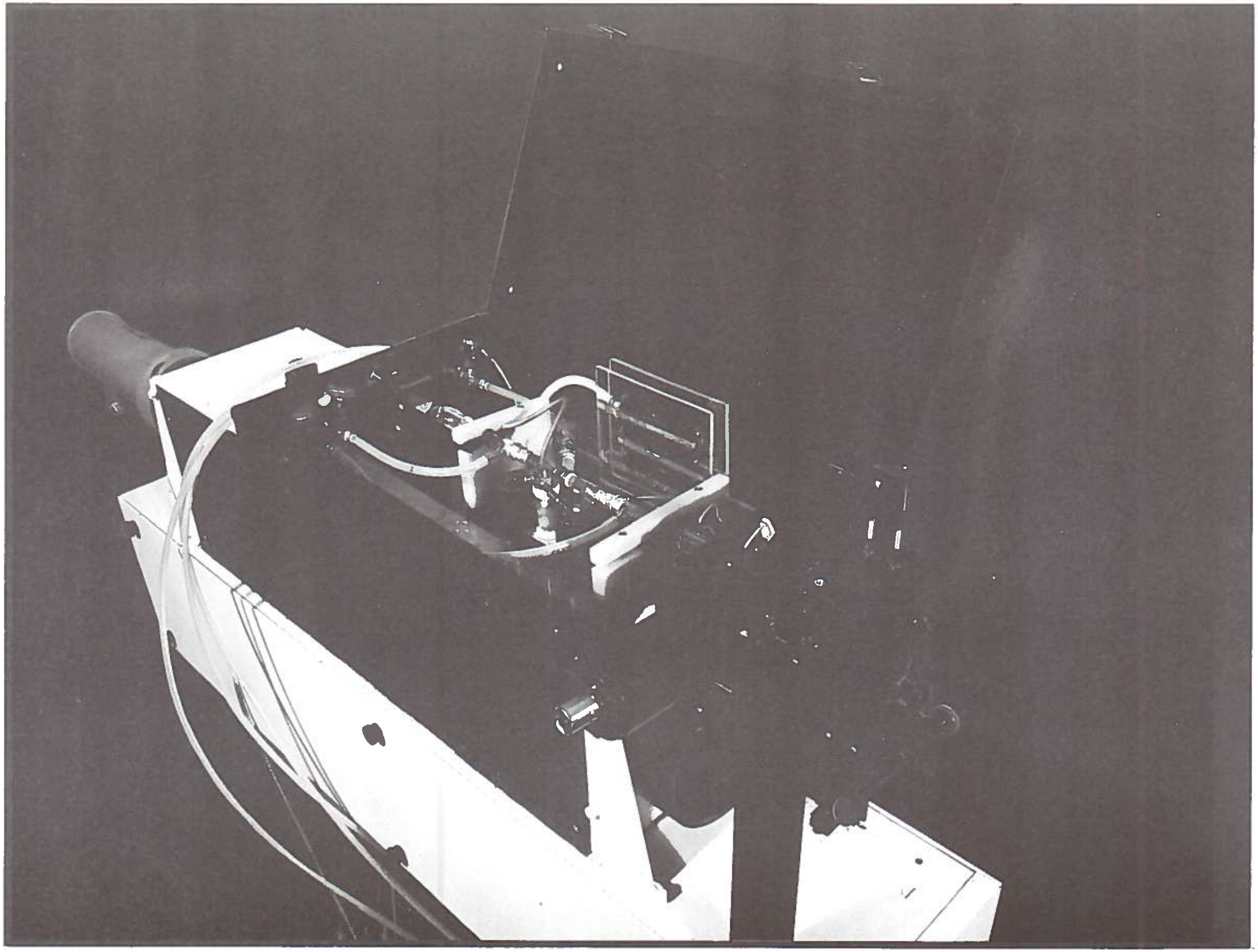

Figure 5.2 - Laser Transmitter

The photomultiplier is an EMI 9558 with S-20 photocathode, chosen because a weatherproof housing was available for it in-house. It differs in spectral and temporal response from the C31025C tube used in Sections 4.1 & 4.2 and the 1P28 tube used in Section 4.3.

The sensor was installed in the dock house at the USCG Station in Point Allerton, Hull, Massachusetts, which is shown in Figure 5.3.

Figure 5.4 shows the location of the sensor, which is just inside the left window of Figure 5.5. A mirror is mounted at dockside (top left of Figure 5.5) to direct the sensor field-of-view to the water surface. An oil-slick retainer, consisting of a rubber inner tube supporting a stiff polyethylene cylinder, floats on the water below the mirror. In Figure 5.6, an oscilloscope, the sensor, and the accessory cart are shown in the foreground. Outside the window, the reflection of part of the inner tube can be seen in the mirror.

5.3.3 Field Results

Figure 5.7 illustrates our ability to distinguish oil from seawater on the basis of intensity alone. Oil sample C5 is a light crude oil of typical fluorescent efficiency, used for the signal-to-noise estimates of Section 6.

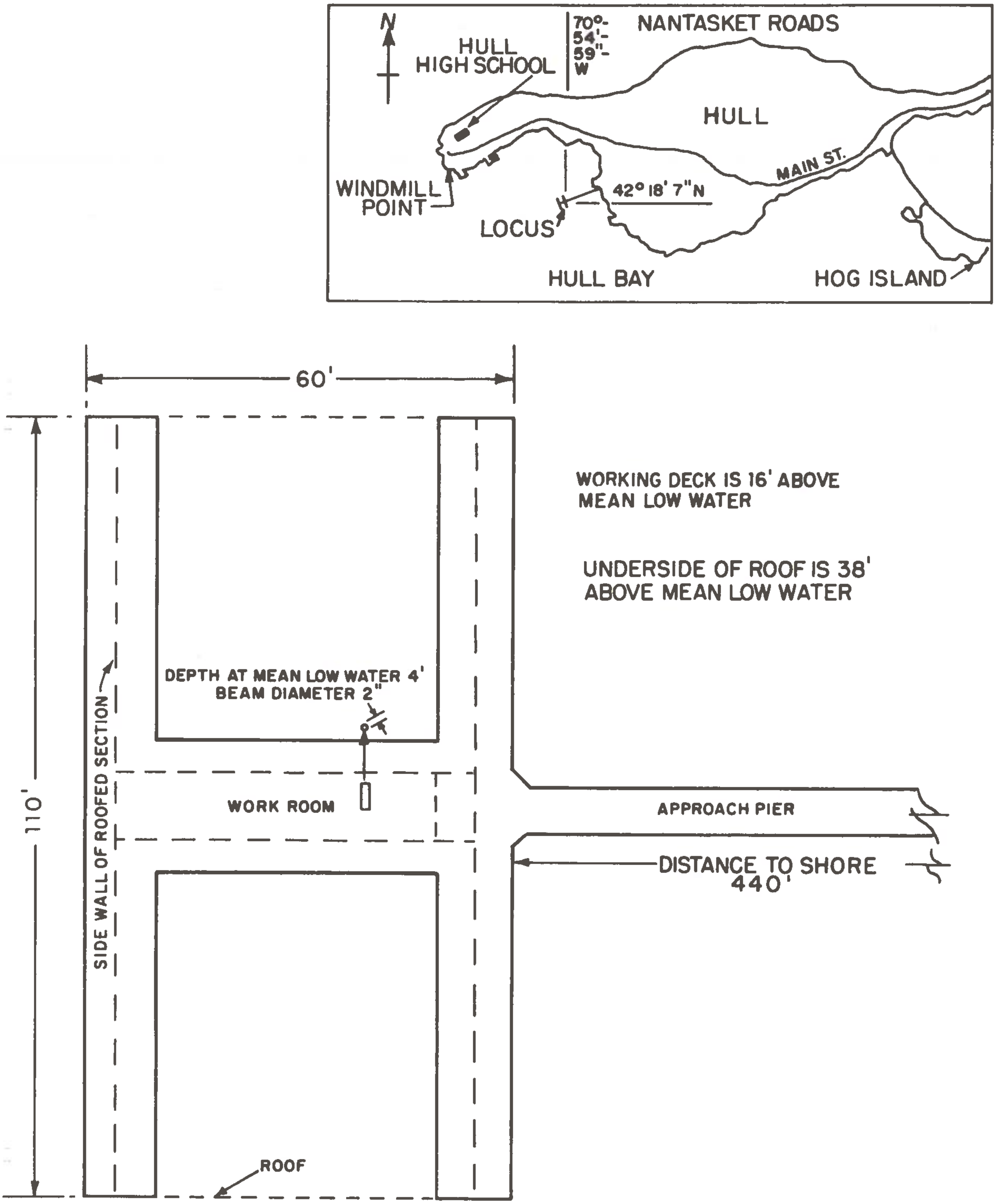

Figure 5.3 - Location and Plan of Dockhouse USCG Station,
Pt. Allerton, Hull, Mass.

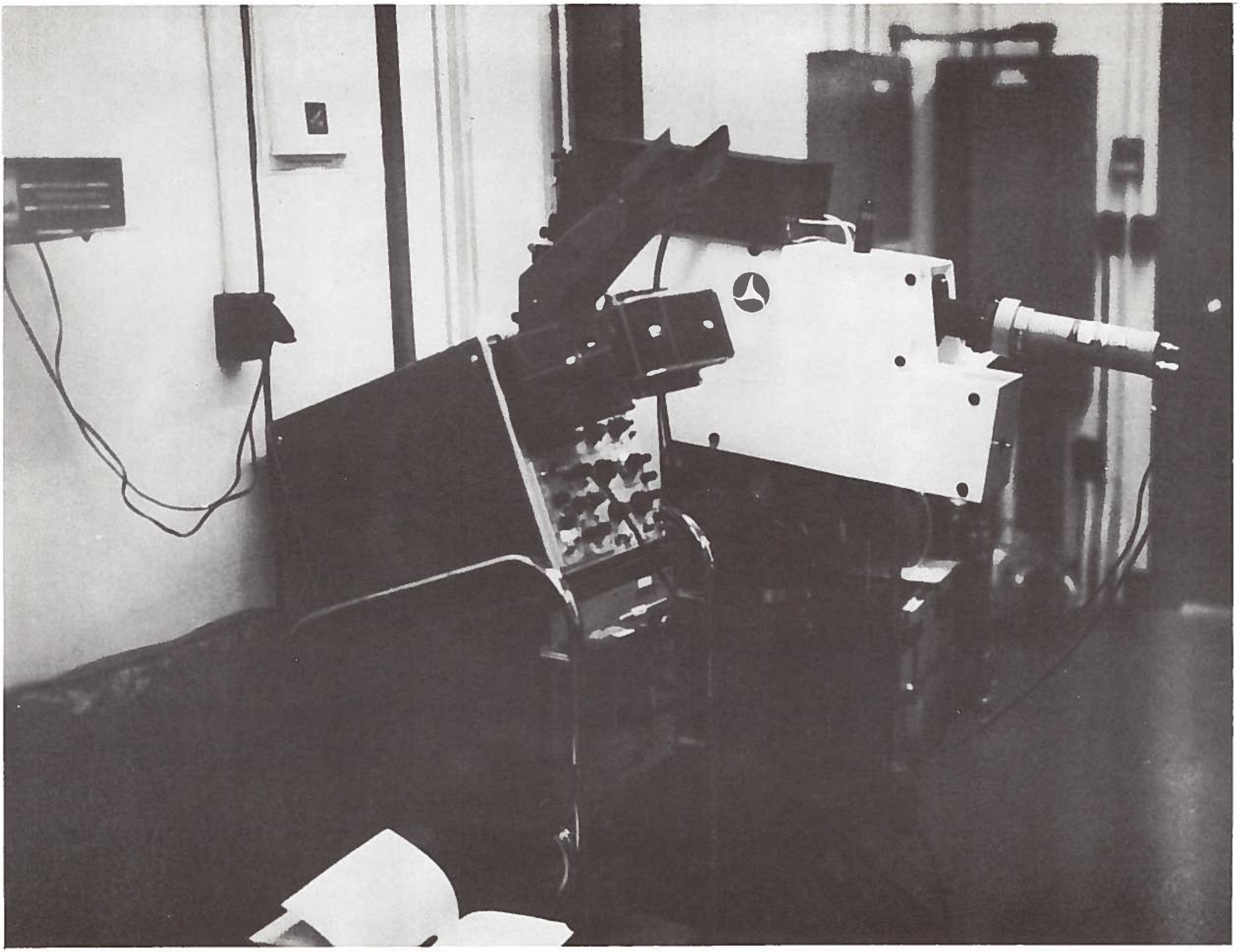

Figure 5.4 - Remote Sensor Configuration at Pt. Allerton (Side View)

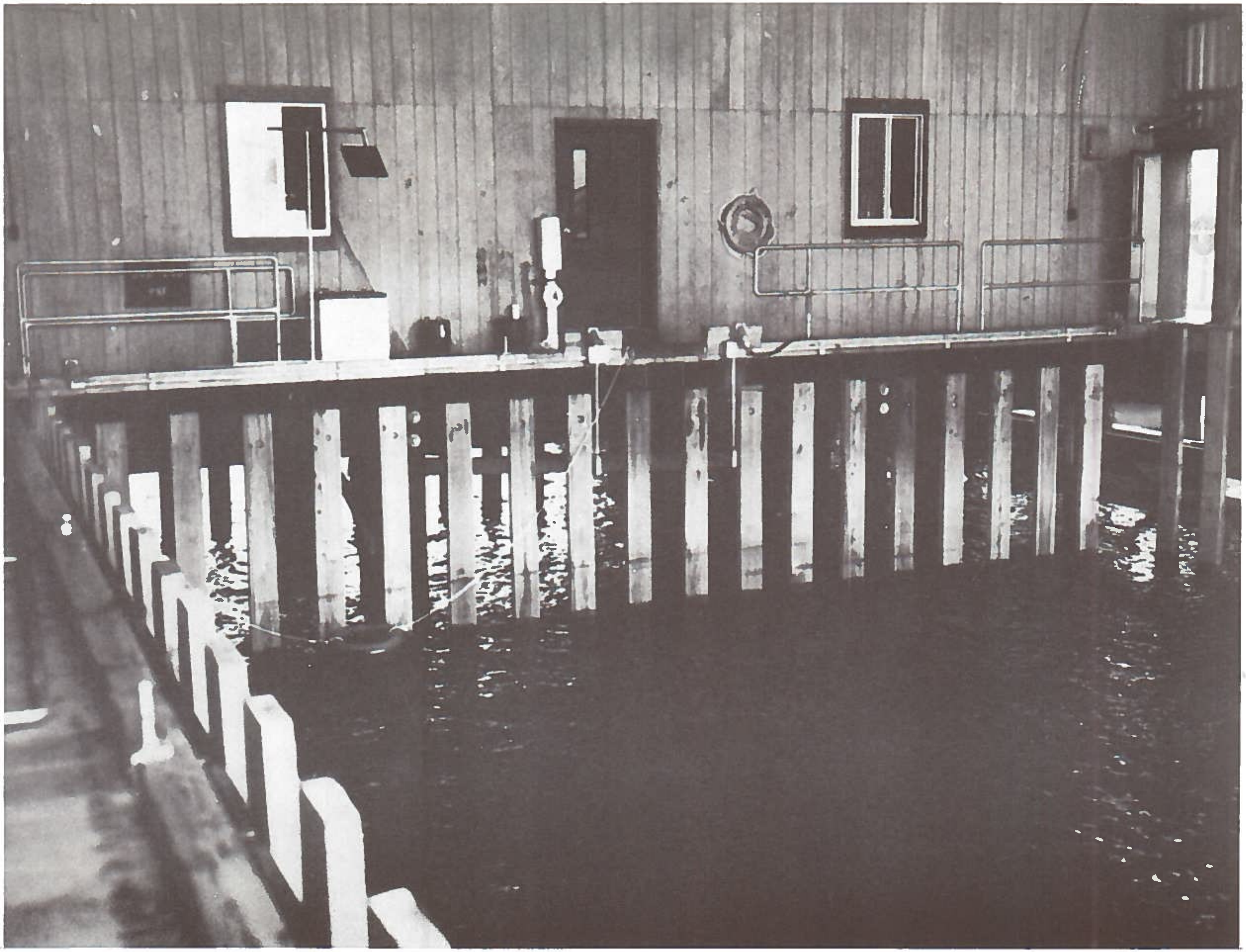

Figure 5.5 - Dockside View at Pt. Allerton

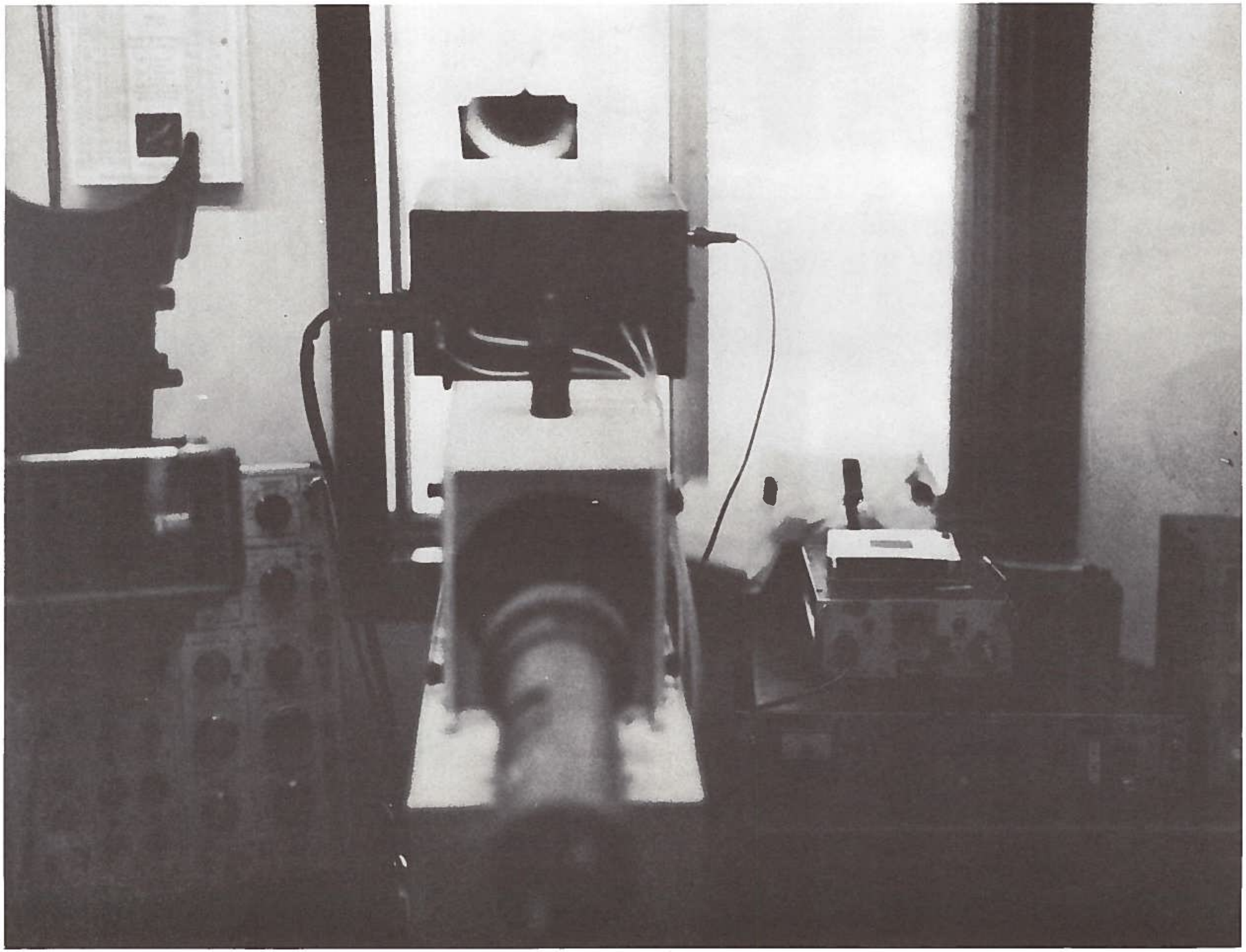

Figure 5.6 - Oil Spill Target. (Shown reflected by head-on mirror.)

FIELD EXPERIMENT, PT. ALLERTON USCG STATION, 11 MAY 1971

SEAWATER

OIL (SAMPLE C5)

HORIZONTAL SCALE : 50 NANOSECONDS PER DIVISION
UPPER TRACE : NITROGEN LASER OUTPUT (700 W PEAK)
LOWER TRACE : FLUORESCENCE SIGNAL DETECTED BY EMI 9558 PHOTOMULTIPLIER. 1200 V BIAS; DC BACKGROUND LEVEL 4 X 10^{-5}A; CORNING 3-74 UV REJECTION FILTER; 30 NM BANDPASS FILTER CENTERED AT 433 NM. CLEAR SKY, ABOUT 1:00 P.M.

Figure 5.7 - Fluorescent Signal Return of Target Oil and Seawater Background

Similar data were taken on several oils, using narrow-band filters at 433 nm and 533 nm. The ratio of fluorescent emission at these two wavelengths enabled us to distinguish between the oils. The observed ratios did not agree with our expectations; with sea agitation, the polyethylene retaining wall appeared to adsorb the heavier fractions of each oil, leaving a film with altered emission spectrum on the water.

Figure 5.8 shows our ability to detect an oil film 0.2 micrometers thick with the above arrangement.

5.3.4 Supplemental Results

With the benefit of field experience, additional measurements with the same remote sensor were made in the laboratory at TSC.

The ratio of emission at 433 nm to that at 533 nm was measured for thick oil samples on seawater (results shown in Table 5.3). Such a ratio is the simplest form of spectral comparison that can be made, yet it clearly enables us to discriminate between the oils. More information could be obtained by using more than two spectral channels.

The ratios for the lightest oils (C9 and D1) decreased measurably within one hour after each oil was spread on the water. This corresponds to a shift of the emission to longer wavelength, which would be expected after evaporation of the lighter components of each oil.

SEAWATER

ONE DROP SAMPLE B7
ON 2200 cm^2 AREA
=0.2 MICROMETER OIL FILM

HORIZONTAL SCALE: 20 NANOSECONDS PER DIVISION
UPPER TRACE: NITROGEN LASER OUTPUT (700 W PEAK)
LOWER TRACE: FLUORESCENCE SIGNAL DETECTED BY EMI 9558 PHOTOMULTIPLIER.
1100 V BIAS: CORNING 3-74 UV REJECTION FILTER; 30 NM BANDPASS FILTER
CENTERED AT 433 NM.

Figure 5.8 - Fluorescent Signal Return of 0.2 Micrometers Thick Film and Seawater Background

TABLE 5.3 REMOTE IDENTIFICATION OF OILS BY TWO-WAVELENGTH RATIO TECHNIQUE

Ratio of signal at 433 nm to signal at 533 nm, measured with the remote sensor described in the text. The oils are described in Appendix .

TSC OIL SAMPLE	Ratio	API Gravity
B2	0.7	12.8
C5	1.1	27.1
B7	1.4	30.3
C9	1.7	42.3
D1	5.4	46.3

Fluorescence versus film thickness is graphed in Figure 5.9 for a typical crude oil. The upper signal limit is taken from measurements on this oil, and would differ for other oils, depending on their extinction coefficients.

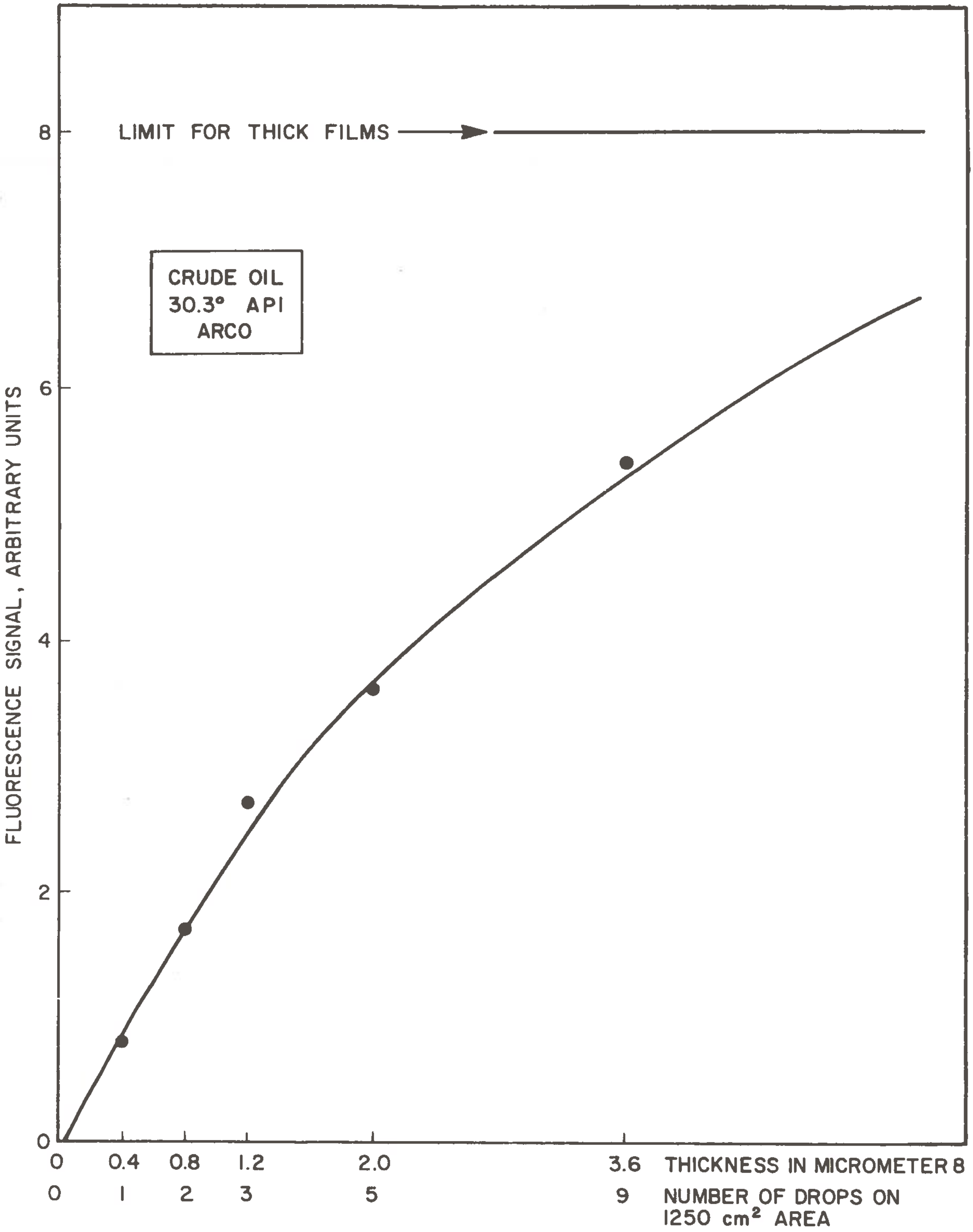

Figure 5.9 - Fluorescence vs. Film Thickness

SECTION 6

FEASIBILITY OF A LASER EXCITED OIL FLUORESCENCE TECHNIQUE FOR THE REMOTE SENSING OF OIL SPILLS

6.1 DETECTION FEASIBILITY

The theoretical analysis of section 5.2, on signal-to-noise considerations for detecting oil spills using the phenomenon of oil fluorescence, indicates that detection is possible.

To confirm theoretical expectations, field measurements were conducted at a USCG station in Hull, Mass. The results of these measurements, see section 5.3, clearly show that oil spill detection can be made, in an ocean environment.

It is now necessary to determine the limits of detection using the fluorescence technique. This can only be done by constructing a flight-qualified prototype and measuring the system performance.

6.2 CLASSIFICATION FEASIBILITY

Perhaps the most important result of our investigation is the discovery that this technique can be used to identify the oil slick as to its type. Four features have been measured and analyzed both in the laboratory and in the field. Separately they can be used for identification or when combined and correlated a more certain identification can be made. (Note the correlation parameters are not limited to those we have measured.) The following correlation parameters have been measured: Fluorescent Emission Spectrum, Fluorescent Power Conversion Coefficient, API Gravity and Fluorescent Lifetime. The values measured are shown together in Table 6.1. Figure 6.1 is a graphical illustration of the individual spectral signatures of all the oil samples measured. Figure 6.2 is a semi-logarithmic plot of the measured fluorescent coefficients of the oil samples versus their peak emission wavelengths. The trend is for the oil samples with shorter wavelength peaks to have a higher fluorescent coefficient. Figure 6.3 is a plot of API gravity versus peak emission wavelength for each sample. Here the trend is for those samples lower in API gravity to emit at a longer wavelength. Figure 6.4 is a plot of fluorescent lifetime versus the peak emission wavelength of each oil sample. The trend is not linear but the lifetime decreases with longer wavelengths, becoming shorter than the pulse width of the laser beyond 500 nanometers. When all of these parameters are correlated, a comprehensive pattern emerges. For heavy oils such as A1, A4, and D4, we expect their peak emission wavelength to be toward the longwave end of the spectrum; also, they should have a low fluorescent power conversion coefficient, and finally, their lifetime will be short. Likewise, for the medium weight oils and light weight oils, the tendencies are in the opposite direction. We can conclude from this work that this technique can be used to classify oil.

6.3 QUANTIFICATION FEASIBILITY

To determine the amount of oil in a given oil spill, it is necessary to know the total area and thickness of the oil slick. To measure the area of the spill, the received signal would be monitored along with spatial information, to produce a contour map. Thickness of the oil slick is measurable by this technique, up to a maximum value which is different for each oil type. The maximum value is related inversely to the extinction coefficient at the excitation and emission wavelengths. This extinction is high for crude oils and heavy refined oils, limiting the quantifying measurements to the range below 10 micrometers thickness. An example is shown in Figure 5.9.

TABLE 6.1 - CORRELATION PARAMETERS

TSC OIL SAMPLE	°API GRAVITY	FLUORESCENT EMISSION λM (nanometer)	FLUORESCENT COEFFICIENT ε_o	FLUORESCENT LIFETIME t (nanosec)
A3	-1.7	597	2.31×10^{-4}	10
D4	5.7	565	1.84×10^{-5}	9
A4	7.2	553	7.77×10^{-6}	9
A1	8.7	545	1.38×10^{-5}	9
B1	9.9	495	7.66×10^{-6}	9
A2	10.0	505	1.09×10^{-5}	9
D2	10.2	514	6.48×10^{-5}	10
B2	12.8	530	8.09×10^{-5}	10
B3	15.5	530	5.77×10^{-5}	10
B8	17.4	505	4.76×10^{-5}	9
D3	19.0	490	2.98×10^{-5}	10
B4	19.2	495	4.18×10^{-5}	9
B5	25.0	459	1.28×10^{-3}	19
C5	27.1	472	5.72×10^{-4}	11
B7	30.3	458	6.74×10^{-4}	16
C7	31.0	480	6.72×10^{-4}	12
C1	31.3	481	8.97×10^{-5}	10
B6	32.6	502	9.38×10^{-5}	10
C2	33.9	490	2.67×10^{-4}	10
C11	34.6	480	1.53×10^{-4}	10
C3	39.0	480	6.04×10^{-4}	13
C8	39.9	474	4.62×10^{-4}	12
C12	40.6	450	4.77×10^{-4}	17
C13	40.6	470	2.50×10^{-4}	11
C9	42.3	446	7.32×10^{-4}	15
C6	42.5	459	8.40×10^{-4}	13
C4	43.7	487	1.62×10^{-4}	11
D1	46.3	406	2.28×10^{-3}	21
C10	46.5	456	5.14×10^{-4}	12

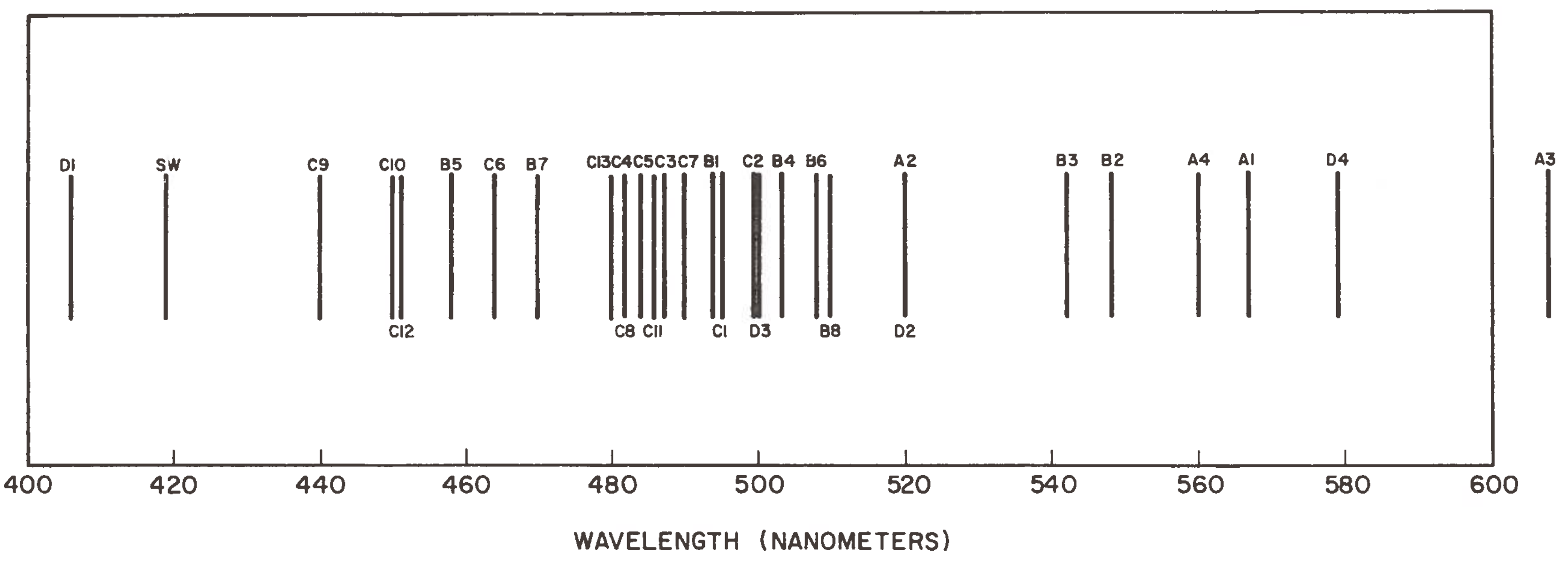

Figure 6.1 - Peak Fluorescent Emission Wavelength of Oil Samples

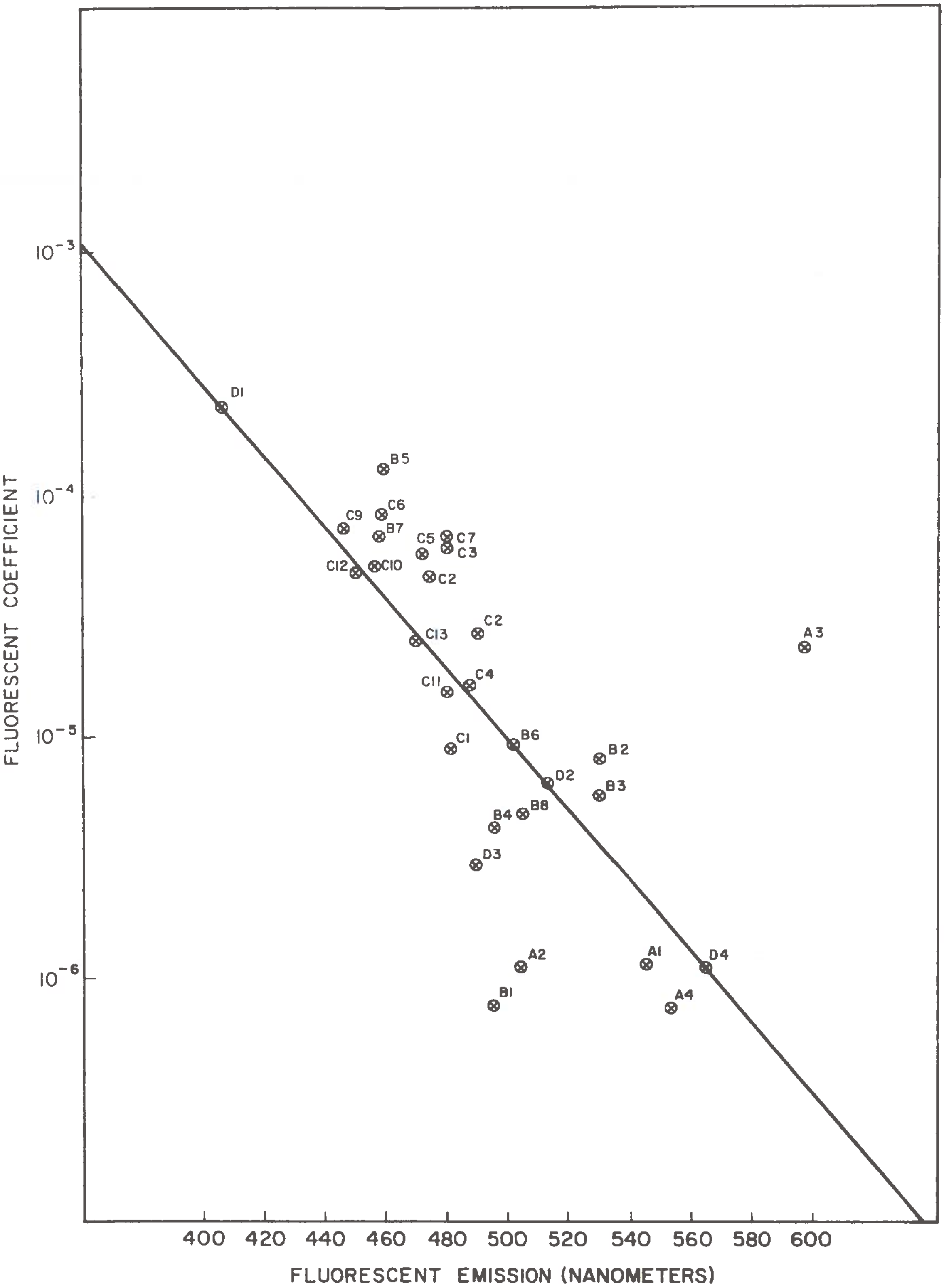

Figure 6.2 - Peak Fluorescent Emission Wavelength Versus Fluorescent Coefficients

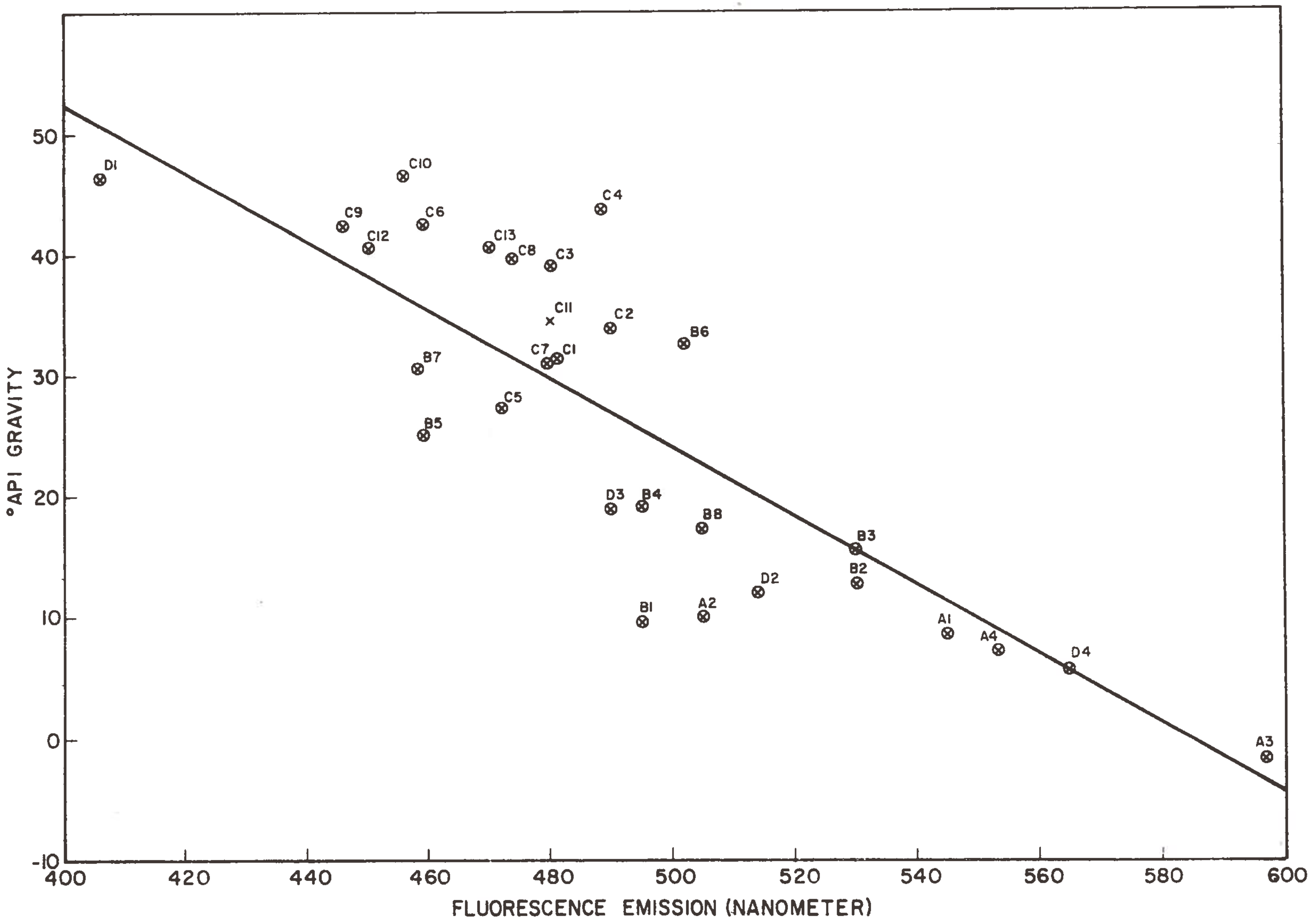

Figure 6.3 - Peak Fluorescent Emission Wavelength versus ^{O}API Gravity

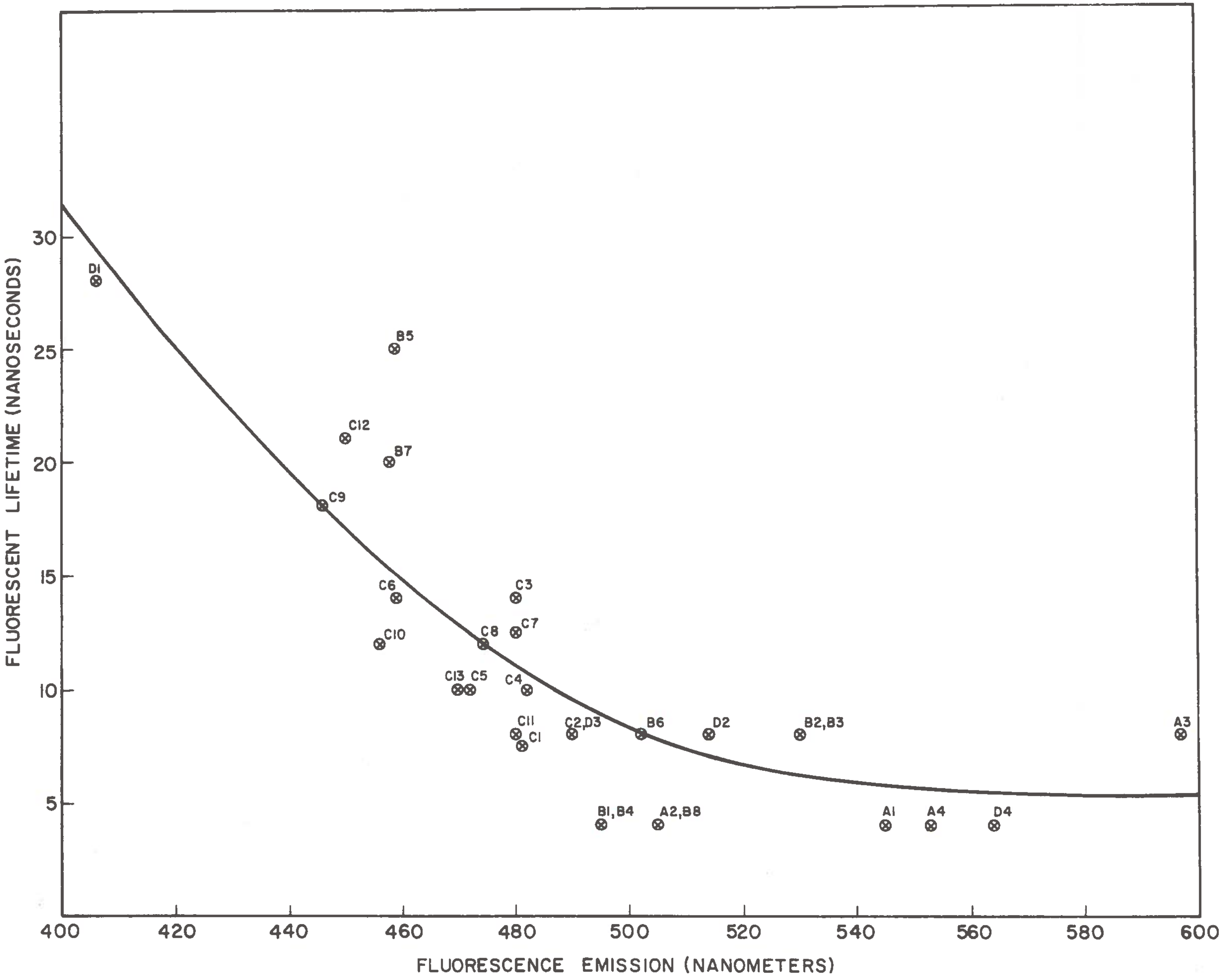

Figure 6.4 - Peak Fluorescent Emission Wavelength versus Fluorescent Lifetime

SECTION 7

RECOMMENDATIONS

The technical feasibility of the remote sensing, i.e., detecting, identifying and mapping oil spills by laser excited fluorescence has been established. A two part program is recommended for further development of this technique.

Part I

A flyable system can be built and used to measure actual oil spills at sea.

Part II

Positive identification of oil types can be greatly improved by additional measurements of oil sample parameters, such as: extinction coefficient, API gravity, fluorescent coefficient, fluorescent emission, and fluorescent lifetime, after the samples have been subjected to the ocean environment for a prolonged period.

SECTION 8

APPENDIX

8.1 DEFINITIONS AND CONVERSION TABLE[25]

API GRAVITY: An empirical scale for measuring the density of liquid petroleum products, the unit being called the "degree API."

ASH: Inorganic residue remaining after ignition of combustible substances determined by definite prescribed methods.

ASPHALTS: Black, solid or semisolid bitumens which occur in nature or are obtained as residues during petroleum refining.

BILGE OIL: Waste oil which accumulates, usually in small quantities, in the lower spaces in a ship, just inside the shell plating. Usually mixed with larger quantities of water.

BLOWOUT: A sudden violent escape of gas and oil from an oil well when high pressure gas is encountered and preventive measures have failed.

BOILING POINT: The temperature at which the vapor pressure of a liquid is equal to the pressure of the atmosphere.

BUNKER "C" OIL: A general term used to indicate a heavy viscous fuel oil.

BUNKER FUEL: A general term for heavy oils used as fuel on ships and in industry. It often refers to No. 5 and 6 fuel oils.

BUNKERING: The process of fueling a ship.

COKER FEED (OR FUEL): A special fuel oil used in a coker furnace, one of the operating elements of a refinery.

CRUDE OIL: Petroleum as it is extracted from the earth. There may be several thousands of difference substances in crude oil some of which evaporate quickly, while others persist indefinitely. The physical characteristics of crude oils may vary widely. Crude oils are often identified in trade jargon by their regions of origin. This identification may not relate to the apparent physical characteristics of the oil. Commercial gasoline, kerosene, heating oils, diesel oils, lubricating oils, waxes and asphalts are all obtained by refining crude oil.

DEMULSIBILITY: The resistance of an oil to emulsification, or the ability of an oil to separate from any water with which it is mixed. The better the demulsibility rating, the more quickly the oil separates from water.

DENSITY: Density is the term meaning the mass of a unit volume. Its numerical expression varies with the units selected.

DISCHARGE: Includes, but is not limited to, any spilling, leaking, pumping, pouring, emitting, emptying or dumping.

EMULSION: A mechanical mixture of two liquids which do not naturally mix as oil and water. Water-in-oil emulsions have the water as the internal phase and oil as the external. Oil-on-water emulsions have water as the external phase and the internal phase is, oil.

FIRE POINT: The lowest temperature at which an oil vaporizes rapidly enough to burn for at least 5 seconds after ignition, under standard conditions.

FLASH POINT: The lowest temperature at which an oil gives off sufficient vapor to form a mixture which will ignite, under standard conditions.

FRACTION: Refinery term for a product of fractional distillation having a restricted boiling range.

FUEL OIL GRADE: Numerical ratings ranging from 1 to 6. The lower the grade number, the thinner the oil is and the more easily it evaporates. A high number indicates a relatively thick, heavy oil. No. 1 and 2 fuel oils are usually used in domestic heaters, and the others are used by industry and ships. No. 5 and 6 oils are solids which must be liquified by heating. Kerosene, coal oil, and range oil are all No. 1 oil. No. 3 fuel oil is no longer used as a standard term.

HAZARDOUS SUBSTANCE: An element or compound, other than oil as defined, which when discharged in any quantity into or upon the navigable waters of the United States or adjoining shorelines or the waters of the contiguous zone, presents an imminent and substantial danger to the public health or welfare, including, but not limited to, fish, shellfish, wildlife, shorelines and beaches.

INNAGE: Space occupied in a product container.

IN PERSONAM: An action in personam is instituted against an individual usually through the personal service of process, and may result in the imposition of a liability directly upon the person of a defendant.

IN REM: An action in rem is one in which the vessel or thing itself is treated as offender and made defendant without any proceeding against the owners or even mentioning their names. The decree in an action in rem is enforced directly against the res by a condemnation and sale thereof.

LOAD ON TOP: A procedure for ballasting and cleaning unloaded tankers without discharging oil. Half of the tanks are first filled with seawater while the others are cleaned by hosing. Then oil from the cleaned tanks, along with oil which has separated out in the full tanks, is pumped into a single slop tank. The clean water in the full tanks is then discharged while the freshly-cleaned tanks are filled with seawater. Ballast is thus constantly maintained.

MAJOR DISASTER: Any flood, drought, fire, hurricane, earthquake, storm, or other catastrophe in any part of the United States which, in the determination of the President, is or threatens to become of sufficient severity and magnitude to warrant disaster assistance by the Federal Government to supplement the effort and available resources of states and local governments in alleviating damage, hardship or suffering.

MAJOR SPILL: A discharge of oil of more than 10,000 gallons in offshore waters or a discharge of any size of such nature and in quantity that human health or welfare are substantially threatened.

MINOR SPILL: A discharge of oil less than 100 gallons in internal waters, or less than 1000 gallons in offshore waters, or a spill of small quantities of other substances. Discharges that: (1) occur in or endanger critical water areas; (2) generate critical public concern; (3) become the focus of an enforcement action; or (4) pose a threat to public health or welfare, should be classified as moderate or major spills depending on their degree of impact.

MODERATE SPILL: A discharge of oil of 100 gallons to 10,000 gallons in the internal waters or 1000 gallons to 10,000 gallons in offshore waters, or a discharge of any material of any size that poses a threat to the public health or welfare.

OIL: Means oil of any kind or in any form, including, but not limited to, petroleum, fuel oil, sludge, oil refuse, and oil mixed with wastes other than dredged spoil.

OIL FILMS: A slick thinner than .0001 inch may be classified as follows:

STANDARD TERM	GALLONS OF OIL PER SQUARE MILE	APPEARANCE
barely visible	25	barely visible under most favorable light conditions.
silvery	50	visible as a slivery sheen on surface water

STANDARD TERM	GALLONS OF OIL PER SQUARE MILE	APPEARANCE
slightly colored	100	first trace of color may be observed
brightly colored	200	bright bands of color are visible
dull	666	color begins to turn dull brown
dark	1332	much darker brown

NOTE: Each one-inch thickness of oil equals 5.61 gallons per square yard or 17,378,709 gallons per square mile.

OUTAGE: Space left in a product container to allow for expansion during temperature changes it may undergo during shipment and use. Measurement of space not occupied.

pH: Term used to express the apparent acidity or alkalinity of aqueous solutions; values below 7 indicate acid solutions and values above 7 indicate alkaline solutions.

POLLUTION INCIDENT: A spill, including an imminent threat of spill, of oil or other hazardous substance of such magnitude or significant as to require immediate response to contain, clean up, or dispose of the material to prevent a substantial threat to public health or welfare, which includes threats to fish, shellfish, wildlife, shorelines and beaches.

POTENTIAL SPILL: Any accident or other circumstances which threatens to result in the discharge of oil or other hazardous substance. A potential spill shall be classified as to severity based on the guidelines above.

POUR POINT: The lowest temperature at which an oil will flow or can be poured under specified conditions of test.

RESIDUAL OIL: A general term used to indicate a heavy viscous fuel oil.

SCUPPERS: Openings around the deck of a vessel which allow water falling onto the deck to flow overboard. Should be plugged during fuel transfer.

PRIMARY AGENCIES: Those Departments or agencies which are designated to have primary responsibility to promote effective operation of this Plan. These agencies are: DOI, DOT, OEP, DHEW, and DOD.

REMOVE OR REMOVAL: The removal of oil from the water and shorelines or the taking of such other actions as may be necessary to minimize or mitigate damage to the public health or welfare.

SLUDGE OIL: Muddy impurities and acid which have settled from a mineral oil.

SPECIFIC GRAVITY: The ratio of the weight of a given volume of the material at a stated temperature to the weight of an equal volume of distilled water at a stated temperature.

SPONTANEOUS IGNITION TEMPERATURE: (S.I.T.): The temperature at which an oil ignites of its own accord in the presence of air oxygen under standard conditions.

STOKE: The unit of kinematic viscosity.

TONNAGE: There are various tonnages applied to merchant ships. The one commonly implied is gross tonnage although in these days tankers and other bulk-carriers are often referred to in terms of deadweight.

GROSS TONNAGE: 100 cubic feet of permanently enclosed space is equal to one gross ton-nothing watever to do with weight. This is usually the registered tonnage although it may vary somewhat according to the classifying authority or nationality.

NET TONNAGE: The earning capacity of a ship. The gross tonnage after deduction of certain spaces, such as engine and boiler rooms, crew accommodation, stores, equipment etc. Port and harbor dues are based on this tonnage.

DISPLACEMENT TONNAGE: The actual weight in tons, varying according to whether a vessel is in light or loaded condition. Warships are always spoken of by this form of measurement.

DEADWEIGHT TONNAGE: The actual weight in tons of cargo, stores etc., required to bring a vessel down to her load line, from the light condition. Cargo deadweight is, as its name implies, the actual weight in tons of the carge when loaded, as distinct from stores, ballast etc.

ULLAGE: The amount which a tank or vessel lacks of being full (see also OUTAGE).

UNITED STATES: Means the States, the District of Columbia, the Commonwealth of Puerto Rico, the Canal Zone, Guam, American

Samoa, the Virgin Islands, and the Trust Territory of the Pacific Islands.

VISCOSITY: The property of liquids which causes them to resist instantaneous change of shape, or instantaneous rearrangement of their parts, due to internal friction. The resistance which the particles of a liquid offer to a force tending to move them in relation to each other. Viscosity of oils is usually expressed as the number of seconds at a definite temperature required for a standard quantity of oil to flow through a standard apparatus.

VISCOUS: Thick, resistant to flow having a high viscosity.

VOLATILE: Evaporates easily.

Conversion Tables

KNOWING	MULTIPLY BY FACTOR BELOW TO OBTAIN				
	GALLON U.S.	BARREL U.S.	GALLON IMPERIAL	CUBIC FEET	LITRE
Gallon (U.S.)	1.000	0.023810	0.83268	0.13368	3.7853
Barrel	42.0*	1.0000	34.9726	5.6146	158.984
Gallon (Imp.)	1.2009	0.02859	1.000	0.1605	4.546
Cubic Feet	1.2009	0.1781	6.2288	1.000	28.316
Litres		0.00629	0.2199	0.03532	1.000

	POUND	TON (SHORT)	TON (LONG)	TON (METRIC)
Pounds	1.00	0.00050	0.000446	0.00045359
Ton (Short)	2000.0*	1.0000	0.89286	0.90718
Ton (Long)	2240.0*	1.120	1.0000	1.0160
Ton (Metric)	2204.6	1.1023	0.98421	1.000

One Hectolitre equals 100 Litre.
One Ton (Metric) equals 1000 Kilograms.
Conversions marked (*) are exact by definition.

2503.12 APPROXIMATE CONVERSIONS

MATERIAL	BARRELS PER TON (LONG)
crude oils	6.7-8.1
aviation gasolines	8.3-9.2
motor gasolines	8.2-9.1
kerosenes	7.7-8.3
gas oils	7.2-7.9
diesel oils	7.0-7.9
lubricating oils	6.8-7.6
fuel oils	6.6-7.0
asphaltic bitumens	5.9-6.5

(As a general rule-of-thumb use 6.5 barrels or 250 gallons per ton of oil.)

8.2 FEDERAL STATUTES AND REGULATIONS

The Congress has declared that it is the policy of the United States that there should be no discharges of oil into or upon the navigable waters of the United States, adjoining shorelines, or into or upon the waters of the contiguous zone. Further, the discharge in harmful quantities of oil into or upon the navigable waters of the United States, adjoining shorelines or into or upon the waters of the contiguous zone is prohibited except where permitted under Article IV of the International

Convention for the Prevention of Pollution of the Sea by Oil, 1954, as amended, and where permitted in quantities and at times and locations or under such circumstances or conditions as the President may, by regulation, determine.

The pertinent federal statutes and regulations are summarized[26] on pages 105-111.

TABLE 8.1 FEDERAL STATUTES AND REGULATIONS

Federal Statutues, Regulations and Administration orders relative to oil pollution control **are** administered by several Departments and Agencies. The following is a tabular summation of the more important of these legal authorities.

Federal Oil Pollution Control Statutes

STATUTES	OPERATING AGENCIES INVOLVED	PROHIBITED ACT OR AUTHORIZATION	TERRITORIAL APPLICATION	SANCTIONS	EXCEPTED DISCHARGES
Refuse Act 1899 (33 U.S.C.407 et seq)	1.COE 2.U.S.C.G. 3.Customs 4.Dept. of Justice	To discharge from ship. . . (foreign & domestic) or from shore or water front facility, any refuse matter of any kind or description (even commercially valuable petroleum).	1.U.S.navigable waters (USNW) 2.Tributaries, if refuse floats or washes into USNW 3.On banks, If likely to be washed into USNW.	1.$500.00 - $2500.00; 30 days to 1 yr. or both 2.Vessel liable "in rem" for penalties.	"sewage" flowing from streets and sewers.
* * * *	* * * *	* * * *	* * * *	* * * *	* * * *
Water Quality Improvement Act of 1970 PL 91-224	**1. DOT** **2. DOI (FWQA)** **3. COE** **4. Customs** **5. Dept. of Justice**	**The discharge of oil into the water in harmful quantities**	**U.S. navigable waters, adjoining shorelines, the contiguous zone**	**1.Failing to report prohibited discharges-(a)fine up $10K(b)imprisonment up to one year, or both.** **2.Knowingly discharging-penalty up to 10K.** **3.Violating regulations-penalty up to $5K.** **4.Cleanup costs(a)vessels-up to $14M or $100 per GRT(b)offshore/shoreside facilities-up to $8M.**	**1.As permitted by regulation.** **2.In the contiguous zone as permitted by '54 Convention.**
* * * *		* * * * *	* * * *	* * * *	* * * *
Oil Pollution Act 1961 as amended (33 U.S.C. 1001-1015)implements International Convention on Prevention of Pollution of Sea by Oil.	1.U.S.C.G. 2.Customs 3.COE 4.Dept. of Justice 5.Dept. of State	1.Any discharge or escape of persistant oil from vessels subject to Act ie. all U.S. seagoing vessels including tankers (whose tanks carry only oil). Except: (a)Tankers under 150 gross tons;. (b)Other vessels under 500 gross tons;. (c)Vessels on whaling operations; (d)Vessels while using Great Lakes & tributaries; and, (e)Naval vessels and auxiliaries.	1.Prohibited zone: (a)Measured from baseline from which territorial sea is established; (b)Generally extends 50 miles to sea; (c)Extends 100 miles to sea off Northeast Coast of U.S.; (d)Extends out 100 miles to sea off West Coast of Canada; and, (e)Modifications published in Notices to Mariners.	1.Penalty: (a)$500.00 to $2500.00 or 1 yr. or both- any person or company; (b)Ship other than one owned & operated by U.S. liable "in rem" for above penalty, and (c)Suspension or revocation of license.	1.Discharges: (a)To secure safety of ship, cargo or life at sea (b)Due to damage to vessel or unavoidable leakage, if all reason able precautions taken after damage occured or leakage discovered (c)Of residue from fuel or lube oil purification or clarification as far from land as possible.

TABLE 8.1 FEDERAL STATUTES AND REGULATIONS

		2.Any discharge of oil from vessel subject to Act, of 20,000 or plus gross tons, whose bldg. contract executed on or after May 18, 1967. 3.Vessels, subject to Act, which are tankers or use oil fuel must keep <u>Oil Record Book</u> with entries <u>of certain</u> discharges or escapes of oils. 4.Forward to State Dept. evidence of discharge or escape from foreign vesl.	2.Unlimited - Except if in Master's opinion special circumstances make it neither reasonable nor practicable to retain oil on board, discharge, outside prohibited zone is permitted. 3.Penalties re. <u>Oil Record Book</u> (a)Person failing to comply-fine of from $500.00 to $1000.00 (b)Person making false entry (i)fine - $500.00 to $1000. (ii)imprisonment for 6 mos. or both. 4.Prohibited zone (No. 1 above).		(d)Oily mixtures from bilges containing only lube oil drained or leaked from machinery spaces. (e)Vessels, other than tanker, proceeding to a port with inadequate reception facilities.
* * * *	* * * *	* * * *	* * * *	* * * *	* * * *
Federal Water Pollution Control Act, as amended (33 U.S.C. 466, <u>et. seq</u>.).	1.Secretary of Interior **(FWQA)**	1.To participate in oil & other hazardous materials pollution incidents & recommend solutions when requested by State or interstate agencies. 2.To provide technical assistance to public & private agencies. 3.To recommend limits on pollutants, including oil & hazardous materials. 4.To "approve" State adopted water quality standards and to establish Federal standards where State standards are not submitted or are inadequate. Standards ordinarily include criteria limiting discharges of oil or hazardous materials.	1.U.S. navigable waters & tributaries. Interstate waters as defined in this Act., including costal waters.	1.Enforcement-conference pursuant to Sec. 10 may result in Federal legal action to enforce recommendations. 2. Abatement action pursuant to Sec. 10(c) (5) where discharge reduces quality below established standard	
Section 12, Fed. Water Pollution Control Act, as amended by P.L. 91-224(Apr. 3,1970) (33 U.S.C.466,<u>et seq.</u>)	**Same as 1712**	**President shall promulgate regulations designating <u>hazardous substances</u> and <u>recommending methods</u> for removal.**	**Same as 1712**	**President shall make recommendation to Congress not later than Nov. 1,1970. Clean up fund of Section 11 available here.**	

TABLE 8.1 FEDERAL STATUTES AND REGULATIONS

Related Federal Statutes

STATUTES	ADMINISTRATIVE AUTHORITY	AUTHORIZED ACTION	TERRITORIAL CONSIDERATIONS
U.S.Navy Ship Salvage Authority (10 U.S.C. 7361)	Secretary of Navy (U.S. Navy Ship System Command, Supervisor of Salvage)	1. To salvage, by contract or otherwise: (a)U.S. Naval vessels; (b)Private vessel (foreign or domestic) subject to availability of salvage forces; and, (i)if not abandoned nor under governmental control nor other salvage facilities reasonably available & competent private authority requests help, i.e. ship's master, owner, or underwriter, (ii)if abandoned or under control of U.S.C.G.,FWPCA, Corps of Engineers, Office of Emergency Preparedness, or federal court - competent requesting agency becomes customer.	1.(a)for U.S. Naval vessels - Navy has direct responsibility anywhere (b)for private vessels (i)U.S. navigable waters and high seas (ii)U.S. navigable waters, U. S. territorial waters and those within the authority of requesting government agency by law or treaty
* * * *	* * * * *	* * * * *	* * * * *
Outer Continental Shelf Land Act of 1953 (43 U.S.C. 1331-1343)	Secretary of the Interior (a) Bur. of Land Mgmt. (b) U.S.G.S.	1. To regulate leases for exploitation of Shelf lands, terms & conditions calculated to prevent pollution in off-shore oil or mining operations. Regulations provide that lessee shall not pollute; shall take certain preventive actions and if pollution occurs, lessee shall make appropriate notifications and shall be liable for clean up.	1. U.S. Continental Shelf Lands
* * * *	* * * * *	* * * * *	* * * * *
Federal Disaster Assistance Act (42 U.S.C. 1855 <u>et seq.</u>) and Disaster Relief Act of 1966 (PL 89-769, 80 Stat. 1316) and Disaster Relief Act of 1969 (PL 91-79) (Expires after Dec. 31, 1970)	The President Director, Office of Emergency Preparedness per E.O. 10427 and 10737	1. To declare a major disaster at the request of a governor of a State 2. If declared, to direct Federal agencies to assist by: (a)Using or lending, with or without compensation, to state & local governments, equipment, supplies, facilities, personnel, etc. other than extension of credit under any act. (b)Performing, on public or private land, work to preserve life and property	(1) major disaster areas as declared by President (2) U.S., its territories & possessions

TABLE 8.1 FEDERAL STATUTES AND REGULATIONS

		(c) Provide temporary housing or emergency shelter (d) Clear debris & wreckage (e) Make emergency repairs & temporary replacements to public facilities of State and local governments. 3.OEP can give direct financial assistance to State & local governments for items in 2 above.	
* * * * *	* * * * *	* * * * *	* * * * *
14 U.S.C. 81 <u>et seq</u>.	U.S.C.G.	1.To aid distressed persons & protect property. Sec. 88 (b) in USNW and on the high seas. 2.To establish, maintain & operate aids to maritime navigation in USNW, waters above the U.S. continental shelf and other specified areas. 3.To mark for protection of navigation any wreck in USNW (Sec. 86) not properly marked by owner (33 U.S.C. 409)	
* * * * *	* * * * *	* * * * *	* * * * *
14 U.S.C. 141 (a)	U.S.C.G.	1.On request may use personnel & facilities to assist any government agency, to perform any activity for which such personnel are especially qualified.	1. Limited only by international law re. Territorial waters
* * * * *	* * * * *	* * * * *	* * * * *
Magnuson Act (50 U.S.C. 191)	designated U.S.C.G. Officers (33 CFR 6) when directed by Executive order (presently implemented by E.O. 10173 as amended)	1.Prevent anything from being placed on board any vessel or waterfront facility as defined in 33 CFR 6.01-4, when necessary to prevent damage to U.S. waters. 2.Establish security zones into which no person or vessel may enter or take anything. 3.Control vessel movement & take full or partial possession or control of any vessel when necessary to prevent danger to U.S. waters 4.Prevent mooring to or compel shifting of any vessel from waterfront facility if it endangers such vessel, other vessels, harbor, any facility therein because conditions exist in or about water front - not limited to fire hazards & unsatisfactory operations.	1. U.S. Territorial waters
Dangerous Cargo Act (46 USC 170)	U.S.C.G.	1. Authority to establish regulations for handling, stowage, storage and use of dangerous articles or substances on board vessels 2. Authority to establish regualtions for disposing of dangerous articles or substances found to be in an unsafe condition	U.S. Territorial waters
* * * * *	* * * * *	* * * * *	* * * * *
Tank Vessel Act (46 USC 391a)	U.S.C.G.	1. Authority to establish additional rules for provision against hazards of life and property created by vessels having on board inflammable or combustible liquid cargo in bulk.	U.S. Territorial waters
* * * * *	* * * * *	* * * * *	* * * * *

Table 8.1 FEDERAL STATUTES AND REGULATIONS

Treaties and International Conventions

TITLE	PARTIES	SUBSTANCE OF AGREEMENT	TERRITORIAL APPLICATION
Treaty re. Reciprocal Rights in Conveyance of Prisoners and Wrecking & Salvage (35 Stat. 2035, TS 502)	U.S. - Great Britain signed for Canada (1908)	1. Vessels & wrecking equipment of U.S. or Canada permitted to salvage wrecks, render aid to vessels in distress or disabled across the international boundary line.	1. In portion of St. Lawrence River through which boundary line passes. 2. Lakes Ontario, Erie, St. Clair, Huron, Superior. 3. Niagara, Detroit, St. Clair & Ste. Marie River. 4. Canals at Sault Ste. Marie. 5. Shores & territorial waters on Pacific & Atlantic within 30 miles of boundary line.
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Boundary Waters Treaty (35 Stat. 2448, TS 548)	U.S. - Great Britain signed for Canada (1909)	1. Established International Joint Commission with jurisdiction over all cases re. use, obstruction or diversion of waters including water pollution. No mechanism for enforcement directly by Commission findings & recommendations reported to respective governments for enforcement action within its territorial limits.	1. U.S. - Canadian boundary waters
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Treaty to Facilitate Assistance to & Salvage of Vessels in Territorial Waters (49 Stat. 3359, TS 905)	U.S. - Mexico (1936)	1. Vessels & rescue apparatus, public & private, may aid vessels and crew of its own nationality, when disabled or in distress. 2. Captain, master or owner of rescue vessel of either country must notify that country when entering or intending to enter territorial waters of the other country as early as possible and may freely proceed with rescue unless advised by the other country that adequate assistance is available or for any other reason rescue is not necessary.	1. On shores or within territorial waters of the other nation - (a)Within 720 mile radius of intersection of international boundary line & Pacific Coast or (b)within 200 miles radius of intersection of international boundary line & coast of Gulf of Mexico.

TABLE 8.1 FEDERAL STATUTES AND REGULATIONS

Convention of High Seas (1958) TIAS 5200) (13 U.S.T. 2312)	U.S. (1962)-Denmark, Finland, Italy, Japan, Mexico, Netherlands, U.K., USSR, inter alia	1.Article XXIV - Member nations responsible for drafting regualtions to prevent pollution of seas by oil. 2.Article XXV - same for radioactive wastes & other harmful agents by vessels under its control	High Sea
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Geneva Convention on Territorial Sea & Contiguous Zone (1958) (15 U.S.T. 1606) (TIAS 5639)	U.S. (1964)-Denmark, Finland, Italy, Japan, Netherlands, U.K., USSR, inter alia	1.To exercise necessary controls to prevent infringement of nations sanitary regualtions within its territory or territorial sea.	1.Not to exceed 12 miles outward from the baseline from which the territorial sea is measured.
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Convention on Continental Shelf (1958) (TIAS 5578) (15 U.S.T. 471)	U.S. (1964)-Denmark, Finland, France, Mexico, Netherlands, U.K., USSR, inter alia	Coastal government has: exclusive & sovereion right to explore and exploit natural resources of the Shelf as long as it does not unjustifiably interfere with navigation, fishing or conservation of living sea resources nor with fundamental oceanographic or other scientific research destined for open publication.	U.S. Continental Shelf - 200 meter isobath curve contiguous to land or to a depth that admits of the exploitation of said area.
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Convention for Prevention of Pollution by Sea by Oil, (1954) (12 U.S.T. 2989: (1962) amended 17 U.S.T. 1523)	U.S. (1961)-Belgium, Denmark, Finland, France, West Germany, Greece, Italy, Japan, Liberia, Mexico, Netherlands, Nigeria, Norway, Panama, Spain, Sweden, U.K., inter alia,	1.To prevent discharge or escape of oily substances by sea-going vessels - See Oil Pollution Act of 1961 as amended in 1966 for U.S. implementation. (33 U.S.C. 1001-1015) (Note: Oily substance is defined as presistant oil) 2. Maintenance of Oil Record Book.	1.Prohibited zone: All seas within 50 miles from nearest land (baseline from which territorial sea is established) and other areas as defined in the conventicr..

8.3 U.S.C.G. SEARCH AND RESCUE AIRCRAFT CHARACTERISTICS

Aircraft	Power	Weight (lbs)		Range (nmi)	Speed (knots)		Service Ceiling (feet)	Cargo Area (feet) LxWxHt	Cabin Pressurized	Environmental Control
		Empty	Gross		Cruise	Max				
HU-16E	two prop	24,000	35,000	1,400	160	215	11,500	(25'x5'x5')	no	heater
HC-130B	four turbo-prop	67,000	135,000	3,200	290	320	23,000	(41'x10'x9')	yes	air conditioned
HH-52A	one gas-turbine	5,900	8,300	350	90	109	11,200	12x5x6	no	heater
HH-3F	two gas-turbine	13,750	22,050	6,000	130	142	13,600	25x6x6	no	heater

8.4 OIL SAMPLE DESCRIPTION

We gratefully acknowledge the named oil companies for the donation of the following crude and refined oil samples.

Sample A1 - Asphalt - ex Midcontinent crude flashed residual stock blended with Cutter Stock. 100/120 Penetration Grade - °API Gravity 8.7 Shell Oil Company

Sample A2 - Asphalt - 180/2.00 Penetration Grade - °API Gravity 10.0 Chevron Oil Company

Sample A3 - Heavy Residuum (Delaware Refinery) - Bunker C - °API Gravity -1.7 Getty Oil Company

Sample A4 - Asphalt - Bayway Refinery - Virgin bottoms from vacuum distillation - 85/100 Penetration Grade - °API Gravity 7.2 Humble Oil & Refining Co.

Sample B1 - Heavy Crude - Foreign - °API Gravity 9.9 Chevron Oil Company

Sample B2 - Heavy Crude - Domestic - Southern California - Asphaltic - °API Gravity 12.8 - not refined Shell Oil Company

Sample B3 - Heavy Crude - Foreign - Guapo (Trinidad) - °API Gravity 15.5 Getty Oil Company

Sample B4 - Heavy Crude - Foreign - Lagunillas (Venezuela) - not refined - °API Gravity 19.2
Humble Oil & Refining Co.

Sample B5 - Heavy Crude - Domestic - Jackson Miranda (Gulf Coast) - °API Gravity 25.0 Getty Oil Company

Sample B6 - Heavy Crude - Domestic - Hawkins (Texas) - not refined - °API Gravity 32.6
Humble Oil & Refining Co.

Sample B7 - Heavy Crude - Domestic - Barbers Hill (Texas)- °API Gravity 30.3 Atlantic Richfield Company

Sample B8 - Heavy Crude - Foreign - Lagunillas (Venezuela) - °API Gravity 17.4 Atlantic Richfield Company

Sample C1 - Light Crude - Foreign - Ceuta (Venezuela) - °API Gravity 31.3 Getty Oil Company

Sample C2 - Light Crude - Domestic - West Texas Sour (Texas) - °API Gravity 33.9 Getty Oil Company

Sample C3 - Light Crude - Foreign - Abu Dhabi (Persian Gulf) - not refined - °API Gravity 39.0
Shell Oil Company

Sample C4 - Light Crude - Domestic - Alabama - mixed base - not refined - °API Gravity 43.7
Shell Oil Company

Sample C5 - Light Crude - Domestic - Perkins Crude - (Lake Charles, La.) - °API Gravity 27.1

Cities Service Oil Company

Sample C6 - Light Crude - Foreign - North Zeta (Venezuela) - not refined - °API Gravity 42.5

Humble Oil & Refining Co.

Sample C7 - Light Crude - Domestic - °API 31.0

Chevron Oil Company

Sample C8 - Light Crude - Domestic - North Texas - °API Gravity 39.9

Continental Oil Company

Sample C9 - Light Crude - Domestic - Kingfisher (Oklahoma) - °API Gravity 42.3

Continental Oil Company

Sample C10- Light Crude - Domestic - Sweden (Texas) - not refined - °API Gravity 46.5

Humble Oil & Refining Co.

Sample C11- Light Crude - Foreign - °API Gravity 34.6

Chevron Oil Company

Sample C12- Light Crude - Domestic - Southwest, Texas - °API Gravity 40.6

Atlantic Richfield Company

Sample C13- Light Crude - Foreign - Zueitina (Libya) - °API Gravity 40.6

Atlantic Richfield Company

Sample D1 - Refined Fuel Oil - Lake Arthur Condensate - °API Gravity 46.3
Cities Service Oil Company

Sample D2 - Low Sulphur Fuel Oil (Bunker) - African Crude - Bottoms cut from atmospheric distillation - °API Gravity 10.2
Humble Oil & Refining Co.

Sample D3 - Low Sulphur #6 Fuel Oil - °API Gravity 19.0
Chevron Oil Company

Sample D4 - No. 6 Fuel Oil - Thermal cracked residual stock - ex Midcontinent - °API Gravity 5.7
Shell Oil Company

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