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A Laboratory Study of the Potential of Time-Resolved Laser Fluorosensors: Supplement

RESORS

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Contents

1. Introduction

This Supplement to 'A Laboratory Study of the Potential of Time-Resolved Laser Fluorosensors' describes the fluorescence properties of an additional twenty-five samples of likely fluorosensor targets (Table 1). As well as some further examples of the type of oils studied for the main report the new selection contains samples related to other roles of fluorosensing besides marine oil spill detection. Included are dyes which may be used as tracers in hydrographic studies, samples from mine tailing ponds, oils which may pollute inland waters, a high boiling point aromatic oil used in coal liquifaction, pulp mill effluent and fish oil.

The fluorescence spectra are presented using the same scales and format as in the main report. Thus direct comparison between the spectra in the main report and in the supplement is possible. In the supplement we have omitted the actual decay profiles which are in any case dependent on the lamp profile. Should they be required in future the decay profiles are stored on floppy disk at NRC.

Experimental techniques were exactly the same as those used in the main study apart from the additional use of a Perkin-Elmer MFP-44A spectrofluorimeter to obtain the spectra of the low optical density mine tailings using right angle rather than front surface viewing.

Table 1: Sample selection

Code #	Description	
S1	T.J. Light Crude Sample M-75-53	
S2	Venezuelan Crude	
S3	Shell Midate Crude	
S4	Leduc Crude	
S5	Punta Cardon #6	
S6	Bunker Oil MOT Oct. 22/76	
S7	Marine Diesel MOT Oct. 22/76	Oils
S8	Bilge Water MOT Oct. 22/76	
S9	Outboard Motor Oil/Gasoline Mixture	
S10	Outboard Motor Oil	
S11	10W50 Oil	
S12	10W30 Oil	
S13[+]	Pulp Mill Effluent - Masson	Pulp Mill Effluent
S14	Pulp Mill Effluent - Hawkesbury	
S15[+]	Plant Tailings Pond Outlet, McIntyre Mines, Grande Cache	
S16[+]	North Side of Tailings Pond, McIntyre Mines	Coal Mine Tailings
S17[+]	Below Settling Pond, Cardinal Creek Coals, May 9/77	
S18[+]	Pond Outlet, Cardinal Creek Coals, May 9/77	
S19	High Boiling Point Aromatic - Coopers Creek Chemicals	
S20	Cod Liver Oil	
S21	Pontamine White S.P. Paper Whitener	
S22	Rhodamine WT	
S23	Rhodamine B	Dyes and Standards
S24	POPOP in Ethanol	
S25	Quinine Sulphate in 0.5 M H_2SO_4	

[+]These optically dilute samples were also studied by right-angle viewing (see Appendix II).

2. Fluorescence Spectra

Samples S1 to S7 are oils of similar types to those covered in the main report. The spectra of all seven are consistent with the classification in that report of oils into three main groups (crude, light refined and heavy refined).

Bilge water (S8) has a broad fluorescence spectrum similar in intensity and shape to a crude oil. It should therefore be possible to police illegal bilge pumping using a laser fluorosensor.

Outboard motor oil (S10) behaves as a typical light refined petroleum product and on mixing with gasoline (S9) shows the same spectral shape but with reduced intensity.

Motor oils 10W50 (S11) and 10W30 (S12) also fluoresce strongly. The structure in their spectra in the 350 to 450 nm range is typical of a light refined petroleum product. The fluorescence at higher wavelengths is possibly due to dyes added after production.

Pulp mill effluent (S13 and S14) emits with an unstructured spectrum narrower than that shown by oils and with a peak at 400 nm. The high tail in the red for sample S13 is due to the sample not being optically dense at 337 nm giving a large amount of scattered light which is overemphasized by the correction factor. The same applies to the coal mine tailing pond samples. Although they are included here the spectra of S13, S15, S16, S17 and S18 are of limited use. They were therefore repeated using a right-angle viewing arrangement. The right-angle spectra give the shape to be expected for the fluorescence of these samples. However efficiencies cannot be estimated by comparison with the front surface spectra. In practice the intensity of fluorescence of such low optical density targets can be large as large depths of penetration are possible compared with the few millimetres possible in the laboratory.

When viewed using a right-angle arrangement the coal mine tailings (S15→18) show a broad band fluorescence with λ_{max} = 420-430 nm. However their efficiency is low. Their quantum yields are around 0.01 (cf ϕ = 0.54 for quinine sulphate in 0.5 MH_2SO_4).

A high boiling point aromatic (S19) typical of the solvents used in coal liquifaction plants shows broad band emission of the strength of many crude oils with λ_{max} = 490 nm. Mapping of accidental spills should therefore be possible, especially with a custom built instrument.

Cod liver oil (S20) fluoresces with the efficiency of a crude oil. Although the band is somewhat narrower than most crude oils confusion could arise between the two when only spectral measurements are made.

Samples S20 and S21 are dyes commonly used in tracer studies. Rhodamine WT, sold as a water soluble dye, is a very poor fluorescer. Pontamine white fluoresces strongly but is reported to be unstable under UV light.

Samples S23-S25 have been suggested as standards for performance tests on fluorosensors. One other suggested standard, 1-napthol at pH 9, was found to be too unstable and is not included.

3. Fluorescence Decay Times

The fluorescence decay times of the samples are recorded in Table 2. The same two channels, 'blue' and 'red', as those described in the main report were used.

For the extended set of oil samples the conclusions of the main report still hold with samples S1 to S7 having decay times in the ranges predicted therein. As with its spectral properties bilge water (S8) shows decay properties which would classify it in the crude oil category. Outboard motor oil also shows decay properties which reinforce its classification by spectral comparison, this time as a light refined product. Interestingly on dilution with gasoline (S9) the decay times of outboard motor oil shorten markedly. This is consistent with the reduced fluorescence efficiency of the mixture. Of the two motor oils the lighter 10W30 (S12) shows the long decay times associated with light petroleum products. The heavier 10W50 (S11) shows much shorter decay times more typical of a crude oil. Only the structure in its spectrum in the low wavelength region distinguishes it from a light crude oil.

Pulp mill effluents also show larger decay times in the red channel as do mine tailing pond samples. Both these aqueous sets of samples show fairly short decay times with $\tau_{blue} \approx 1.5$ and $\tau_{red} \approx 3.0$.

Table 2: Fluorescence lifetimes of possible fluorosensor targets

	τ_{Blue}	τ_{Red}
S1	1.64 ± 0.06	4.57 ± 0.09
S2	1.60 ± 0.07	4.52 ± 0.10
S3	0.96 ± 0.05	2.72 ± 0.06
S4	2.29 ± 0.07	6.16 ± 0.11
S5	-	1.07 ± 0.04
S6	0.60 ± 0.03	1.51 ± 0.05
S7	8.49 ± 0.17	16.6 ± 0.17
S8	1.05 ± 0.05	3.60 ± 0.08
S9	2.85 ± 0.08	6.32 ± 0.14
S10	7.23 ± 0.26	12.71 ± 0.24
S11	1.45 ± 0.07	4.58 ± 0.10
S12	11.16 ± 0.36	19.95 ± 0.24
S13	1.35 ± 0.05	2.6 ± 0.07
S14	1.50 ± 0.06	2.82 ± 0.07
S15	1.39 ± 0.05	2.77 ± 0.05
S16	1.28 ± 0.04	2.64 ± 0.06
S17	1.40 ± 0.05	3.05 ± 0.07
S18	1.39 ± 0.05	2.82 ± 0.07
S19	1.05 ± 0.05	5.85 ± 0.11
S20	3.02 ± 0.08	5.82 ± 0.13
S21	2.90 ± 0.11	5.88 ± 0.08
S22	-	0.32 ± 0.03
S23	-	3.30 ± 0.07
S24	1.58 ± 0.06	-
S25	-	19.06 ± 0.12

Disappointingly cod liver oil cannot be definitely distinguished from crude mineral oil by its decay times. Although the lengthening on going to the red channel is less than generally found for the crude oils it is by no means small enough to allow classification.

4. Conclusions

All the crude oil and petroleum products examined in this supplementary study show fluorescence properties consistent with the conclusions of the main report.

Of the new classes of targets studied all show some potential for fluorosensing. Pulp mill effluent fluoresces efficiently and should be detected easily. Coal mine tailing pond water also fluoresces, although less strongly than pulp mill effluent, and would be detectable providing the optical depth were great enough. The potential for the sensing of these aqueous targets will be affected significantly by the background fluorescence of the waters in the absence of effluent. We have no information on this topic. A large scale survey of the induced background fluorescence of Canadian waters would be invaluable in the assessment of fluorosensor roles. Although background fluorescence will not add to the signal from optically dense oil slicks it could be important where a spill has spread significantly to allow laser light to penetrate into the water below, and in estimating the contrast to be expected between open water and an oil spill.

Besides reinforcing the conclusions of our main report the preliminary studies in this supplement show that several other roles of fluorosensing appear feasible.

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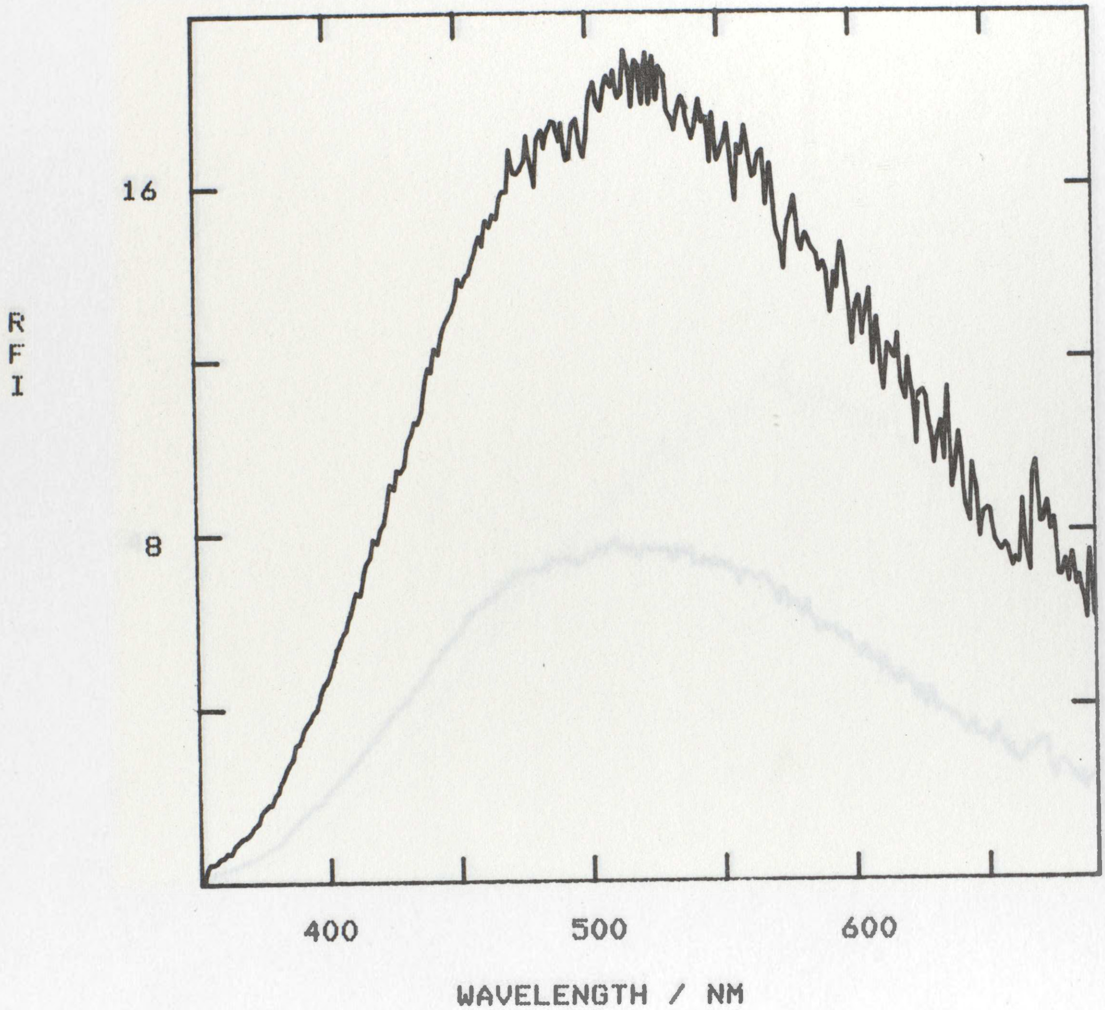
Besides reinforcing the conclusions of our main report the preliminary studies in this supplement show that several other roles of fluorosensing appear feasible.

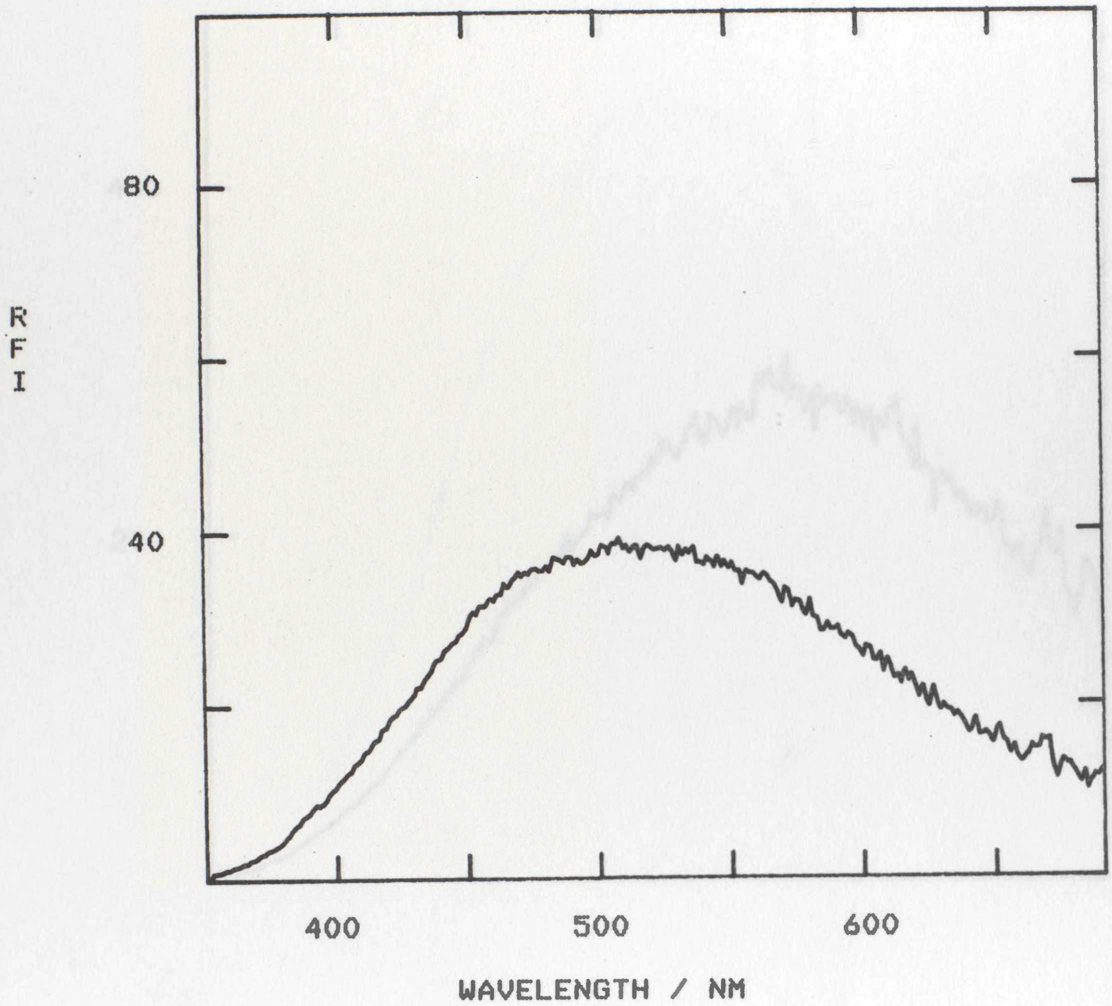
Appendix I

Fluorescence Spectra

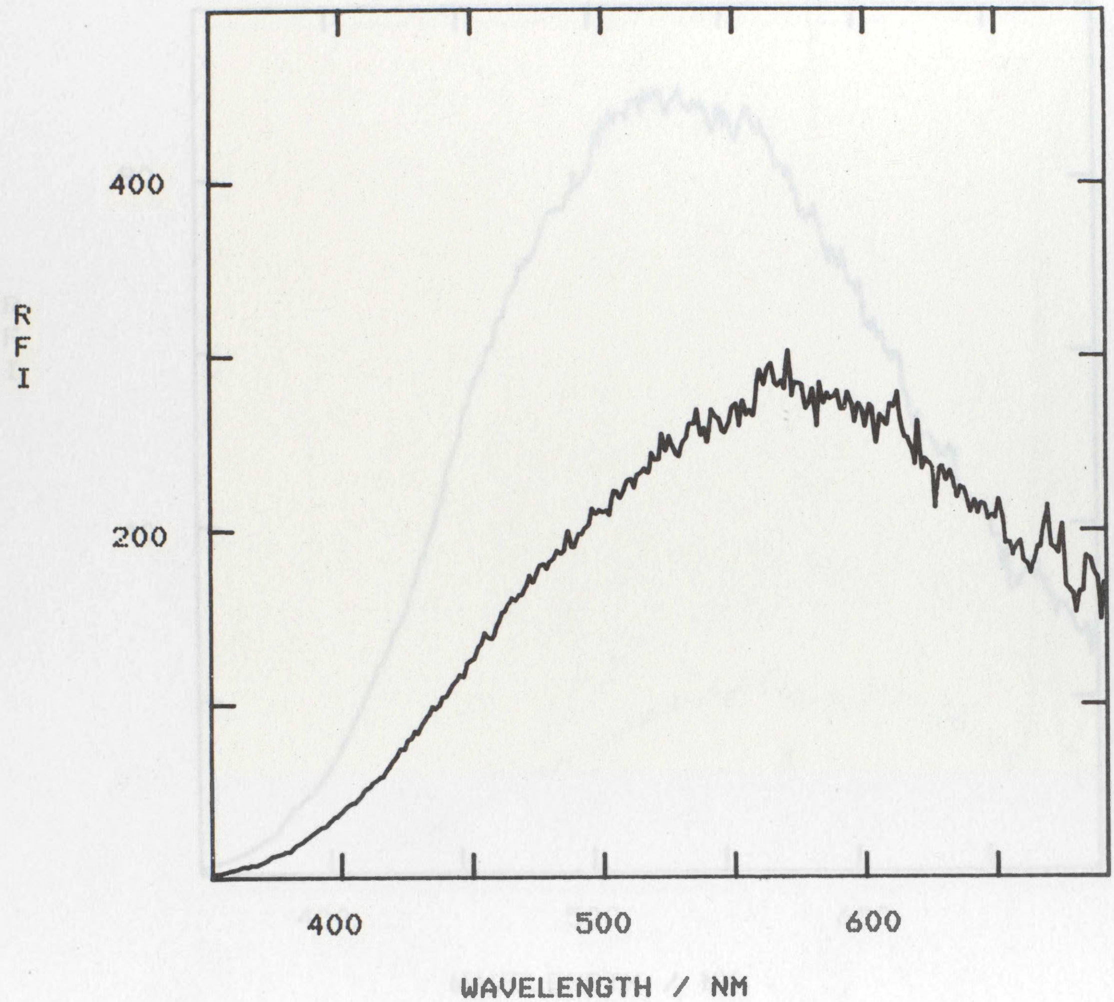
Spectra are plotted showing relative fluorescence intensity (RFI) as a function of emission wavelength. The excitation wavelength was 337 nm in all cases (where a spurious peak is observed at 674 nm this is due to second order transmission of reflected exciting light by the emission monochromator). All spectra in Appendix I can be directly compared with each other and with those in the main report taking their vertical scales into account.



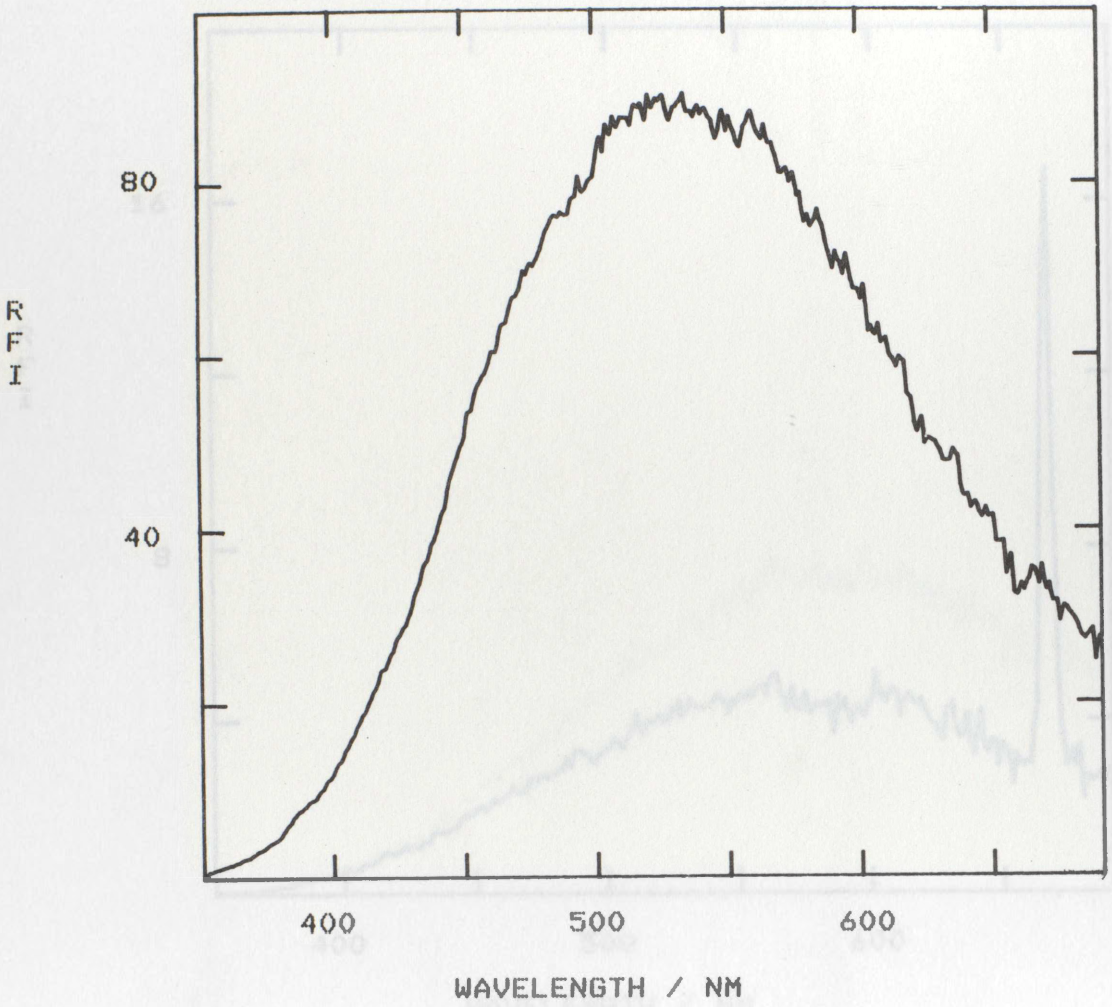
S1: T.J. LIGHT CRUDE SAMPLE M-75-53



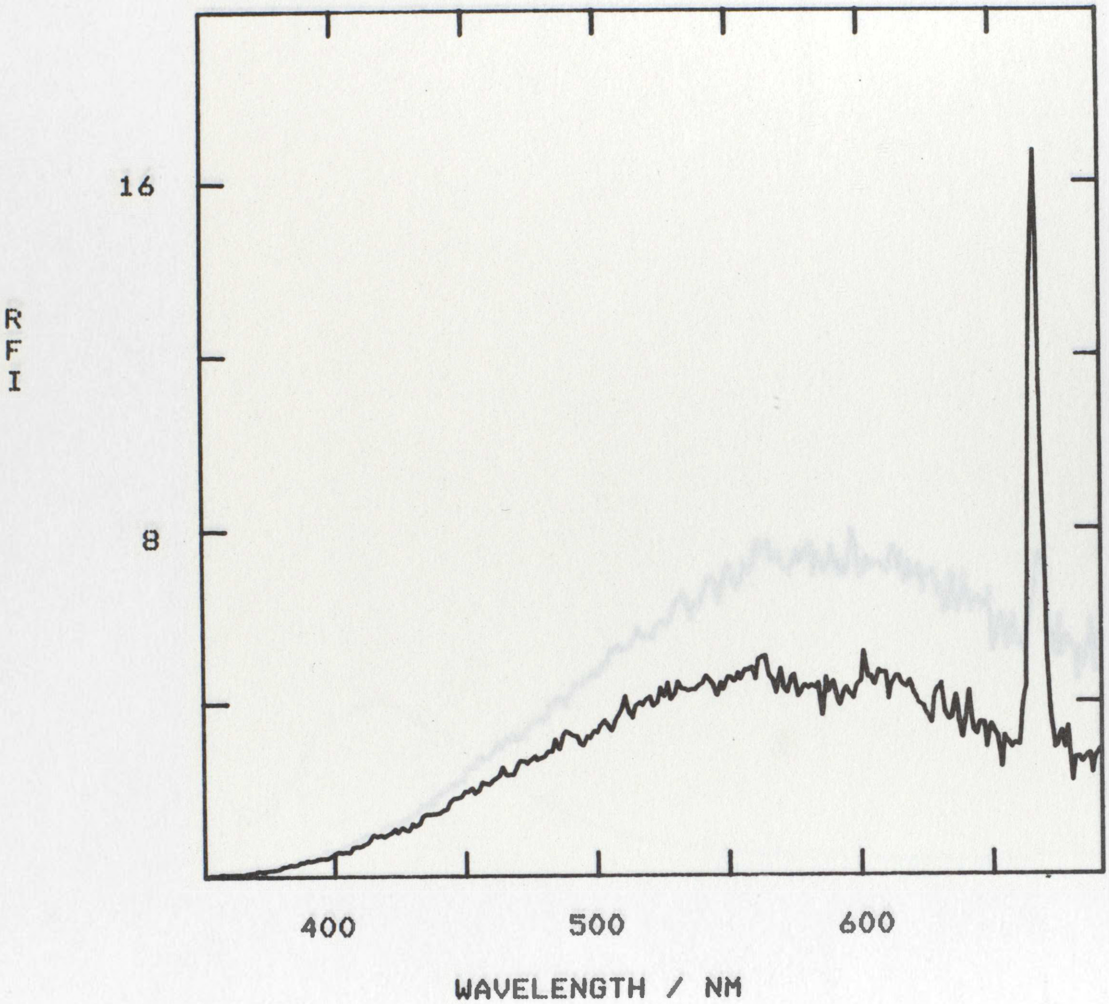
S2: VENEZUELAN CRUDE



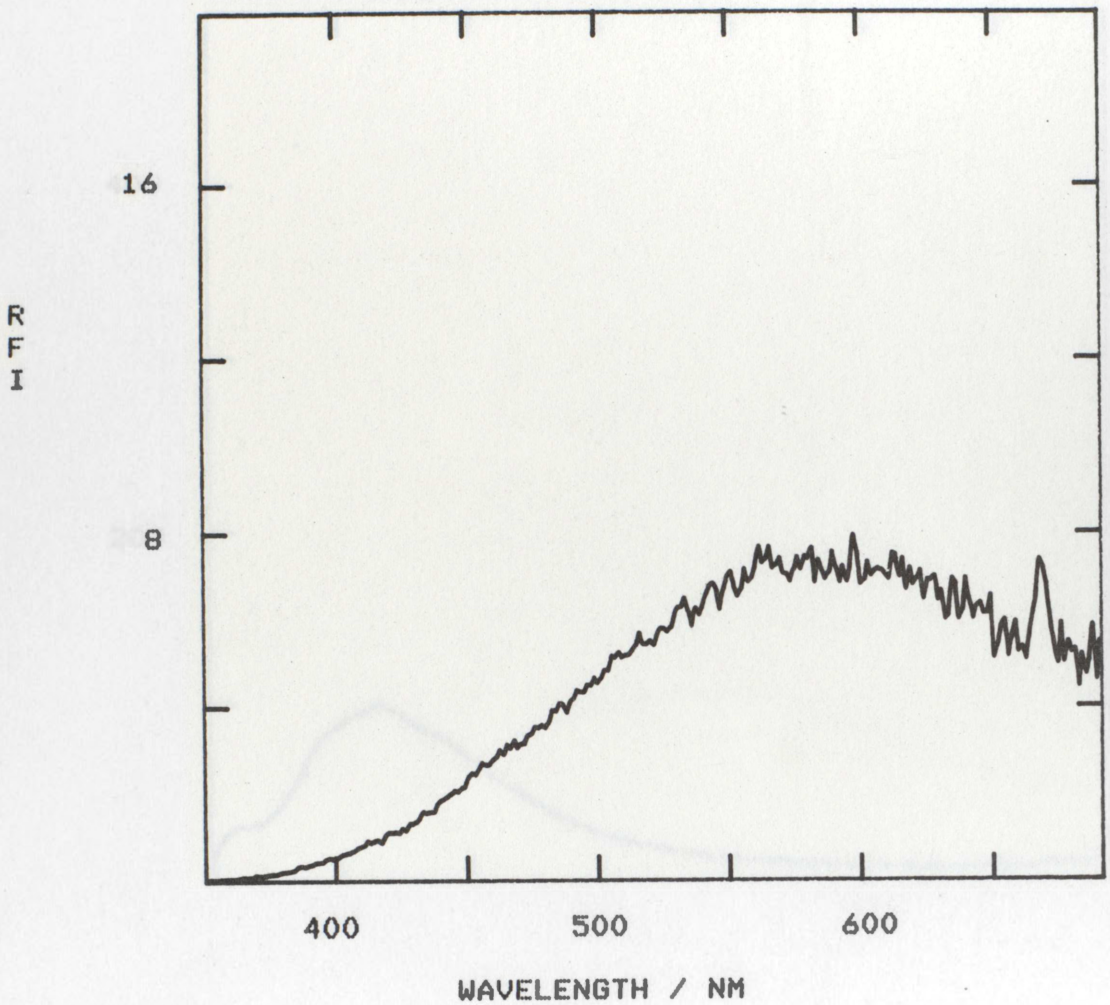
S3: SHELL MIDALE CRUDE



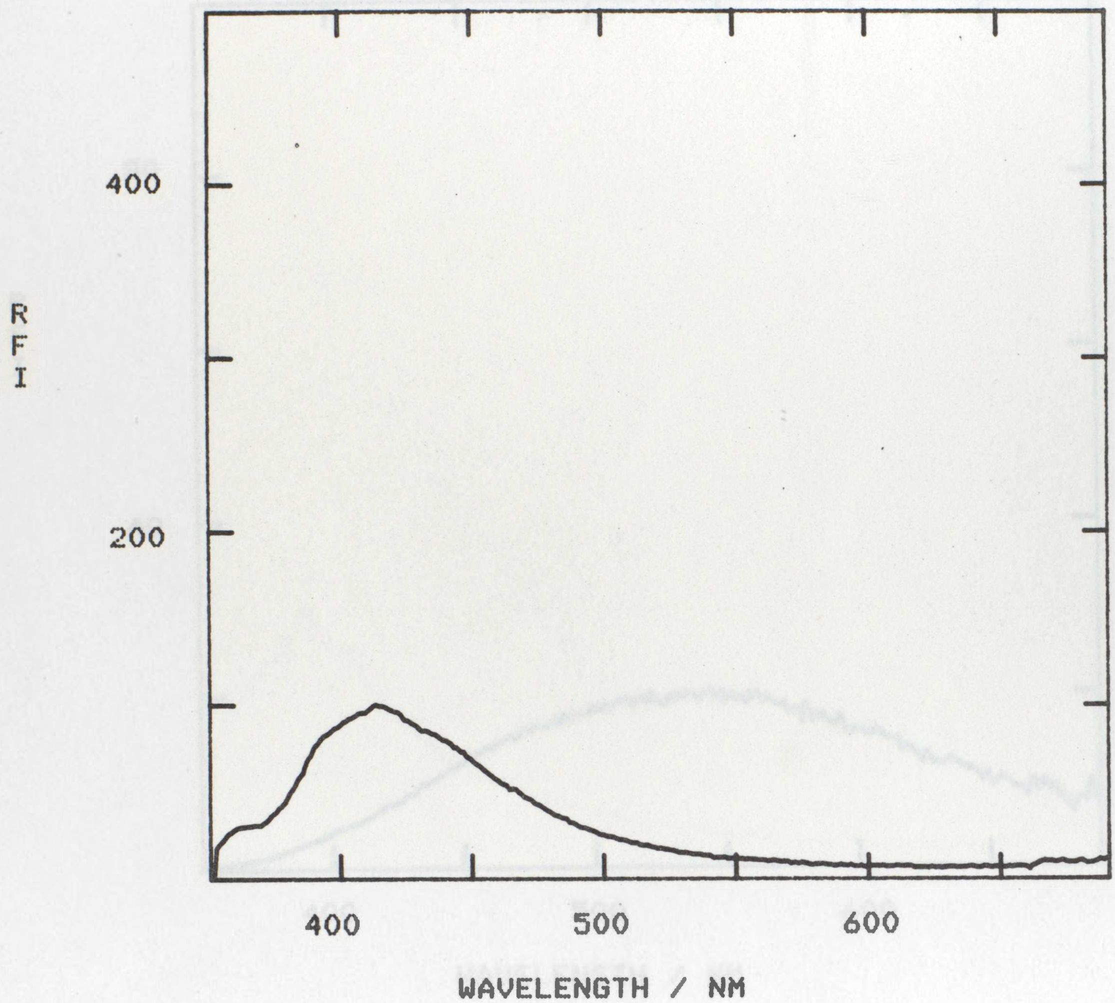
S4: LEDUC CRUDE



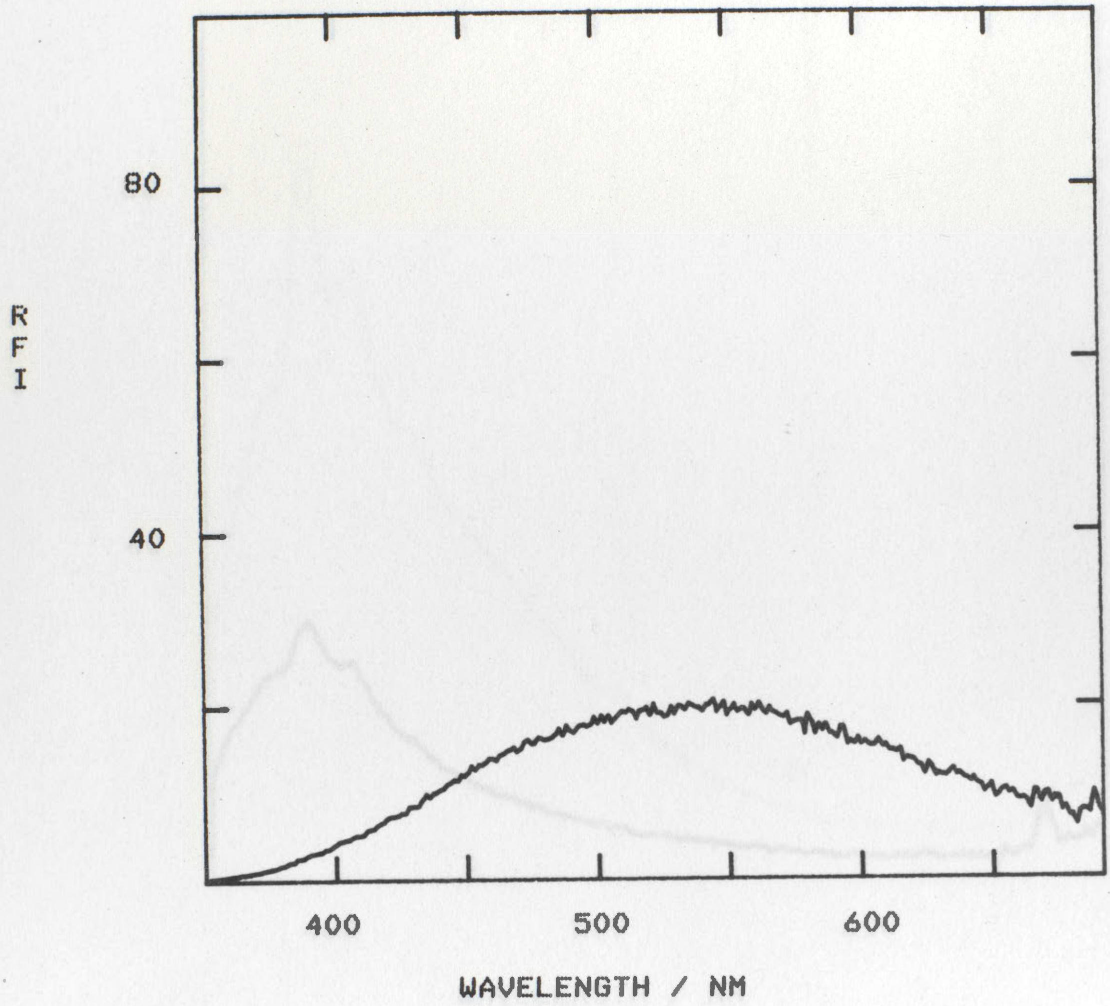
S5: PUNTA CARDON #6



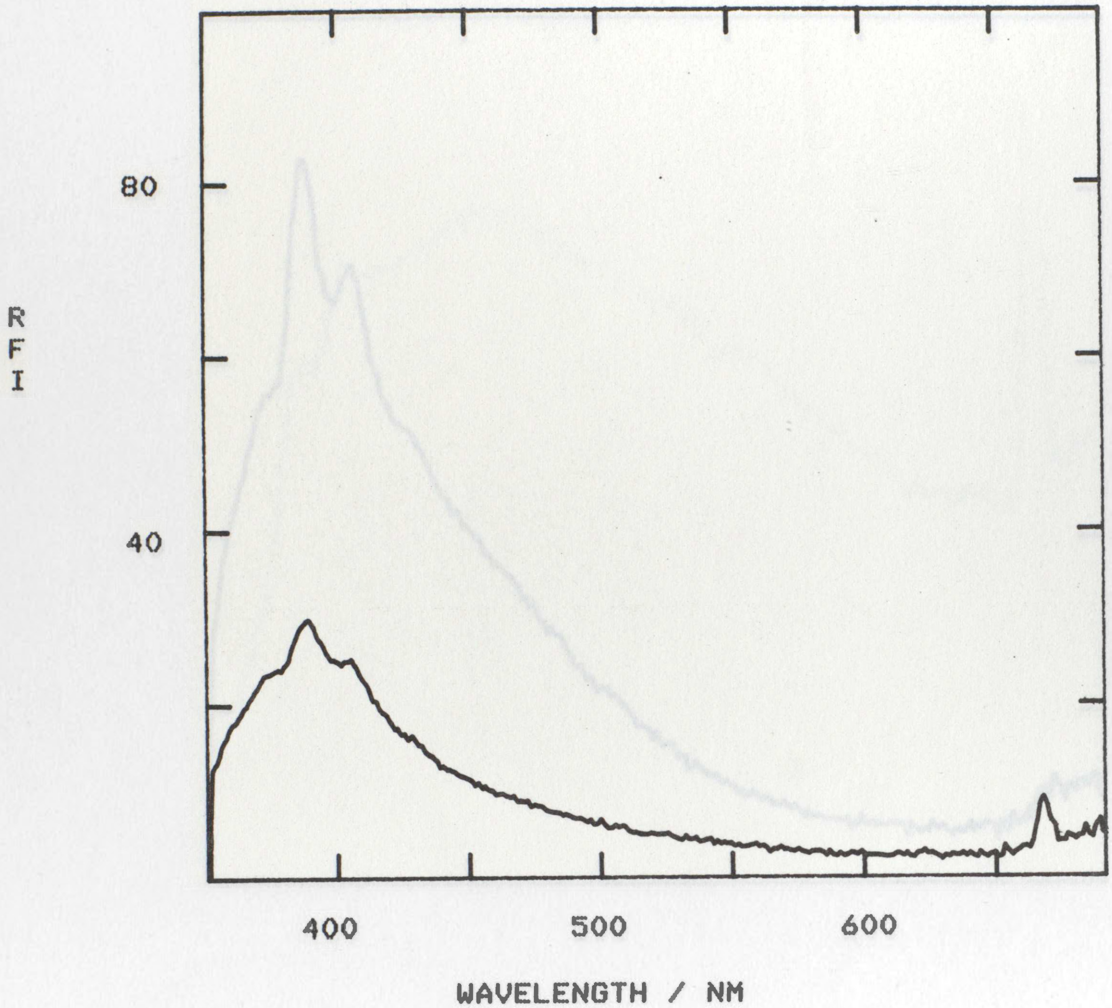
S6: BUNKER OIL M.O.T. OCT/76



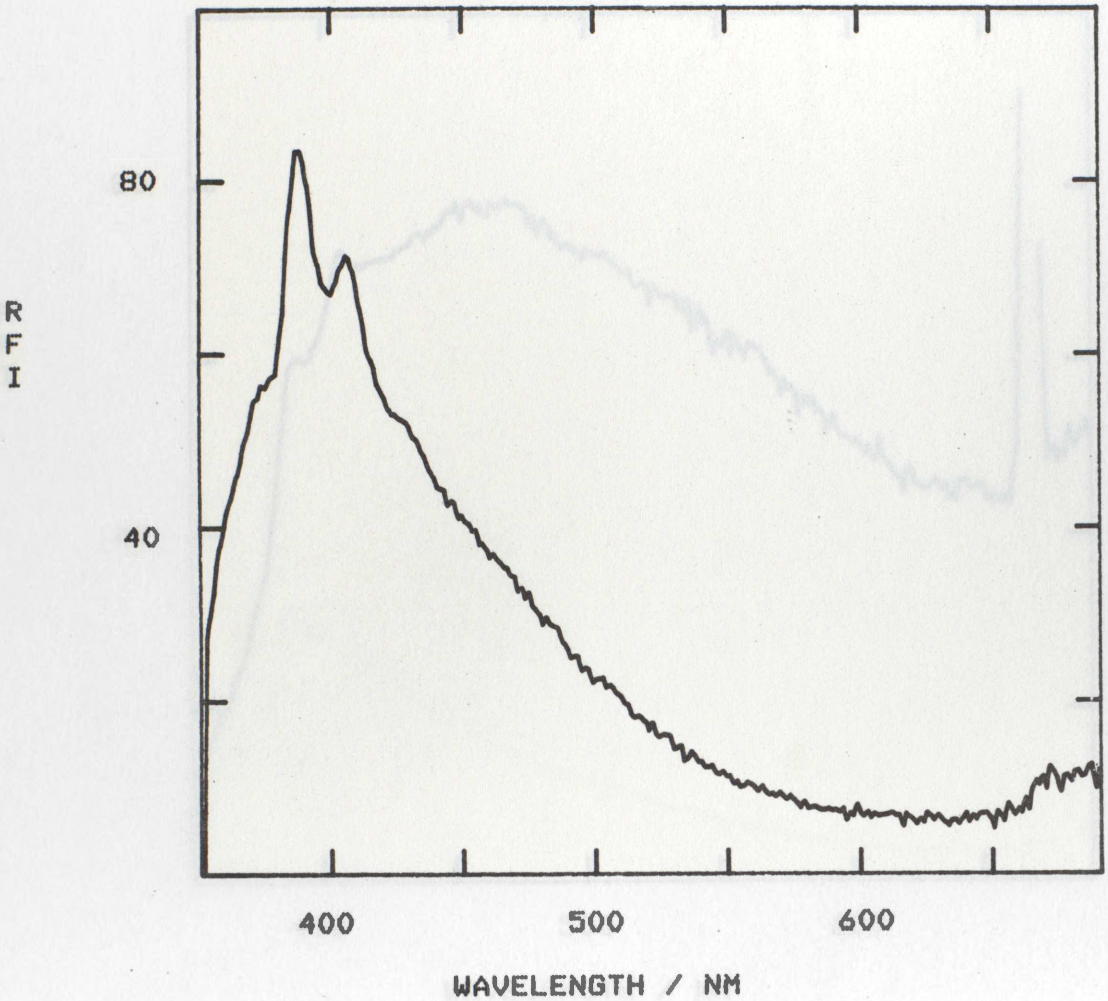
S7: MARINE DIESEL M.O.T. OCT/76



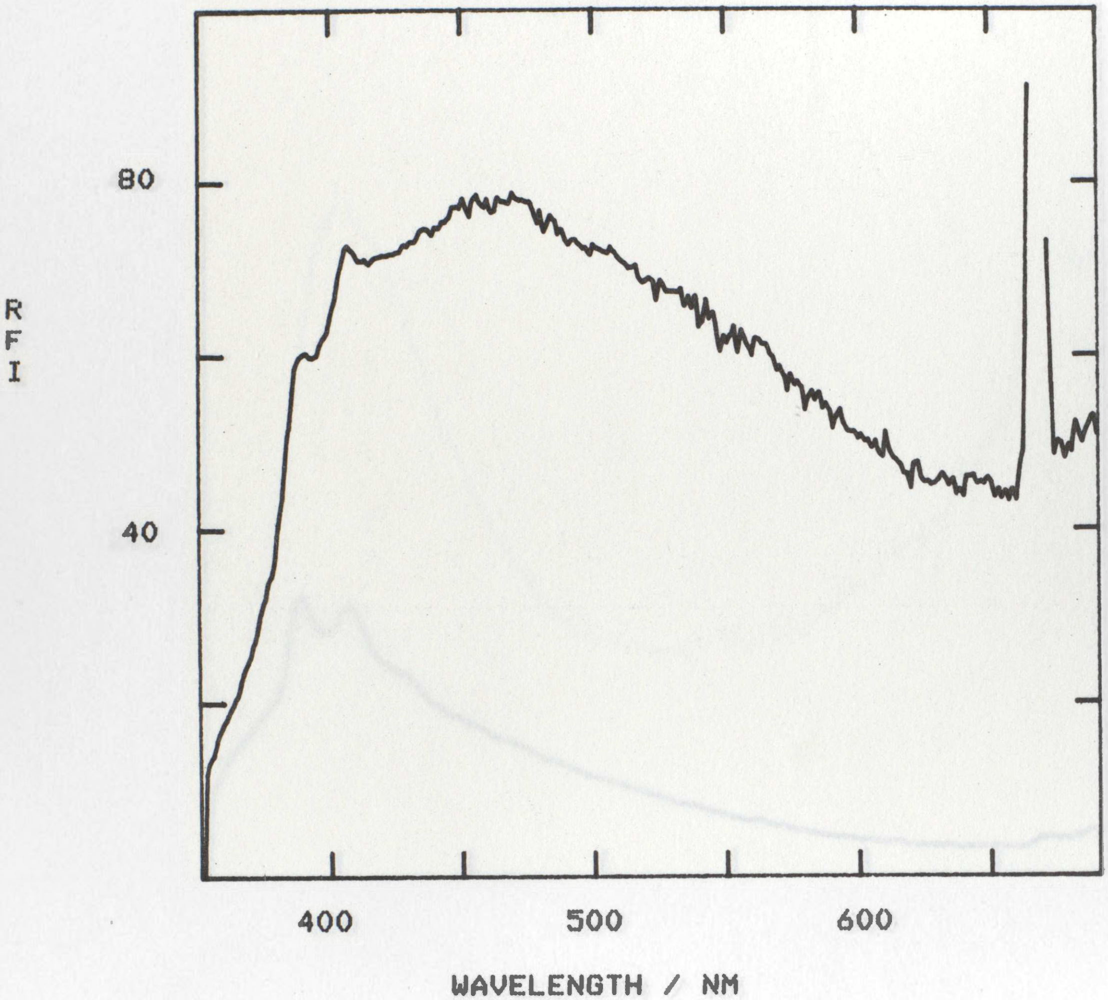
S8: BILGE WATER M.O.T. OCT/76



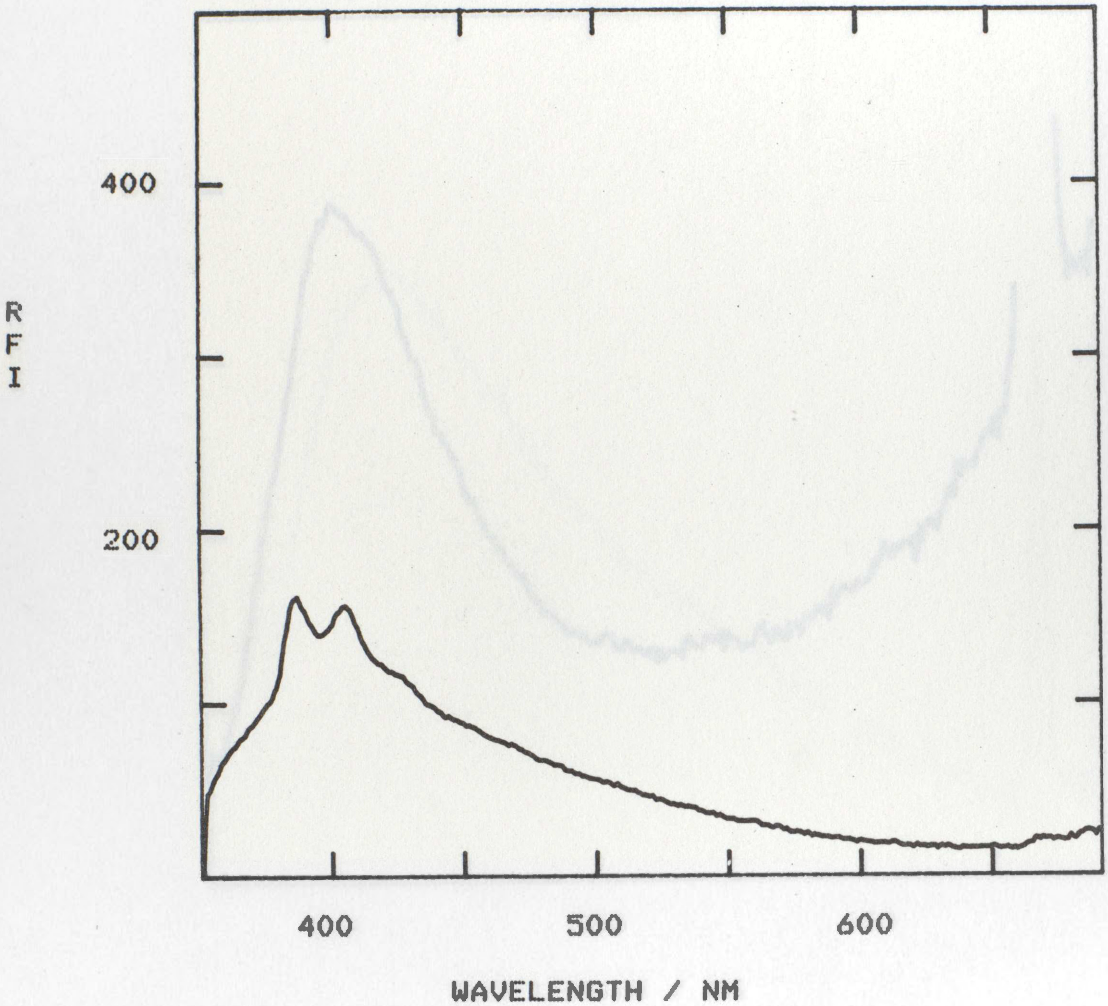
S9: OUTBOARD MOTOR OIL / GASOLINE MIXTURE



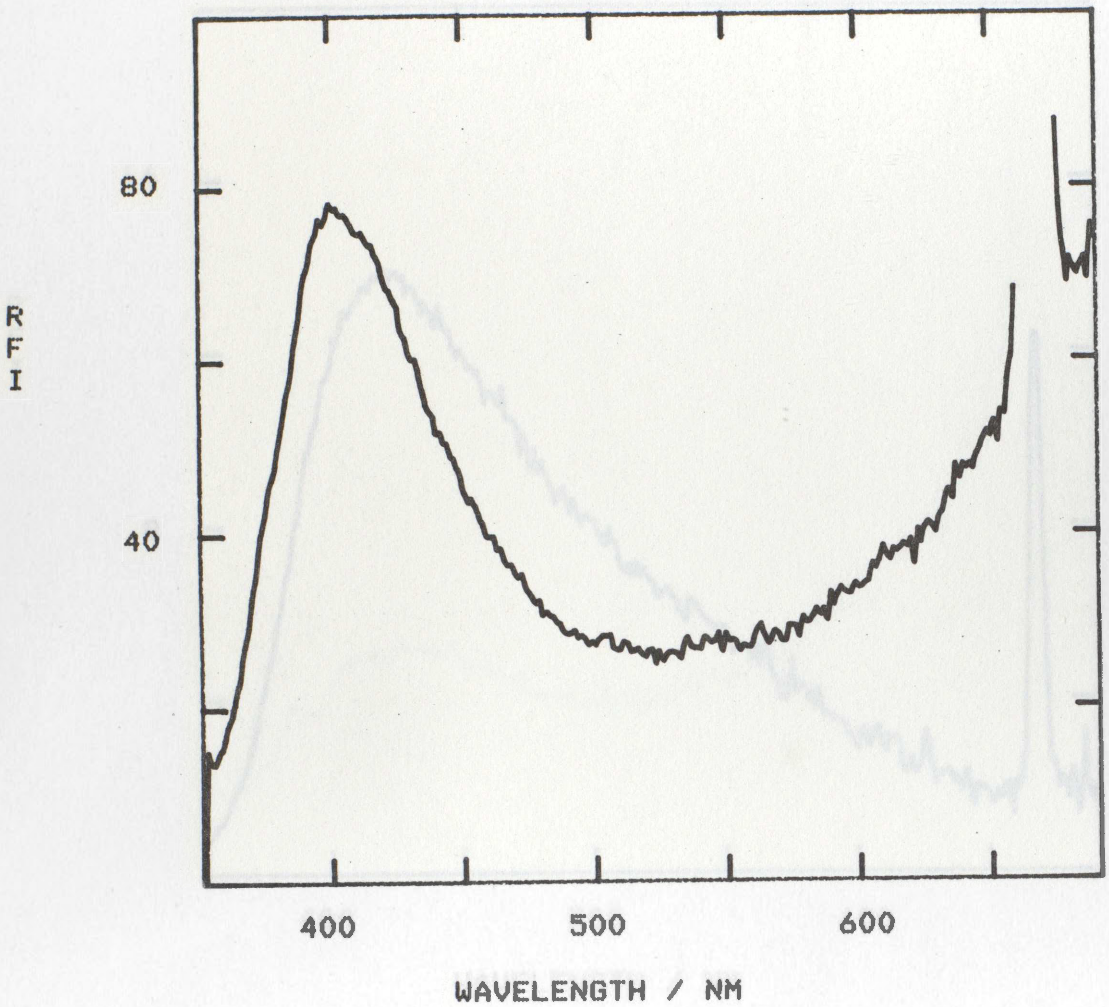
S10: OUTBOARD MOTOR OIL



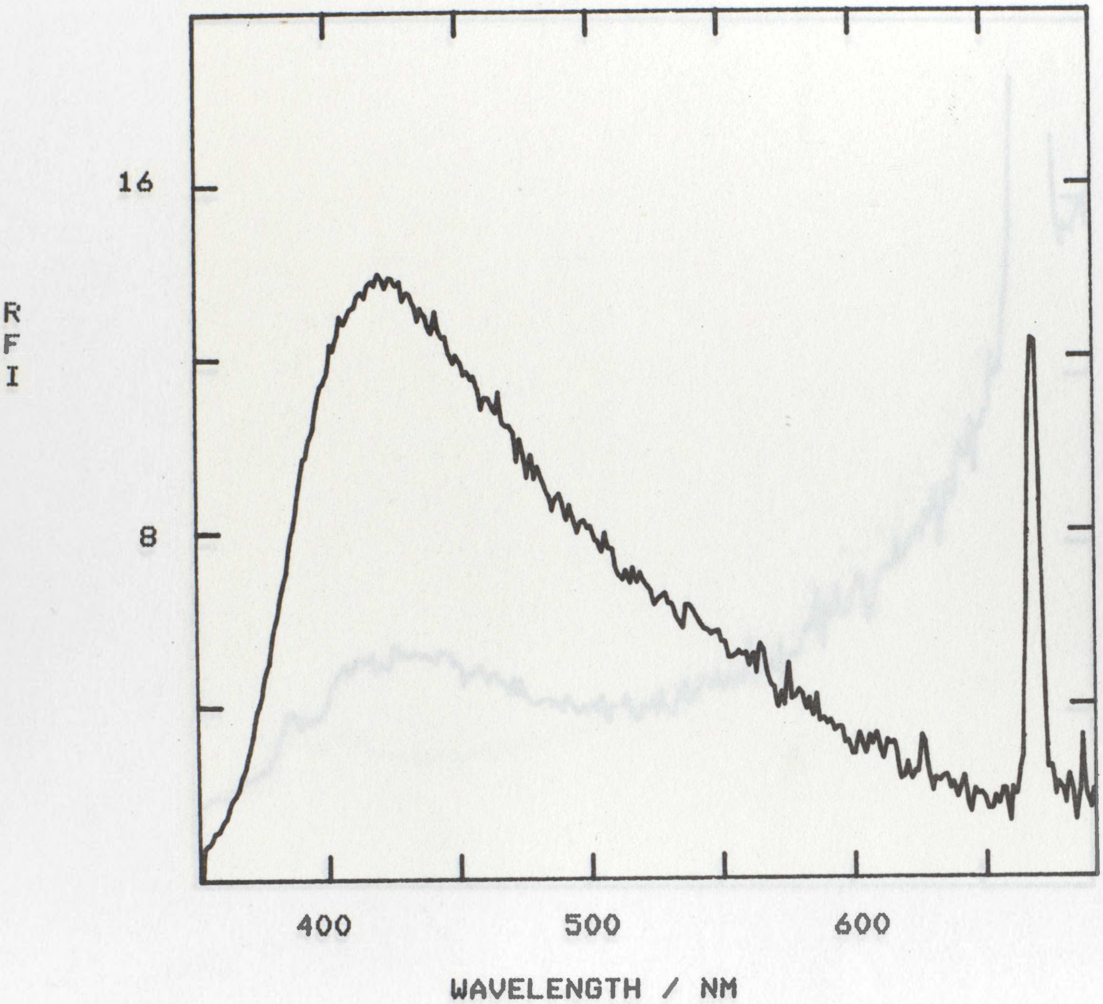
S11: 10W50 OIL



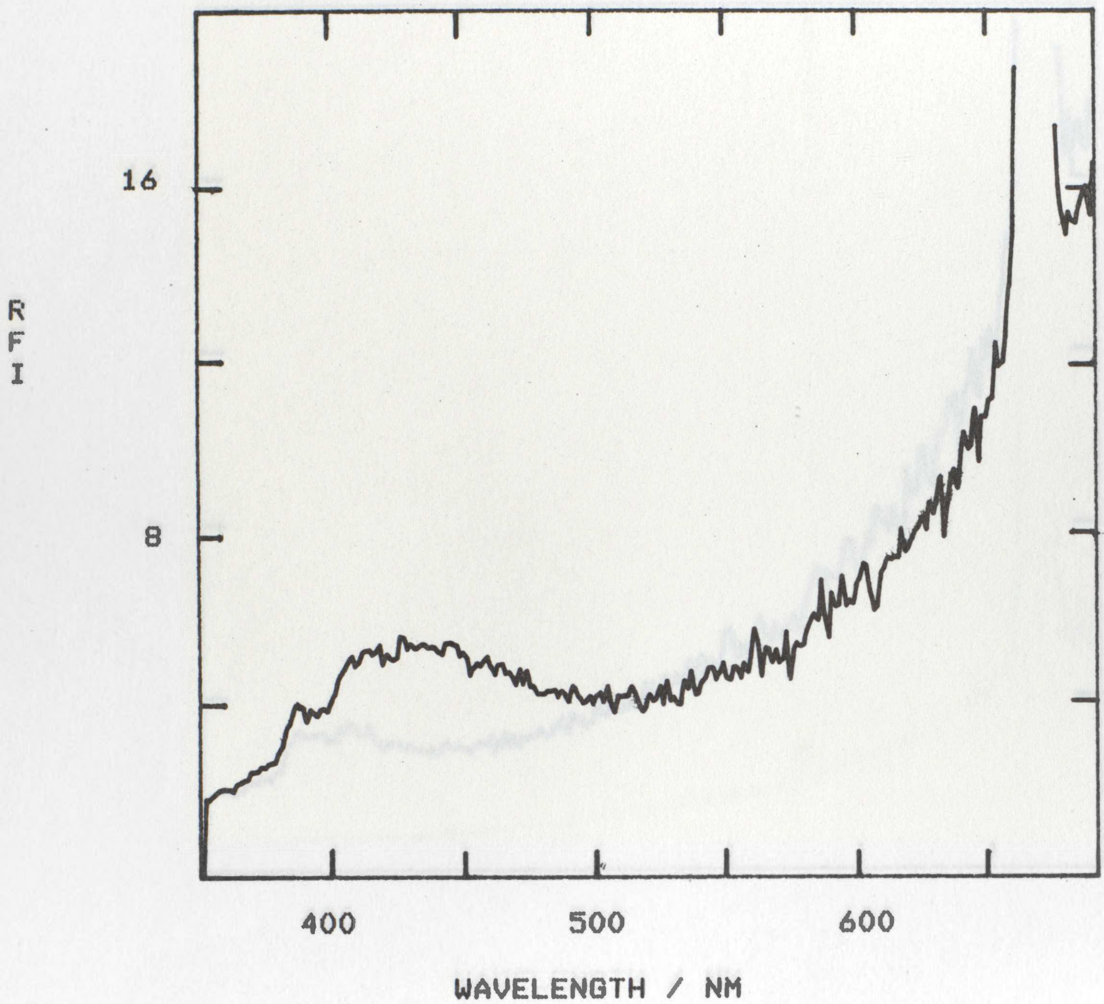
S12: 10W30 OIL



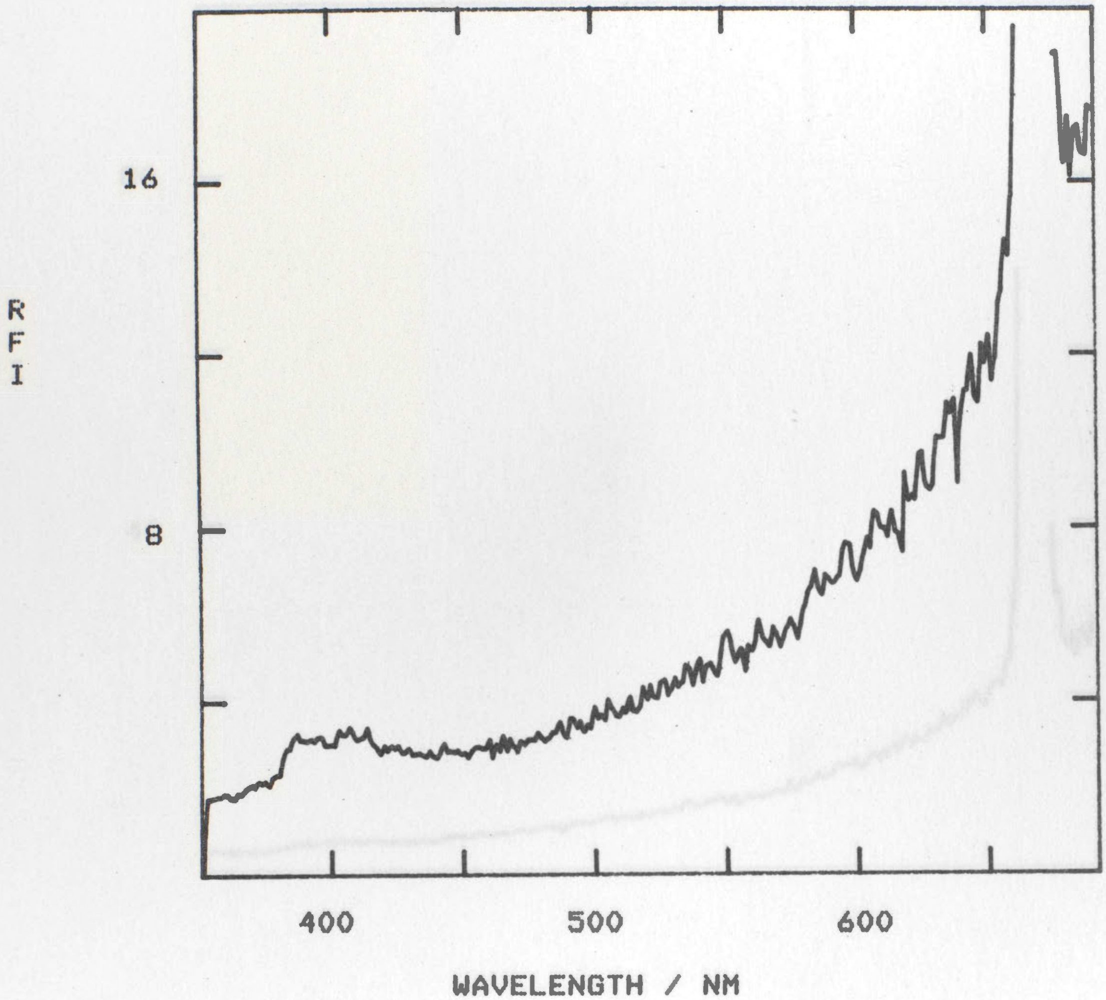
S13: PULP MILL EFFLUENT - MASSON



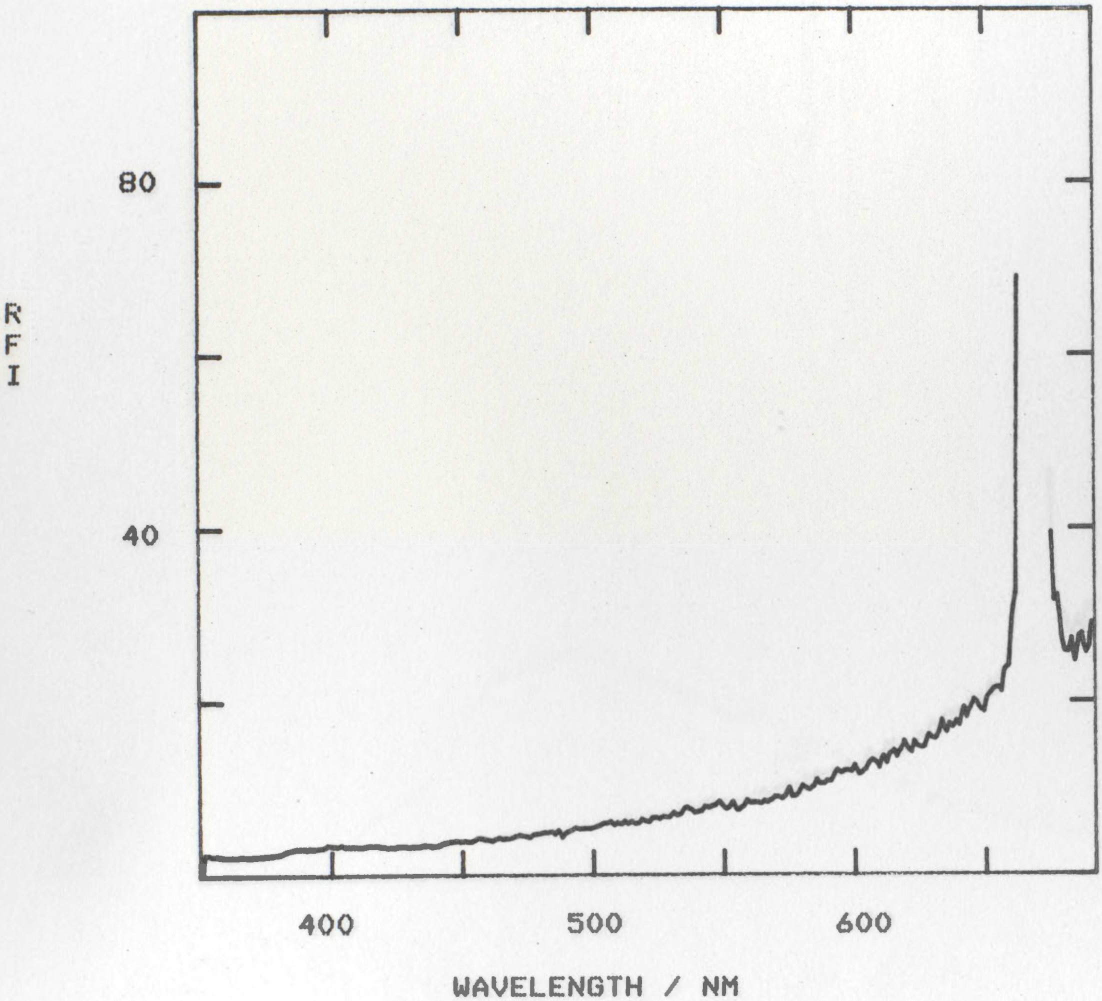
S14: PULP MILL EFFLUENT - HAWKESBURY



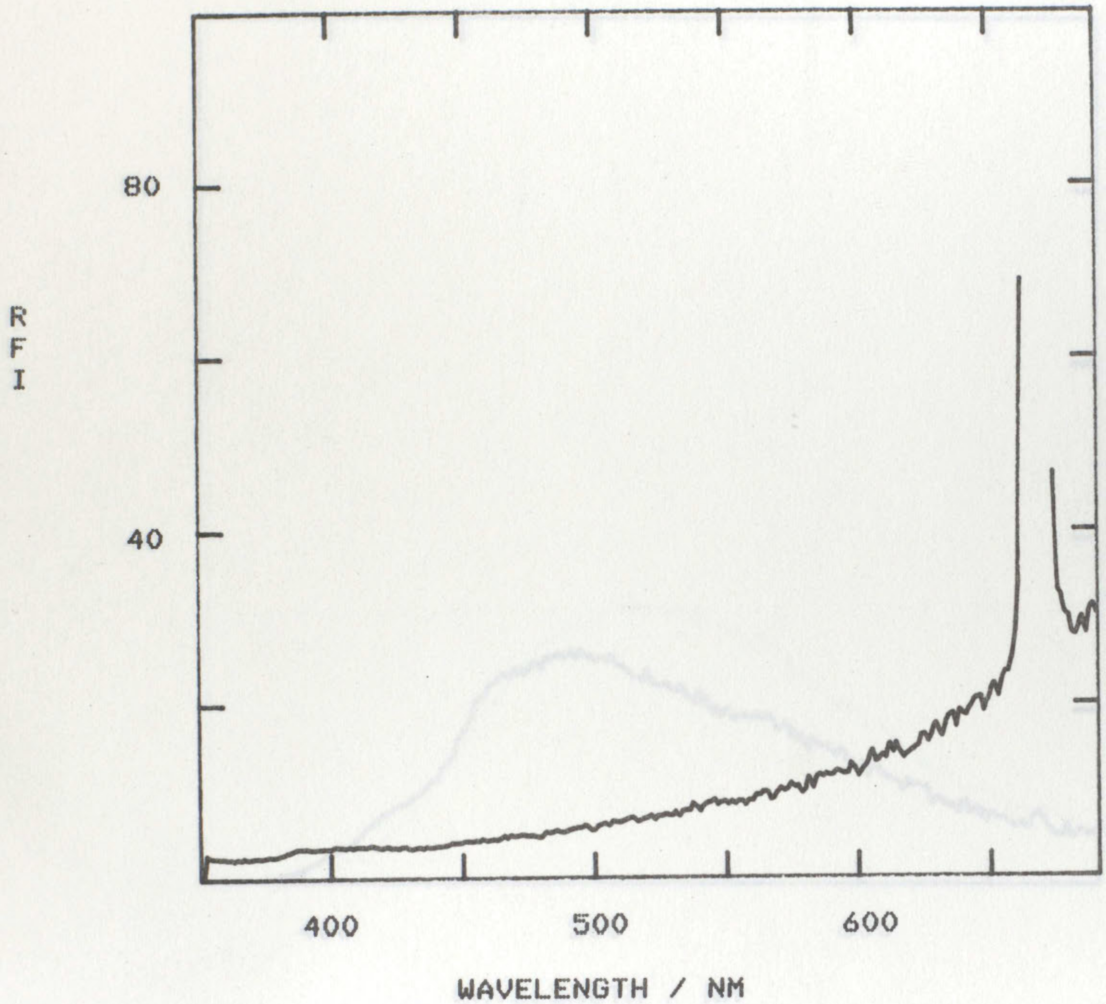
S15: PLANT TAILINGS POND OUTLET
MCINTYRE MINES, GRAND CACHE



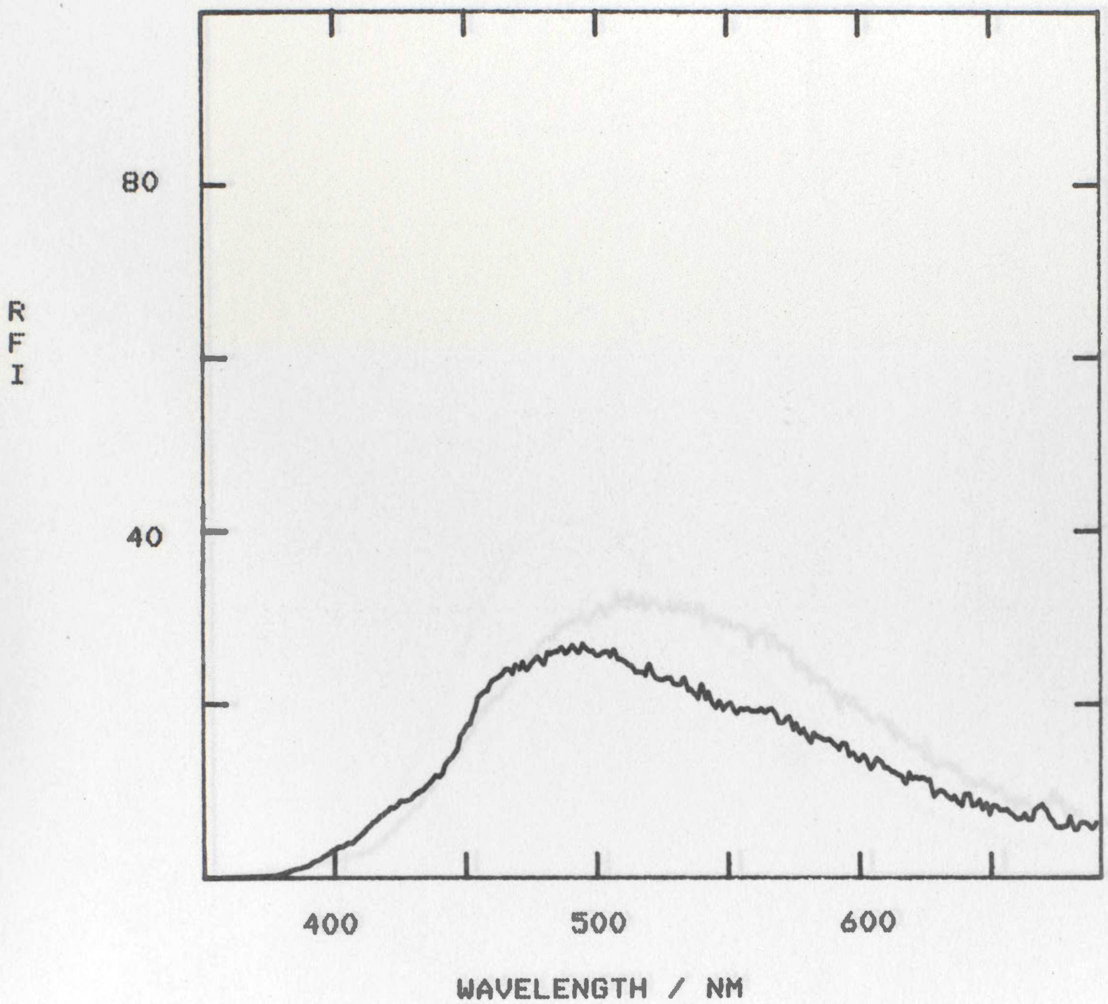
S16: NORTH SIDE OF TAILINGS POND
MCINTYRE MINES, GRAND CACHE



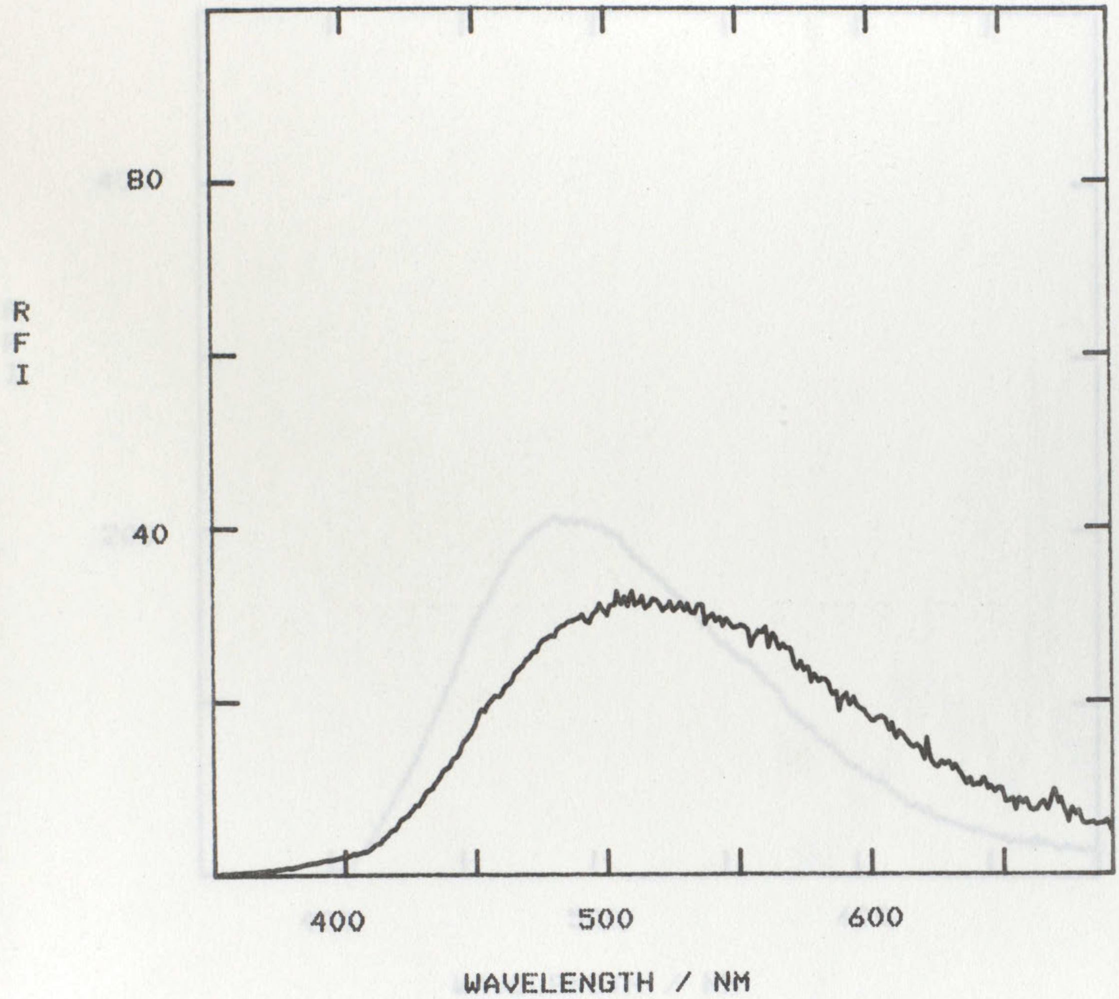
S17: BELOW SETTLING POND
CARDINAL CREEK COALS MAY/77



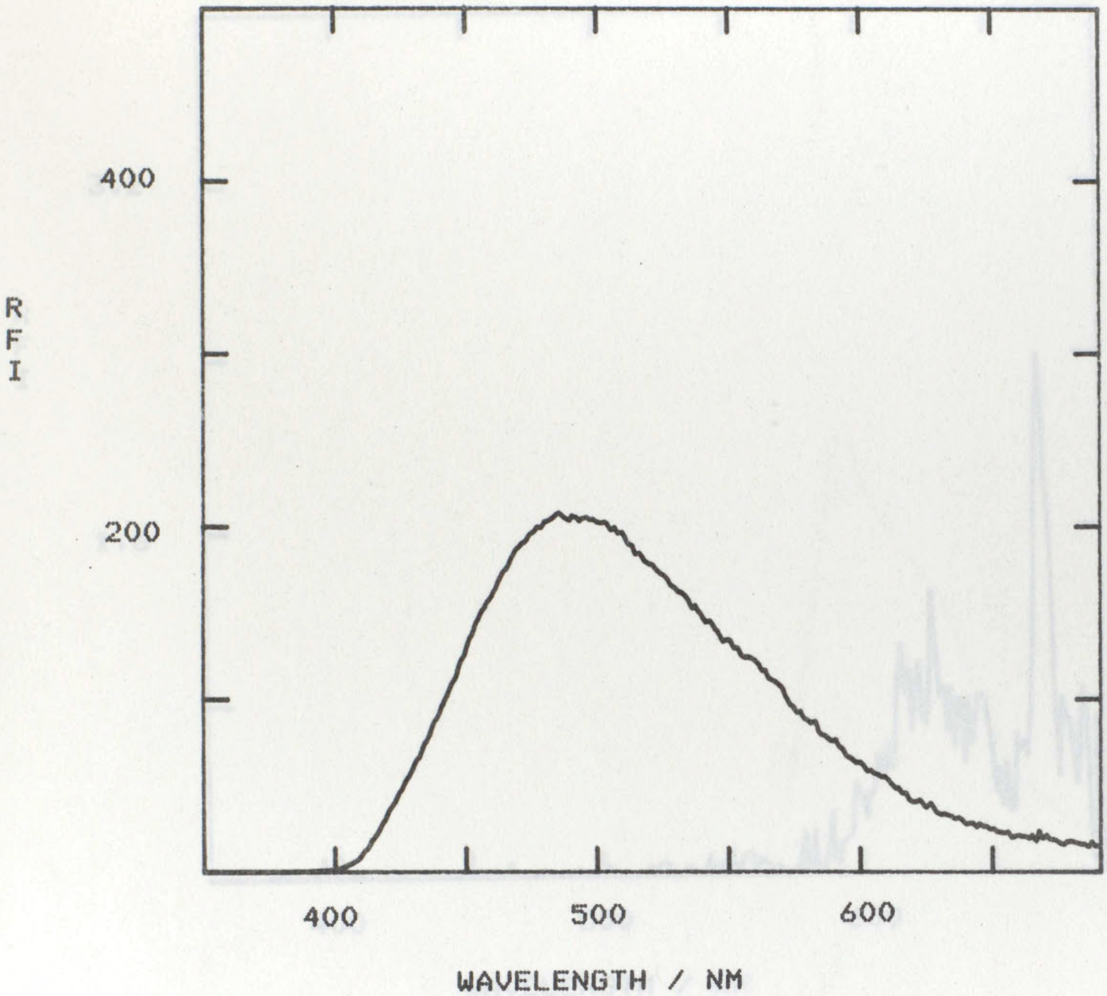
S18: POND OUTLET
CARDINAL CREEK COALS MAY/77



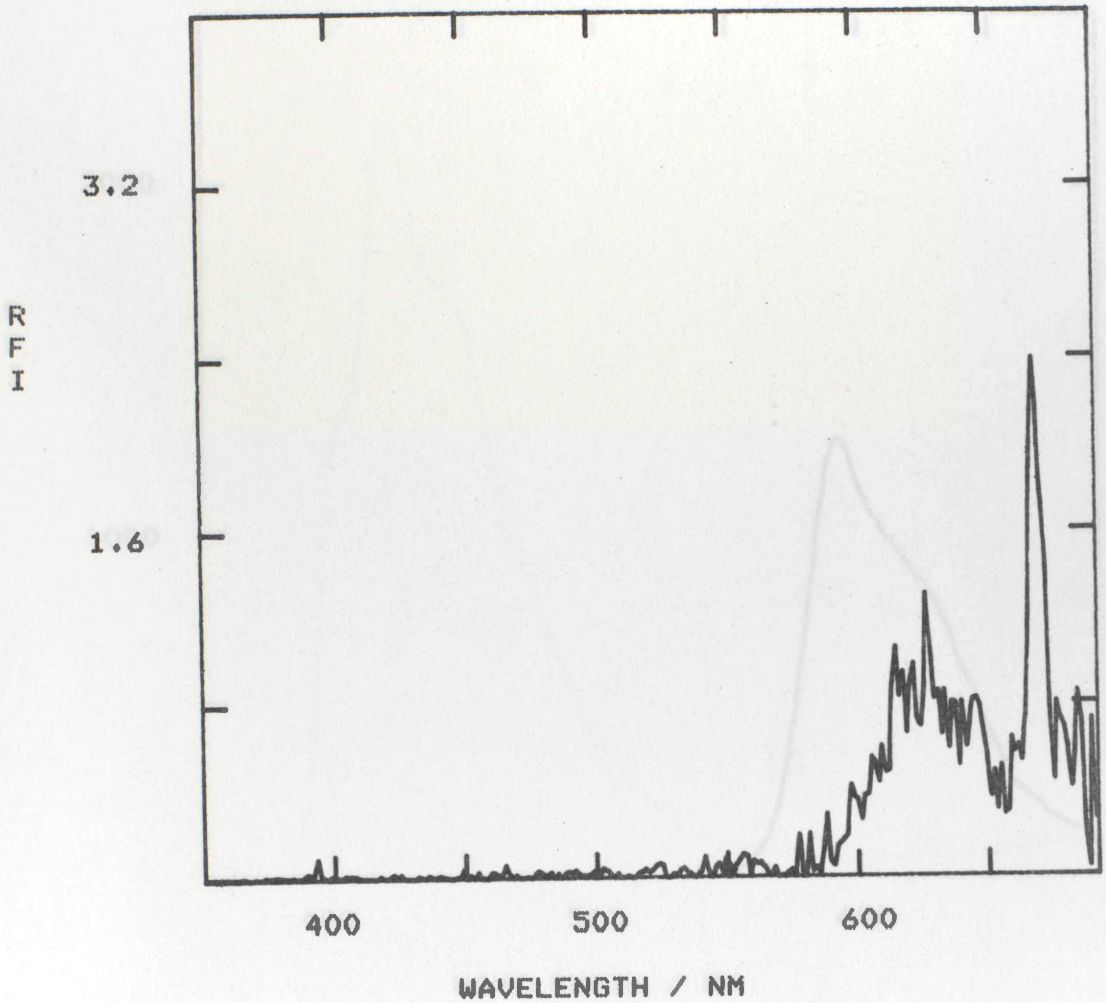
S19: HIGH BOILING POINT AROMATIC
COOPERS CREEK CHEMICALS



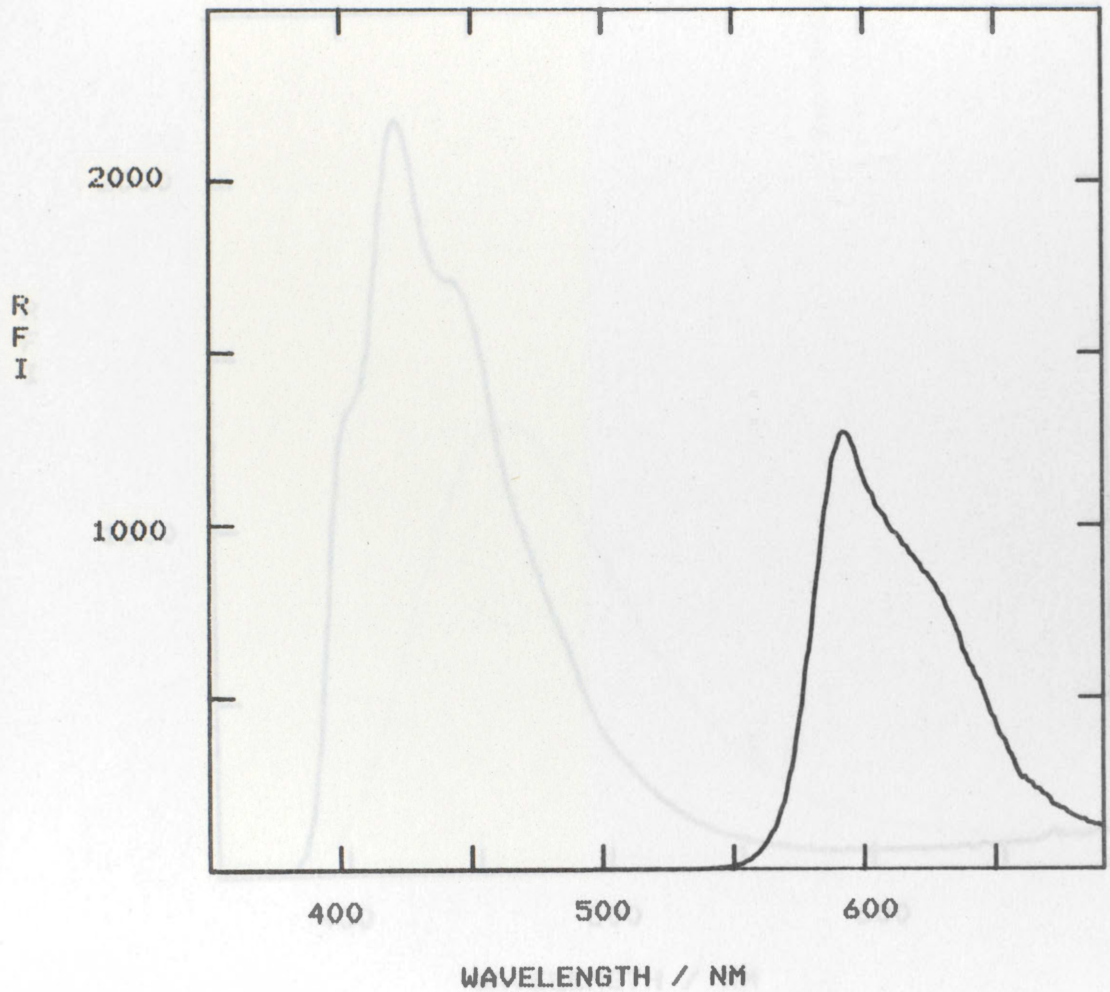
S20: COD LIVER OIL



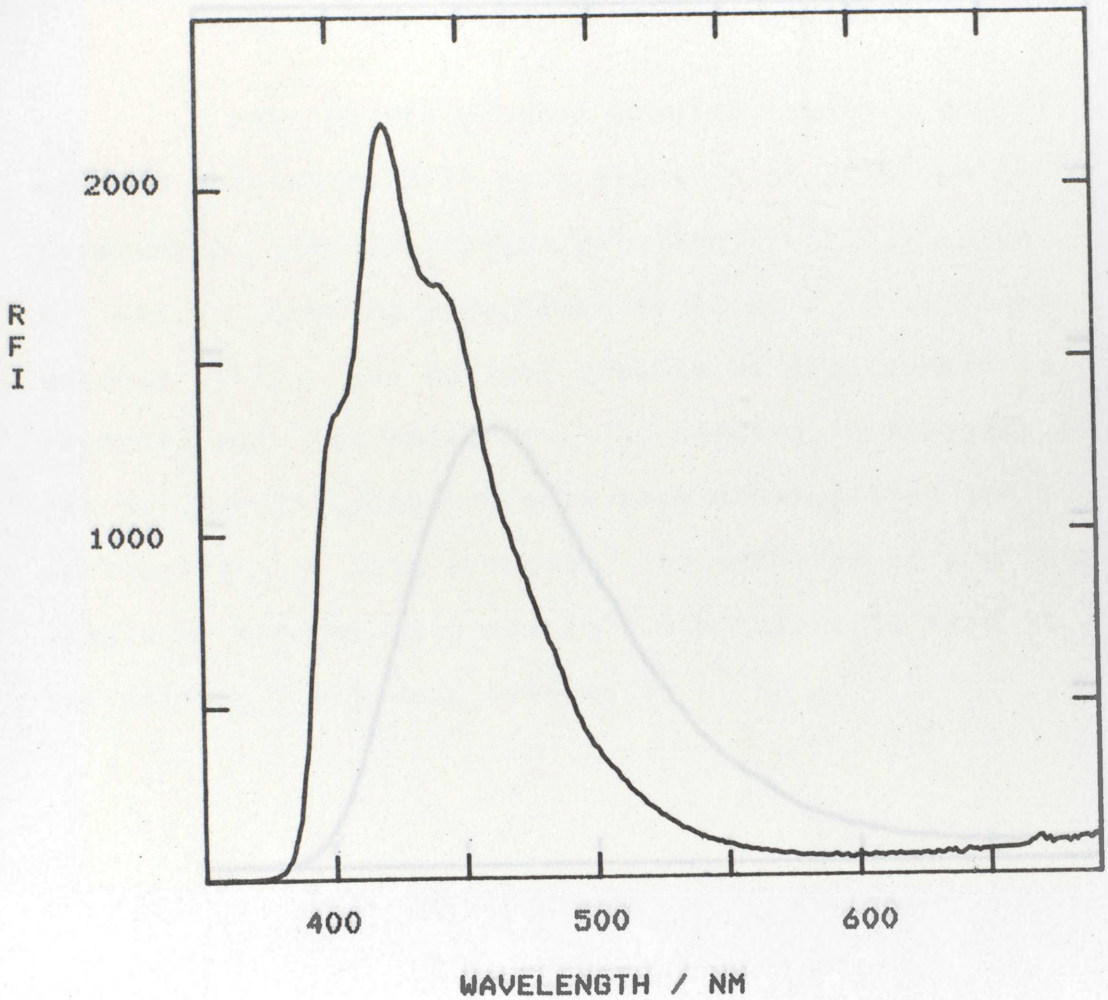
S21: PONTAMINE WHITE S.P. PAPER
WHITENER



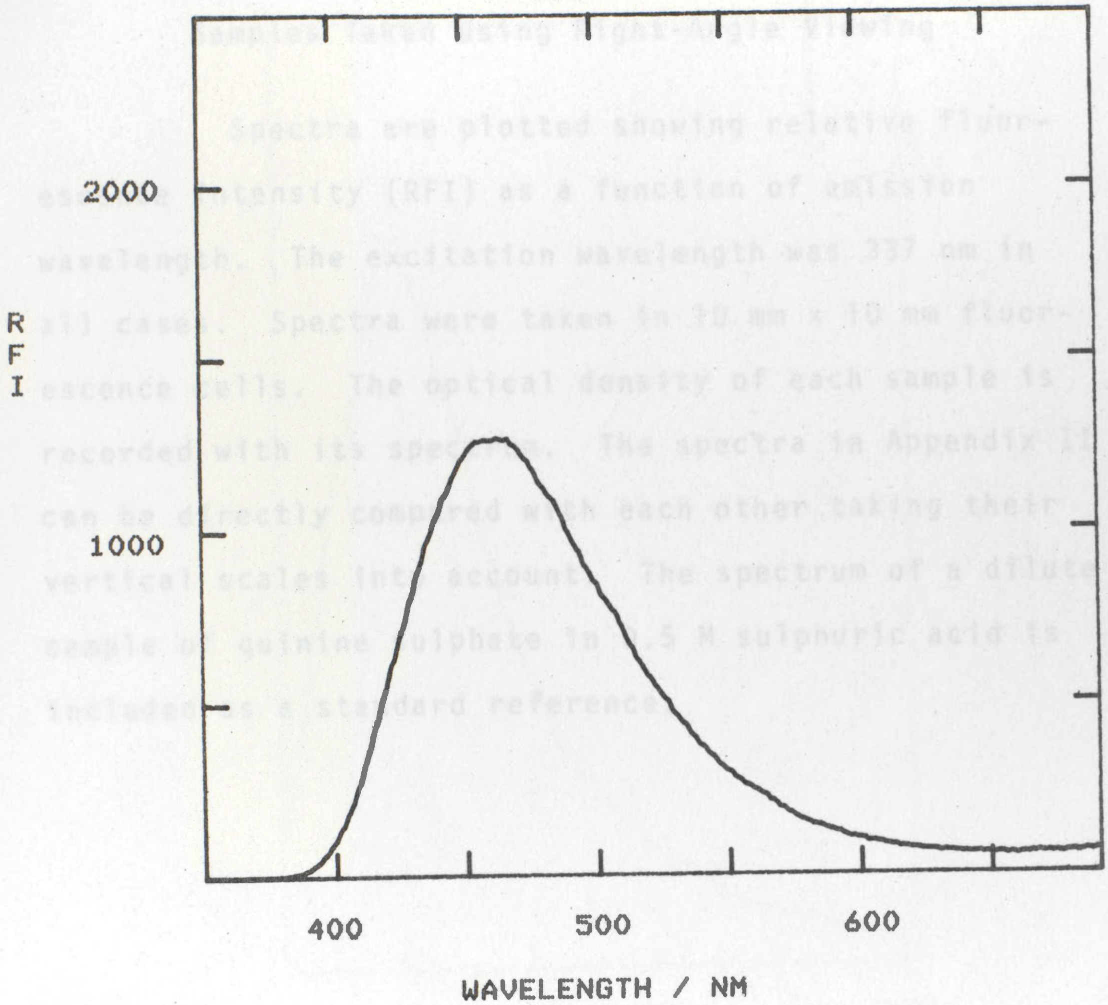
S22: RHODAMINE WT



S23: RHODAMINE B IN ETHANOL



S24: POPOP IN ETHANOL

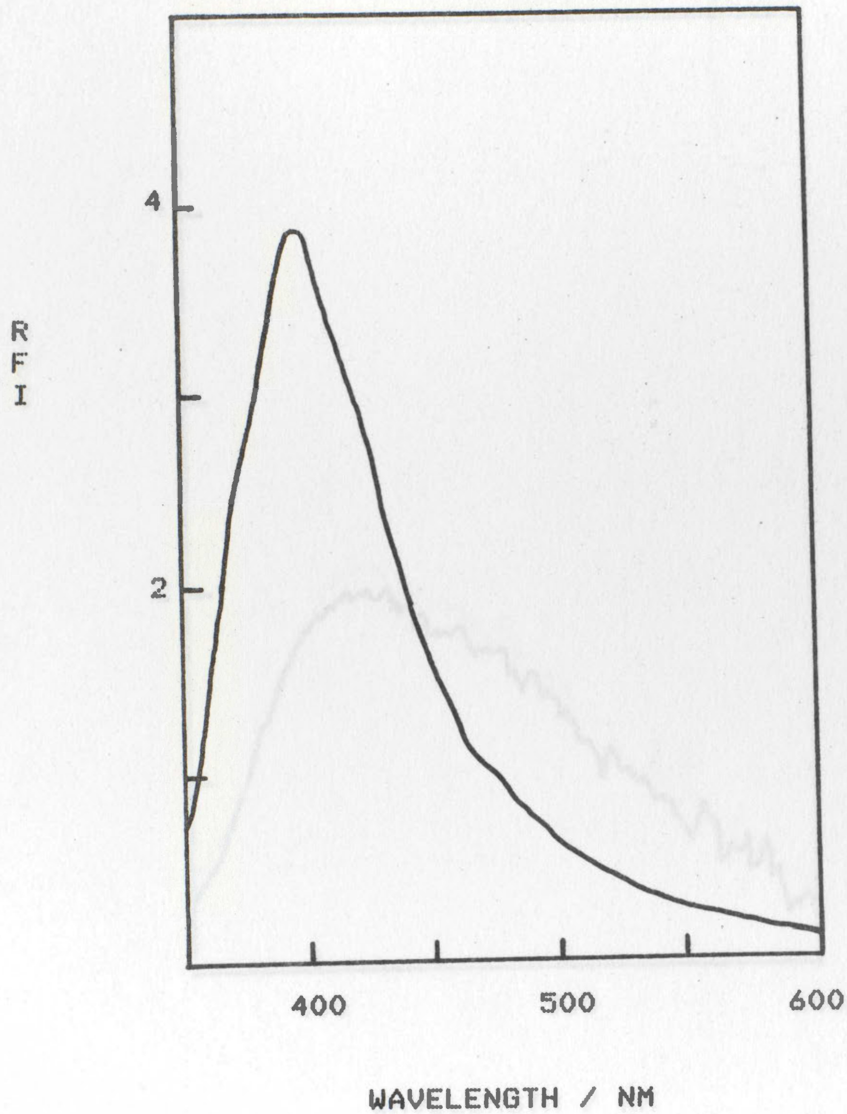


S25: QUININE SULPHATE IN 0.5 M
SULPHURIC ACID

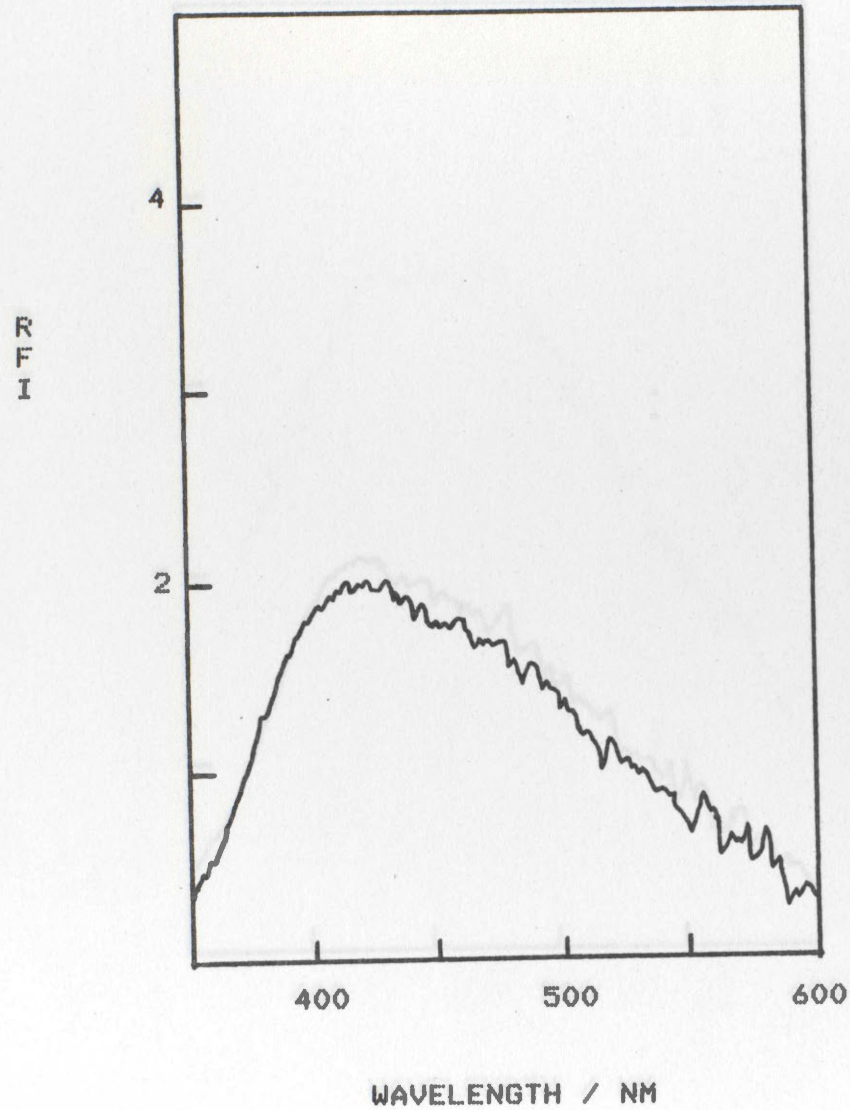
Appendix II

Fluorescence Spectra of Low Optical Density Samples Taken using Right-Angle Viewing

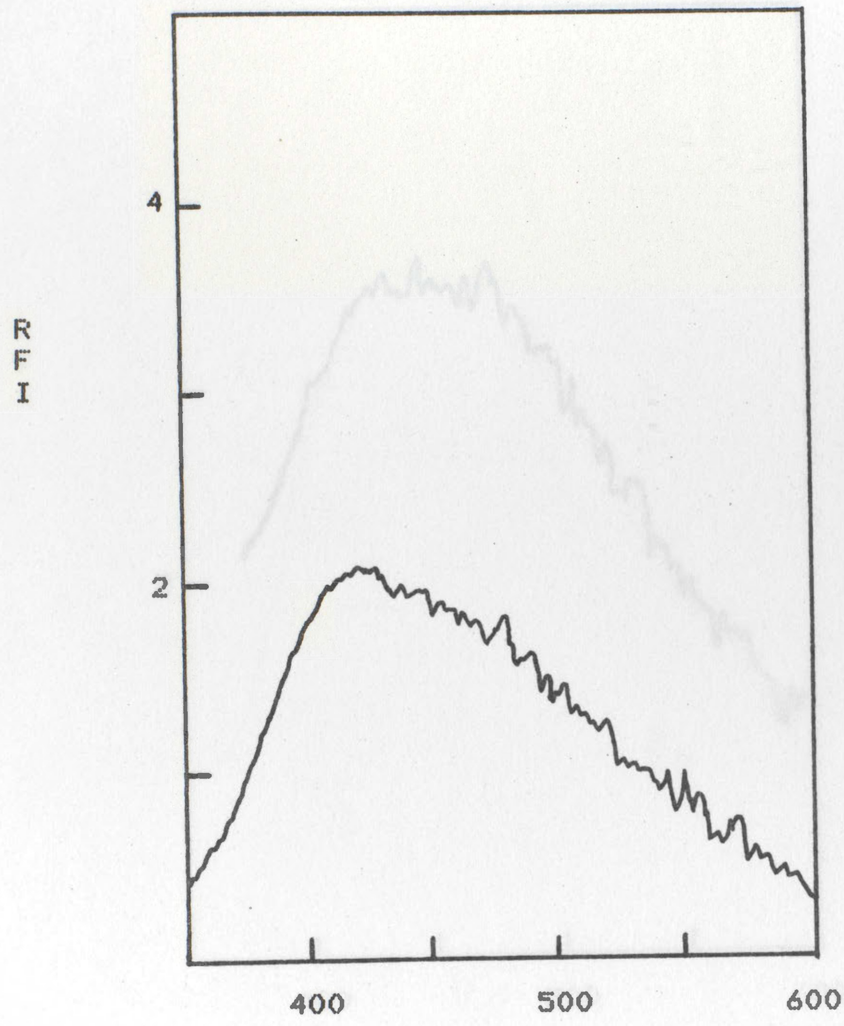
Spectra are plotted showing relative fluorescence intensity (RFI) as a function of emission wavelength. The excitation wavelength was 337 nm in all cases. Spectra were taken in 10 mm x 10 mm fluorescence cells. The optical density of each sample is recorded with its spectrum. The spectra in Appendix II can be directly compared with each other taking their vertical scales into account. The spectrum of a dilute sample of quinine sulphate in 0.5 M sulphuric acid is included as a standard reference.



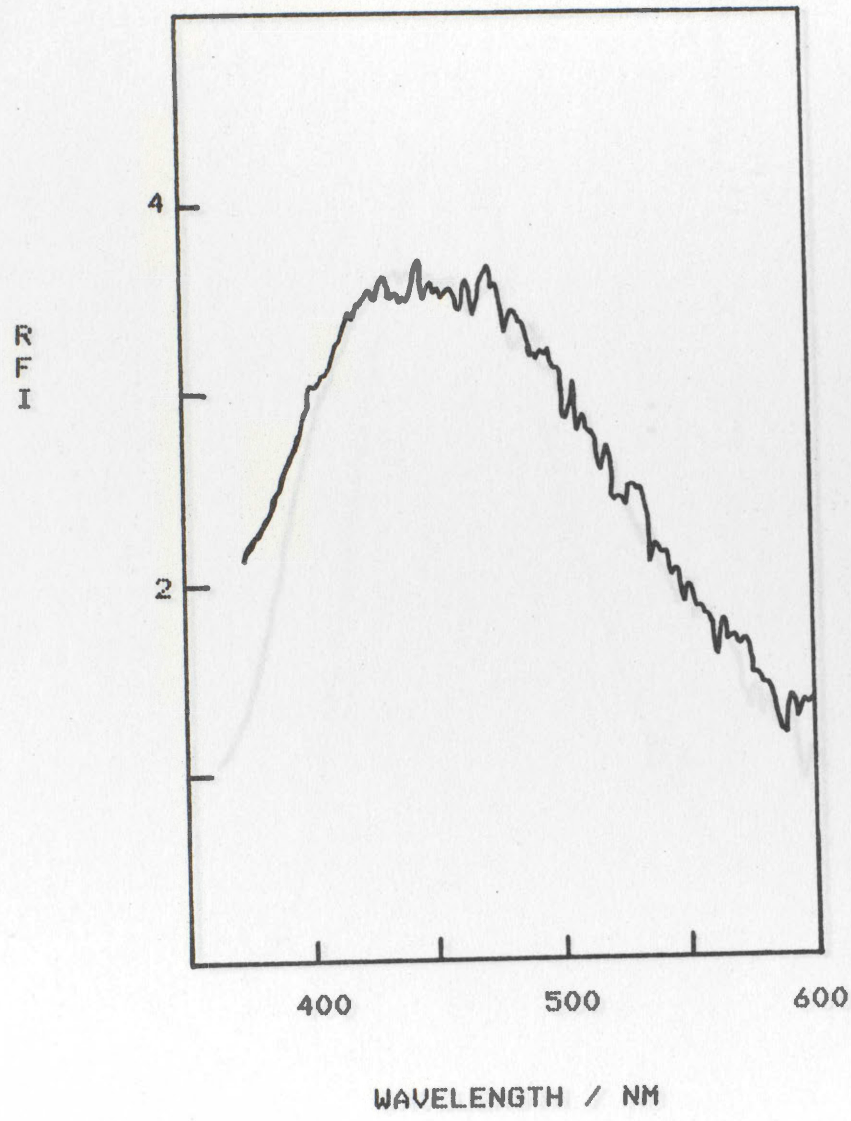
S13: PULP MILL EFFLUENT - MASSON
OD > 2 / MM AT 337 NM



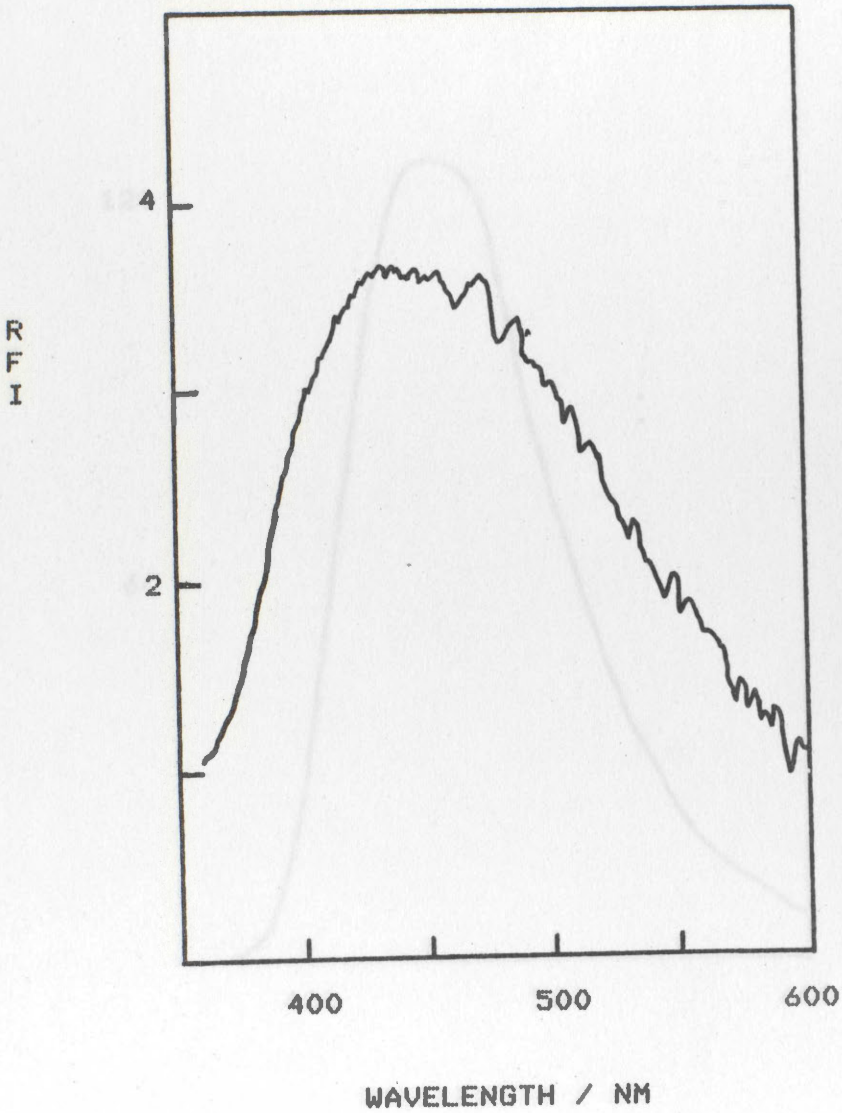
S15: PLANT TAILINGS POND OUTLET
MCINTYRE MINES, GRAND CACHE
OD = 0.0043 / MM AT 337 NM



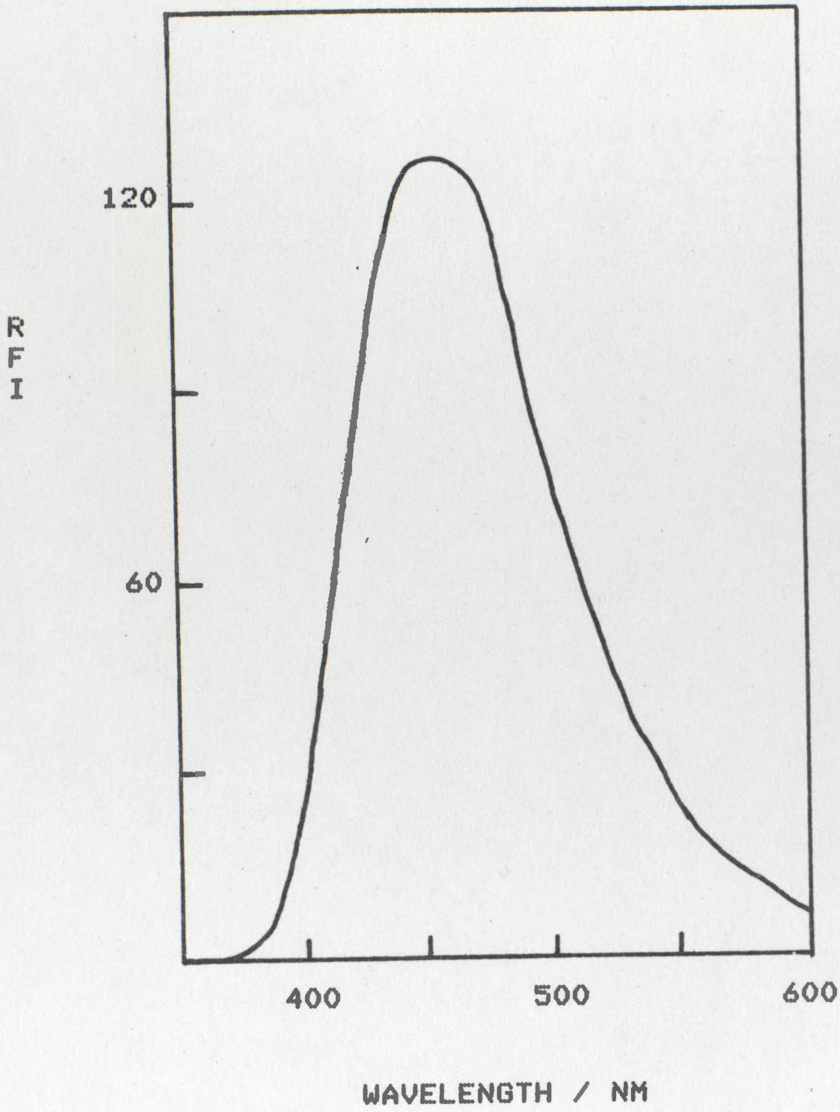
S16: NORTH SIDE OF TAILINGS POND
MCINTYRE MINES, GRAND CACHE
OD = 0.0052 / MM AT 337 NM



S17: BELOW SETTLING POND
CARDINAL CREEK COALS MAY/77
OD = 0.035 / MM AT 337 NM



S18: POND OUTLET
CARDONAL CREEK COALS MAY/77
OD = 0.015 / MM AT 337 NM



S25: QUININE SULPHATE IN 0.5 M
SULPHURIC ACID
OD = 0.0051 / MM AT 337 NM