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Thin Oil Film Detection Limits of Laser Fluorosensors

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THIN OIL FILM DETECTION LIMITS OF LASER FLUOROSENSORS

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ABSTRACT

Fluorosensor equations were derived for the case of thin translucent oil films. Absorption coefficients were measured for five crude oils as a function of wavelength within the 230 to 400 nm range. Fluorescence efficiencies were also measured over a range of film thicknesses at three excitation wavelengths for these oils. This experimental data allowed verification of the fluorosensor equations and justified certain simplifications. Thin film detection limits were calculated for a sensor with current specifications and means of improving sensor performance were discussed.

RÉSUMÉ

Des équations concernant les fluorodétecteurs ont été établies dans le cas de pellicules d'hydrocarbures translucides. Les coefficients d'absorption ont été mesurés pour cinq types de pétroles bruts en fonction de la longueur d'onde pour une gamme de 230 à 400 nm. Le rendement de fluorescence a également été mesuré pour diverses épaisseurs de films à trois longueurs d'onde d'excitation. Ces données expérimentales ont permis de vérifier les équations des fluorodétecteurs et ont justifié certaines simplifications. Les limites de détection de films ont été calculées pour un capteur de spécifications courantes et des moyens d'améliorer le rendement des capteurs ont été examinés.

FOREWORD

This study was conducted by the National Research Council on behalf of the Canada Centre for Remote Sensing. Funding for the study was provided by the Canada Centre for Remote Sensing and the Environmental Emergency Branch of the Environmental Protection Service. The study was conducted as part of the Arctic Marine Oilspill Program (AMOP).

TABLE OF CONTENTS

	Page
ABSTRACT	i
RÉSUMÉ	ii
FOREWORD	iii
LIST OF FIGURES	vi
LIST OF TABLES	vii
CONCLUSIONS	viii
1 INTRODUCTION	1
2 THEORY	2
3 EXPERIMENTAL	5
3.1 Oil Selection	5
3.2 Absorption Studies	5
3.3 Fluorescence Studies	5
4 ABSORPTION COEFFICIENTS OF CRUDE OILS	8
5 EFFECT OF FILM THICKNESS ON OIL FLUORESCENCE SPECTRA	10
6 EFFECT OF FILM THICKNESS ON APPARENT FLUORESCENCE YIELD	12
7 THIN FILM DETECTION LIMITS OF LASER FLUORESENSORS	14
REFERENCES	19

LIST OF FIGURES

Figure		Page
1	FLUORESCENCE SPECTRA OF CRUDE OILS. $\lambda_{\text{ex}} = 337 \text{ nm.}$	6
2	ABSORPTION COEFFICIENTS OF CRUDE OILS AS A FUNCTION OF WAVELENGTH.	9
3	EFFECT OF VARYING FILM THICKNESS ON THE FLUORESCENCE SPECTRUM OF CRUDE OIL (CO7). $\lambda_{\text{ex}} = 270 \text{ nm.}$	11
4	DEPENDENCE OF THE APPARENT FLUORESCENCE YIELD OF CRUDE OILS, η_d , ON FILM THICKNESS.	13
5	DEPENDENCE OF THE SIGNAL - TO - NOISE RATIO AS CALCULATED FOR THE CCRS MK III FLUOROSENSOR FOR THE CRUDE OILS.	16

LIST OF TABLES

Table		Page
1	OIL SELECTION	5
2	ABSORPTION COEFFICIENTS OF CRUDE OILS	8
3	THIN FILM DETECTION LIMITS (S/N = 3) CALCULATED AS DESCRIBED IN TEXT	15
4	COMPARISON OF SINGLE SHOT SIGNAL - TO - NOISE RATIOS OF 2 μ m FILMS USING N ₂ AND KrF LASER BASED FLUOROSENSORS	18

CONCLUSIONS

The oil properties on which the thin film detection limit depends are the fluorescence efficiency ($\eta(\lambda)$) and the absorption coefficient (α) at the excitation wavelength. Reabsorption of emitted fluorescence can be neglected due to the nature of the dependence of α on wavelength (i.e. α_{ex} is found to be significantly greater than α over the emission band). Consequently spectral distributions are not affected appreciably by film thickness. Our crude oil samples became translucent at thicknesses under 5 to 20 μm at 337 nm depending on the oil. The current minimum detectable film thickness is about 1 μm for all the oils at 337 nm. Marked improvement in fluorosensor performance can be expected if advantage is taken of the increase in absorption coefficient at lower wavelengths by exciting at such wavelengths. Eximer lasers are available which not only allow this but also offer more power leading to a further improvement in performance.

1 INTRODUCTION

Various studies on fluorosensing have shown the technique to be feasible for the detection of oil spills (Rayner and Szabo, 1978; Rayner, Lee and Szabo, 1978; Fantasia, Hard and Ingaro, 1971; Horvath, Morgan and Stewart, 1971; Eldering and Webb, 1975; O'Neil, Davis, Gross and Kruss, 1975; Measures, Garleck, Houston and Stephenson, 1975). The bulk of this work has been restricted to optically dense spills. While most workers recognize that the thickness of the spill becomes important when the spill is not opaque, there has been little experimental work to determine the point at which films become translucent. Fantasia et al. (1971) reported the thickness dependence of the fluorescence yield of one crude oil. Horvath et al. (1971) gave the calculated effect of slick thickness on the fluorescence properties of three oils and also pointed out that, in the circumstance of a thin film of a weakly emitting oil over water with a large background fluorescence, the total fluorescence signal may even be attenuated in the presence of an oil spill. Eldering and Webb (1975) varied the thickness of their oil samples but their thinnest film was a wiped film of undetermined thickness. In a theoretical paper Kung and Itzkan (1976) have presented a method to deduce the fluorescence efficiency of an oil from the fluorescence of a thin film using the seawater Raman return as a reference.

With the front surface viewing geometry of a fluorosensor one might expect the spectral distribution of the fluorescence to be dependent on film thickness if there is appreciable absorption at the emission wavelengths. Studies of the fluorescence of several oils in films of known thickness were undertaken to investigate this. The strength of the fluorescence return is determined in part by the amount of light absorbed by the film. The absorption coefficients of several oils at wavelengths likely to be used in laser fluorosensing were therefore measured by absorption spectroscopy of thin films. These extinction coefficients can be used in a modified fluorosensor equation to estimate lower limit oil spill thicknesses below which the return signal is lost in noise. The validity of the modified equation can also be checked by working back from the results of the thin film fluorescence studies to estimate the absorption coefficients.

2 THEORY

It is convenient to derive the fluorosensor relationships for an optically dense target first and then consider the effects of film thickness.

For a pulsed fluorosensor and an opaque target the number of signal photons detected per pulse (S_{∞}) is given by:

$$S_{\infty} = P T_L \int_{\lambda_1}^{\lambda_2} \eta(\lambda) \cdot C(\lambda) d\lambda \frac{A_R}{4\pi h^2} \cdot T_S \cdot T_F \cdot T_R \quad (1)$$

where:

- P - is the number of photons per laser pulse;
- $\eta(\lambda)$ - is the fluorescence quantum efficiency per wavelength interval of the target at the particular excitation wavelength;
- $C(\lambda)$ - is the detector cathode quantum efficiency per wavelength interval;
- A_R - is the receiver area;
- h - is the height of the sensor over the target;
- T_L - is the attenuation of the laser pulse by the beam steering optics; the atmosphere and the air-target interface;
- T_S - is the attenuation of the return fluorescence due to reflective losses at the target air interface;
- T_F - is the attenuation of the return signal; and
- T_R - is the attenuation of the return signal by the receiver optics.

The field of view of the receiver is assumed to overlap the excited area of the target completely. T_S , T_F and T_R are assumed to be independent of wavelength. The limits of the fluorosensor bandpass are represented by λ_1 , and λ_2 .

The number of background photons detected per pulse (B) is given by:

$$B = \int_{\lambda_1}^{\lambda_2} I_q(\lambda) C(\lambda) d\lambda A_T \frac{A_R}{h^2} \cdot T_F T_R \tau \quad (2)$$

where:

- $I_q(\lambda)$ - is the quantum spectral irradiance of the target in the absence of laser illumination;
- A_T - is the area of the receiver field of view; and
- τ - is the gate width of the detection system.

Spectral irradiances are often quoted in power units ($I_e(\lambda)$). The quantum spectral irradiance can be calculated from the relationship:

$$I_q(\lambda) = \frac{\lambda}{hc} I_e(\lambda) \quad (3)$$

where "h" is Planck's constant and "c" the speed of light.

Assuming Poisson statistics, the noise (N) is given by;

$$N = \sqrt{S+B} \quad (4)$$

and the signal to noise ratio by;

$$S/N = S/\sqrt{S+B} \quad (5)$$

We can now consider the effect of reducing the oil thickness. The number of signal photons detected per pulse (dS) from a layer of thickness (dx) at a depth (x) from the surface is given by;

$$dS = PT_L \int_{\lambda_1}^{\lambda_2} \eta^1(\lambda) C(\lambda) e^{-\alpha_{ex}x} \alpha_{ex} e^{-\alpha_{em}(\lambda)x} dx d\lambda \frac{A_R}{4\pi h^2} T_S T_F T_R \quad (6)$$

where α_{ex} and $\alpha_{em}(\lambda)$ are absorption coefficients of the oil at the excitation and emission wavelengths respectively and η^1 is the molecular fluorescence efficiency of the oil. Integrating for a slick of thickness (d) we obtain :

$$S = PT_L \int_{\lambda_1}^{\lambda_2} \eta^1(\lambda) \frac{\alpha_{ex}}{\alpha_{ex} + \alpha_{em}(\lambda)} \cdot C(\lambda) (1 - e^{-(\alpha_{ex} + \alpha_{em}(\lambda))d}) d\lambda \cdot \frac{A_R}{4\pi h^2} T_S T_F T_R \quad (7)$$

The optically dense case may be examined by letting (d) tend to infinity:

$$S_\infty = PT_L \int_{\lambda_1}^{\lambda_2} \eta^1(\lambda) \frac{\alpha_{ex}}{\alpha_{ex} + \alpha_{em}(\lambda)} C(\lambda) d\lambda \frac{A_R}{4\pi h^2} T_S T_F T_R \quad (8)$$

The fluorescence efficiency measured experimentally, $\eta(\lambda)$ in equation 1, already contains a factor for the reabsorption of emitted light, being given by:

$$\eta = \eta^1(\lambda) \frac{\alpha_{ex}}{\alpha_{ex} + \alpha_{em}(\lambda)} \quad (9)$$

Then in the general case;

$$S = P T_L \int_{\lambda_1}^{\lambda_2} \eta(\lambda) C(\lambda) (1 - e^{-(\alpha_{ex} + \alpha_{em}(\lambda)) d}) d\lambda \cdot \frac{A_R}{4\pi h^2} T_S T_F T_R \quad (10)$$

In order to estimate the effect of slick thickness on the performance of a laser fluorosensor, the absorption coefficient of the oil at the excitation wavelength and over the emission band must be known. Assumptions concerning the relative sizes of α_{ex} and $\alpha_{em}(\lambda)$ which might allow the simplification of equation 10 will be discussed later. Calculation of the signal from equation 10 using experimental absorption coefficients for a range of thicknesses will allow the dependence of the signal - to -noise ratio on thickness to be studied.

3 EXPERIMENTAL

3.1 Oil Selection

A series of crude oils was chosen from the larger selection used in earlier studies on the feasibility of laser fluorosensing (Rayner and Szabo, 1976). They span the crude oils in fluorescence properties. Their spectra are shown in Figure 1 and their fluorescence properties are summarized in Table 1.

TABLE 1 OIL SELECTION

Oil Type	$(\lambda_{\text{ex}} = 337 \text{ nm})$	
	$\lambda_{\text{max}}/\text{nm}$	$\lambda_{\text{max}}/10^{-4} \text{ nm}^{-1}$
CO3 Texaco Arabian Crude	510	1.2
CO4 Texaco Nigerian Crude	480	3.5
CO5 Texaco Venezuelan 'Lago Medio' Crude	500	0.7
CO7 Gulf Oil B.C. Light Crude	480	4.2
CO19 Shell Oil Peace River Crude	500	2.3

3.2 Absorption Studies

Absorption coefficients were measured using a Carey 118 spectrophotometer. Cells were assembled by clamping two quartz flats together with a suitable spacer. The minimum pathlength obtainable was approximately $1 \mu\text{m}$ using flats upon which silicon oxide spacers had been deposited by optical coating techniques. The even spacing of the flats was checked by inspection of the reflected interference pattern under a sodium D lamp. The pathlength was determined from the transmitted interference fringes measured in the Carey 118 with the cell empty. Where possible the cells were filled by capillary action. The heavier oils required that the cell be dismantled and reassembled squeezing out an excess of oil. In this case the pathlength was not known to better than about $1 \mu\text{m}$.

3.3 Fluorescence Studies

Fluorescence measurements were made using a Perkin-Elmer MPF-44A spectrofluorimeter. A specially constructed module was used in place of the standard sample

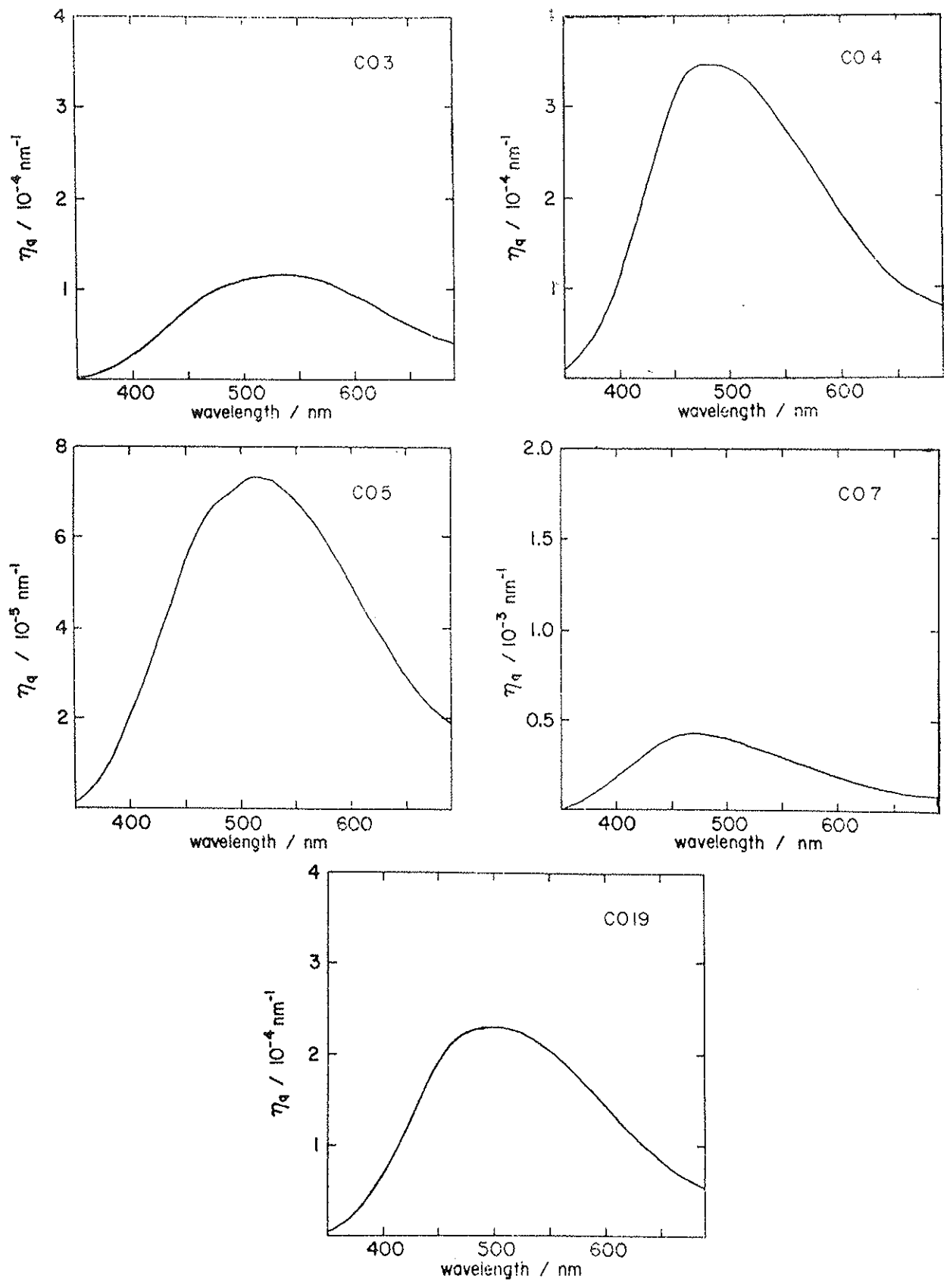


FIGURE 1 FLUORESCENCE SPECTRA OF CRUDE OILS. $\lambda_{\text{ex}} = 337\text{nm}$.

cell housing module to allow the front surface monitoring of liquid samples. Spectra were corrected for the wavelength dependence of the detection system using a microprocessor based Corrected Spectra Unit which was calibrated with a standard tungsten lamp. Fluorescence spectra are presented in quantum efficiency per unit wavelength interval. Thin oil films were prepared by dropping a known volume of oil from a Hamilton syringe onto a water surface of known area. Visual inspection showed that most oils spread evenly except for thicker films where the film was usually opaque at wavelengths of 337 nm and less. It was important to use scrupulously clean glass sample cells to ensure even spreading. Only poor films could be obtained in disposable plastic cells.

4 ABSORPTION COEFFICIENTS OF CRUDE OILS

The absorption coefficients of the five crude oils are shown as a function of wavelength in Figure 2 and listed in Table 2. All show increasing absorption as wavelength decreases. As expected from their appearance, the lighter oils have lower absorption coefficients than the heavier ones. The shoulder at approximately 260 nm seems general for all the oils and can be attributed to a major, common component present in the oils.

TABLE 2 ABSORPTION COEFFICIENTS OF CRUDE OILS

λ/nm	CO3	CO4	CO5	CO7	CO19
400	0.18	0.06	0.15	0.02	0.10
390	0.22	0.07	0.17	0.02	0.11
380	0.25	0.08	0.20	0.03	0.14
370	0.30	0.09	0.24	0.03	0.16
360	0.38	0.12	0.30	0.04	0.20
350	0.47	0.15	0.37	0.06	0.25
340	0.58	0.19	0.45	0.09	0.32
330	0.73	0.26	0.57	0.12	0.41
320	0.85	0.33	0.67	0.16	0.49
310	1.07	0.48	0.80	0.23	0.66
300	1.32	0.74	1.06	0.33	0.89
290	1.61	0.98	1.29	0.43	1.10
280	1.91	1.19	1.53	0.54	1.36
270	2.32	1.41	1.86	0.67	1.62
260	2.54	1.60	2.08	0.77	1.82
250	2.68	1.51	2.14	0.76	1.83
240	3.55	2.49	2.86	1.04	2.45
230	4.21	4.21	3.91	1.78	3.92

The absorption coefficients are used in the following sections in assessing laser fluorosensor performance.

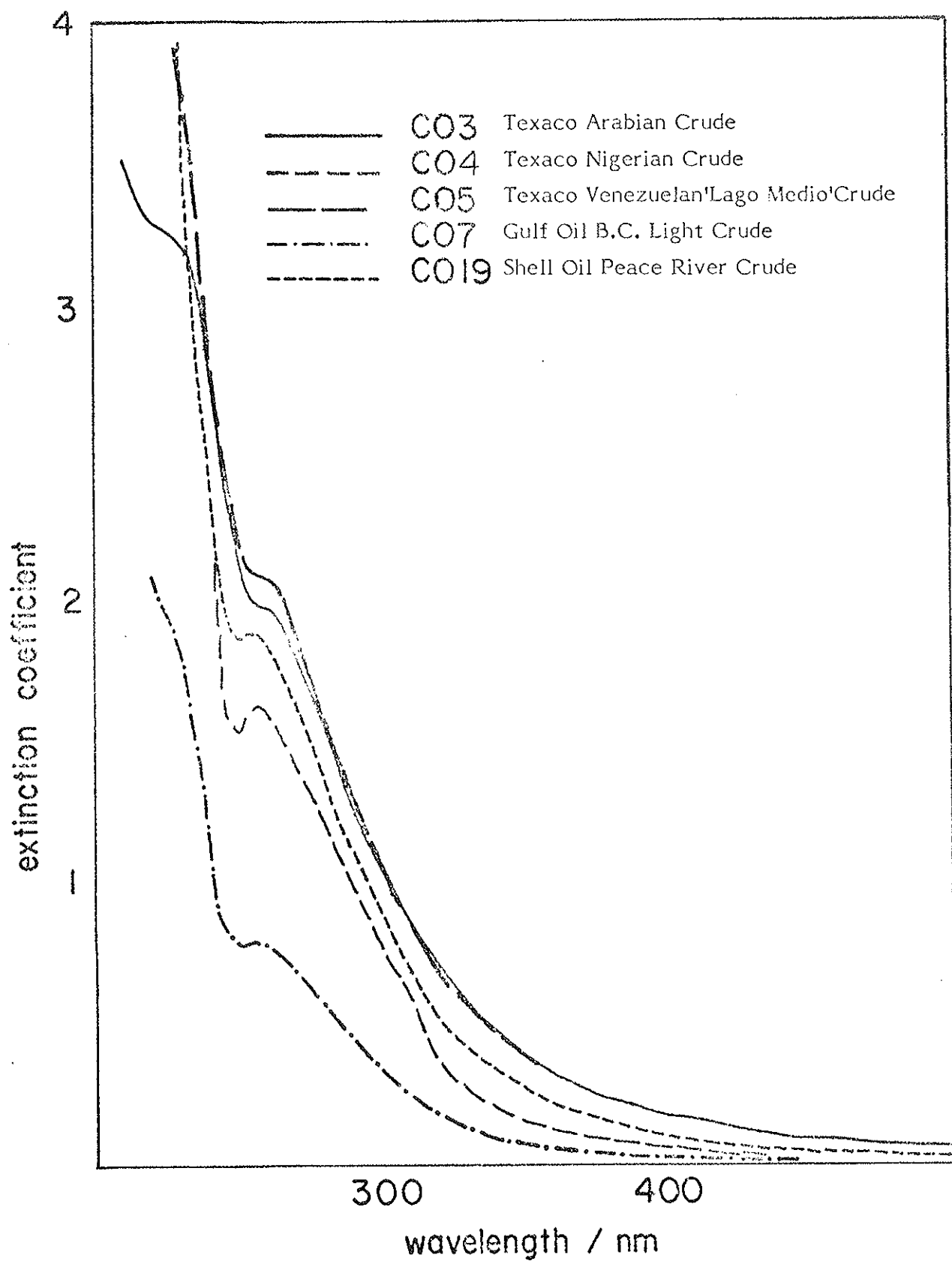


FIGURE 2

ABSORPTION COEFFICIENTS OF CRUDE OILS AS A FUNCTION OF WAVELENGTH

5 EFFECT OF FILM THICKNESS ON OIL FLUORESCENCE SPECTRA

The spectral shape of the fluorescence return to a fluorosensor is theoretically dependent on the film thickness due to reabsorption of the emitted fluorescence. Equation 10 can be differentiated to give:

$$\frac{dS}{d\lambda} = P T_L n(\lambda) C(\lambda) (1 - e^{-(\alpha_{ex} + \alpha_{em}(\lambda))d}) \frac{A_R}{4\pi h^2} T_S T_F T_R \quad (11)$$

The effect of the film thickness on the spectral shape is determined by the relative sizes of α_{ex} and the range of $\alpha_{em}(\lambda)$ and by the variation in α_{em} over the emission spectrum. That is, for there to be no effect on the spectrum, α_{ex} must be significantly greater than any value of $\alpha_{em}(\lambda)$ over the range of the emission spectrum and/or α_{em} must be constant over the range.

For excitation at 240 and 270 nm the former condition applies. As is demonstrated for one oil (CO7) in Figure 3, there is no significant change in spectral shape between the extremes of film thickness used in this study for all five oils. The emission maximum and spectral shape is independent of exciting wavelength in the UV range for these crude oils. The sharp increase in α with wavelength (see Figure 2), results in α_{ex} being significantly greater than $\alpha_{em}(\lambda)$ over the emission band. Even for excitation at 337 nm this condition holds over most of the emission band and the distortion at thin film thicknesses is evident, if at all, only in the high wavelength tail. As absorption at 337 nm is at the lowest in our excitation range these spectra are the noisiest and distortion is often of the order of or less than the noise. In no case was the distortion significant enough to shift the maximum emission wavelength (λ_{max}).

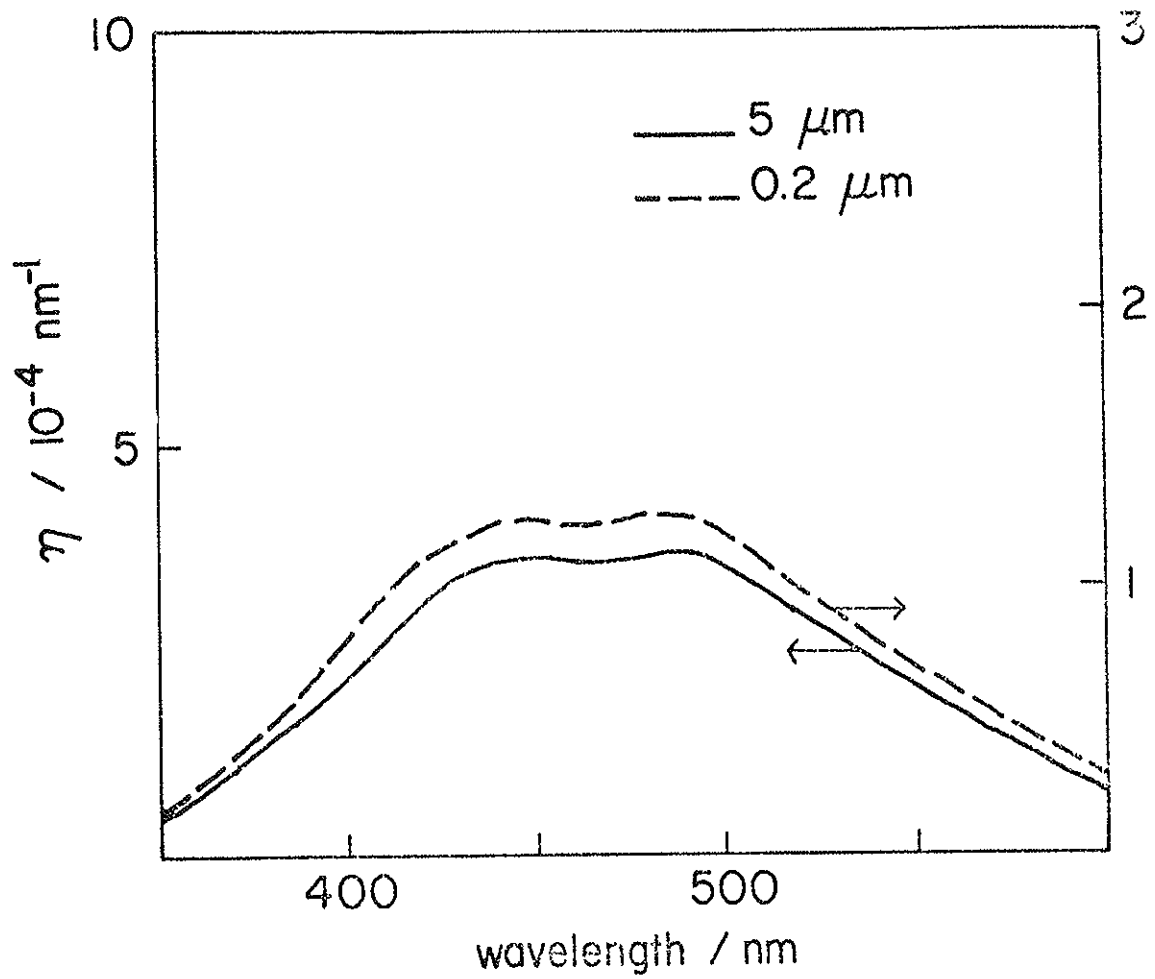


FIGURE 3 EFFECT OF VARYING FILM THICKNESS ON THE FLUORESCENCE SPECTRUM OF CRUDE OIL (CO7). $\lambda_{\text{ex}} = 270 \text{ nm}$.

6 EFFECT OF FILM THICKNESS ON APPARENT FLUORESCENCE YIELD

The apparent fluorescence yield (η_d) was measured at various values of film thickness (d) for all five oils at their emission maxima. From Equation 11 it can be seen that the apparent yield is:

$$\eta_d(\lambda) = \eta(\lambda) (1 - e^{-(\alpha_{ex} + \alpha_{em}(\lambda))d}) \quad (12)$$

Inspection of Figure 2 shows that $\alpha_{ex} \gg \alpha_{em}(\lambda_{max})$ for all oils. We can therefore simplify Equation 12 to give:

$$\eta_d(\lambda_{max}) = \eta(\lambda_{max}) (1 - e^{-\alpha_{ex}d}) \quad (13)$$

The measured values of $\eta_d(\lambda_{max})$ are shown as a function of film thickness in Figure 4. Also shown in this figure are theoretical curves of η_d against film thickness calculated using Equation 13 and measured values of α_{ex} and $\eta(\lambda_{max})$. Agreement is found within experimental error between the experimental and theoretical curves. The greatest error is in the measurement of the film thickness, especially for the thinner films of light oils where evaporation has the greatest effect.

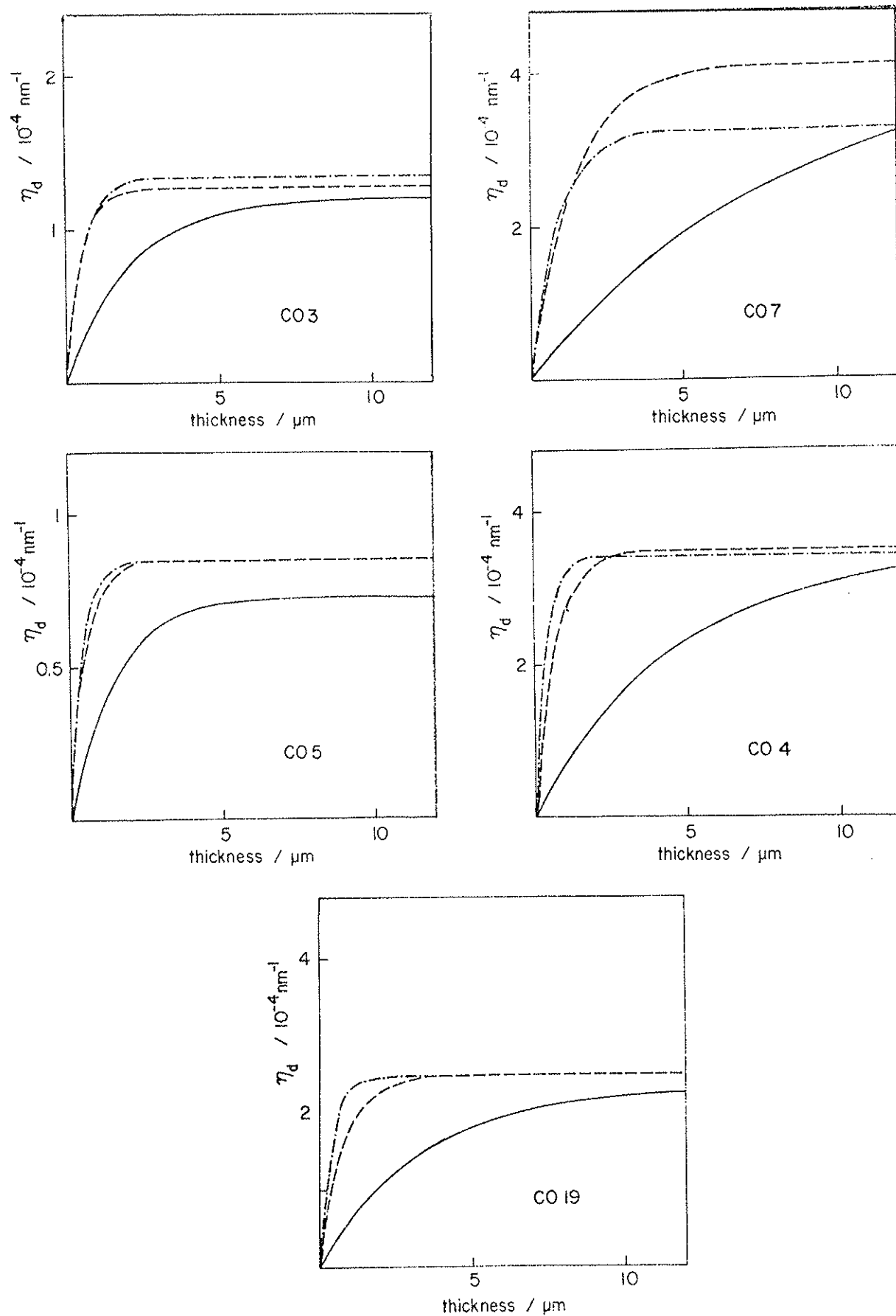


FIGURE 4 DEPENDENCE OF THE APPARENT FLUORESCENCE YIELD OF CRUDE OILS (η_d) ON FILM THICKNESS.
 — $\lambda_{\text{ex}} = 337 \text{ nm}$, --- $\lambda_{\text{ex}} = 270 \text{ nm}$, -.-.- $\lambda_{\text{ex}} = 240 \text{ nm}$.

7 THIN FILM DETECTION LIMITS OF LASER FLUOROSENSORS

In the last two sections it has been shown that reabsorption of emitted light can be neglected for crude oils in the laser fluorosensor equation. The equation can then be written as follows:

$$S = PT_L \int_{\lambda_1}^{\lambda_2} \eta(\lambda)C(\lambda) (1 - e^{-\alpha \text{ex}^d}) d\lambda \frac{A_R}{4\pi h^2} T_S T_F T_R \quad (14)$$

This equation can be used to calculate signal-to-noise ratios as outlined in the theory section.

The signal - to - noise ratios are considered to be expected in the channel at λ_{max} of a multichannel fluorosensor having the following specifications and operational parameters:

P	- number of photons/laser pulse, (i.e. 2.5 mJ/pulse at 337nm)	4.2×10^{15} photons
$\lambda_1 - \lambda_2$	- channel width	20 nm
$C(\lambda)$	- cathode quantum efficiency constant over $\lambda_1 - \lambda_2$	0.15
T_L	- attenuation of laser pulse by the beam steering optics, atmosphere, and the air-target interface	0.6
T_S	- attenuation of the return fluorescence due to reflective losses at the target air interface	0.9
T_F	- attenuation of the return signal by the atmosphere	0.9
T_R	- attenuation of the return signal by the receiver optics	0.12
A_R	- receiver area (radius of receiver = 10 cm)	$\pi(0.01)^2 \text{m}^2$
h	- height of sensor over target	300 m
$I_q(\lambda)$	- quantum spectral irradiance of target in absence of laser illumination (i.e. $2 \times 10^{-7} \text{mW cm}^{-2} \text{sr}^{-1} \text{nm}^{-1}$ as measured experimentally for a sun angle of 55° over open water).	4.4×10^{15} photons $\text{s}^{-1} \text{m}^{-1} \text{sr}^{-1} \text{nm}^{-1}$
A_T	- area of receiver field of view	$3.75 \times h^2 \times 10^{-6} \text{m}^2$
τ	- gate width of detection system	50 ns

Figure 5 shows the variation of signal - to - noise ratio with film thickness for all five crude oils at three excitation wavelengths calculated using the above parameters in Equations 2, 5 and 14. These calculations apply to single shot measurements. If several consecutive shots are averaged then the signal - to - noise ratio is improved by \sqrt{N} where N is the number of shots averaged.

If we take the minimum detection limit to be at a signal - to - noise ratio of 3 we arrive at the thin film detection limits recorded in Table 3. It is interesting to note that over a set of oils whose fluorescence efficiencies vary from 0.73×10^{-4} to $4.1 \times 10^{-4} \text{ nm}^{-1}$ the minimum detectable thickness for excitation at 337 nm varies only between 0.6 and 1.3. This is due to the lighter oils, which generally have higher fluorescence efficiencies, and lower absorption coefficients. Indeed the most efficiently fluorescing oil (CO7) has a higher minimum detection limit than CO5.

TABLE 3 THIN FILM DETECTION LIMITS (S/N = 3) CALCULATED AS DESCRIBED IN TEXT

	$\lambda_{\text{ex}} = 337 \text{ nm}$			$\lambda_{\text{ex}} = 270 \text{ nm}$			$\lambda_{\text{ex}} = 240 \text{ nm}$		
	η $/10^{-4} \text{ nm}^{-1}$	α	d $/\mu\text{m}$	η $/10^{-4} \text{ nm}^{-1}$	α	d $/\mu\text{m}$	η 10^{-4} nm^{-1}	α	d $/\mu\text{m}$
CO3	1.2	0.49	0.9	1.3	1.8	0.2	1.3	3.6	0.1
CO4	3.5	0.22	0.6	3.5	1.4	0.1	3.4	2.5	0.05
CO5	0.7	0.69	1.3	0.9	1.8	0.4	0.9	2.4	0.3
CO7	4.8	0.11	0.9	4.1	0.7	0.2	3.3	1.05	0.1
CO19	2.3	0.30	0.7	2.5	1.3	0.2	2.5	2.4	0.1

The parameters used in these calculations are based on the specifications of the CCRS MkIII Laser Fluorosensor currently undergoing field trials. The results therefore represent detection limits which one expects to attain using presently available technology. The signal - to - noise calculations also allow the design aspects of a fluorosensor where future improvements will have their greatest impact, to be pinpointed. Inspection of Equation 13 shows the obvious advantages of increasing laser power and the importance of optical efficiencies of the transmitter and receiver. Improvement can also be made by matching the detector cathode sensitivity wavelength range with the emission of the target. This is achieved presently for crude oils with their $\lambda_{\text{max}} \approx 500 \text{ nm}$. The

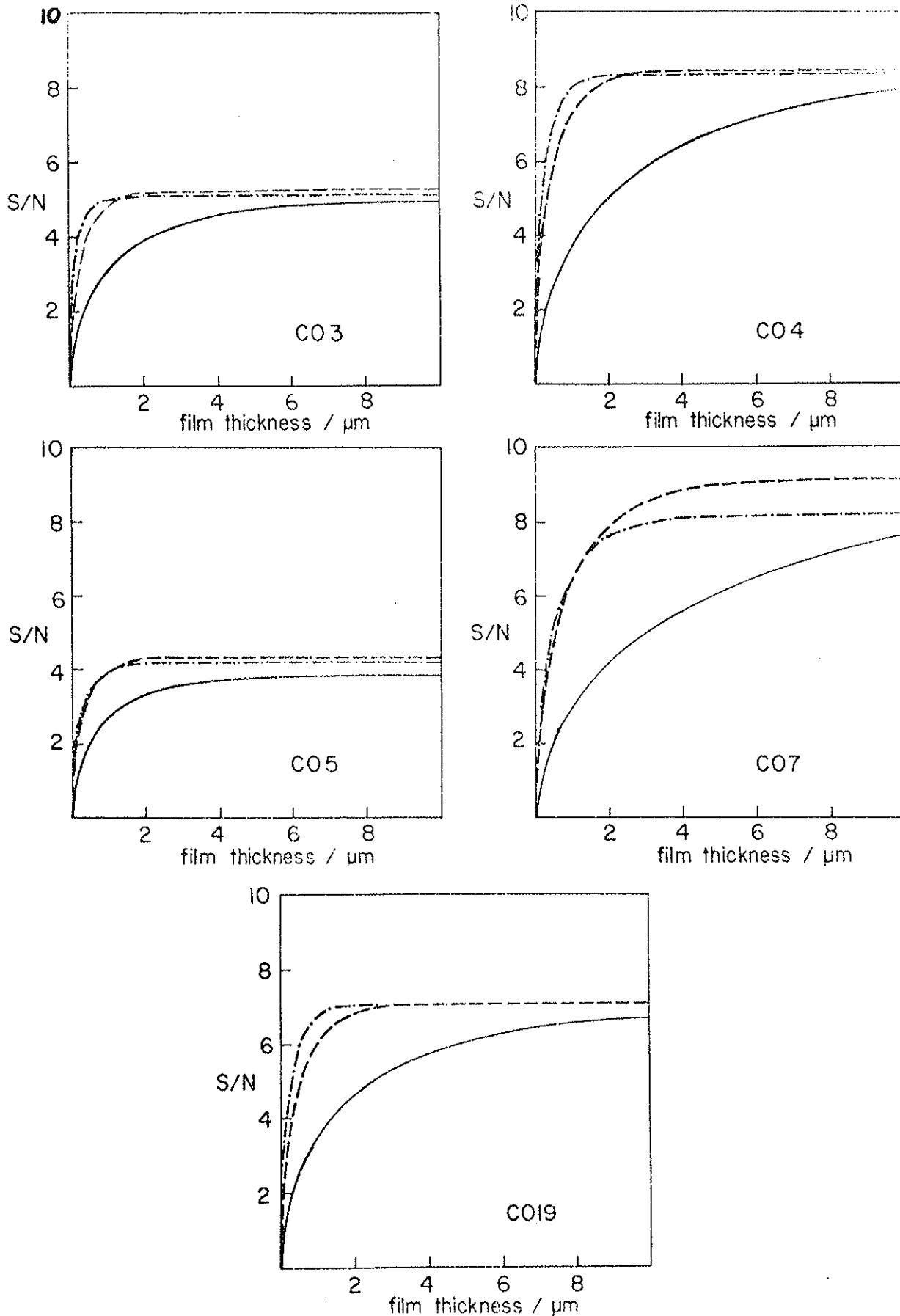


FIGURE 5

DEPENDENCE OF THE SIGNAL - TO - NOISE RATIO AS CALCULATED FOR A CCRS MkIII TYPE FLUOROSENSOR OVER CRUDE OILS.

— $\lambda_{\text{ex}} = 337 \text{ nm}$, --- $\lambda_{\text{ex}} = 270 \text{ nm}$, -.-.- $\lambda_{\text{ex}} = 240 \text{ nm}$.

availability of UV sensitive image intensifier tubes would; for sensors which are based on such devices MkIII, improve the performance of a sensor over targets which fluoresce in the near UV such as light refined petroleum products and oil based insecticide sprays. Alternatively one could design a fluorosensor using photomultiplier tubes specifically for this type of target.

A less obvious, but probably the most effective, means of lowering the thin film detection limit emerges from this work. It has been shown that the absorption coefficient of crude oils increases dramatically with decreasing wavelength. Thus lowering the excitation wavelength will result in a marked improvement in laser fluorosensor performance. The detection limits reported for excitation at 270 and 240 nm in Table 3 are calculated using the same laser power and sensor specifications as at 337 nm.

As an example, to effect the decrease in thin film detection limit, as found on going from 337 to 240 nm excitation for CO₃, one would have to increase the laser power by a factor of eight.

The recent rapid development of eximer lasers promises a source which can take advantage of these oil absorption properties. Not only can one excite in the UV, using for example krypton-fluoride to give 248 nm, but the optical power available from the eximer laser is far in excess of that from the nitrogen lasers currently used in fluorosensors. Commercial lasers are available which offer 10 W continuous power at a 70 Hz repetition rate (i.e. 140 mJ or 1.8×10^{17} photons per pulse). Just the power increase alone promises a six-fold improvement in signal - to - noise ratio. Table 4 shows calculated single shot signal - to - noise ratios for otherwise identical sensors using either a 2.5 mJ per pulse nitrogen laser or the krypton-fluoride laser described above. Film thickness was 2 μ m. Power and absorption effects combine to give a total ten-fold signal - to - noise ratio improvement.

TABLE 4 COMPARISON OF SINGLE SHOT SIGNAL - TO - NOISE RATIOS OF
2 μ m FILMS USING N₂ AND KrF LASER BASED FLUOROSENSORS

	Single Shot		S/N
	N ₂		KrF
CO3	3.9		34
CO4	5.0		54
CO5	3.3		28
CO7	4.4		50
CO19	4.6		46

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