AN INVESTIGATION OF THE FLUORESCENCE OF BRITISH BITUMINOUS COALS

THE ANALYSIS OF FLUORESCENT SPECTRA OF COAL MACERALS

by

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Investigation of the Fluorescence of British Bituminous Coal.

The analysis of fluorescent spectra of Coal Macerals.

A thesis submitted for the degree of Master of Philosophy

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SUMMARY

Two British Bituminous coals (Cortonwood and Frickly) were separated using 'float and sink' techniques into their respective macerals.

The fluorescent excitation and emission spectra of the pyridine extracts of these maceral groups are investigated along with the respective synchronous fluorescence spectra. The effect of concentration on the fluorescence of these extracts and comparisons to model compounds is also reported. All spectra including the simplified synchronous spectra are compared and correlated, so conclusions can be drawn.

The effect of sodium hypochlorite is also investigated along with ultra-violet spectra and comparisons to text and standard spectra.

From these comparisons the theories related to the fluorescence of coal macerals are discussed.

KEYWORDS: FLUORESCENCE, COAL MACERALS, PYRIDINE, BITUMINOUS COAL, STRUCTURAL ANALYSIS

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LIST OF ABBREVIATIONS

B.S.	British Standard
Em	Emission
Ex	Exinite
F	Fluorescence intensity
ν	Frequency
I.C	Intersystem Conversion
λ_{max}	Wavelength of maximum fluorescence intensity
N.M.R.	Nuclear Magnetic Resonance
rpm	revolutions per minute
s.g	specific gravity
Vit	Vitrinite
λ	Wavelength

CHAPTER ONE

1. INTRODUCTION

1.1. Introduction

The fluorescence properties of solid coal are well known and may be observed for polished surfaces of the material excited by blue or ultra-violet light[1]. Preliminary observations, by a member of the Solid Fuel Research Group at Aston, revealed that a pyridine extract of a coal maceral showed fluorescence properties. This phenomenon seemed worthy of further investigation in the hope that it would lead to an understanding of the nature, structure and properties of 'solutions' of coal macerals.

Hence the origin of the initiation of the study described in this report in which the excitation, emission and synchronous fluorescence spectra of two maceral groups, exinite and vitrinite, have been examined in some detail, along with the effect of sodium hypochlorite on these maceral extracts. This fluorescence technique has two main advantages over other analytical studies.

First, this is a non-degradative technique and it is the first time the optical properties of coals have been studied in detail, in their most soluble medium (pyridine). So this study might also assist in understanding the nature of coal solubility. In addition to these benefits the differences between the fluorescence of exinites and vitrinites may also be seen due to the high sensitivity of fluorescence analysis.

1.2 The Nature of Coals

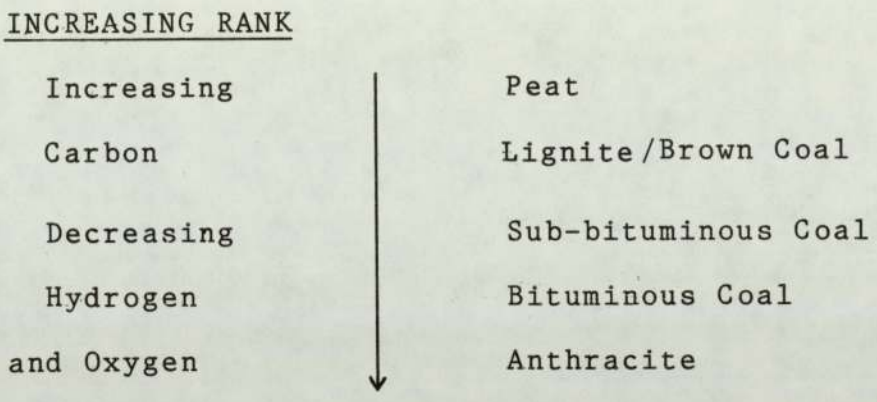
This brief outline of the formation of coal is required to explain the differences between the basic composition of coals. An understanding of the origins of the constituents of coals is essential when discussing the microscopic grouping in coals (coal macerals). These distinguishable microscopic groupings are useful in the explanation of the properties of coals as they can be considered to be physically and chemically distinctive. This is particularly useful as coals are not a simple, black, non-uniform mixture of carbon, hydrogen, oxygen, sulphur and other minor elements, nor is coal a complex repeating aromatic structure.

1.2.1 Coal Formation

Coal is a sedimentary rock laid down millions of years ago from dead, rotting vegetation in 'swamp-like' conditions. These conditions allowed little oxidation, thus preventing the complete biological degradation of the plant material. This material was sandwiched between layers of inorganic material. Thus providing a source of the inorganic 'pollutant' material present in coals, such as ash. These layers of partly decomposed matter then undergo further changes over geological time eventually forming coals as we know them today. This process is very complex with several factors such as the pH, the oxygen content, and the temperature during the initial decomposition influencing the formation. In addition variations over geological time and the rate of burial, all affect the composition of coals.

The age of the coal and the speed of 'coalification' means that some basic sequence is required to initially classify coals. The position of coal in this sequence is called its rank:-

Figure 1.1



COAL CLASSIFICATION BY RANK

As rank is purely qualitative, the composition of coal can also be classified according to its macroscopic, or its microscopic structure along with other chemical and physical properties.

1.3 Coal composition

The macroscopic composition of coals has been described by the way the coal 'looks'. In bituminous coals, four "lithotypes" were described by Stopes[18] in 1919. (See table 1.1).

The lithotypes can be seen in the individual seams as bands formed from different types of plant material; in fact the reflectivity of coal is still used today to assess a coal's rank.

1.3.1. Microscopic structure (coal macerals)

Lithotypes are composed of complex aggregates of microscopic entities known as "macerals". Perhaps the most important way of looking at the components of coals is to examine the macerals in coal petrography. These macerals are divided into three principal groups, each representing a distinct decompositional environment.

The macerals are categorised by their appearance and optical characteristics, and in general, the specific plant debris from which the coal was formed can then be identified. Table 1.1 shows the composition of the lithotypes, the maceral groups and their origins.

The variation in factors described (p18), along with the nature of the sources means that the maceral composition in coals differs dramatically from one coal to another. This change in the maceral composition alters the physical properties of coals. Thus, by carrying out research on nearly "pure" maceral groups, the overall characteristics and properties of coals will become more clearly understood.

Macroscopic Lithotypes	Microlithotype Group	Principal maceral groups	Maceral Group	Maceral	Composed of or derived from
VITRAIN	vitrite	V	Vitrinite - V	Collinite	Humic gels
	clarite	V + E			
	vitrinertite	V + I		Tellinite	Wood, bark and cortical tissue
	trimacerite	V + E + I			
DURAIN	clarite	V + E	Exinite - E	Sporinite	Fungal and other spores
	durite	I + E		Cutinite	Leaf cuticles
	vitrinertite	V + I		Resinite	Resin bodies and waxes
	trimacerite	V + E + I		Alginite	Algal remains
FUSAIN	inertinite	I	Inertinite - I	Micrinite	Unspecified detrital matter $< 10\,\mu m$
				Macrinite	Similar, but 10-100 μm grains
				Semifusinite	"Carbonised" woody tissues
				Fusinite	
CLARAIN	Irregularly alternating, thin layers of variously proportioned vitrain - durain mixtures.			Sclerotinite	Fungal sclerotia and mycelia

Table 1.1 The Petrographic Composition of Macroscopic Lithotypes and Microscopic Coal Macerals with maceral groups as recognised by the International Committee for Coal Petrography[2]

1.3.2. Organic composition of Coal

From the early days when coal was used for industrial purposes, there has been difficulty in characterising them in order that their properties could be known prior to use. However, this proved to be awkward and to be specific was impossible, so holistic properties of coals were used, such as ash content, calorific value and swelling number so that coal could be valued on some agreed basis. In fact, coal merchants still use these calculations to assess the usability for coals from each pit.

During the oil crisis emphasis was placed on understanding and characterising coals. Over recent years there have been many studies looking at the structure, chemical and physical properties of alternative fuels, and chemical feed stocks including coals.

These studies have led to more information relating to coal and its 'structure(s)'. (See Figure 1.2). These studies fron Van Krevelen [4] through to the present day have led to some general conclusions about coals:-

1. Coals have a high molecular weight and a non-uniform structure.
2. As rank increases, the number of fused aromatic rings increases, along with the number of aliphatic substituents. Also, the amount of oxygen, carboxylic acid and carbonyl groups decrease whilst the ether and phenolic groups increase.

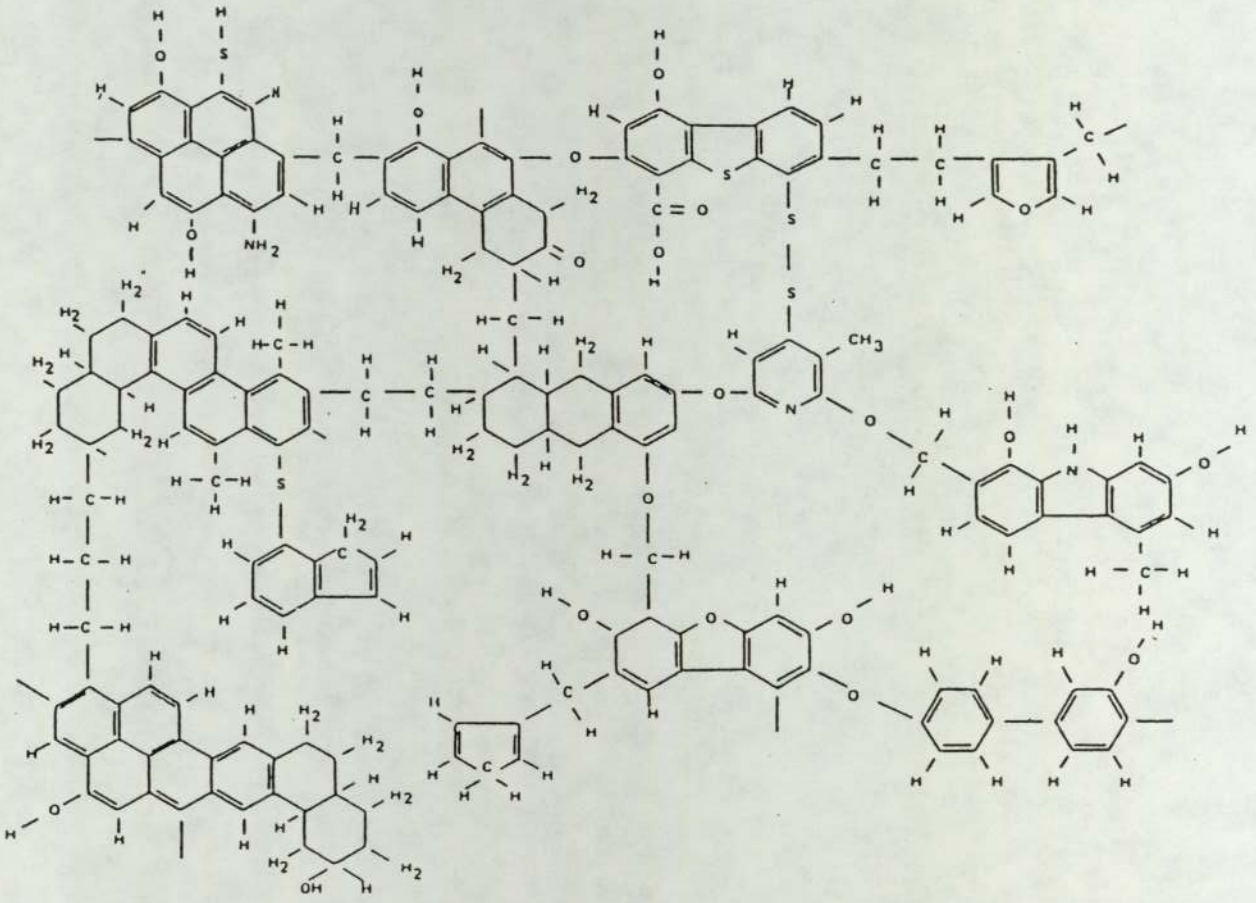


Figure 1.2 Given's[3] Schematic Representation of the Structure and Connecting Bridges in Bituminous Coals

3. There are several types of 'bridging bonds' between clusters such as hydro-aromatics, hetero-atoms, (oxygen, sulphur and nitrogen), and alkyl groups (methylene and ethylene).
4. Secondary bonding holds some of the coal structure together including hydrogen bonding, π interactions.

It is not a surprise, due to the heterogeneous nature of coal, that many of these conclusions and models are still non-specific and at times confusing. However, the existence of π-π interactions, other non-skeletal bonding and the extent of aromatisity in bituminous coals suggests that some part of the coal structure will be of particular interest in a fluorescence study.

1.4 Fluorescence Theory

Fluoresence is a process in which radiation is emitted by atoms or molecules that have been excited by the asbsorption of radiation. Prior to excitation, the molecule is usually in the singlet ground electronic state S_0. After the emission of radiation, the electron returns to the ground electronic state from the excited electronic states, although frequently the electron would then be in a vibrationally excited state. This movement between different electronic states is often shown. (See Figure 1.3).

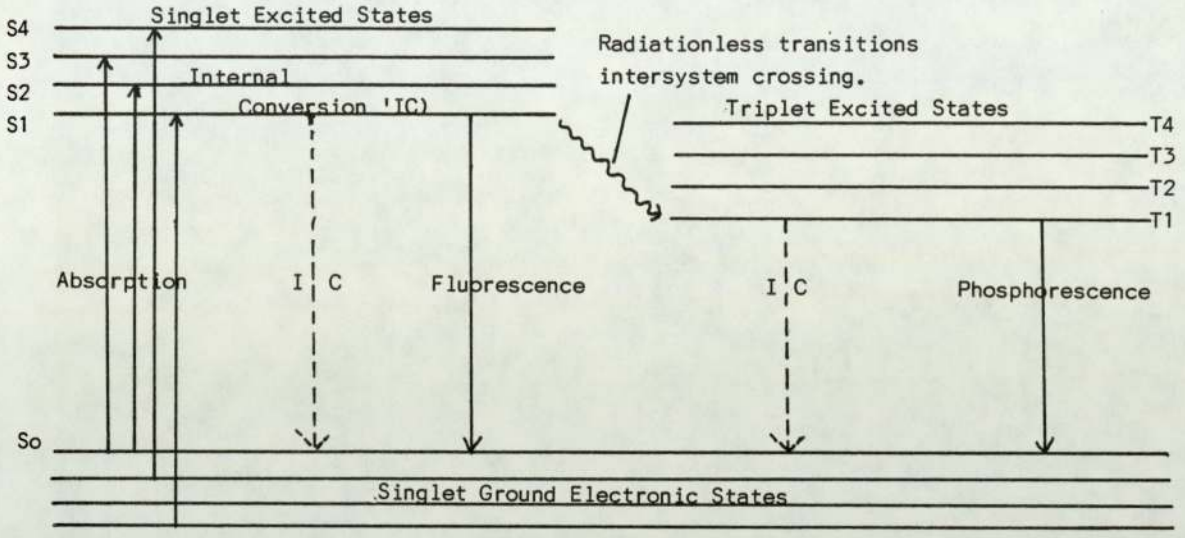


Figure 1.3 Fluorescence Theory

From the diagram it can be seen that state multiplicities are important since the nature of the emission processes depends on them. If the states from which the emission originates and terminates have the same multiplicity, the emission is called Fluorescence.

This most commonly occurs between the first excited S_1 and the ground singlet state S_0. However, if the states from which the emission originates and terminates differ in spin multiplicity, ($\Delta S \geq 1$), then the emission is known as phosphorescence. ($T_1 \rightarrow S_0$). As highly probable transitions can only occur when $\Delta S = 0$, phosphorescence emissions have a relatively long life time (10^{-3} to 10 seconds), while fluorescence has a short life time (10^{-7} to 10^{-10} seconds).

In addition to the radiative processes, there are two radiationless processes that are possible. These occur from the conversion of electronic energy into vibrational or rotational energy, known as internal conversion. When a radiationless process occurs between the first excited singlet and the lowest excited triplet state, it is known as intersystem crossing.

Excitation to any excited singlet state above the first is normally followed by internal conversion, such that fluorescence or intersystem crossing occurs only from the first excited singlet state. The internal conversion process is more than 10^3 times more likely to occur than emission directly from any excited singlet state above the first excited singlet. Internal conversion from the first excited singlet state can occur, thus competing with and quenching fluorescence and intersystem crossing. But internal conversion from the first excited singlet is less likely than among the higher excited states and the complete quenching of fluorescence is extremely rare. An outline of the processes involved in fluorescence is:-

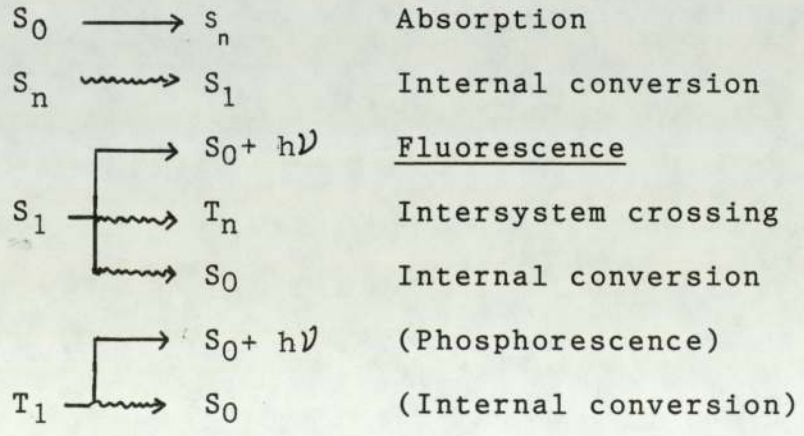


Figure 1.4 Fluorescence Interaction Processes

The energy associated with the fluorescence photon is given by $h\nu$.(See Figure 1.4). So the frequency and wavelength of emitted radiation is fixed depending on the energy difference between S_0 and S_1.

If the ground state and lowest excited state potential energy curves cross or mix, then the fluorescence intensity may be weak or absent. The molecules can also lose energy from the first excited state by collisions and the energy is lost as heat:

$$S_1 \longrightarrow S_0 + \text{heat}$$

The "amount" or efficiency of the solute to fluoresce is called the quantum yield. For example, if each molecule that absorbs one quantum of activating light returns to its ground state by emitting a quantum of fluorescent light, then the fluorescent efficiency (quantum yield) would be 1 (or 100%). However, due to the processes already mentioned, internal conversion and intersystem crossing, along with collisions, the fluorescent efficiency is less than 1. Thus the fluorescent intensity can be written:-

(1) $F = (I_o - I)\ \phi$

where

F = fluorescent intensity

I_o = intensity of exciting light

I = intensity of transmitted light

ϕ = quantum efficiency

The quantitative relationship between fluorescence intensity and concentration can be derived from Beer's Law:-

$I = I_o e^{-kct}$ or $I = I_o 10^{-\varepsilon ct}$

where:

C = concentration

t = thickness of light path

ε = Molar extinction coeficient

$k = \varepsilon \times 2.303$

when substituted in (1) this gives:-

$$F = (I_o (1 - e^{-kct})) \phi$$

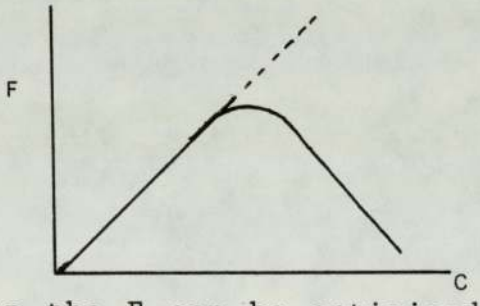
Assuming that the concentration is very small then:-

$$F = I_0 (kCt) \phi$$

From this it can be seen that by keeping I_0 constant, the effect of concentration can be investigated and vice versa:-

with I_0 constant

this is a representation of the result for a typical fluorescent material.



From this graph it can be seen the F can be optimised to give greater sensitivity.

In general, it is assumed that fluorescence occurs in molecules which have 'loosely' held electrons. Thus, fluorescence occurs mostly in molecules with conjugated bonds, in particular, in those with delocalised π electrons. This is because these electrons can be promoted relatively easily, thus allowing radiation to be emitted when returning to their ground states. As these delocalised π electrons

are most apparent in organic aromatic compounds, it is this type of compound which is seen to fluoresce more than any other.

Another factor that affects the fluorescence is the "electron density", ie: how closely the π electrons are packed or held. Thus, the polarity of both the fluorescing molecule and the solvent can have an effect on the fluorescence. This electron density is also affected by substituents, electron donors promote fluorescence ($-NH_2$ -OH) as they increase electron delocalisation. While electron withdrawing groups (-CI, $-NO_2$, COOH) decrease or quench the fluorescence. Non-bonding (lone) pair electrons promote fluorescence as they can be excited without disrupting any bonding. The pH of the system can increase or decrease stability, thus also affecting fluorescence. Solvents that produce Van-de-Waal's bonds, with the excited states, promote phosphorescence. Lastly, temperature and viscosity of the system (solute and solvent) can affect the fluorescence by increasing or decreasing internal conversion, through collisions. In addition, the structure of the fluorescing molecule also affects the 'electron density' with planar, rigid molecules being most fluorescent.

1.4.1. Why study the fluorescence of coal macerals ?

Most of the studies on coal are degradative and involve some reaction in which, of course, the structure is disrupted. By studying the 20% -30% of coal maceral, which is soluble in pyridine, we are directly measuring the fluorescence of a large portion of the coals' original material. This method is not totally non-degradative as

there seems to be an affinity between parts of the coal material and the pyridine.* This may even be advantageous when analysing results. However, we can detect a physical property of coal macerals directly. Also the high sensitivity of fluorescence means that differences between maceral groups may be detected. Spectra may be analysed, yielding information relating to the structure of coals. This project will attempt to use fluorescence not only to assess the possibilities of using the fluorescence of coal macerals to assist in the classification of coals, but also to evaluate any structural information which may be gained.

* There is the question of pyridine chemically combining with some of the coal maceral and a colloidal suspension, not a solution, being formed.

CHAPTER TWO

2. ANALYTICAL TECHNIQUES

2.1 Introduction

Polished surfaces of coals fluoresce and phosphoresce when excited by blue or long wavelength ultraviolet light.[1] The intensity of emission by exinite (lipinite) macerals is particularly intense, vitrinite (huminite) macerals generally fluoresce only weakly and inertinite macerals do not fluoresce at all.[5] The morphologies of exinite macerals are clearly delineated by their fluorescence and this is the basis for their petrographic identification.

Fluorescence occurs throughout a broad range of wavelengths and usually has a single peak of maximum intensity. The emission can be characherised by three parameters[6, 7]:-

a) The wavelength of maximum emission.

b) The red/green quotient, being the ratio of emission intensity at 600 nm and 546 nm (or 500 nm).

c) The alteration, being the change in emission intensity which occurs during the first ten minutes of irradiatiion.

These characteristics give further information about the nature and degree of maturity and they often correlate with the technological properties of the fuel. Nevertheless, it must be emphasised that nothing has been established about the chemical origin of the fluorescence. The most commonly occuring fluorescing structure, that a photochemist would recognise in coals, is the naphthalene nucleus.

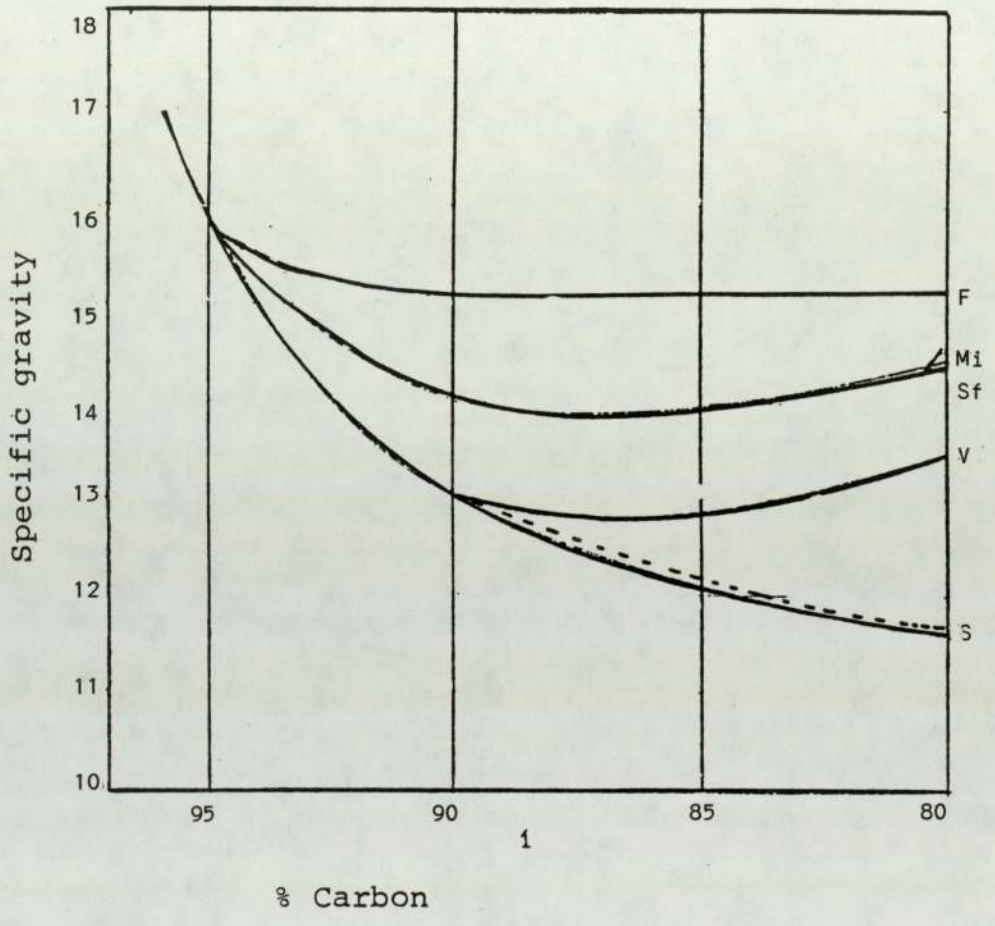
Certain benzenoid structures, more complex polynuclear aromatic structures and porphyrins, though often present only in small or trace quantities, would also fluoresce. Indeed, fluorescence spectroscopy is a standard method of recognising aromatic structures in oil shales[8] and coal liquids.[9] Clearly resolved low temperature fluorescence spectra of carbon disulphide extracts of coals demonstrated the presence of a number of polynuclear aromatic hydrocarbons.[10] Paradoxically, these results emphasise the difficulties in understanding the fluorescence of solid fuels. Firstly, carbon disulphide and similar solvents extract only small quantities of material of coals and that material may be atypical. Secondly, the maximum fluorescence of naphthalene and the smaller hydrocarbons occur at lower wavelengths (by 100 nm) than the maximum emission of solid coals. Thirdly, vitrinites contain higher concentrations than exinites.[11] If fluorescence of solid coals is ever to be interpreted in terms of fluorescence exhibited by structures present in solution, then it would be sensible to examine the fluorescence of pyridine extracts of coals.

2.2. Maceral separation

The coal maceral groups were separated from selected coals using a sink and float technique[12]. Thus the differences in the maceral group densities is crucial in their separation. Figure 2.1 illustrates how the specific gravities of coal macerals vary with the rank of coals. It is seen that the exinites' (sporinite and resinite) specific gravities vary considerably from the s.g. of the vitrinite for low ranked coals easing their separation.

Figure 2.1

Variation of specific gravity for coal macerals[13]



F = Fusinite
Mi = Micrinite
Sf = Semifusinite
V = Vitrinite
S = Sporinite
--- = Resinite

However, for the higher ranked coals, used in this study, the specific gravities of exinites and vitrinites converge at about 90% carbon content. For this reason the selection of the source material is important.

Also, during grinding the differences in the mechanical strength of the macerals can also assist in their separation. For example, the exinite (sporinite) will tend to be concentrated in the coarser fractions when grinding and sieving [14]. The hardness of the maceral groups decrease from exinite through to inertinite.

The exinite and vitrinite were concentrated and thus separated by suspending crushed durain using various densities of toluene and perchloroethylene solutions. These solutions were used, as organic liquids were not satisfactory separating media for high rank coals. Also aqueous zinc chloride solutions are unpleasant to handle. Finally, a maceral analysis by microscopic examination was used as a guide to the next step in separation and as an estimation of the maceral 'purity'.

2.2.1 Exinite separation

To obtain a high yield of a specific exinite maceral, such as sporinite, is difficult as the specific gravities of exinites are similar. (Figure 2.1). So to obtain an extract with one main exinite component, it makes sense to use starting material rich in that particular maceral, for example, using durains rich in sporinite.

To assist in this separation, the shiny vitrain particles were picked out by eye, after breaking the durain blocks into small 2 cm lumps.

These lumps were then crushed until all the material passed through a B.S.240 mesh sieve. This material was then mixed with 200 ml of various specific gravity solutions of toluene and perchloroethylene. The resulting suspensions were centrifuged at 2500 rpm for 30 minutes. The floating material was collected and dried at 50°C.

On microscopic examination,a specific gravity of 1.25 was found to give the best separation. This procedure was repeated until there was no further improvement in the purity of the exinite maceral content. This process gave the following exinite purities for the samples used:-

Frickley - 93%

Cortonwood - 90%

2.2.2 Vitrinite separation

For bituminous coals the largest maceral fraction is the vitrinite group. This can be seen from the vitrinite reflectance which increases with rank and is used as a measurement of a coal's rank[2]. (See Figure 2.2).

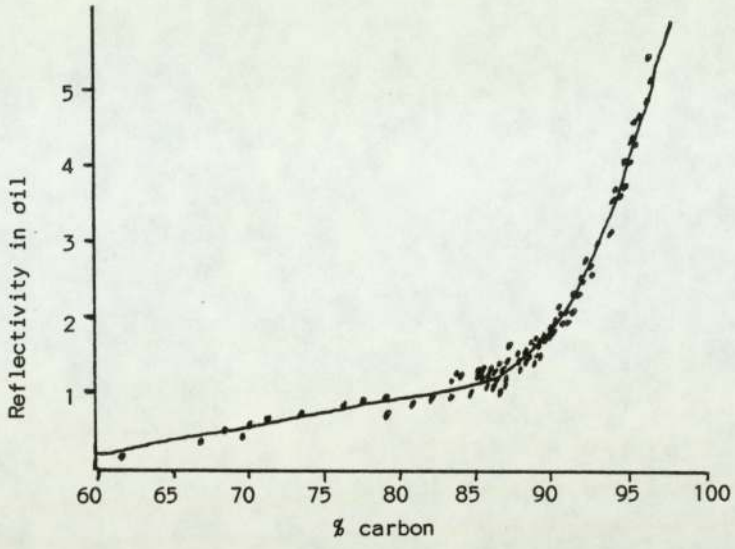


Figure 2.2 Reflectivity

This reflectivity is used when, as for the exinite separation, the bright vitrain concentrates are picked out by eye. These fragments were crushed and passed through a B.S. 120 mesh sieve. This material was then suspended in a toluene/perchloroethylene solution of s.g.1.32. After centrifuging, the wash floats were then dried at 50°C and the analysed purities were:-

Cortonwood vitrinite - 97%

Frickley vitrinite - 99%

These particles were analysed using polished blocks of the maceral material and examined with a reflected light microscope. This follows the procedure, as described in the International Handbook of Coal Petrography [15].

For further details of the separation and maceral analysis see the report by Ms M R Davies from which the four original separated materials were obtained.[11]

2.3 Pyridine extraction

Approximately 2g of the finely ground, separated maceral concentrate was placed in a Soxhlet thimble and refluxed with 200 cm^3 of pyridine. When only pyridine was detected in the extracting solvent on the most sensitive range of a gas chromatograph, the extraction was considered complete. The pyridine was partly removed from the extracted material by vacuum evaporation. The final stage of evaporation and drying was achieved by passing a nitrogen stream over the surface of the concentrated extract. Nitrogen was used to reduce oxidation.

2.3.1. Preparation of standard extracts

After twelve hours of drying, the fine granular pyridine material was used to prepare standard coal maceral extracts. Drying was carried out in the same flask as used in the extraction to reduce handling. This dried maceral material was redisolved in pyridine to obtain solutions of known concentration. These solutions are referred to in the text as the "original concentration" solutions.

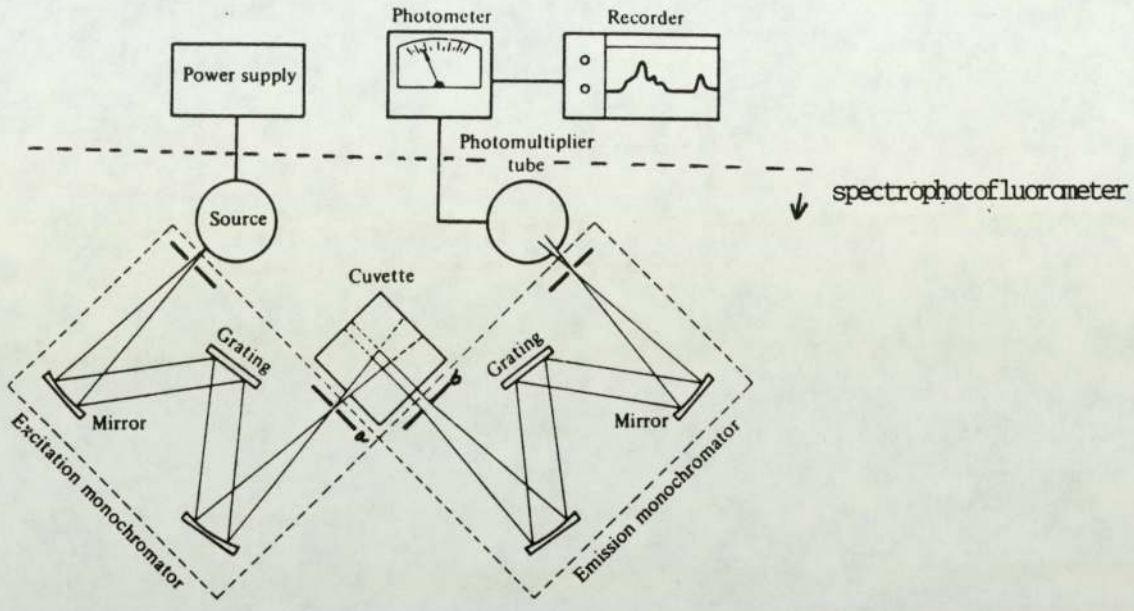
These "original" solutions were then diluted to obtain a suitable range of solutions. The extent of dilution was determined by the first set of results, after which more 'accurate' concentration ranges were investigated.

The pyridine used for all solutions was initially passed through a silica gel column (100 m mesh) mixed with finely powdered activated charcoal. This reduced interference from any impurities to a minimum.

After obtaining the spectra, the extracts were kept at room temperature in air tight containers. Spectra were repeated with these samples during the next year. The standard solutions in this section and those used in the sodium hypochlorite experiments were made by weighing dry weights of the standard compounds, then dissolving these weights in pyridine so that the concentration corresponded to the original concentrations (O) of the maceral solutions.

2.4 Instrumentation

The fluorometer used is an Aminco-Bowman spectrofluorometer from the American Instrument Company, a schematic diagramof which can be seen below.



The power supply and photometer were also obtained from the American Instrument Company, while the plotter was a "J-J" x-y plotter.

This spectrofluorometer is capable of automatically scanning the emission and excitation spectra at varying speed, but is not capable of automatically scanning through a synchronous spectra. The spectra produced are clean, accurate and are of a relatively high resolution, with the weakest link in the apparatus being the plotter. The resolution of the spectra depends on the slit widths at (a) and (b) which, for all the reported spectra was set at the highest resolution, 1 mm. The cell used, for all spectra, was a 10mm² quartz spectrofluorometer cell, which was cleaned with chromic acid, then washed with acetone and dried between every change of solution.

A typical set of results which would be obtained for a single solution are:-

1. Emission spectra with excitation set at 375 nm.
2. Emission spectra with excitation set at 335 nm.
3. Excitation spectra with emission set at 620 nm.
4. Synchronous spectra with $\Delta\lambda$ 30 nm
5. additional readings at fixed excitation and emission would be taken for the concentration graphs.

A problem which has to be overcome is to what extent the spectra are 'real'. This will be clarified by running spectra of more standards with known emission maxima. This will also eliminate any instrumental interference, as at present these spectra are uncorrected.

2.4.1. Synchronous spectra

As the Aminco-Bowman Spectrophotofluorometer cannot automatically, synchronously scan, the spectra have to be produced manually. As the information obtained is not particularly new, just a summary of other data, the process to obtain and plot these spectra is considered time consuming. In addition, because the spectra are produced manually, they are less accurate than the excitation and emission spectra. The readings are taken 10 nm apart with a possible error of $\pm$ 2 nm.

For all synchronous spectra the difference between the excitation and emission spectra is 30 nm ($\Delta\lambda$ = 30 nm).

2.5 Ultra-violet spectra

The pyridine extracts, as used for the fluorescence spectra were pipetted in to a clean 1 cm^3 glass cuvette. This was then placed in a Pye Unicam SP800B spectrometer and ultra-violet spectra obtained.

2.6 Hypochlorite oxidation

The oxidation was carried out by preparing an alkaline solution of sodium hypochlorite, ie 50% sodium hypochlorite with 50% sodium hydroxide. This solution was then added to a pyridine solution of the maceral group or standard of known concentration again in 50/50 proportions. It was then mixed rigorously and left in an oven at 60°C for a set length of time (normally overnight), and shaken periodically. These two phase reaction mixtures were then removed from the oven and spectra recorded at various time intervals. The harshness of this oxidation was altered by varying the alkalinity of the sodium hypochlorite solution.

CHAPTER THREE

3. ANALYSIS OF THE FLUORESCENCE OF PYRIDINE EXTRACTS OF COAL MACERAL GROUPS

To assist in the analysis and the general progress of this study an initial solution of Cortonwood vitrinite was used to find the appropriate fixed wavelengths at which to run the excitation and emission spectra. From this initial investigation it was decided to run the emission spectra with the excitation fixed at 375 nm, and at 335 nm. The emission spectra, with excitation set at 335 nm, were used to support several observations.

It was also decided that the excitation spectra would bee run with the emission fixed at 320 nm thus allowing the peaks around 550 nm and 590 nm to be investigated.

3.1 Emission and excitation spectra of Cortonwood macerals

For the first two sections (3.1 and 3.2) the range of known concentration pyridine extracts were obtained by diluting each concentration in turn by 50%. For example, 10 cm^3 of the original extract (0) was diluted with 10 cm^3 of the filtered pyridine to obtain the diluted extract (1). In turn, this solution was used to produce the diluted extrat (2). This procedure was repeated to produce the full range of 8 diluted extracts, thus the index for the following diagram is as follows:-

0 - Original extract concentration.
1 - 1st 50% dilution
2 - 2nd 50% dilution
. " "
. " "
. " "
8 - 8th 50% dilution

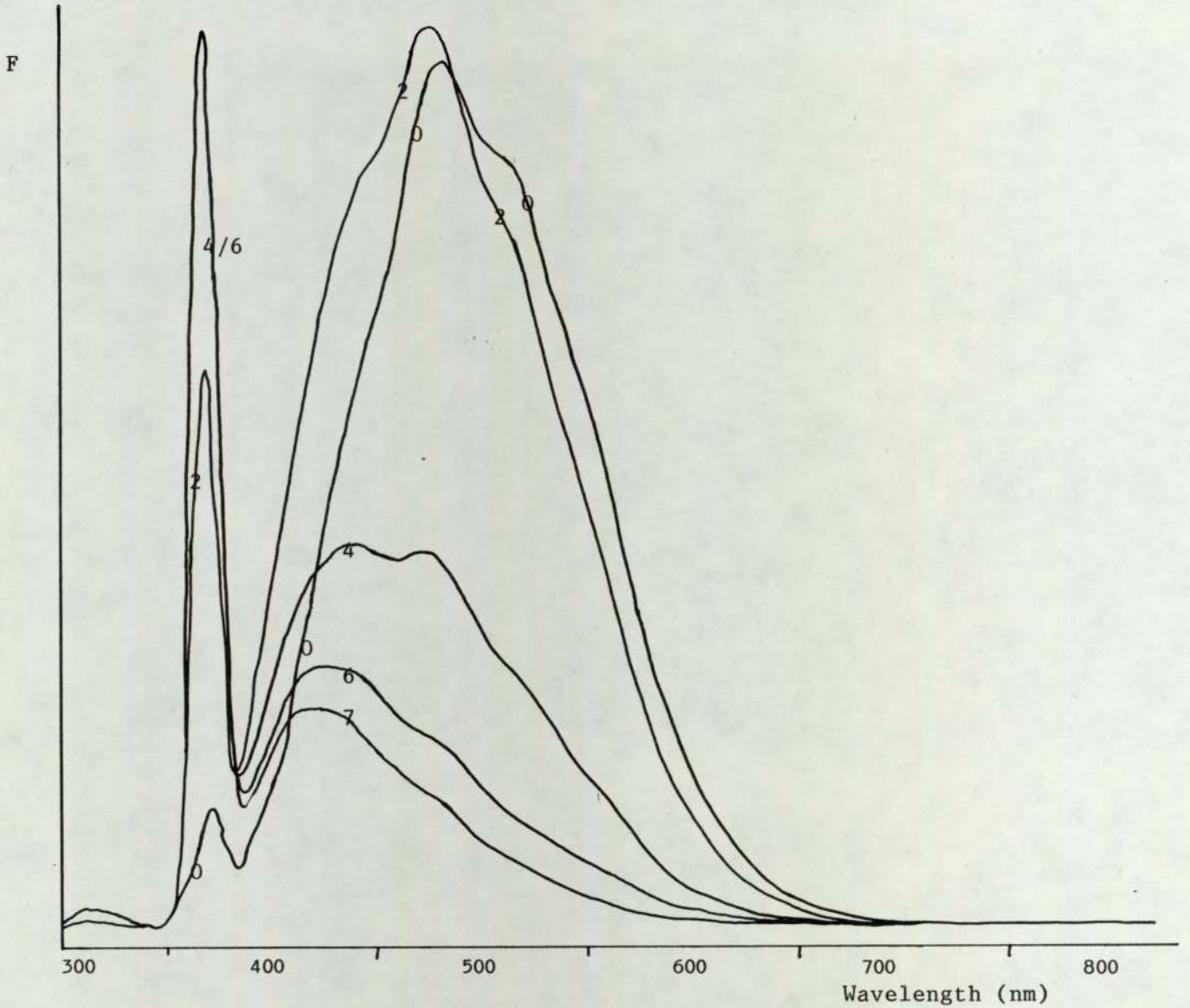


Figure 3.1 Emission Spectra of Cortonwood Vitrinite. Excitation set at 375 nm. Scales - 2/0 - 0.1: 4/6/7 - 0.3.

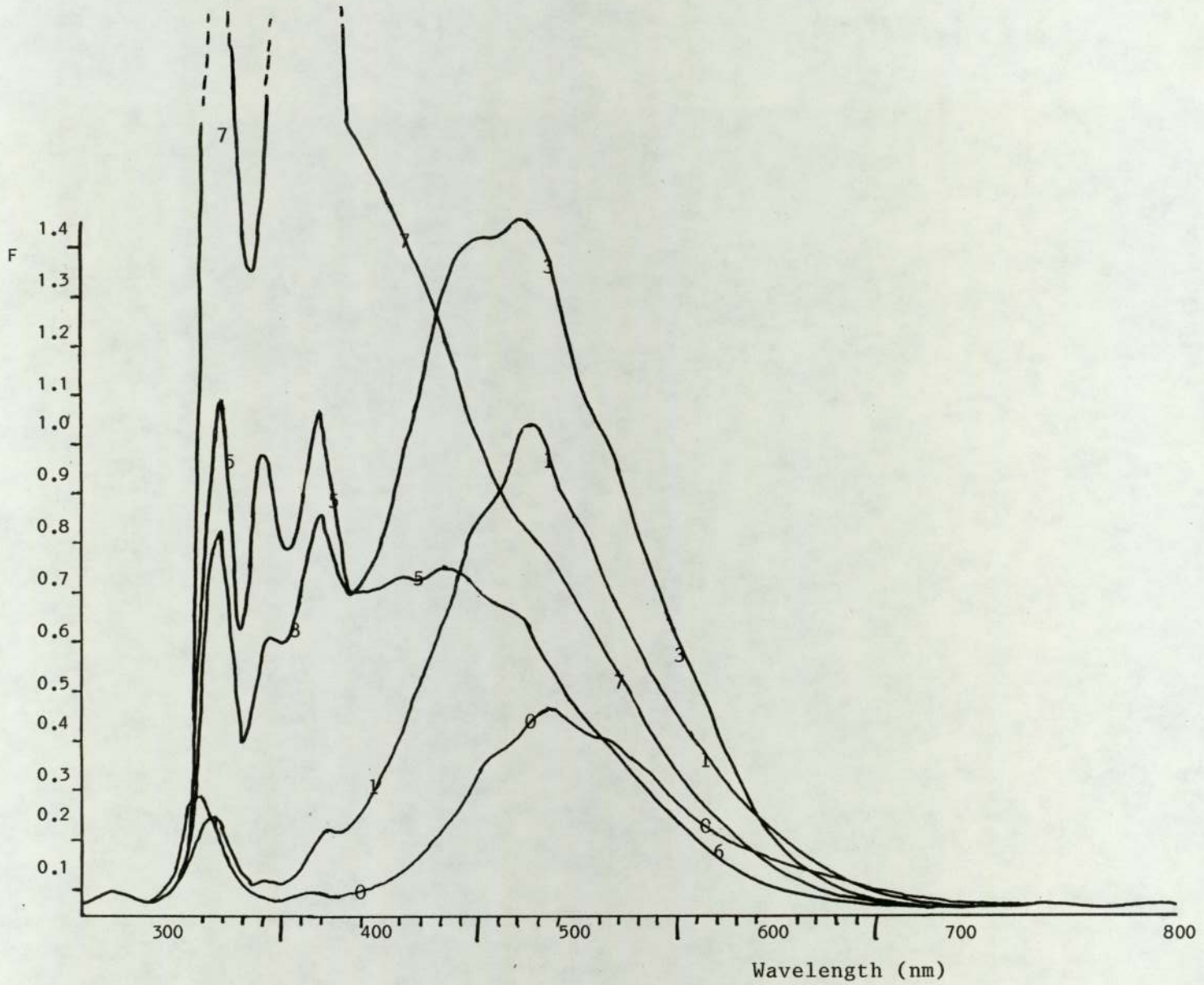


Figure 3.2 Emission spectra of Cortonwood Vitrinite, with varying concentration. Excitation set at 335 nm. Scale 0.03.

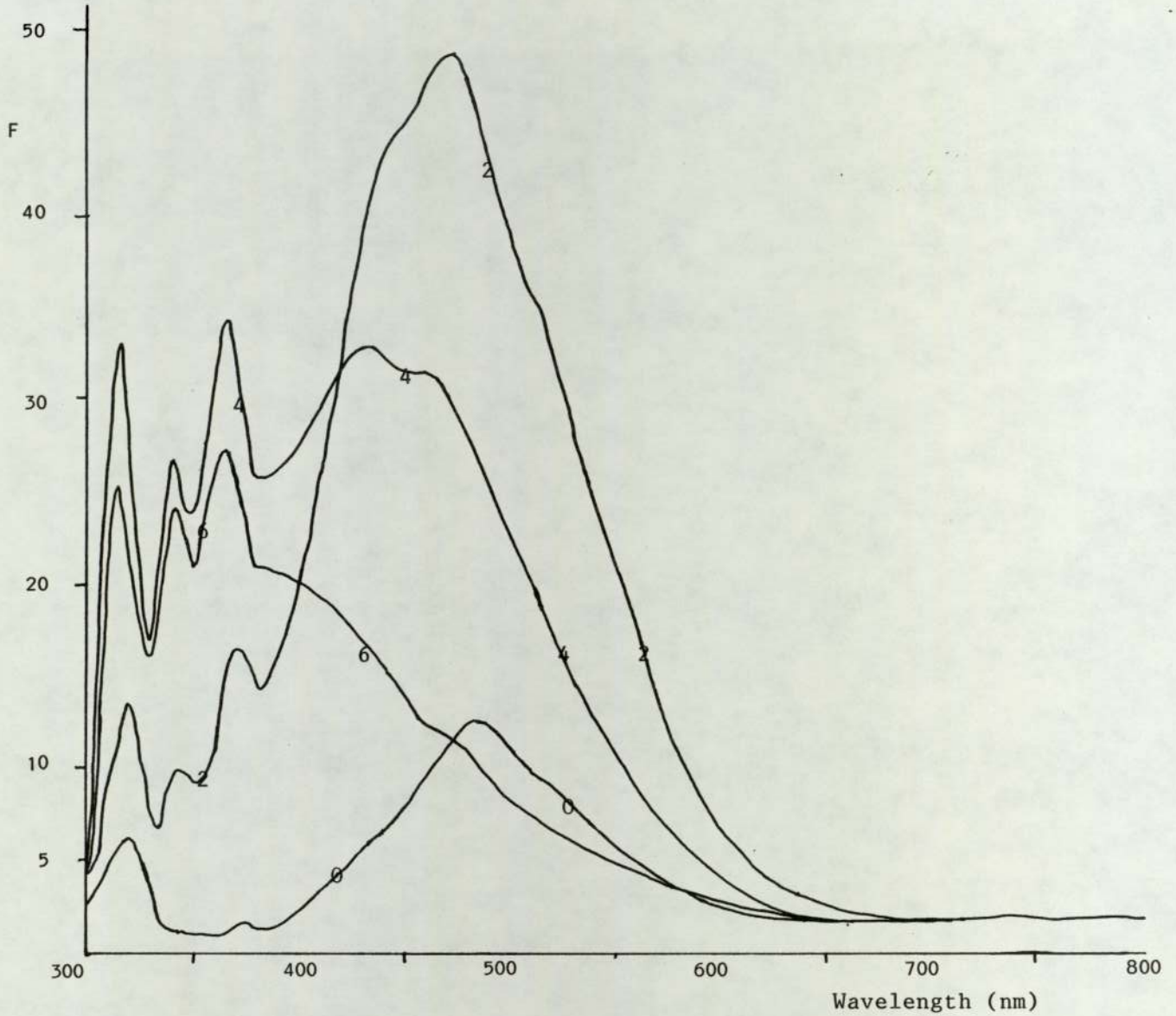


Figure 3.3 Comparison of Emission Spectra of Cortonwood Vitrinite.
Excitation set at 335 nm (ii). Scale 0.03.

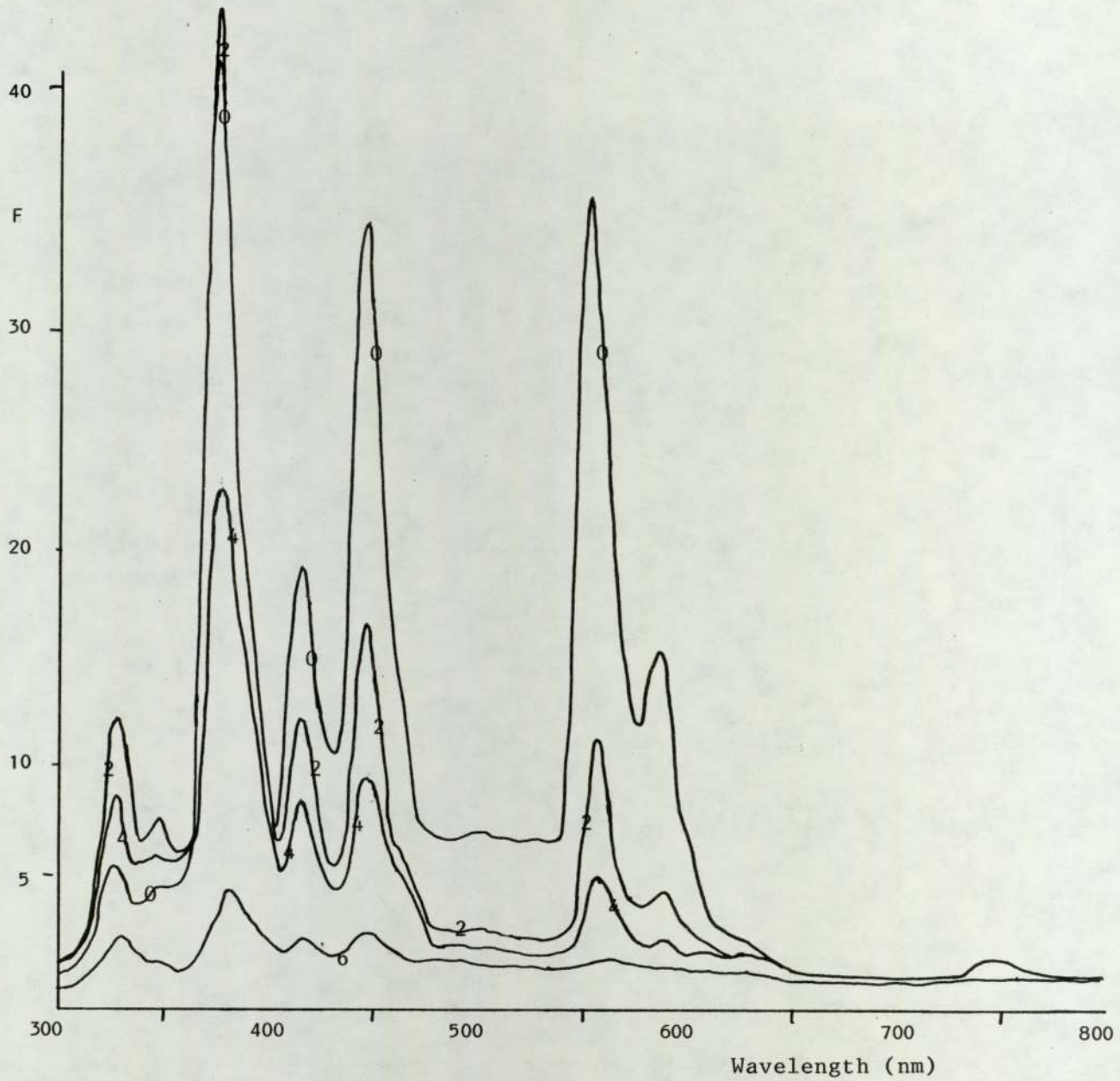


Figure 3.4 Excitation Spectra of Cortonwood Vitrinite. Emission set at 620 nm. Scale 0.01.

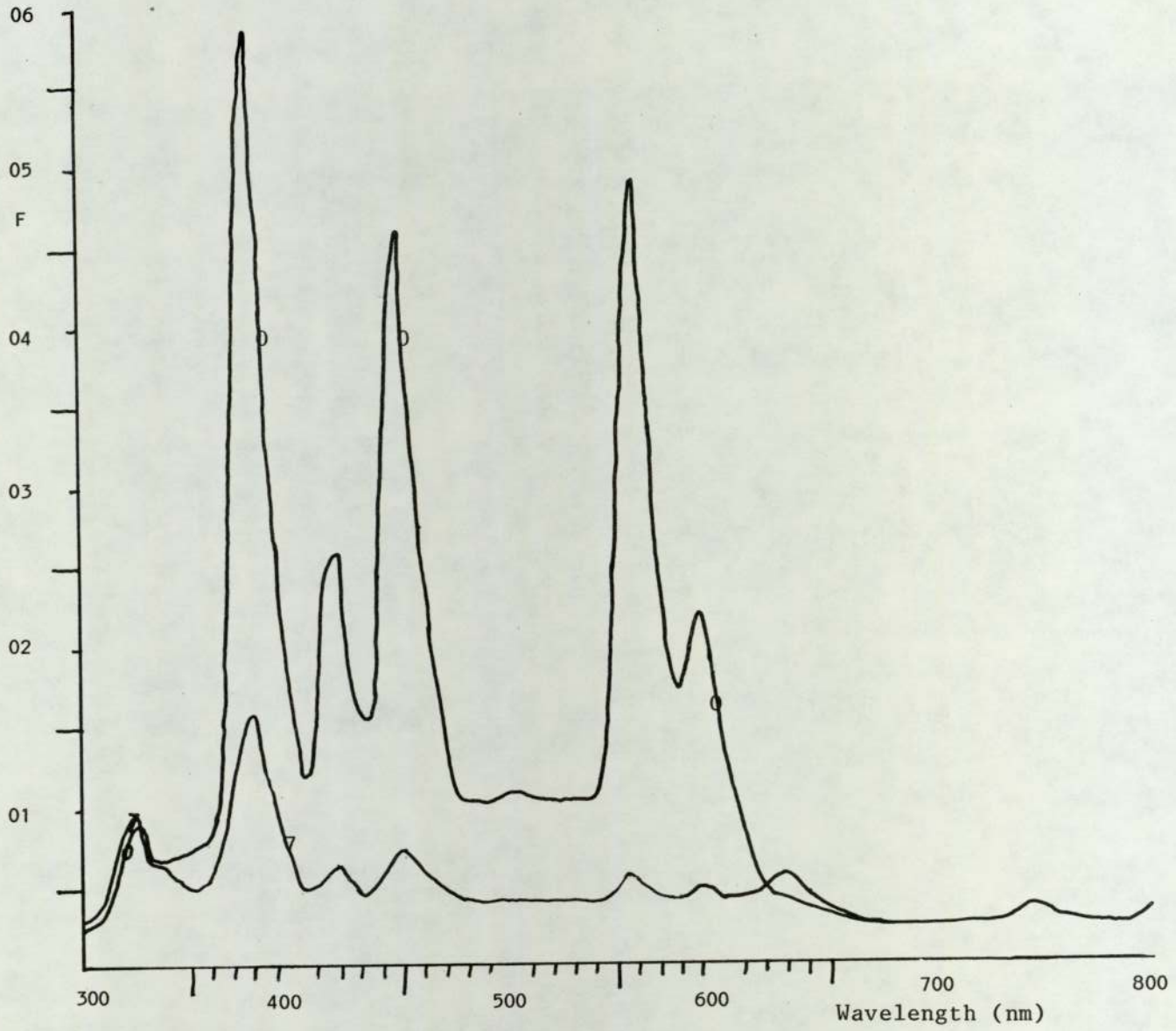


Figure 3.5. Excitation Spectra of Cortonwood Vitrinite. Emission set at 620 nm.

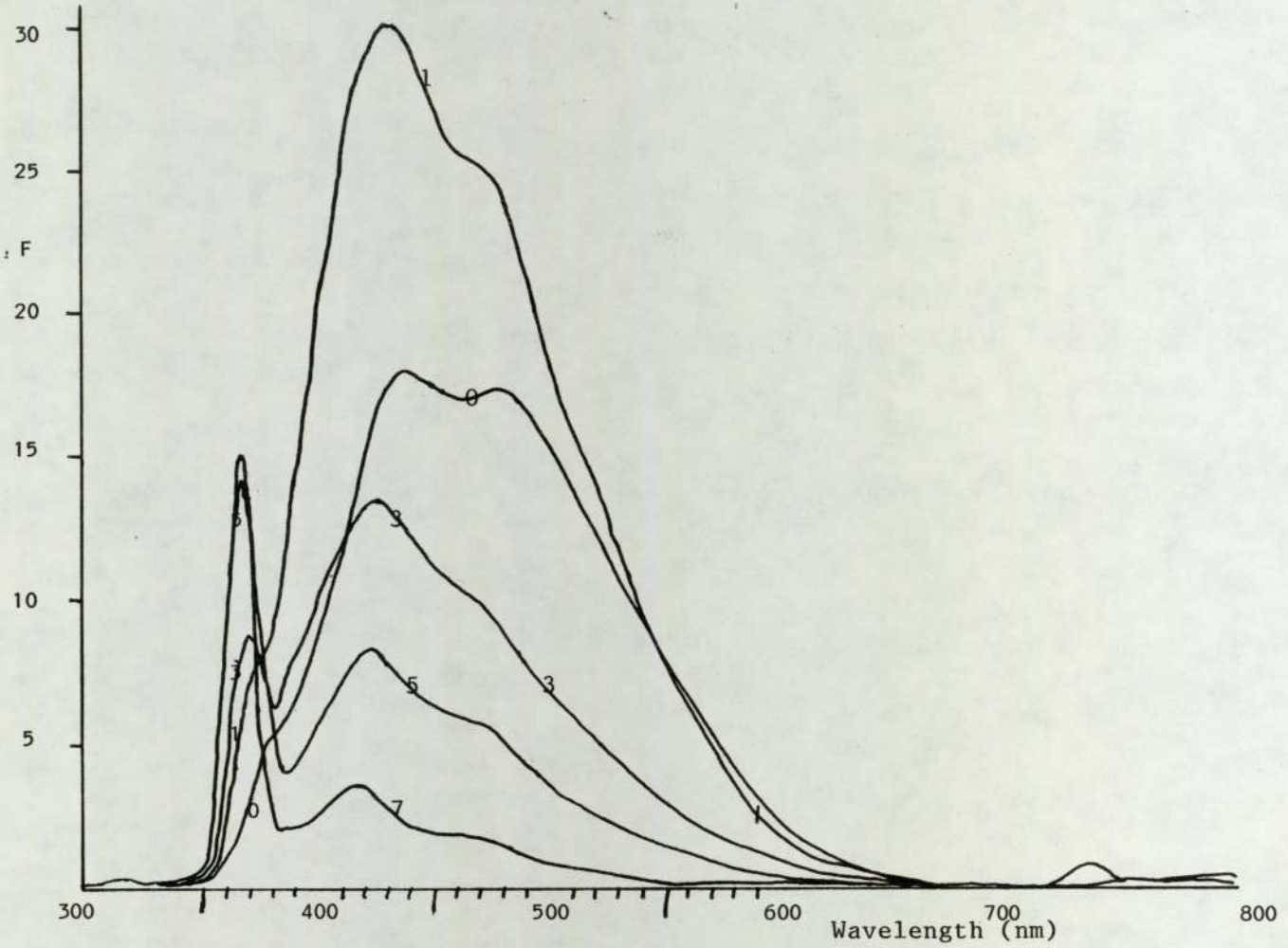


Figure 3.6. Emission spectra of Cortonwood Exinite with varying concentrations. Excitation set at 375 nm.

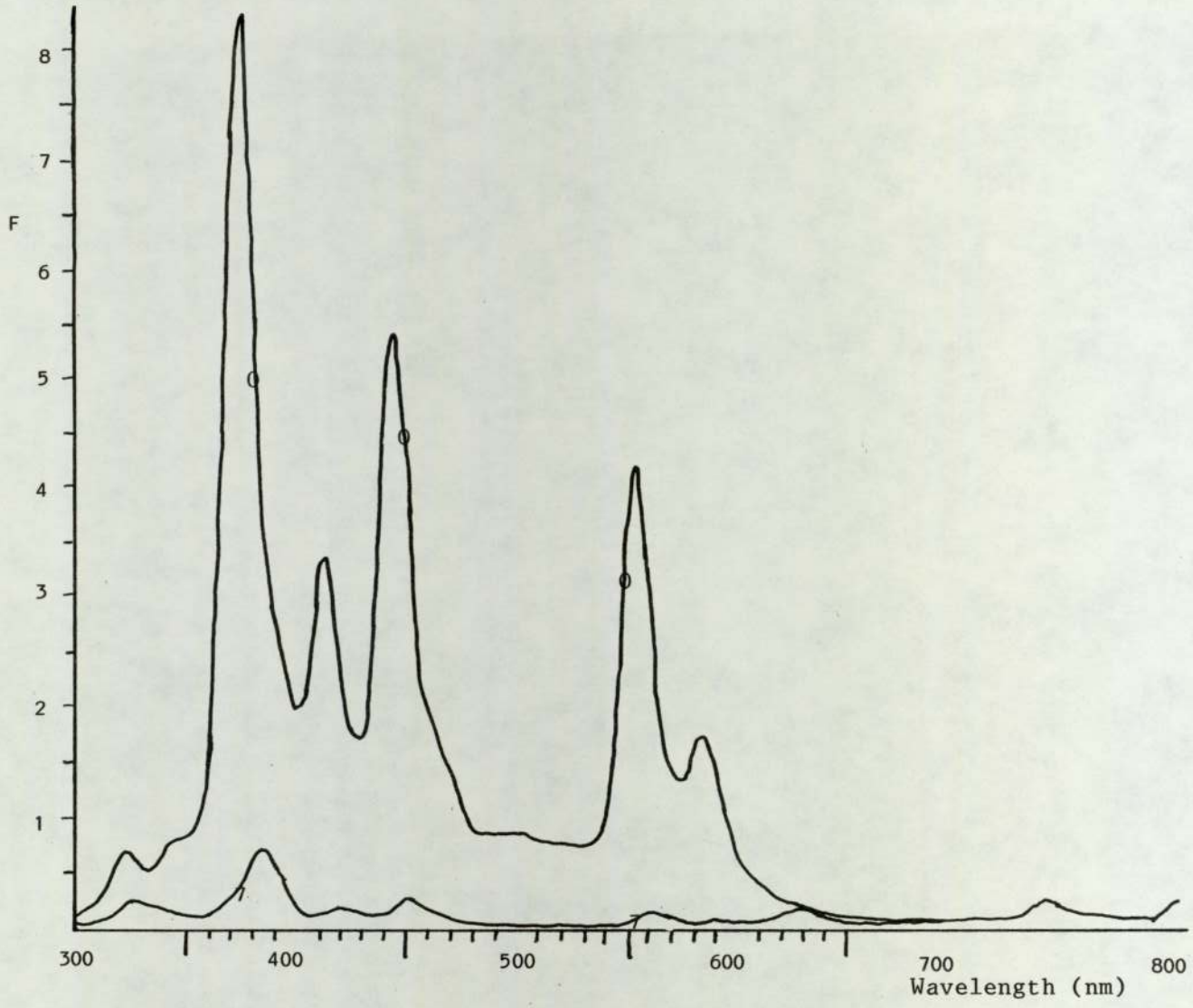


Figure 3.7. Excitation Spectra of Cortonwood Exinite. Emission set at 620 nm. Scale 0.01.

These figures (3.1-3.8) show the increase and decrease in the fluorescence intensity over a range of concentrations. The emission spectra show the wavelengths of maximum fluorescence at 435 nm for the exinite (fig 3.6) and 485 nm for the vitrinite (fig 3.1). It is also noted that there are 'shoulders' on these spectra which vary in prominence over this range of concentrations.

The two spectra of Cortonwood vitrinite with excitation set at 335 nm are of the same set of solutions, showing different concentrations (figs 3.2 and 3.3).

The excitation spectra (figures 3.4, 3.5, 3.7) are of a different nature with six peaks at 325, 375 (strongest), 420, 450, 555 and 590 nm. The fluorescence intensity does increase, for all these peaks, with the 375 nm peak decreasing slightly at the higher concentration.

Note: The spectra of the Cortonwood macerals were drawn manually and not automatically plotted on an X-Y plotter as for the rest of the spectra.

3.1.1 Comparison and concentration curves.

The following spectra show the comparison between Cortonwood exinite and vitrinite.

From these spectra (figs 3.8-3.10) it appears that the exinite solution fluoresces more strongly than the vitrinite solution over this concentration range. Also the maximum peak of intensity occurs at different wavelengths. For the exinite, the peak of maximum intensity occurs at 435 nm, while the vitrinite has a maximum peak of intensity at 480/485 nm (figs 3.8, 3.9).

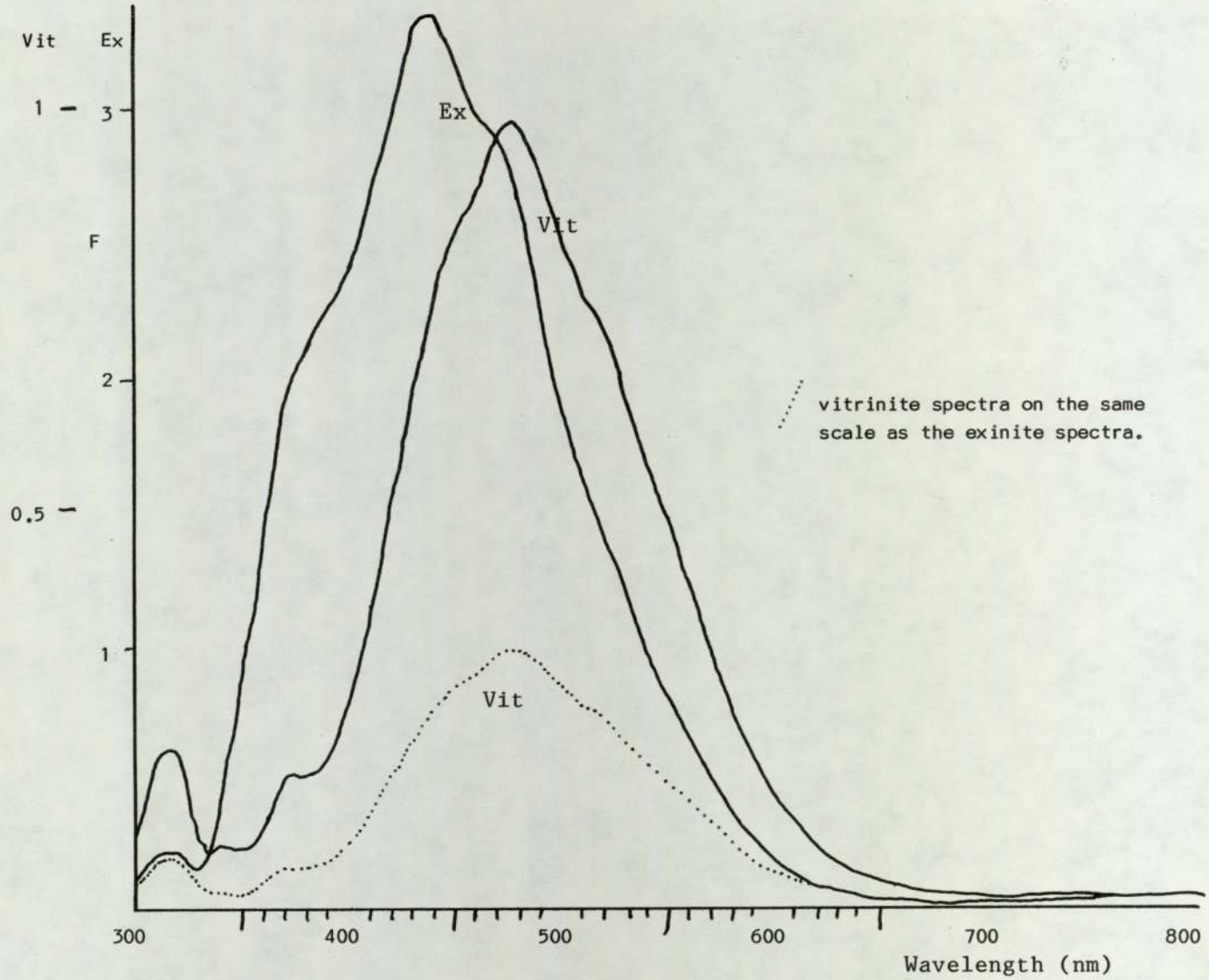


Figure 3.8. Comparison of Cortonwood Exinite and Vitrinite emission spectra. Excitation set at 335 nm - dilution 1.

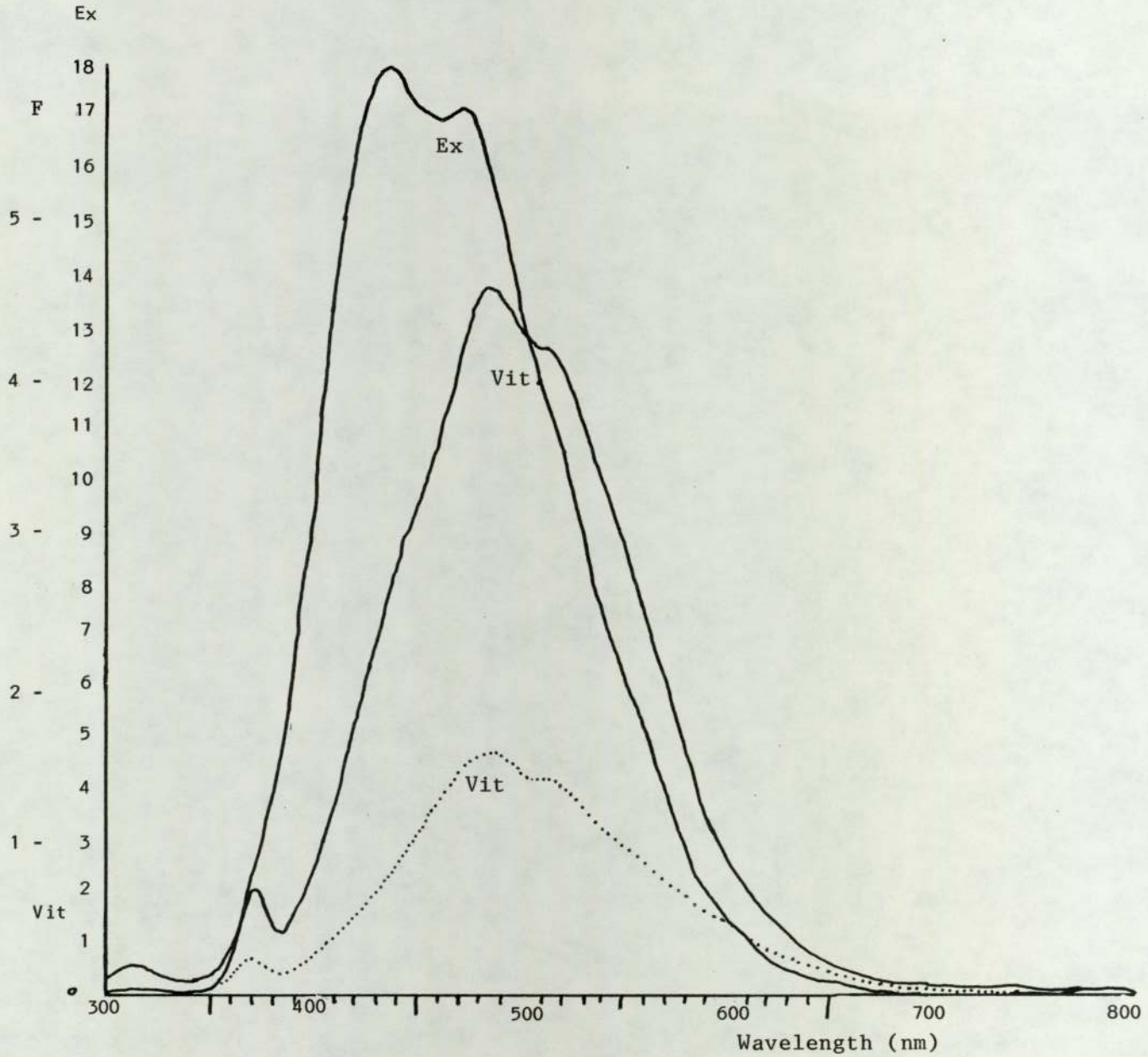


Figure 3.9. Comparison of Cortonwood Exinite and Vitrinite emission Spectra. Excitation set at 375 nmn - original concentrations.

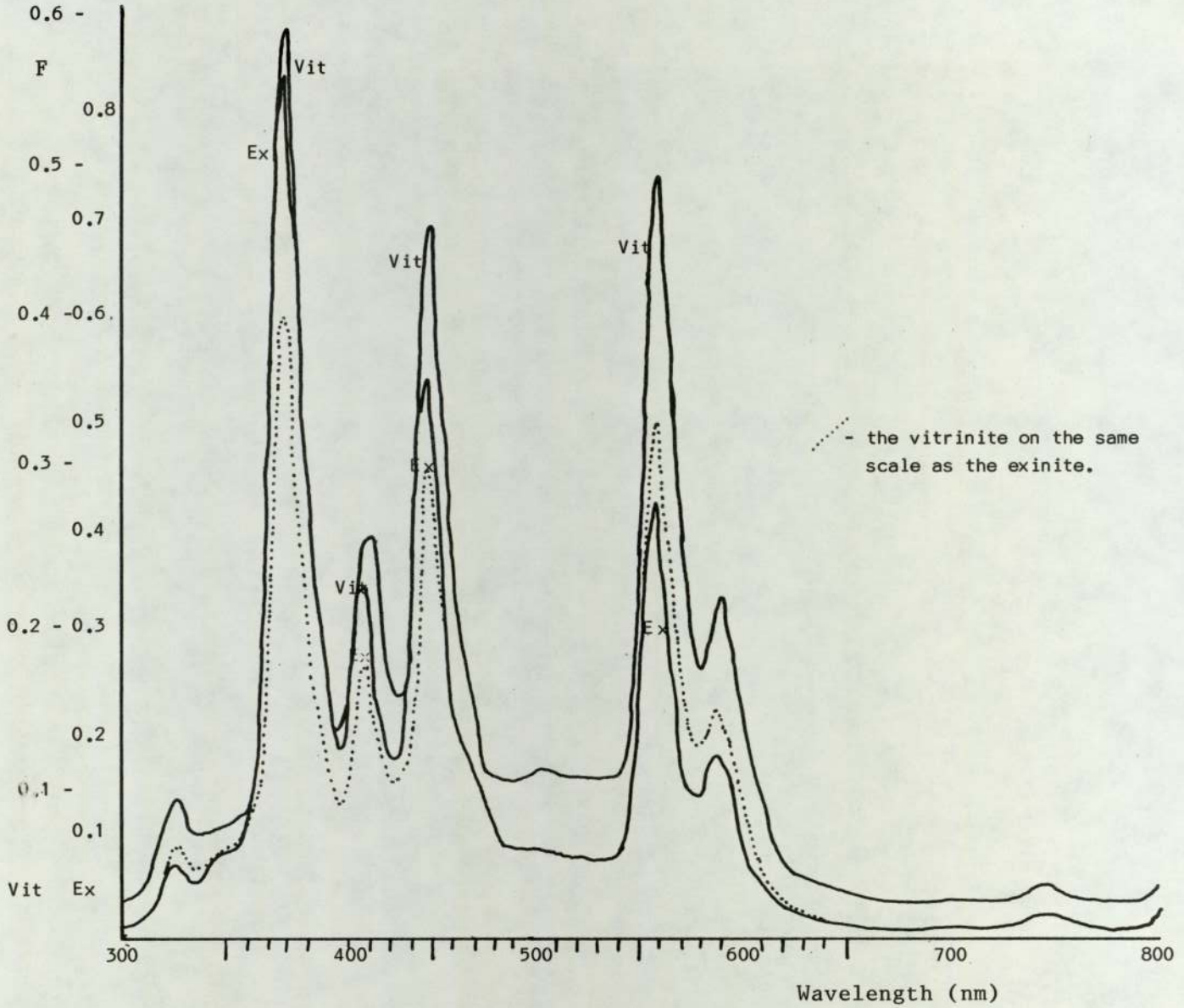


Figure 3.10. Comparison between Cortonwood Exinite and Vitrinite Excitation Spectra. Emission set at 620 nm. - original concentrations.

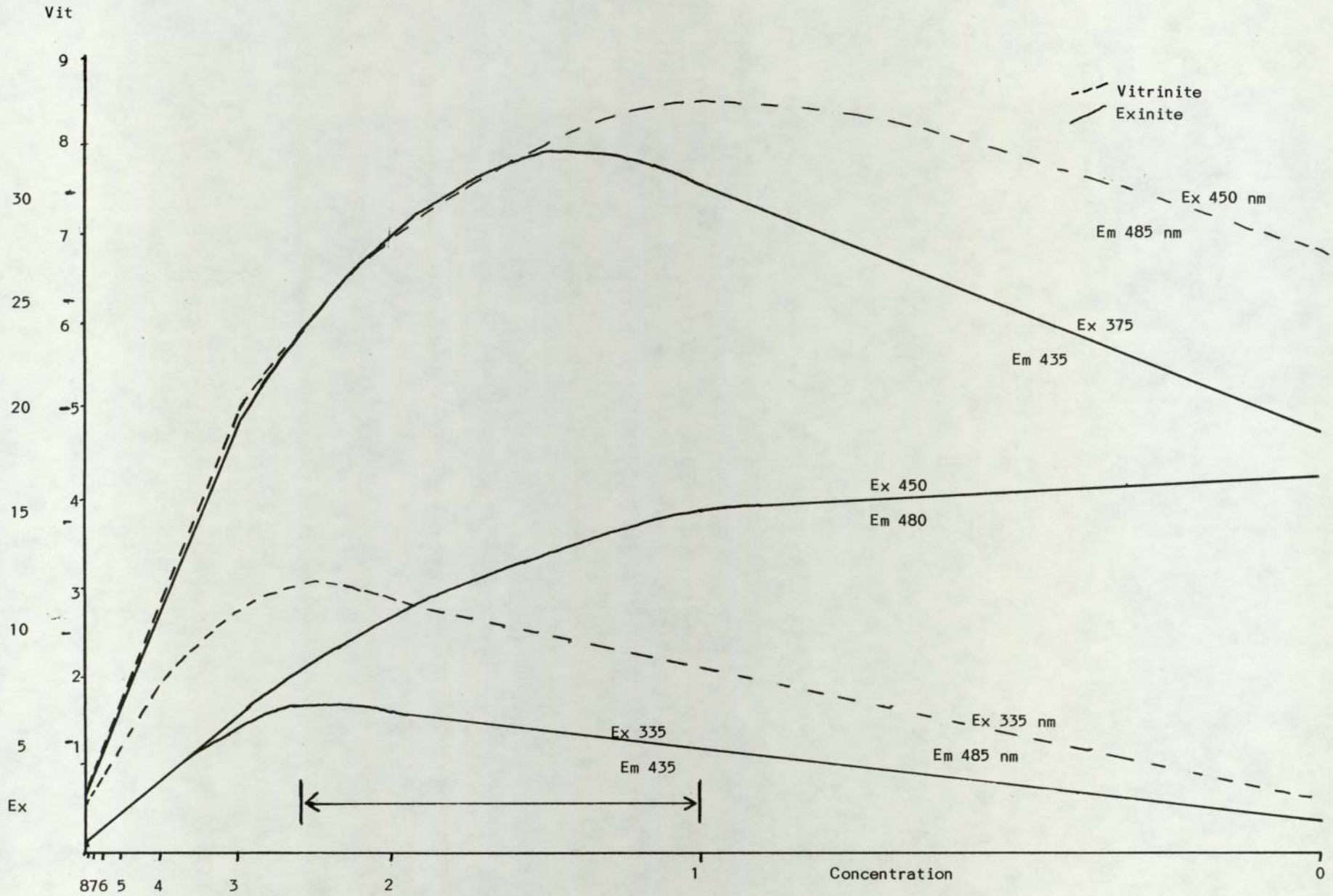


Figure 3.11 Graph showing the variation of fluorescence intensity with concentration for both. Vitrinite and exinite.

It was suspected that the variation of concentration of these solutions could be having an effect on the maximum peak of intensity (λ max), looking at the general drift in the emission spectra (figs 3.8, 3.9). Hence the reason to plot the concentration graph.

From this graph (fig. 3.11), it is seen that for Cortonwood exinite the emission peak at 480/485nm has not yet reached full intensity, while at the same concentration the emission peak at 435nm is being quenched. Due to the heterogeneous nature of coal, it was then necessary to investigate these observations further.

3.2 Emission and excitation spectra of Frickly macerals.

By studying a similar range of concentrations of pyridine extracts of the exinite and vitrinite maceral groups obtained from a Frickly coal sample, it was hoped to increase the consistency of previous results. (See figs. 3.12 - 3.15).

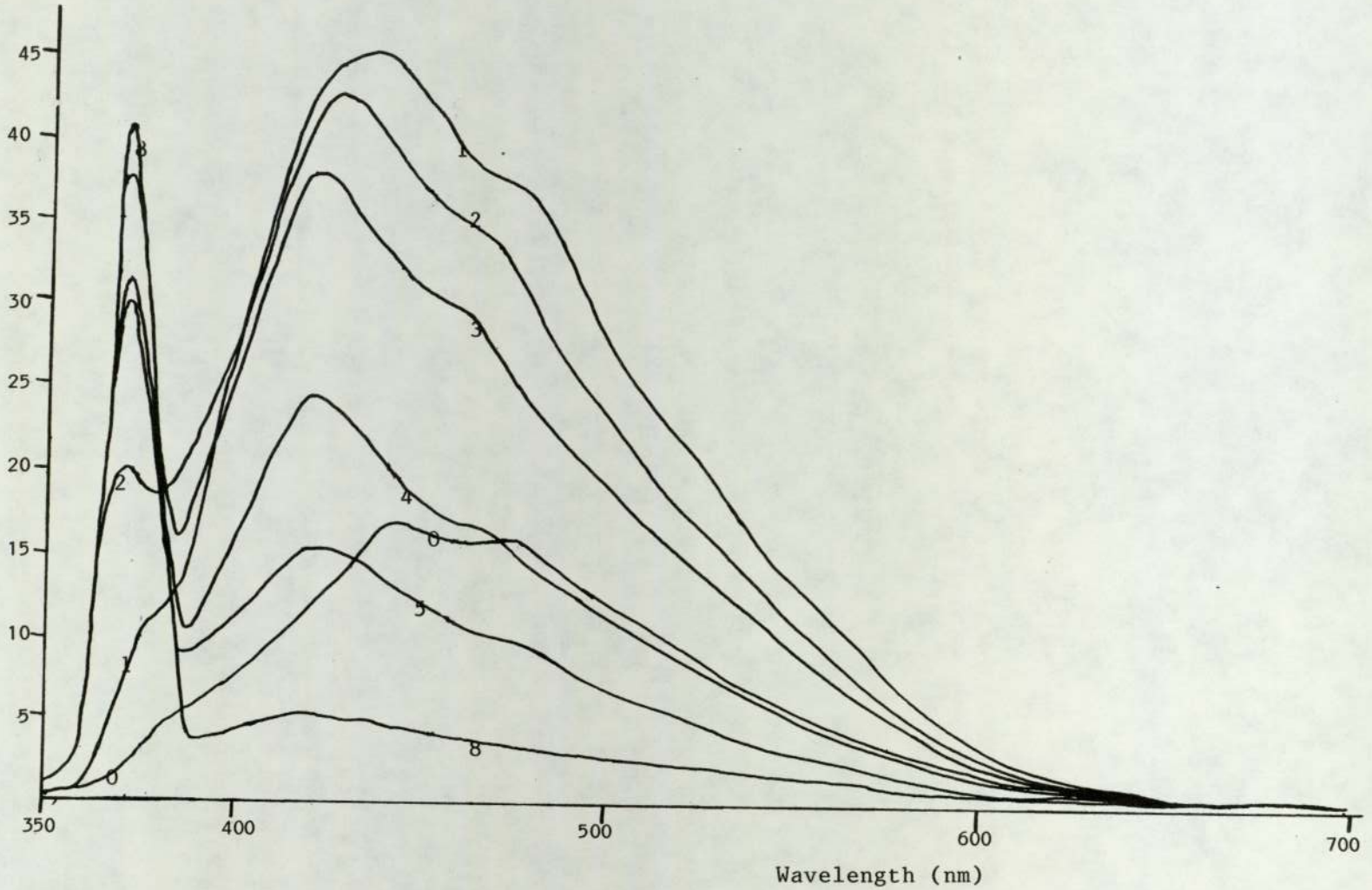


Figure 3.12. Emission Spectra of Frickly Vitrinite with varying concentrations. Excitation set at 375 nm. Scale 0.3.

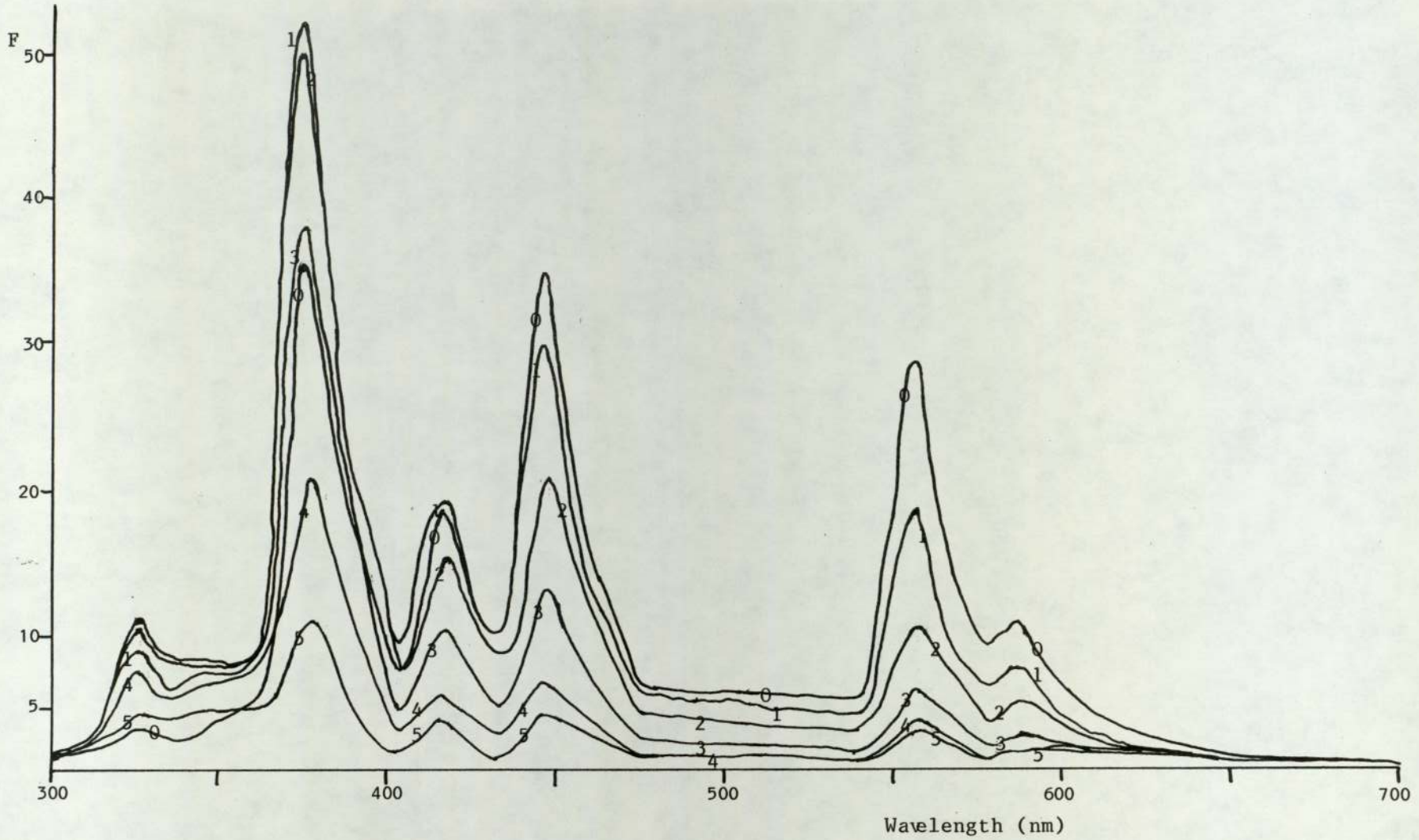


Figure 3.13. Excitation Spectra of varying concentrations of Frickly Vitrinite. Emission set at 620 nm. Scale 0.01.

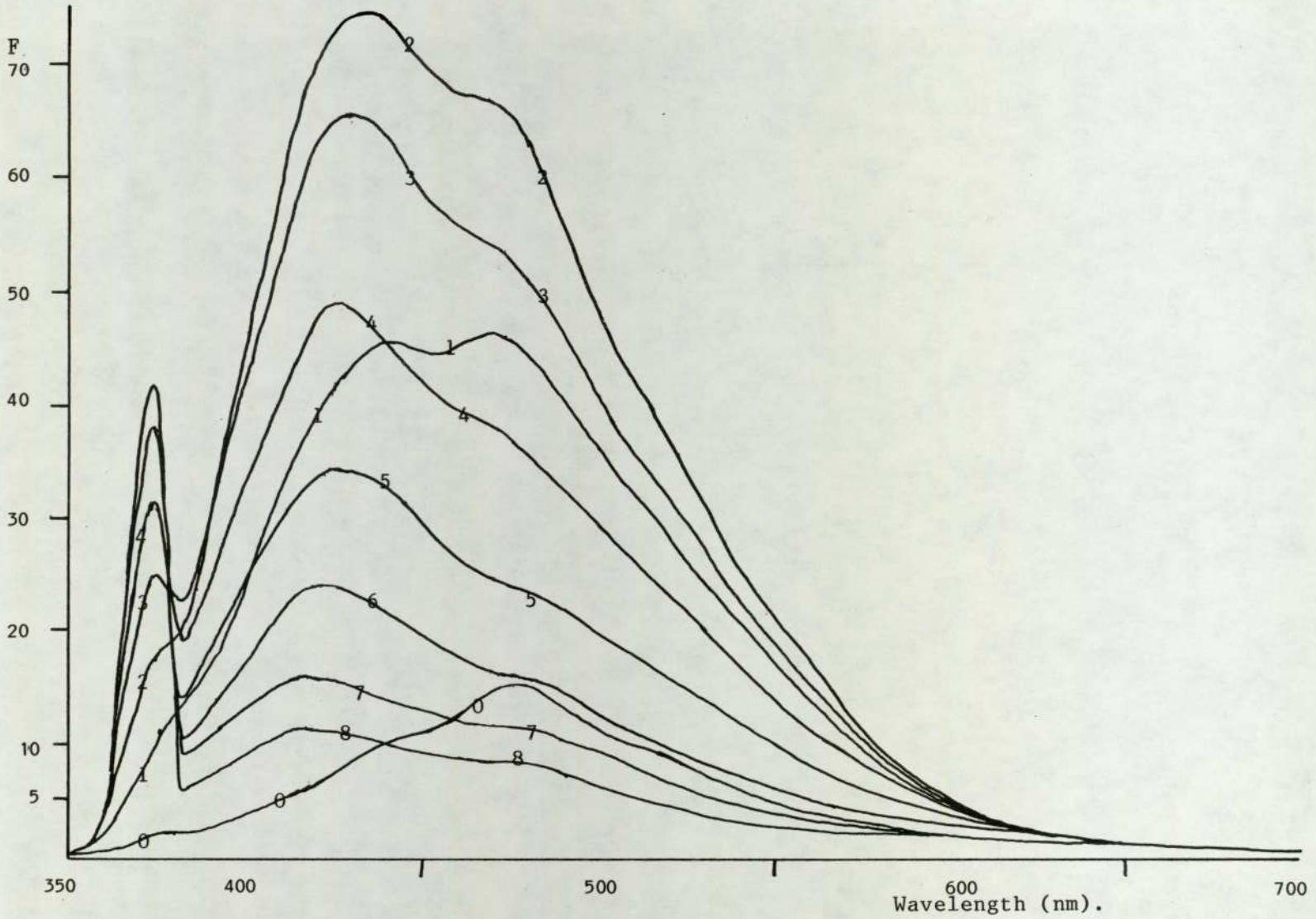


Figure 3.14. Emission Spectra of varying concentrations of Frickly Exinite. Excitation set at 375 nm. Scale 0.3.

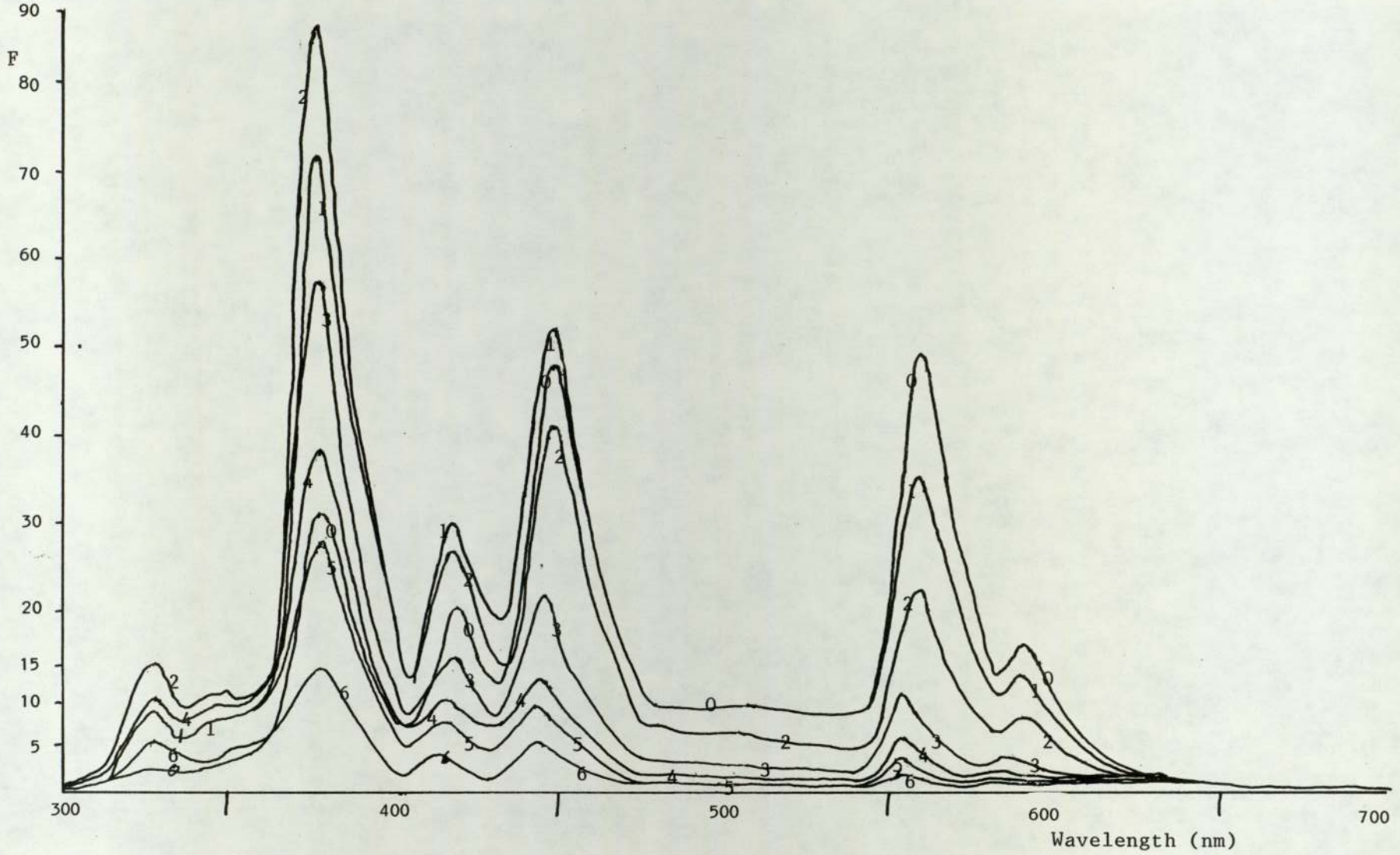


Figure 3.15. Excitation Spectra of Frickly Exinite at various concentrations. Emission set at 620 nm. Scale 0.01.

The emission spectra profile is confirmed by these more comprehensive results. However, these results show that Frickly vitrinite has a maximum fluorescence wavelength of 435 nm, the same as the exinites investigated (fig 3.12.). Also, in this set of results the 485 nm becomes the dominant fluorescence peak at higher concentrations, this is seen in the graph of the 'original' concentration of the exinite (fig 3.14).

The excitation spectra are identical to those for Cortonwood macerals in peak position and they also show the shift to higher wavelengths with concentration more accurately.

3.2.1 Comparison and concentration curves.

For the following spectra of Frickly exinite and vitrinite maceral groups, the scanning range has been reduced from 200 to 800 nm to 300 to 700 nm to increase accuracy.

These spectra appear to show that the Frickly exinite fluoresces more strongly than the vitrinite. However, the difference in fluorescence intensity is far less than that of Cortonwood exinite and vitrinite. Also, unlike the Cortonwood macerals, both emission spectra are almost identical with respect to peak position and profile.

Concentration plots (fig 3.18) are also reported, in order to look at the effect of concentration on fluorescence intensity.

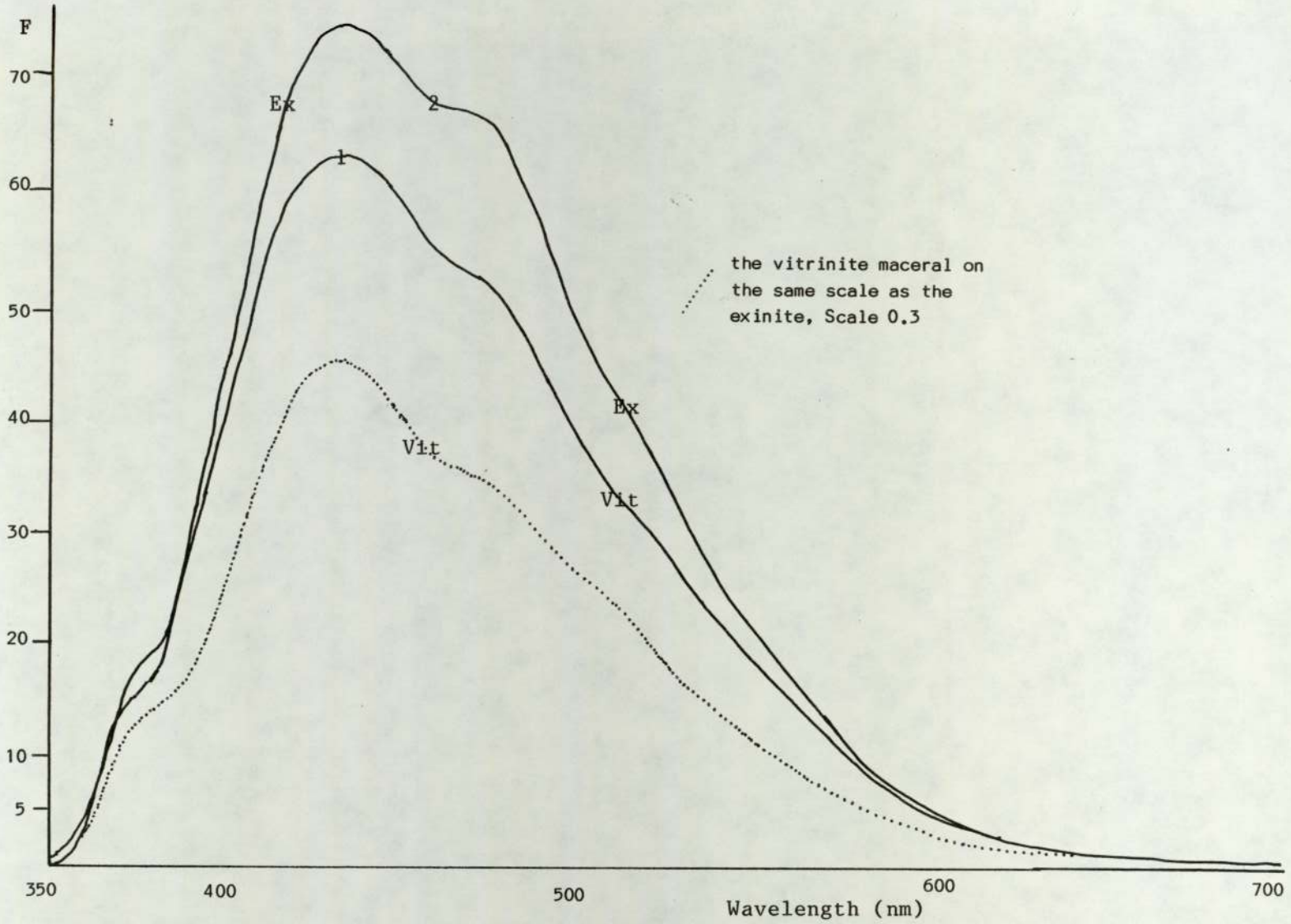


Figure 3.16. Comparison of Frickly Exinite and Vitrinite at maximum emission concentrations. Excitation set at 375 nm.

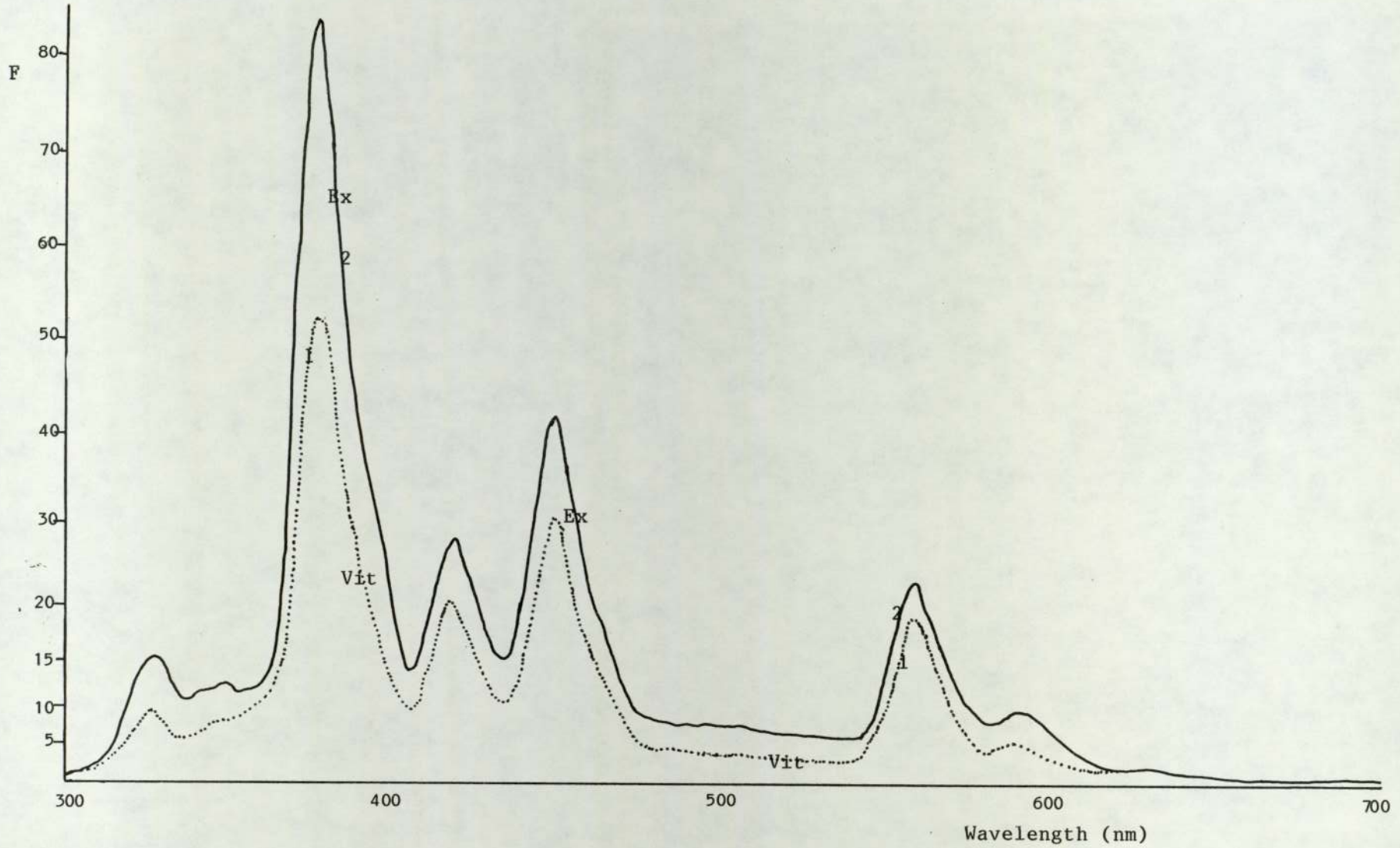


Figure 3.17. Comparison of Frickly Exinite and Vitrinite at maximum emission concentrations. Emission set at 620 nm. Scale 0.01.

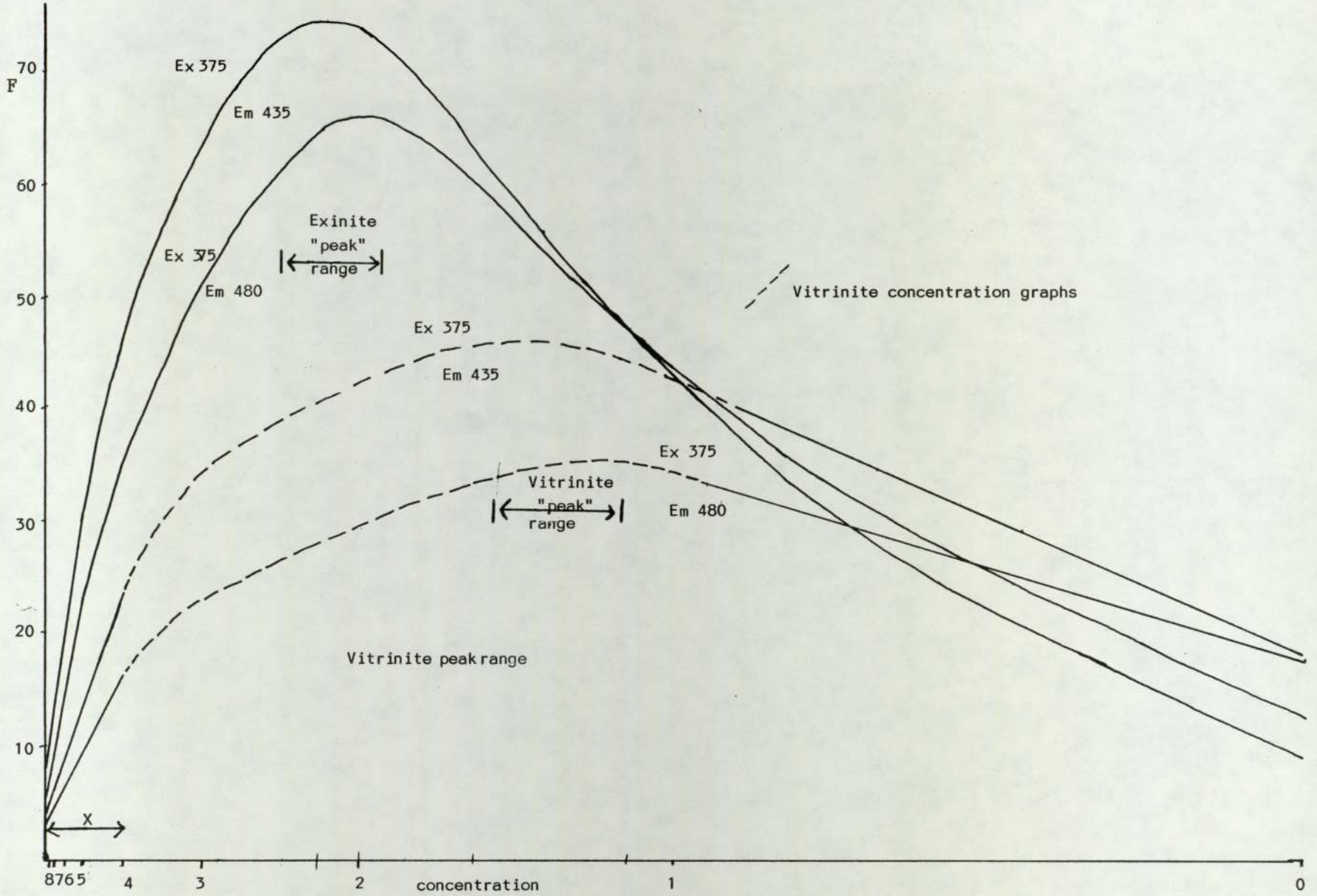


Figure 3.18. The variation of F with concentration for Frickly exinite and vitrinite. (Scale 0.3).

As for the Cortonwood results, these plots can be considered as obeying Beer's Law over the concentration range covered by the solutions up to extracts 4 or 5. (See fig 3.18). More importantly these graphs show the concentration range over which maximum fluorescence occurs. As can be seen, these concentration ranges, which could be narrowed with more accurate concentration intervals, are different for the exinite and vitrinite. In addition, it is also noted that the point at which the 485 nm peak becomes predominant is also at different concentrations for the exinite and vitrinite.

3.3 Detailed study of a concentrated extract of Cortonwood exinite.

After previous results it was felt necessary to look more closely at high concentration solutions of one of the macerals. The results for a 'high' concentration set of solutions of Cortonwood exinite are now reported.

So the concentration effects could be studied more closely, the dilution of the extracts was altered after the first dilution so the concentration of the extracts are closer together, thus enabling the alterations in the fluorescence wavelength and intensity to be studied in more detail. For these more concentrated extracts, 12 cm^3 of the previous dilution is diluted with 8 cm^3 of the filtered pyridine.

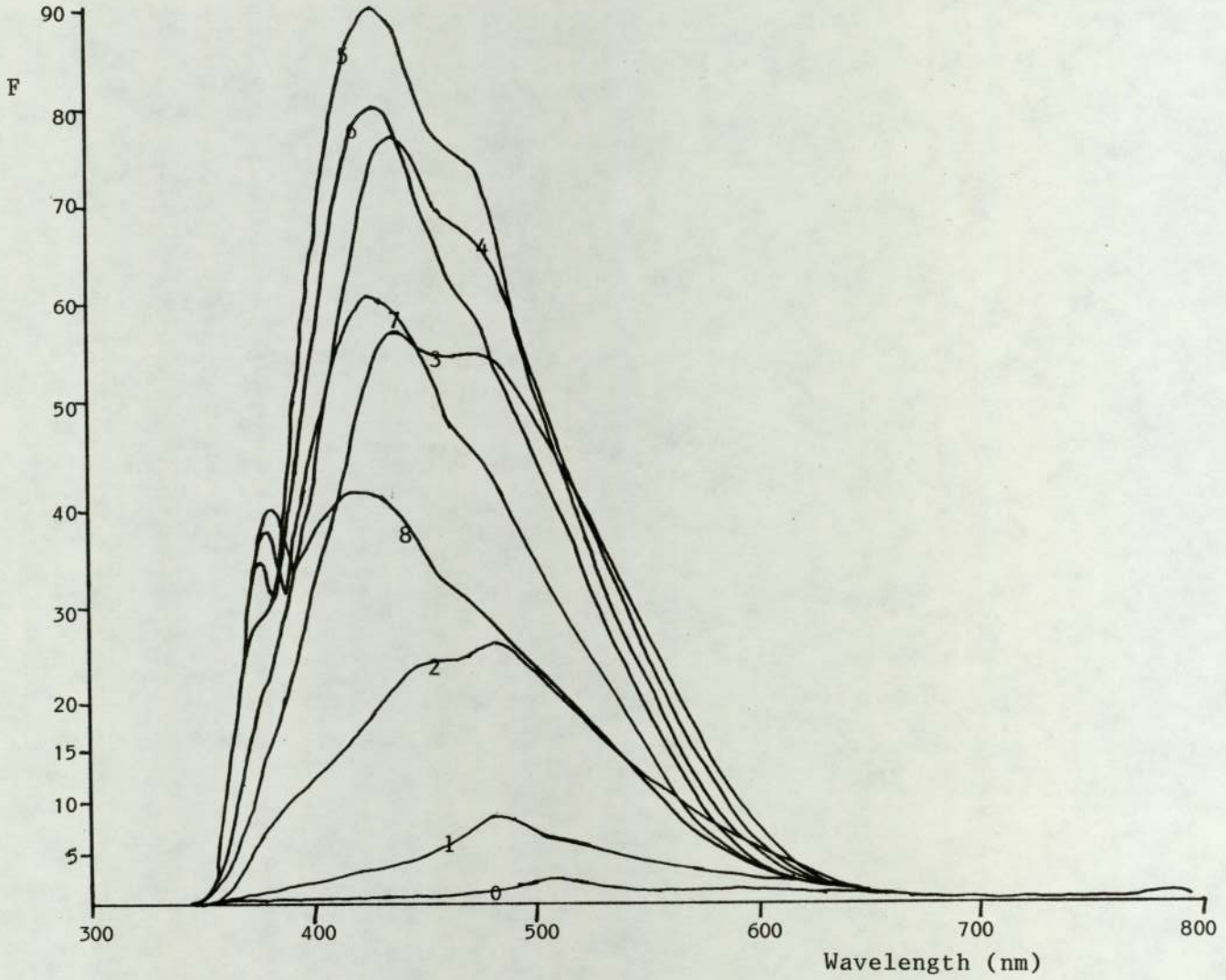


Figure 3.19. Emission Spectra of Cortonwood Exinite (high concentration solution) at varying concentrations. Excitation set at 375 nm. Scale 0.3.

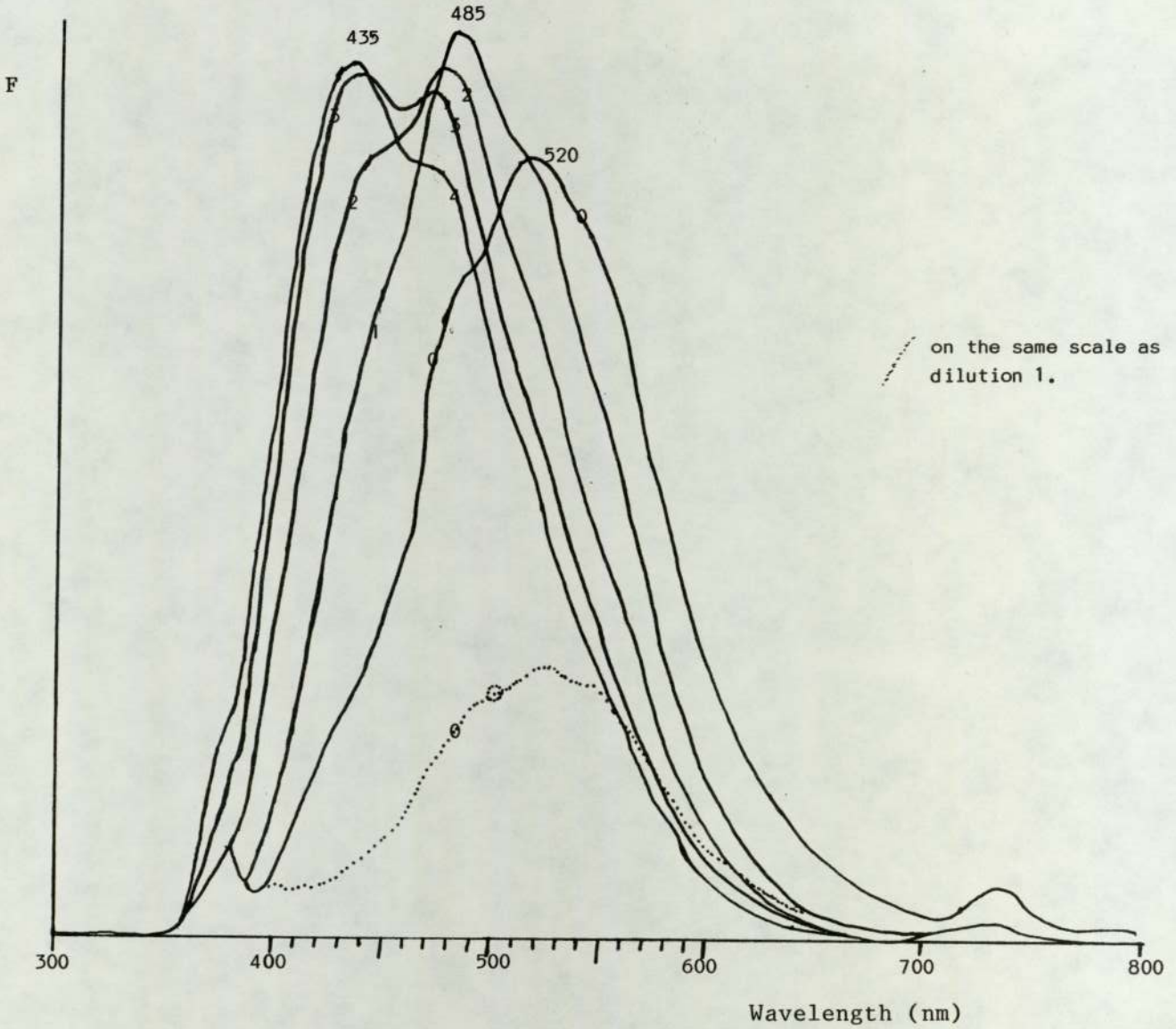


Figure 3.20. Emission Spectra of Cortonwood Exinite (high concentration) over a range of concentrations. Excitation set at 375 nm. (Scale various).

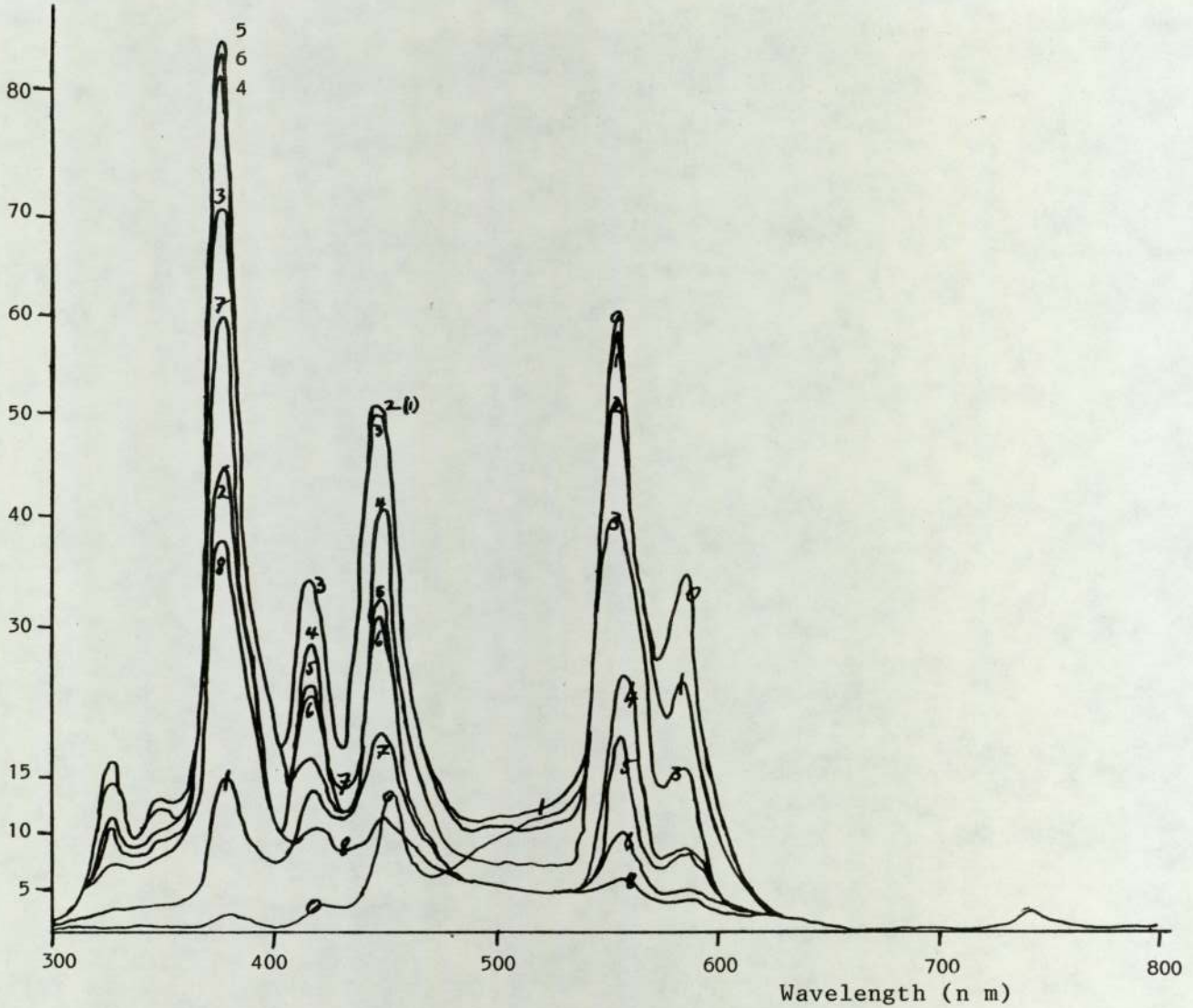


Figure 3.21. Excitation Spectra of Cortonwood Exinite (high concentration) over a range of concentrations. Emission set at 620 nm. Scale 0.01.

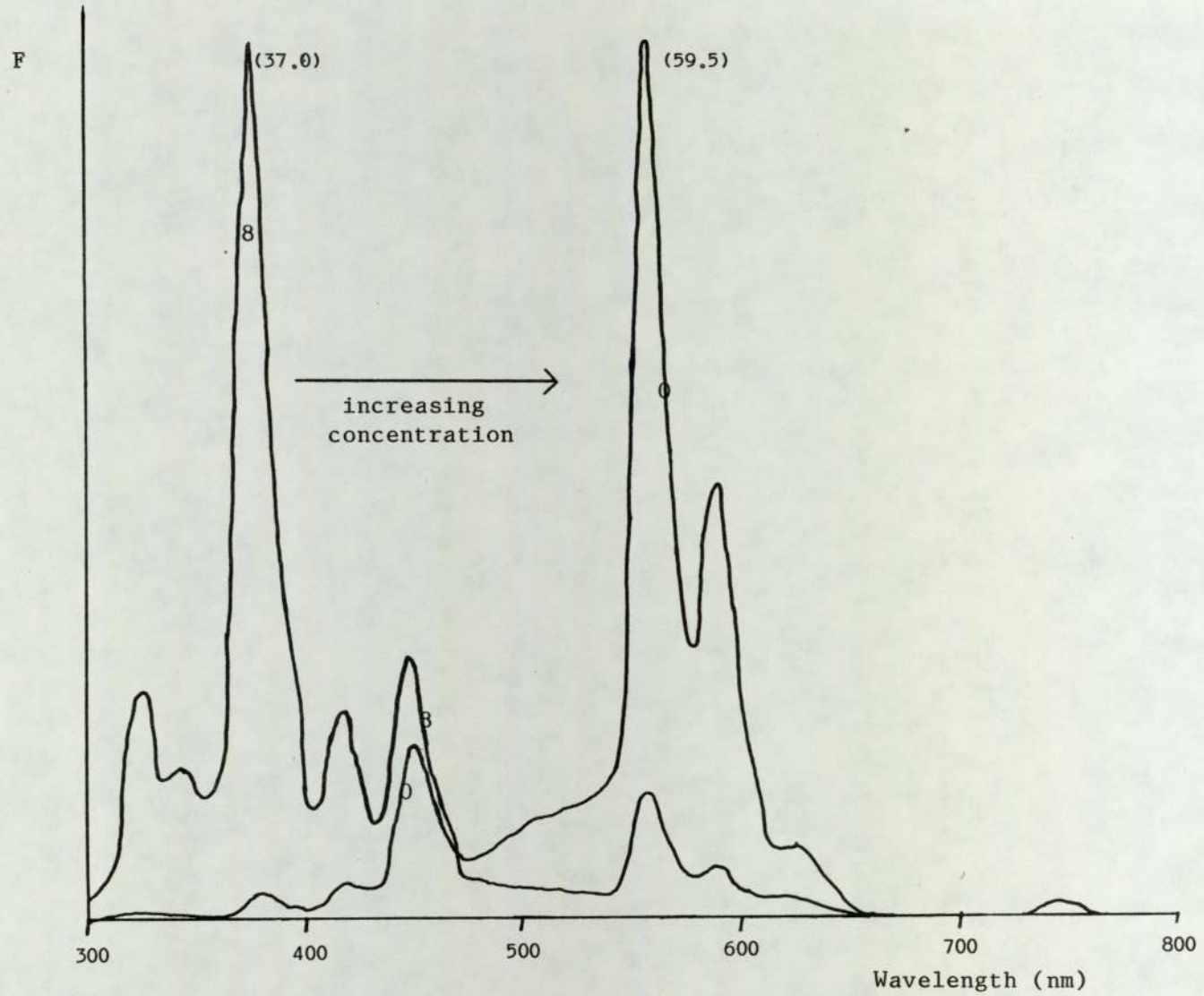


Figure 3.22. Excitation spectra of Cortonwood Exinite (high concentration) at either 'end' of the concentration range. Emission set at 620 nm. Scale 0.01

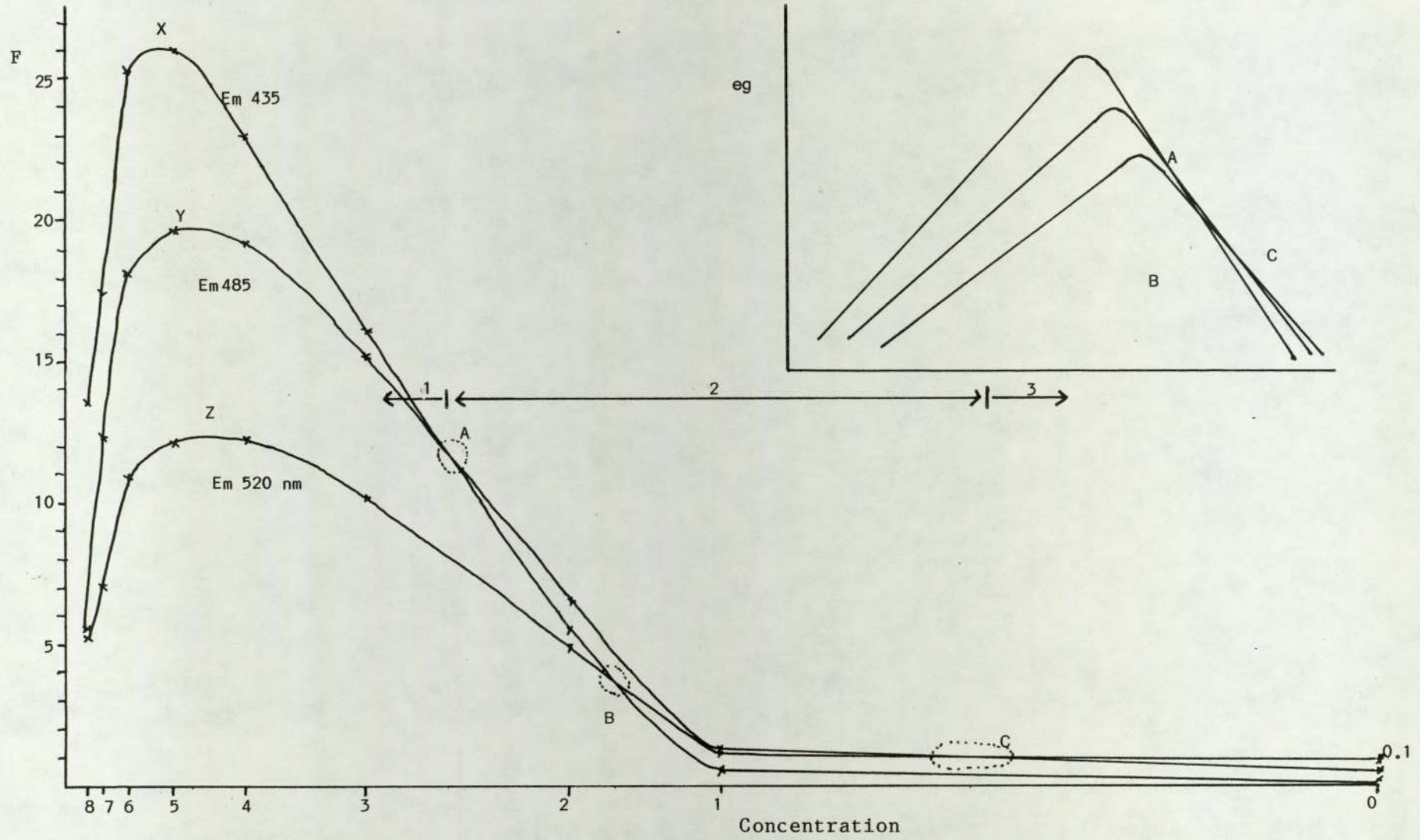


Figure 3.23. Variation of F with concentration following the 435, 485 and 520 nm peaks with fixed excitation frequency of 375 nm.

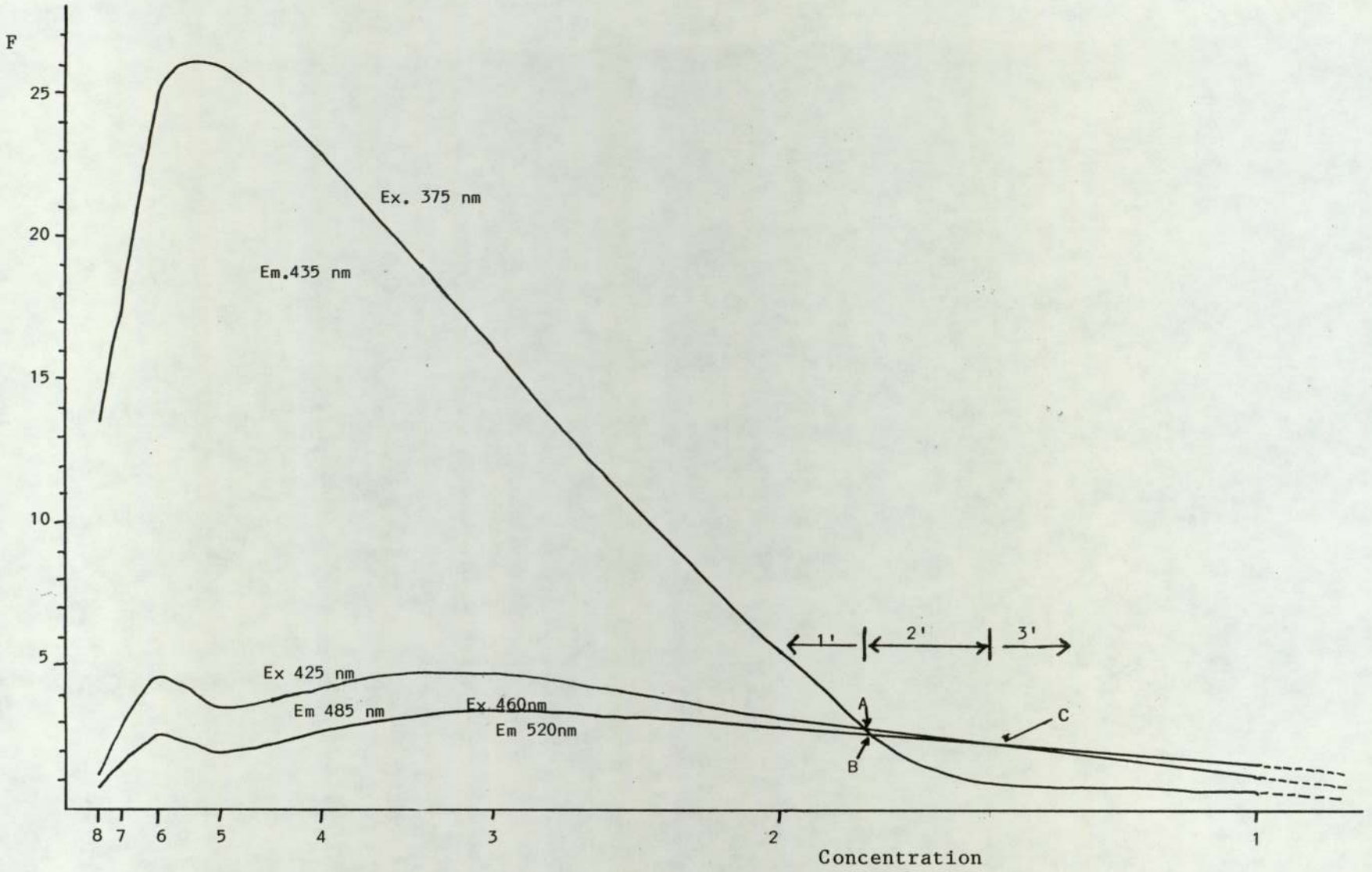


Figure 3.24. Variation of F with concentration following the 3 peaks at 435 nm, 485 nm, 520 nm, with varying excitation frequencies.

From these, a clearer picture of the three fluorescent peaks, with their maxima occurring at different concentration, can be seen (fig. 3.23) These peaks occur at the following wavelengths* in order of strength: ie. the first has the highest F values:-

		concentration range (approximate)
1.	435 nm	X - between Dilutions 6 - 5
2.	485 nm	Y - between Dilutions 5 - 4
3.	520 nm	Z - about Dilution 4

* maximum estimated error $\pm$ 3nm.

Also the shift in the excitation spectra can be easily seen in figure 3.21. This shows the shift in fluorescence intensity from the 375 peak at low concentration to the 555 nm peak at high concentrations. A detailed study on these maceral extracts can be seen in diagrams (3.23 and 3.24) showing a more accurate picture of the effect of concentration on these maceral solutions. In graph 3.23 each of the wavelengths mentioned previously reach their maximum fluorescence at different concentratioins (x, y and z) respectively. The concentration ranges over which each of the peaks are most prominent can be seen; ie. 1, 2 and 3.

These two phenomena can also be seen in figure 3.24 although the results are not compatible. This graph was drawn so that the point C (or rather C) could be more accurately found with the excitation wavelength closer to the emission wavelength. This only assists when investigating the 520 nm peak.

The three points, A, B and C are explained:-

(A) The concentration at which the 485 nm peak becomes more dominant than the 435 nm peak.

(B) The concentration at which the 520 nm 'shoulder' becomes stronger than the 435 nm presence.

(C) The concentration at which the 520 nm peak becomes more dominant than the 485 nm peak.

3.3.1. The comparison of Cortonwood and Frickly macerals.

There is little difference in the fluorescence of the exinites, with the Cortonwood maceral fluorescing more strongly in both the emission and excitation spectra; (see figures 3.25 and 3.26).

However, for the vitrinites there is quite a significant difference in the emission spectra. Figure 3.27. also shows considerable difference in the intensity as well as maximum peak position. The excitation spectra again shows more intense peaks for the Cortonwood maceral. This might be indicating that the Cortonwood maceral has a higher concentration (of fluorescing particles) than that of the Frickly exinite.

These results show that accurate concentrations could possibly be used to obtain 'set' intensity ratios, which could in turn, be used to characterise coals or their macerals.

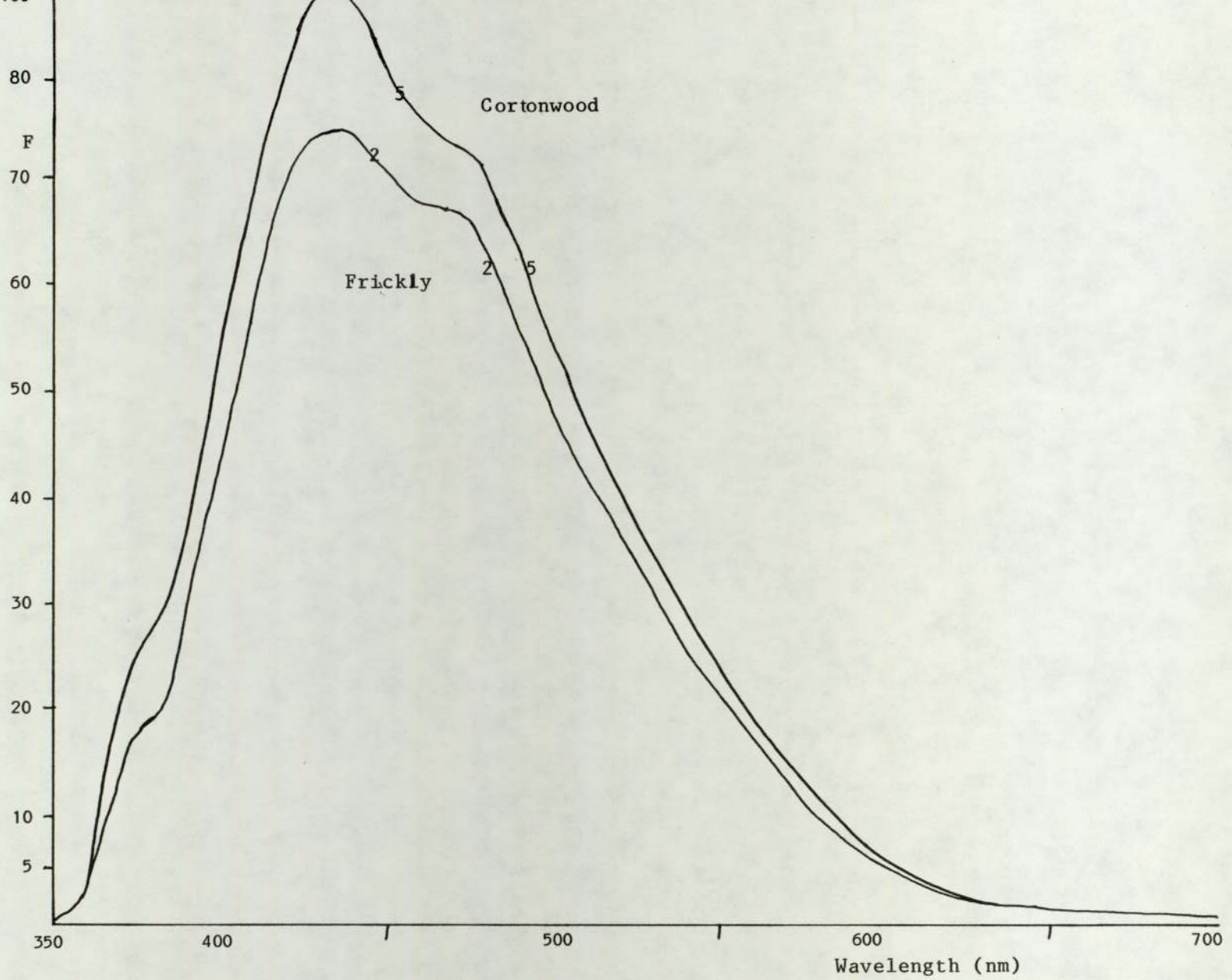


Figure 3.25. Comparison of Frickly and Cortonwood Exinites. Emission Spectra (strongest emission spectra) Excitation set at 375 nm. Scale 0.3

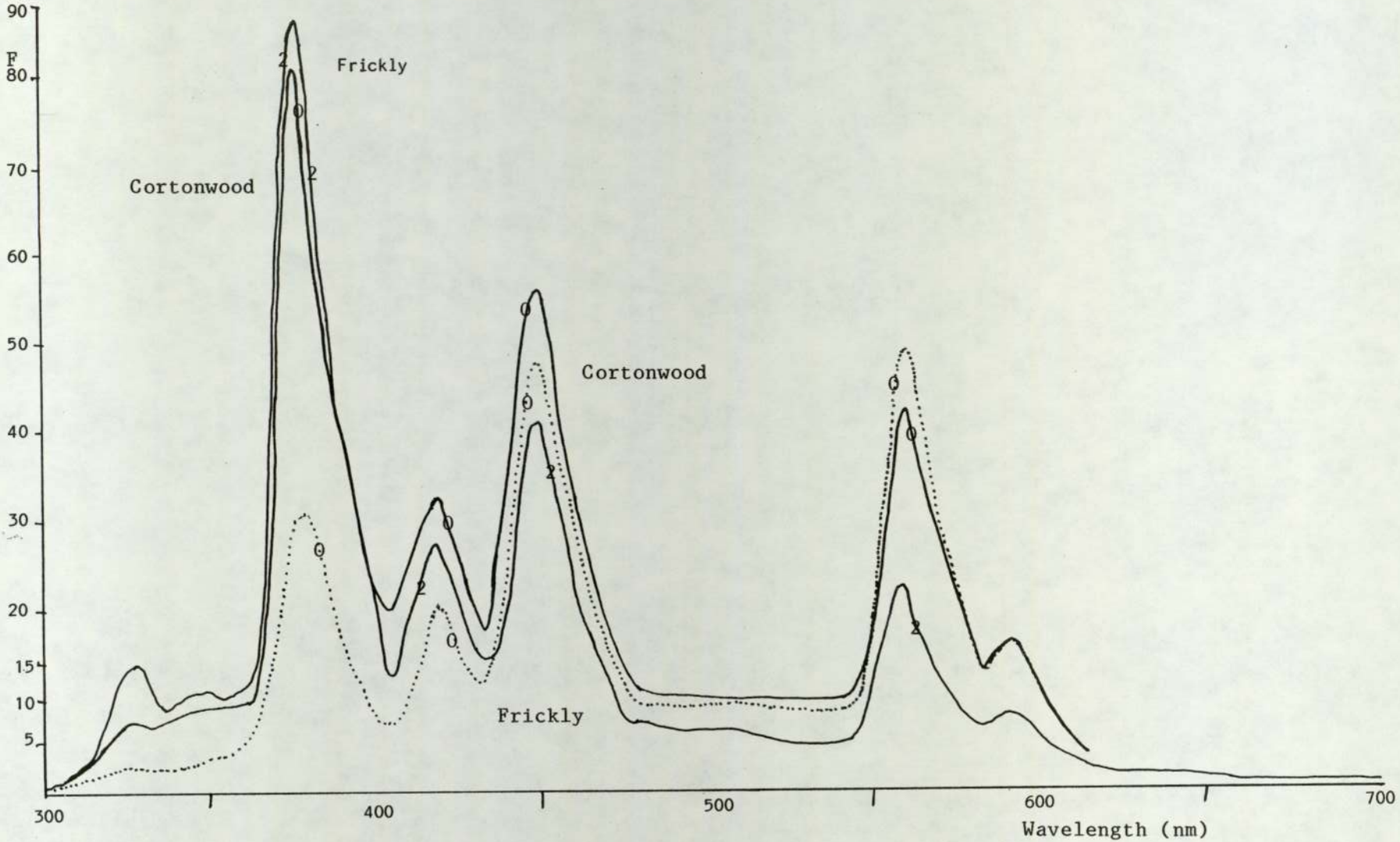


Figure 3.26. Comparison of the excitation Spectra of Frickly and Cortonwood Exinite. Emission set at 620 nm. Scale 0.01

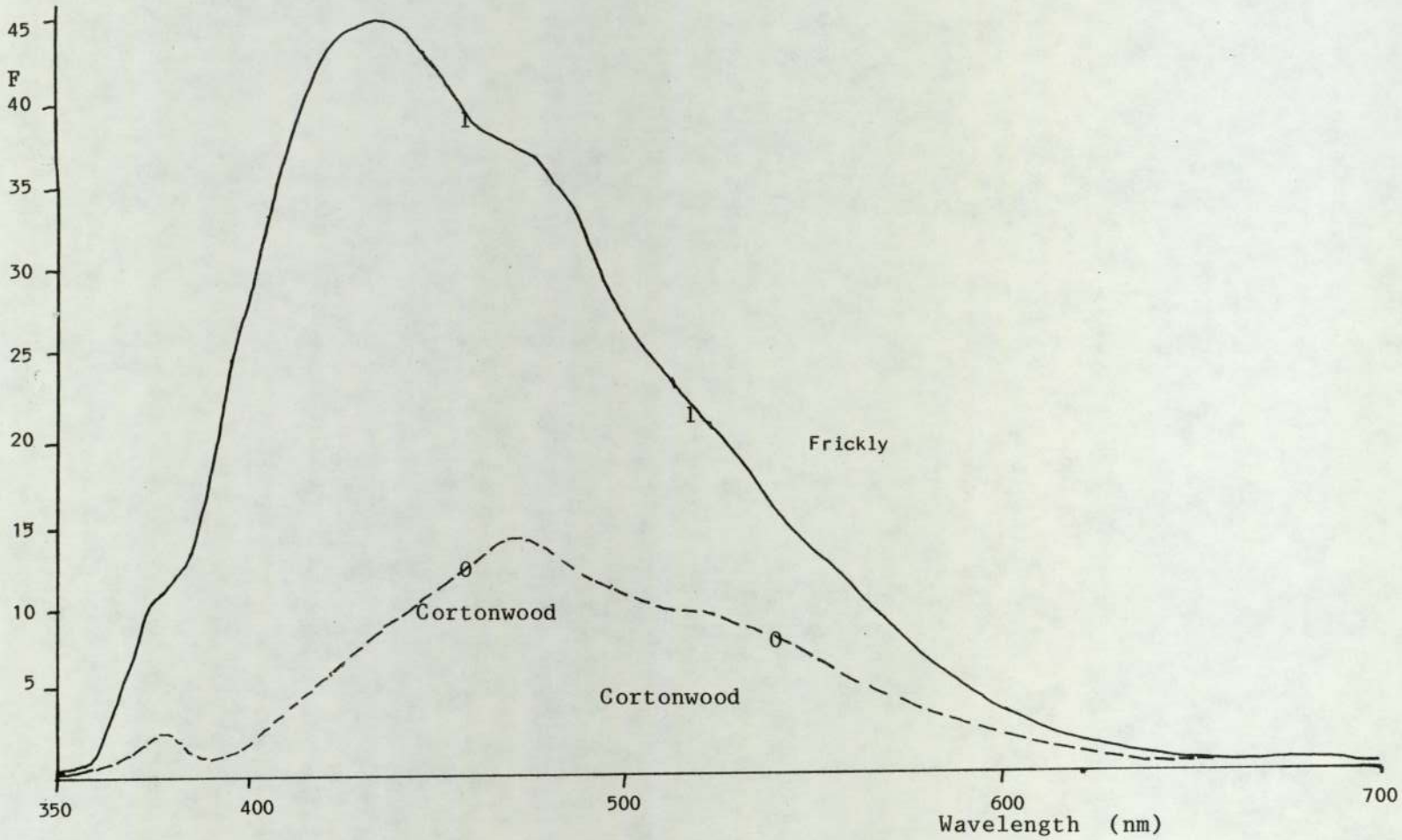


Figure 3.27. Comparison of the Emission Spectra of Frickly & Cortonwood Vitrinite. Excitation set at 375 nm

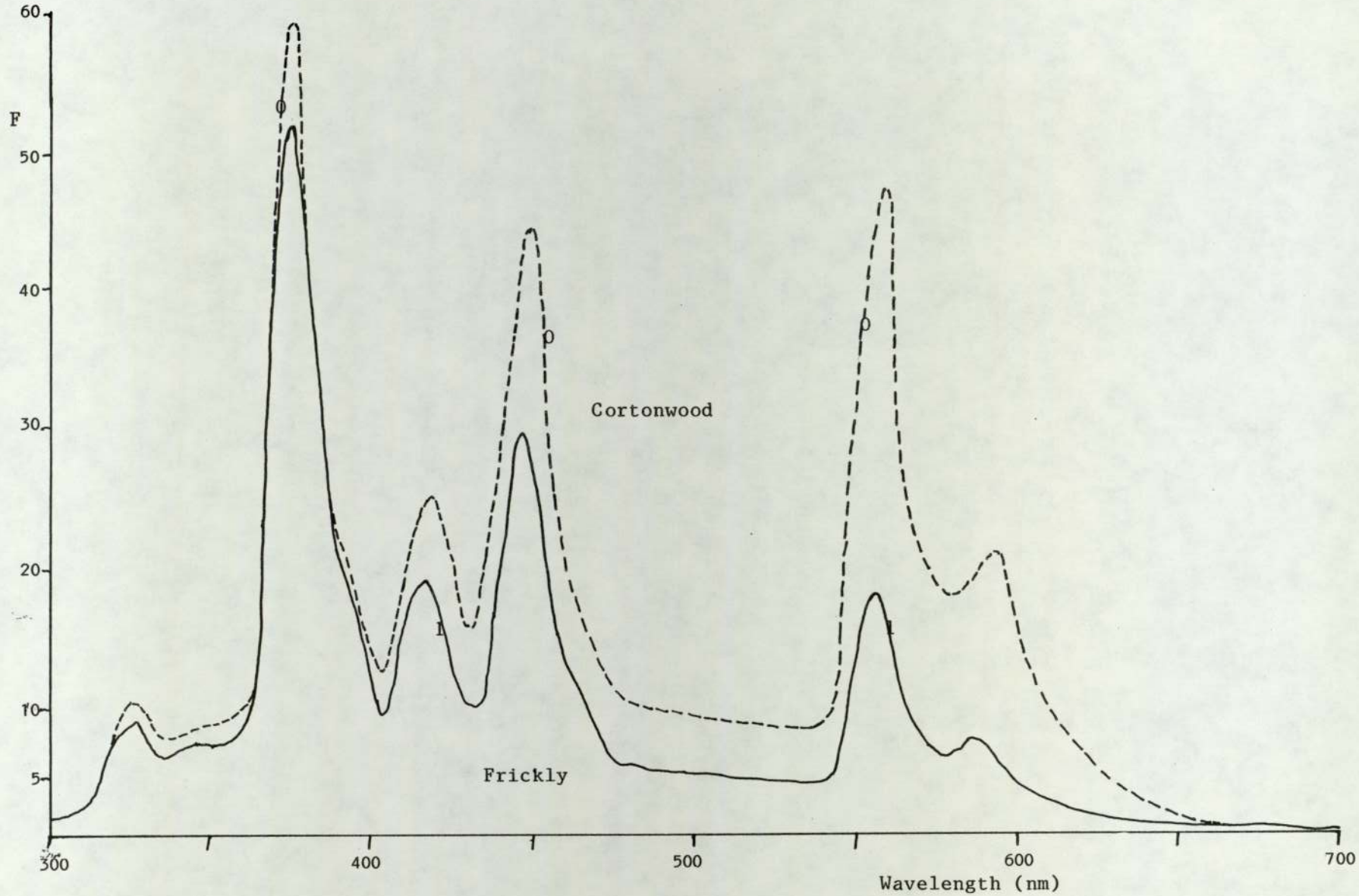


Figure 3.28. Comparison of the excitation spectra of Cortonwood and Frickly Vitrinite. Emission set at 620 nm. Scale 0.01

3.4 Examination of synchronous spectra.

This is an introduction to the synchronous spectra used in the following sections. The synchronous spectra obtained are more precise than the emission and excitation spectra (ie. fewer and clearer peaks), with their nature mostly influenced by the excitation spectra. As it has not been shown whether the excitation spectra are truly characteristic of the coal macerals, only a few spectra have been drawn for initial investigation.

Nevertheless, these spectra do provide another view of the fluorescence of coal macerals and, if automated, could provide a better tool for comparison.

These spectra (figures 3.29 and 3.30) represent a summary of the excitation and emission spectra, the four main peaks observed being 380nm (375nm), 420nm, 450nm and 520nm. The general fluorescence intensity is greater than that of equivalent emission and excitation spectra. This provides greater variation in peak 'heights' which in turn, leads to a slight increase in accuracy when comparing samples (see figure 3.31). Also, the shift in the radiation emitted, to longer wavelengths at high concentration, is more pronounced in the synchronous spectra .

(see figure 3.31).

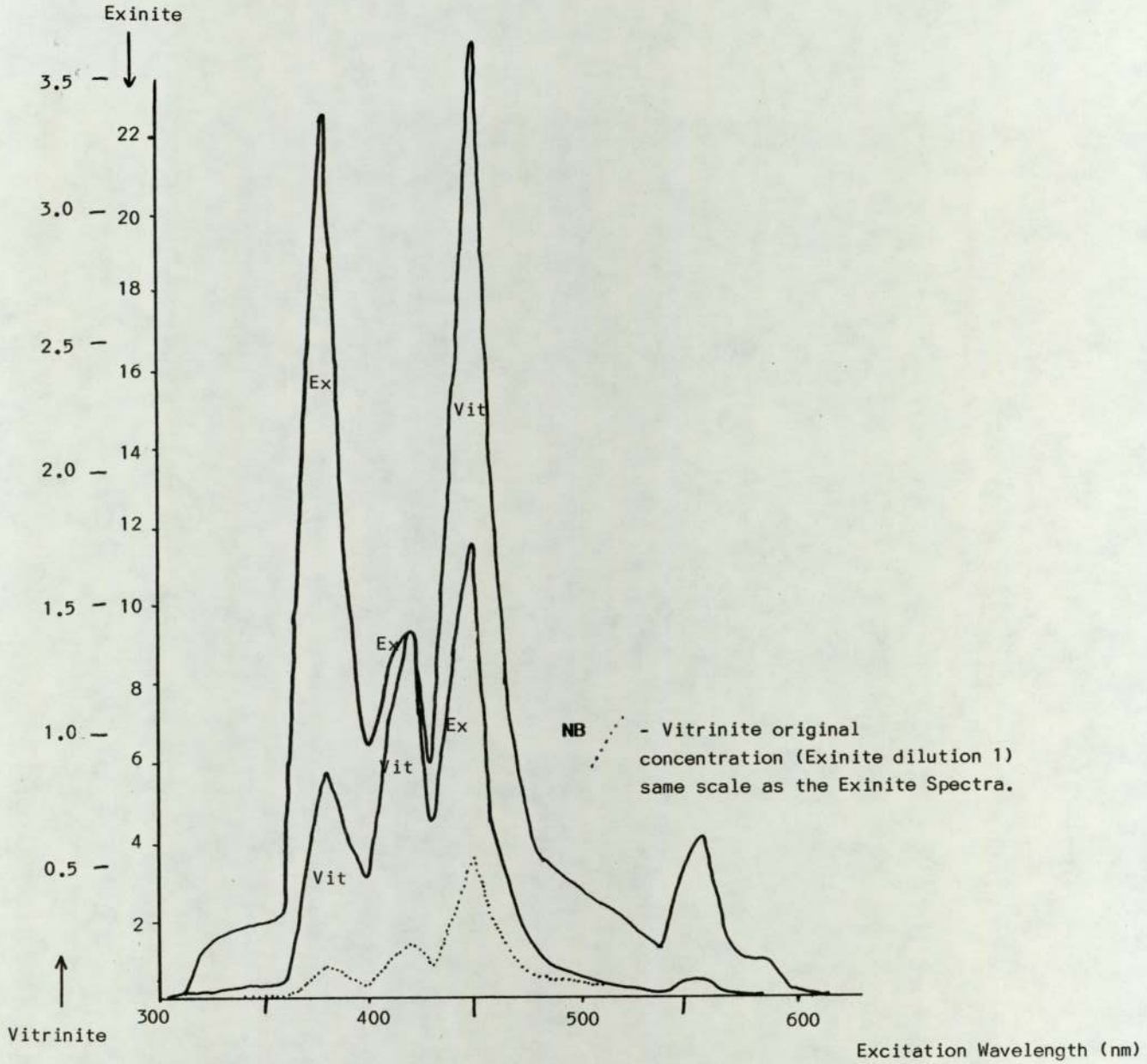


Figure 3.29. Comparison of the Synchronous Spectra of Cortonwood Exinite & Vitrinite. $\Delta\lambda$ 30nm.

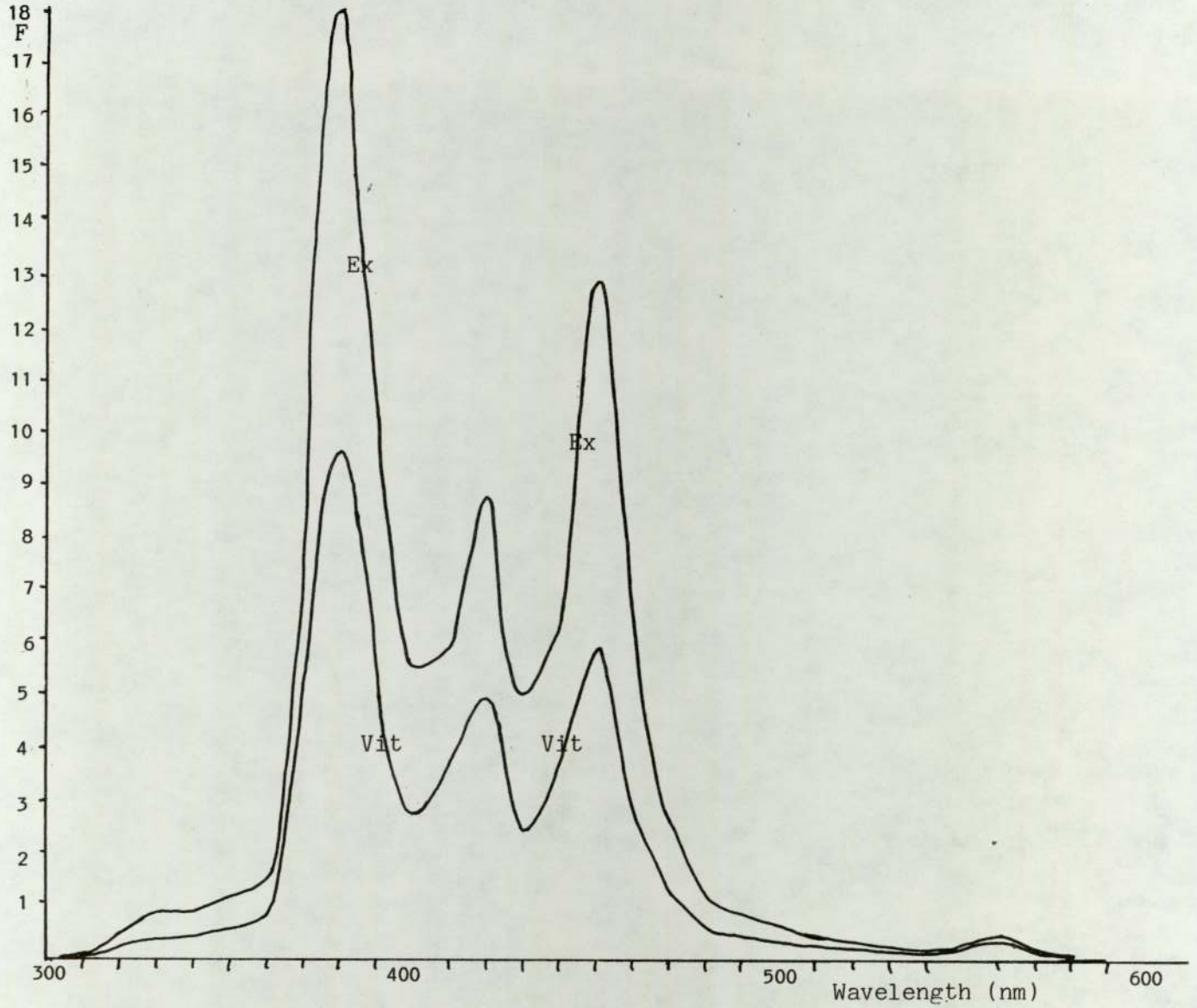


Figure 3.30. Comparison of the Synchronous Spectra of Frickly & Vitrinite. $\Delta\lambda$ 30nm

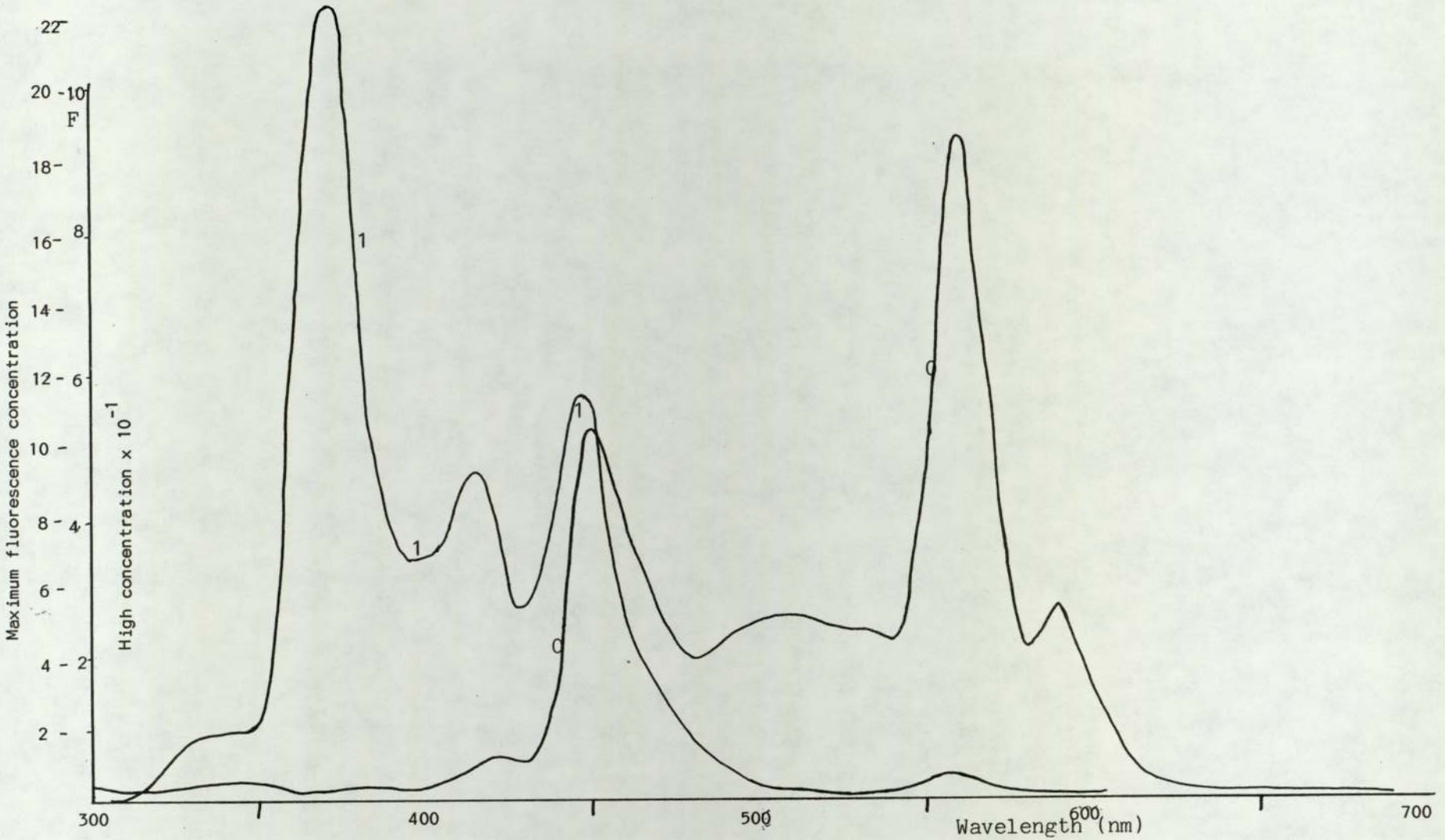


Figure 3.31. Comparison of high concentration and maximum fluorescence concentration $\Delta\lambda_{30}$nm. Scales as shown. Samples from Cortonwood Exinite.

The comparison of the synchronous spectra of macerals from different coal now follows (see figures 3.32 - 3.33). These two figures show that for both macerals the spectra are identical in peak position. Also, the difference in fluorescence intensity is remarkably small, with the Frickley vitrinite and the Cortonwood exinite respectively giving the most intense fluorescence.

As seen later, synchronous spectra can simplify the data to provide a 'cleaner' picture for comparison (see figures 3.32 - 3.33). This type of spectrum is used in the final two sections and has been much reported in the° literature.

The stability of the coal maceral extracts in pyridine has proved useful with no alteration in the spectra over 5 to 7 months, thus allowing confirmatory information and an increased accuracy of results.

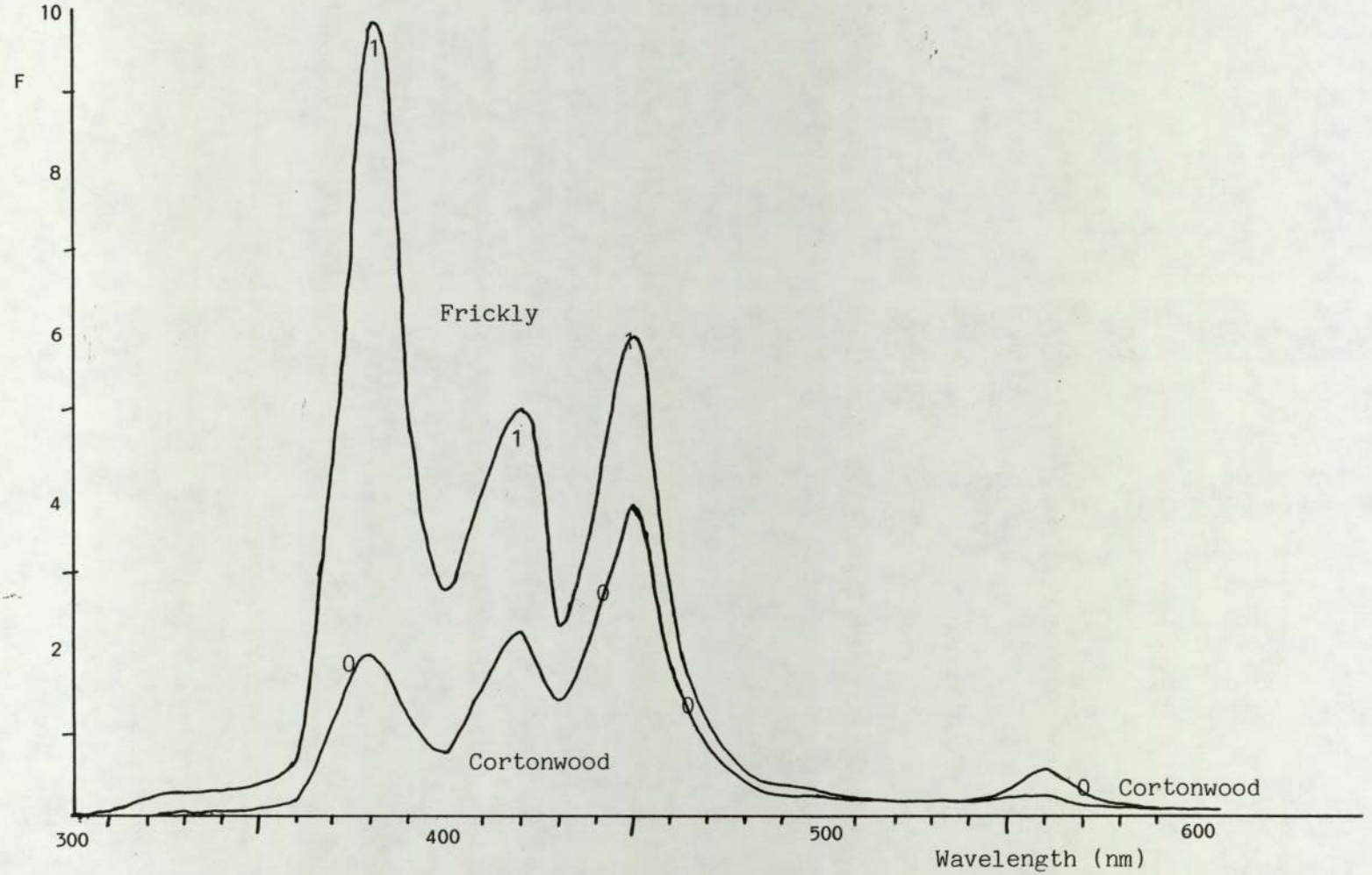


Figure 3.32. Comparison of the Synchronous Spectra of Frickly and Cortonwood Vitrinite. $\Delta\lambda$ 30 nm.

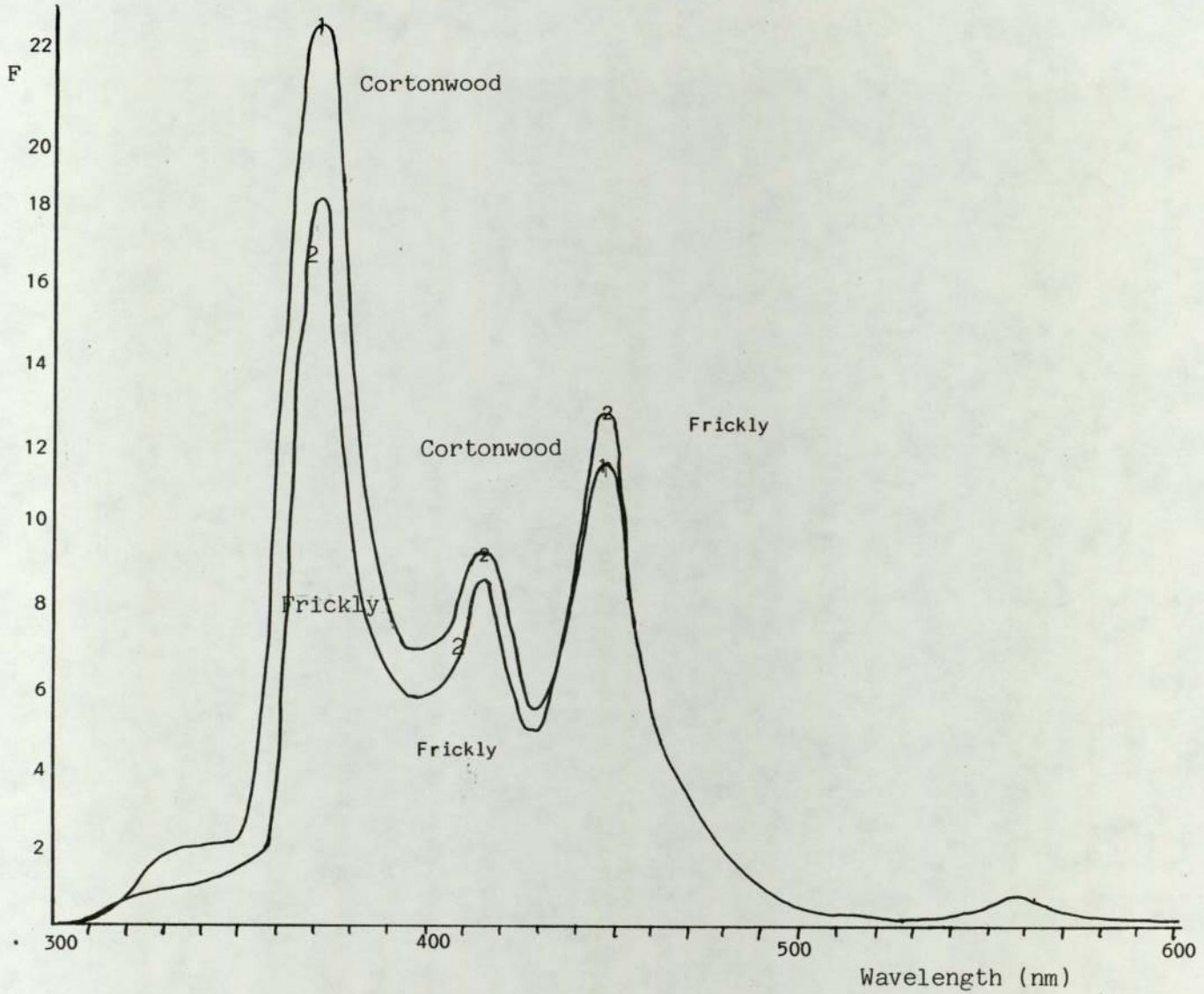
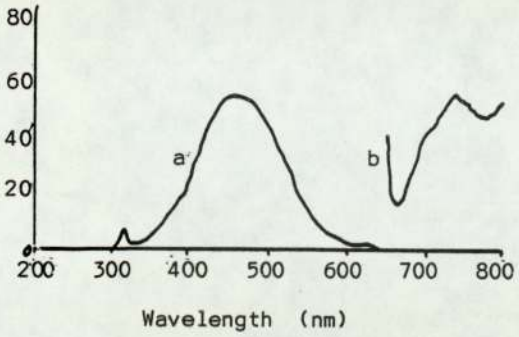


Figure 3.33. Comparison of the Synchronous Spectra of Cortonwood and Frickly Exinite. $\Delta\lambda 30_{nm}$

3.5 Conclusions

The fluorescence spectra of coal maceral groups from two coals, Frickley and Cortonwood, have been reported in this study. The results support the observations of a previous study of emission spectra by Friedel and Retcofsky[16]. This showed that whole coals generally have a peak of maximum emission fluorescence between 440 nm and 455 nm, which in the case of Cortonwood coal would correspond to a mixture of Cortonwood exinite with a higher proportion of the vitrinite. The similarity between the spectra in this study and the spectra reported by Friedel and Retcofsky can be seen in fig 3.34. These results are further supported by another study on humic acids obtained from coals, in which fluorescence at 450 nm were reported[17].

This study has in fact progressed several stages from the work by Friedel and Retcofsky. Firstly, this investigation includes the observation of excitation spectra from coal systems. These are therefore, the first direct observations of the absorption of light by the aromatic nuclei of coal extracts. In principle the relative proportions of di and polyaromatic species can be deduced. The pyridine obscures the presence of monoaromatics. Secondly, the whole coals, after being separated into their maceral group components, have been found to differ in the fluorescence spectra of the exinite and vitrinite maceral groups. Thirdly, the clear resolution emission, excitation and synchronous spectra all show some marked changes with concentration.



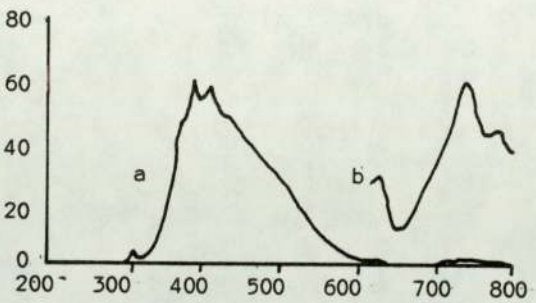
Emission Spectra of a pyridine extract of a coal (Pocahontas No.4)

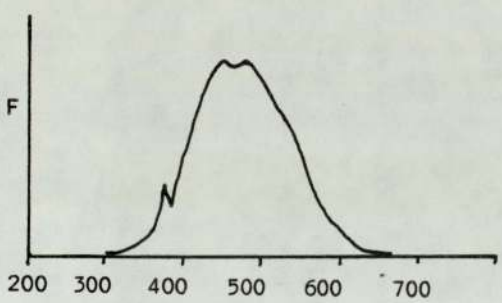
a) 1mm slit width scale 0.01
(b) 2mm slit width scale 0.003)

Emission Spectra of a pyridine extract of Adaville coal

a) -1 mm slit width, scale 0.001
(b) -2 mm slit width, scale 0.001)

Excitation set at 315 nm





Emission spectra of Cortonwood Exinite (high concentration) slit width 1mm,. Scale 0.3. Excitation 375 nm

Emission spectra of Cortonwood Vitrinite low concentration.

Slit width 1 mm, Scale 0.03
Excitation 325 nm

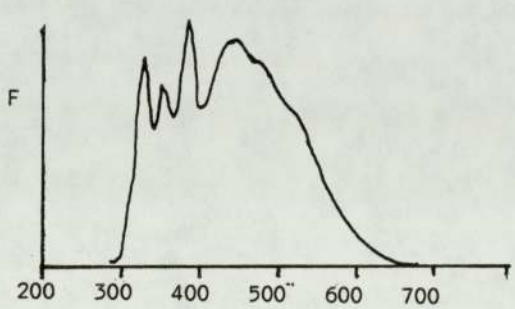
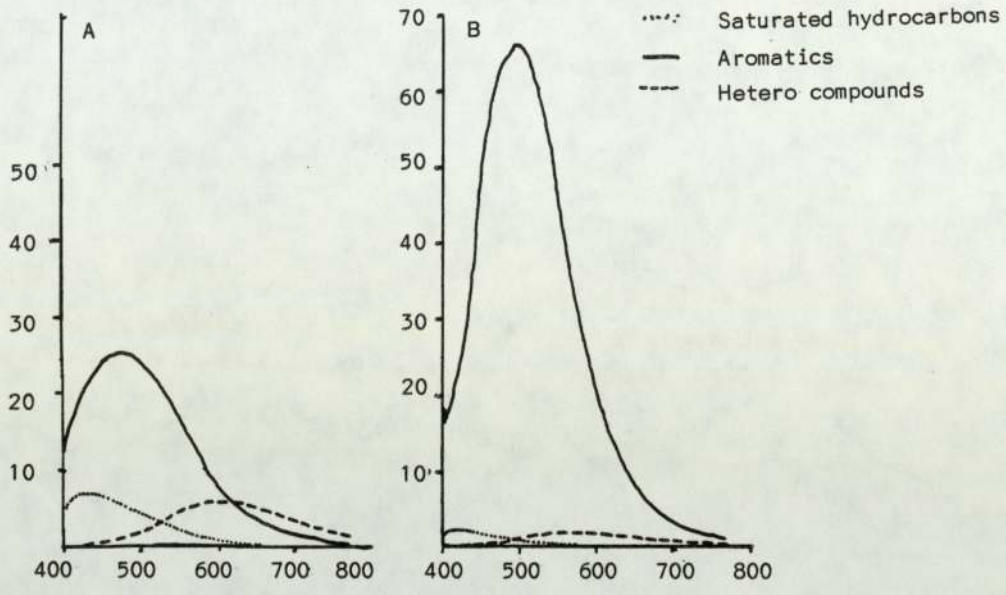


Figure 3.34 Comparison of emission spectra of this study with that of whole coals from a report by Friedel and Retofsky[12].



Fluorescence Spectra of different fractions of extracts from:-

A - a medium-volatile bituminous coal

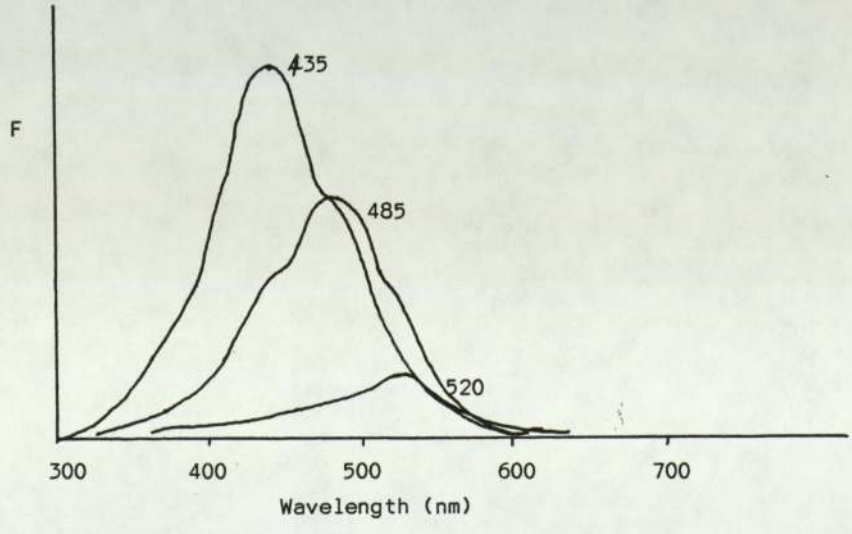
B - a high -volatile bituminous coal

Figure 3.35 The fluorescence of aromatic extracts of coals compared to saturated hydrocarbons and hetero compounds[19].

Overall, this study like others, supports the view that the majority of the fluorescence observed is caused by aromatic compounds. The extent to which aromatic extracts of coals fluoresce more strongly than other extracts can be seen in figure 3.35[19].

The results also show that coal macerals generally have a peak of maximum fluorescence at approximately 435 nm, with the exception of Cortonwood vitrinite, which has been seen to have a peak of maximum fluorescence at 485 nm. This could be due to the concentration range of the extracts of Cortonwood vitrinite 'stepping' over the concentration at which the vitrinite has a 435 nm 'peak' greater than the intensity of the 485 nm 'peak'. Alternatively, this could mean that the Cortonwood vitrinite was incapable of splitting down to a smaller, more fluorescent particle, which fluoresces at 435 nm.

The three fluorescent 'peaks' stated previously were found to be 435nm, 485nm and 520nm, ± 3nm as seen in the following simplified diagram of their relative intensities..



The exinite and vitrinite macerals of both coals investigated displayed the variation in wavelengths as shown in figure 3.20, with the exinite for both coals fluorescing more° strongly than their respective vitrinites, although for the Frickley macerals there was little difference in the maximum fluorescence intensity.

The shift to a longer wavelength emission with an increase in concentration is also seen in the excitation spectra (fig.3.21). The five peaks of spectral activity (absorption) are noted here along with their variation with concentration. The 'peaks' listed in order of intensity at maximum fluorescence are:-

375nm, 450nm, 555nm, 420nm, 590nm.

There was also a weak 'peak' at 325nm for dilute solutions (see fig.3.4). The peaks at 555nm and 590nm became more dominant at high concentrations when the 520 emission 'peak' was dominant and the general fluorescence intensity was weaker (fig.3.22). Most of the conclusions will be drawn from the emission spectra as they vary considerably and are characteristic of fluorescing aromatic systems. The small fluorescent peaks at 740nm in the near infra-red (figs 3.6 and 3.20), also reported by Friedel and Retcofsky[16], have been investigated in other studies in some detail using a repetitive scanning technique and are only mentioned briefly.[20]

The concentration curves, figures 3.11, 3.23 and 3.24 show that Beer's Law[21] is obeyed over the dilute concentrations leading up to a maximum fluorescence. This straight line increase is also true for those wavelengths concentration (see figure 3.11).

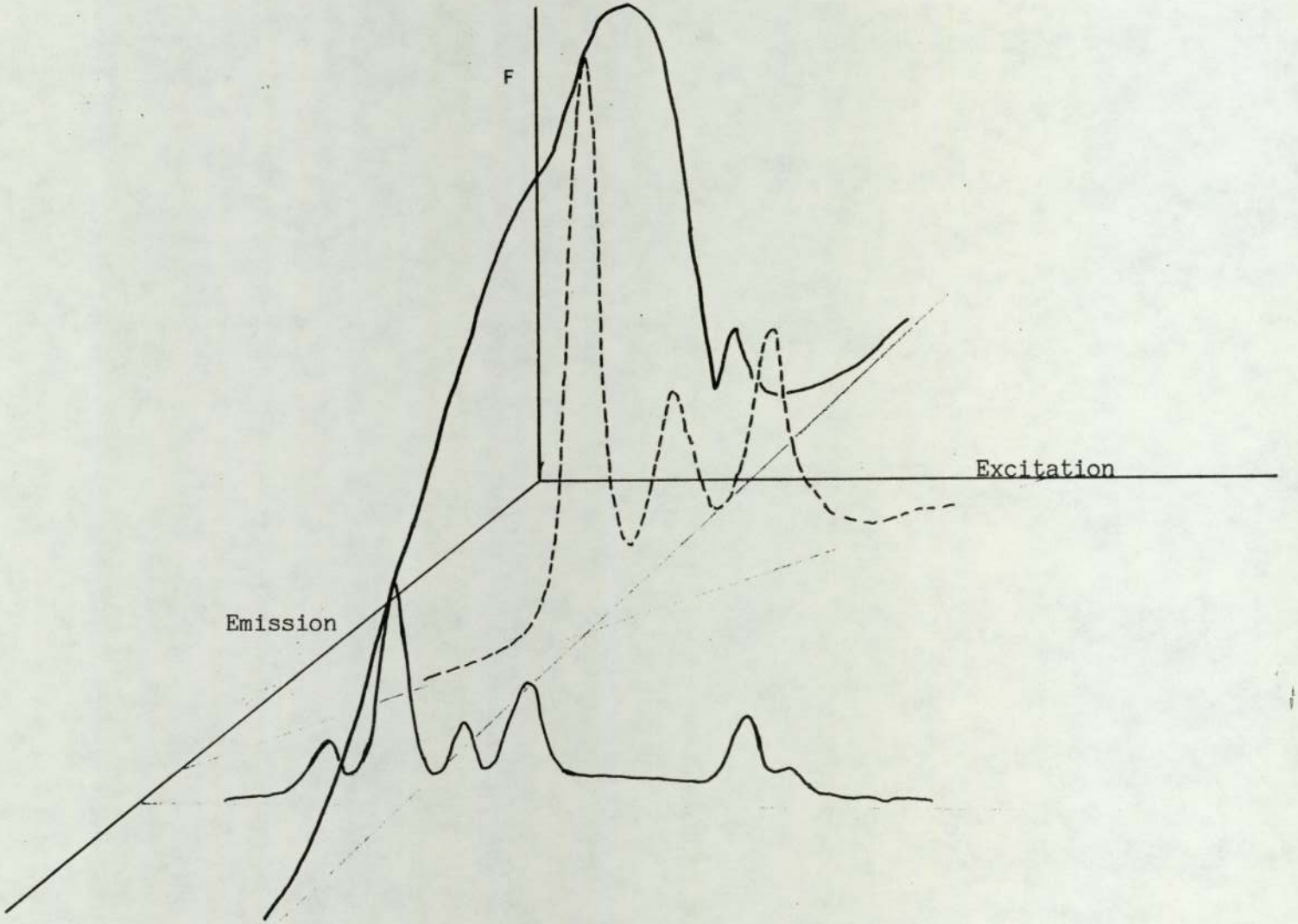


Figure 3.36 Graph showing how fluorescent spectra of coal maceral groups (or whole coals) could be used to "fingerprint" or characterise coals.

It is proposed that the fluorescent properties of coal macerals reported here, could be used to form a table of parameters from which coals could be categorised, along with the Q ratio; the red/green ratio[22] . Table 3.1 shows several possible fluorescent characteristics which might be found useful when studying other physical properties of coals. These characteristics could be particularly useful when studying the photochemical reactions of coals.

The synchronous spectra reported in the final section of this chapter show a simplified picture of the emission and excitation spectra. To explain the relevance of synchronous spectra figure 3.36 has been drawn, which shows the synchronous spectra as a diagonal slice through a fluorescent emission 'map'. Leading from these results later studies have shown that the "fingerprinting" of coals and coal macerals is possible (see fig. 3.37).[23] The use of synchronous spectra to analyse fuels has been reported in other studies[24,25] and has been found useful in analysing aromatic mixtures.

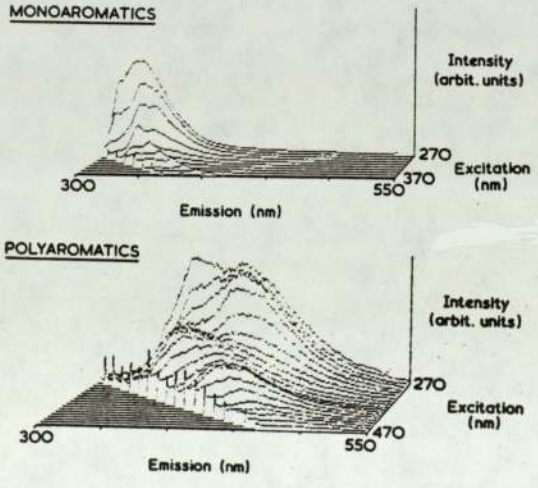


Figure 3.37 Fluorescence spectra of mono and polyaromatic fractions in chloroform.

Table 3.1

Table of Fluorescent characteristics of Coal Macerals which could be used to categorise coals

Characteristic		Coal Macerals: Cortonwood vitrinite	Cortonwood exinite	Cortonwood exinite II (high concn.)	Frickley vitrinite	Frickley exinite
Peak of maximum fluorescence (λ max) Intensity (nm)		485	435	435	435	435
concentration at which maximum fluorescence occurs ($\pm$0.005) grams per litre		0.041	0.0345	0.064	0.051	0.0333
Q ratio Intensity 650 nm / Intensity 500 nm = Q (red/green ratio)		$\frac{0.3}{8.3}$=0.036	$\frac{0.2}{18}$=0.011	$\frac{0.75}{50.5}$=0.015	$\frac{0.5}{28}$=0.018	$\frac{0.5}{23}$=0.022
Exinite/Vitrinite intensity ratio max.F vitrinite / max.F exinite		$\frac{8.5}{32.0}$ = 0.266			$\frac{45.0}{74.0}$ = 0.608	
$\frac{1}{2}$ intensity Bandwidth nm		420 → 450 (130)	390 → 515 (125)	390 → 512 (122)	395 → 517 (122)	400 → 518 (118)
Concentration characteristics (See Fig. 3.23)		concentration ranges				
Maximum fluorescence peak ranges (excitation 375 nm) (grams per litre)	435 nm X		0.046 → 0.023	0.08 → 0.0482	0.068 → 0.034	0.038 → 0.019
	485 nm Y			0.107 → 0.08	0.068 → 0.05	0.057 → 0.0285
	520 nm Z			0.134 0.08		
maximum fluorescence peak change over points (grams per litre) ($\pm$0.005)	435nm· 485 nm A			0.298	0.136	0.0713
	435 nm 520 nm B			0.434		
	485 nm 520 nm C			0.93 (c'0.496)		
relative fluorescent intensity 0 rank.		4	1	1	3	2
Concentration of original solutions grams per litre		0.082 (2.05 mg in 25 ml)	0.092 (2.3 mg in 25 ml)	1.24 (12.4 mg in 10 ml)	0.136 (3.4 mg in 25 ml)	0.152 (3.8 mg in 25 ml)

This study has shown how sensitive fluorescence is to alterations in concentration and how useful it can be in analysing quite complex systems. Also the long term stability of the coal maceral solutions in pyridine (ie no change in 5 months) has proved to be useful with no degradation over time thus allowing for a more comprehensive analysis.

3.5.1 Analysis of concentration effects.

This discussion concerns the observations, most clearly seen in figure 3.20. There are several possible explanations of how and why there are three peaks of maximum emission fluorescence at different concentrations.

A possible explanation of the emission spectra is that there are relatively simple interactions between the coal particles in the extract forming three different particles based on the original fluorescing aromatic unit.
Two possible combinations are:-

$$f_1 \longrightarrow 2f_1 \longrightarrow 3f_1$$

or

$$f_1 \longrightarrow 2f_1 \longrightarrow 2(2f_1)$$

435nm	485nm	520nm	corresponding fluorescent peak.

These 'bonds' effect the energy levels in the electron systems of the aromatic nuclei of f_1 thus reducing the wavelength of the emitted radiation.

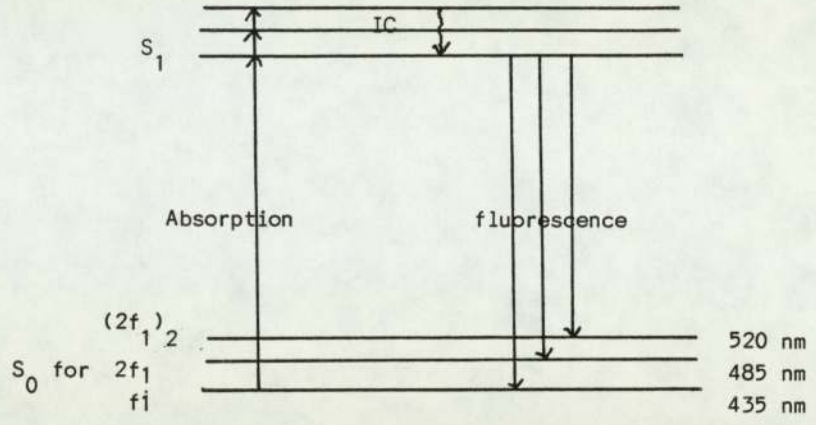


Figure 3.38 Possible explanation of fluorescence

If this was the case and f_1 was the building block of the fluorescing system, then the alternative energy levels would exist all the time and all three peaks would be seen at the same time. These peaks might vary in their levels depending on the equilibrium in the systems, nevertheless, all three would be observed simultaneously. Moreover, if this straightforward combination occurred, then all three peaks would be quenched as the system was affected. No one peak would remain while other peaks were quenched. So the concentration effects are observed, and each of the 'peak' fluorescent wavelengths can be clearly and distinctly seen. Also, there are considerable variations in the concentrations of extracts displaying these separate 'peaks'. Lastly, the significant reduction in the intensity of the peaks from 435nm to 485nm to 520nm points to the fluorescence not only from encumbant π electron systems but also from combined systems.

The fluorescence phenomena observed, although not due to a 'straightforward' chemical attraction between the coal particles, does involve weaker attraction forces and is effected by the solvent pyridine in some sort of 'combined' system. The involvement of pyridine in the fluorescence of the coal particles could explain why such a large percentage of the coal material is removed when extracted with pyridine (20% to 30%)[26]. These observations would suggest that the 'loosely held' more volatile coal material is more attracted to the pyridine than to the skeletal structure of coals (see figure 1.2)[27].

Perhaps one approach is to consider the coal particles to have a radius around them and when another particle encroaches into this three dimensional area, weak Van-der-Waals bonds are formed. This interference could be due to interactions between delocalised π electrons, thus increasing their stability and reducing mobility. Therefore, the energy released through fluorescence is decreased, which is observed by the fluorescence at longer wavelengths, also the possibilities for intersystem crossing increases which reduces the intensity of the longer wavelengths' fluorescence. (See figure 3.20).

The transition to the concentration at which there are more interacting particles than the original fluorescing particles is gradual. This is seen in the results where firstly a shoulder appears (Plot 1 fig.3.6), then the 485nm peak becomes more dominant (Plot 1, fig.3.14), and finally the 435nm peak disappears (Plot 1, fig 3.19). When the fluorescing particles display these properties the resultant combined particle is called an excimer. This phenomena has also been noted in other studies [28]. The principle combinations for this study are listed below.

Possible explanation of the 435nm peak:

$A^* \longrightarrow A^\circ + h\nu$ major fluorescing particle

Possible explanation of the 485nm peak:

$A^* + A \longrightarrow A_2^\circ + h\nu'$ eximer

$A^* + S \longrightarrow AS^* + h\nu''$ exeplex

$A + A \longrightarrow A_2$

$A_2 + h\nu \longrightarrow A_2^* \longrightarrow A_2^\circ + h\nu'''$

Possible explanation of the 520nm peak:

$A_2^* + \bar{A} \longrightarrow A_3^* + h\nu^{IV}$

$AS^* + AS \longrightarrow (AS)_2^* + h\nu^{V}$

$AS^* + A \longrightarrow SA_2^* + h\nu^{VI}$

$A^* + A \longrightarrow (A_2)_2^* + h\nu^{VII}$

$A_2 + A_2 + h\nu \longrightarrow (A_2)^* \longrightarrow (A_2)_2^\circ + h\nu^{VIII}$

* signifies an activated particle

° signifies a particle after emitting fluorescence in a deactivated state

The spectra suggest some sort of exeplex is formed as a transition state in a combined system reducing the intensity of the observed fluorescence of the 485_{nm} and 520nm peaks. The speed of formation of excimers may be increased from their activation by the lone pair of electrons present in pyridine acting on the phenolic groups present in these extracts. An aromatic and phenolic group content was detected in N.M.R. spectra of pyridine extracts of the identical separated coal maceral groups used in this study[29].

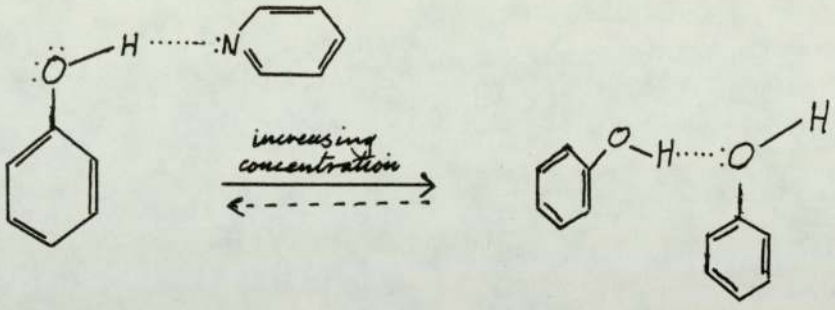


Figure 3.39 Formation of phenolic bridges in pyridine systems

The diagram above shows the possible bonds present in the exeplex with pyridine. This bonding between the phenol group and the nitrogen present in pyridine acts as a donator to the fluorescent coal particle thus assisting in the formation of a phenolic bridge between two separate coal particles (A) thus forming an excimer which fluoresces at 485nm.

These excimers, may, through a similar process also link together using other phenolic bridges. However, it is more likely that the $\pi - \pi$ interactions form links to create dimers. This additional bonding would further limit the π electron movement, thus almost quenching the observed peak at 520 nm.

It is also suggested that the pyridine, through its interactions, may enhance the fluorescence of these coal particles by stretching hydrogen bonds present in the structure thus allowing more π electron movement. This is most prevalent in the dilute solutions. There is the liklihood that in the high concentration extracts some of the emitted radiation from excited particles will be absorbed by other coal particles, thus again reducing the emission of the 520nm peak even further. From this discussion it follows that the solvent pyridine (S) interact with the mainly aromatic fluorescent coal particles. The following simplistic equations show how the three different peaks of maximum fluorescence at different concentrations may be explained through exeplex formation. (See below).

1. $AS + h\nu \longrightarrow AS^*$ Primary emission
2. $AS^* \longrightarrow AS^o + h\nu'$
3. $AS^* + AS \longrightarrow (AS)_2^*$
4. $(AS)_2^* \longrightarrow (AS)_2^\circ + h\nu''$ Secondary emission
5. $(AS)_2 + h\nu \longrightarrow (AS)_2^*$
6. $(AS)_2^* + (AS) \longrightarrow (AS)_3^\circ + h\nu'''$
7. $(AS)_2^* + (AS)_2 \longrightarrow (AS)_4^\circ + h\nu'^{v}$ Tertiary emission

emission at 435nm $\equiv \nu'$

emission at 485nm $\equiv \nu''$

emission at 520nm $\equiv \nu'''$

The emission at 520nm is most likely to be explained as $h\nu'^{iv}$ as the concentration of (AS) particles will be comparatively small to that of the $(AS)_2$ particles.

CHAPTER FOUR

4. ANALYSIS OF THE STRUCTURE AND REACTIVITY OF THE PYRIDINE EXTRACTS OF COAL MACERALS.

Further analysis of the nature of the coal macerals can be investigated along with a possible structure of the major fluorescing coal particle by observing the spectra of standard aromatic solutions in pyridine and other solvents. Also, by studying the reactivity of the original maceral extracts in a mild reaction more information may be gained about the fluorescence of coal macerals.

4.1 Comparison to other studies and analysis of standard aromatic hydrocarbons

Most of the results obtained are compared to spectra produced by Isadore B Berlman in the "Handbook of Fluorescence Spectra of Aromatic Molecules"[30]. This applies to all reported spectra, unless otherwise stated. These comparisons were made in order that the spectra obtained from coal macerals could be used in straight forward analysis. This meant that the analysis of the fluorescing components of these pyridine extracts of coal macerals could be attempted.

Thus it was necessary to directly compare spectra of standards with previously reported standards in the same solvent. (see figure 4.1). The spectra obtained are compatible with the spectra in the literature (figure 4.1). The resolution is higher for the literature spectra, as the slit widths used are approximately one fifth of the slit width used in this study. These spectra in cyclohexane (figure 4.2) are now compared with those in pyridine.

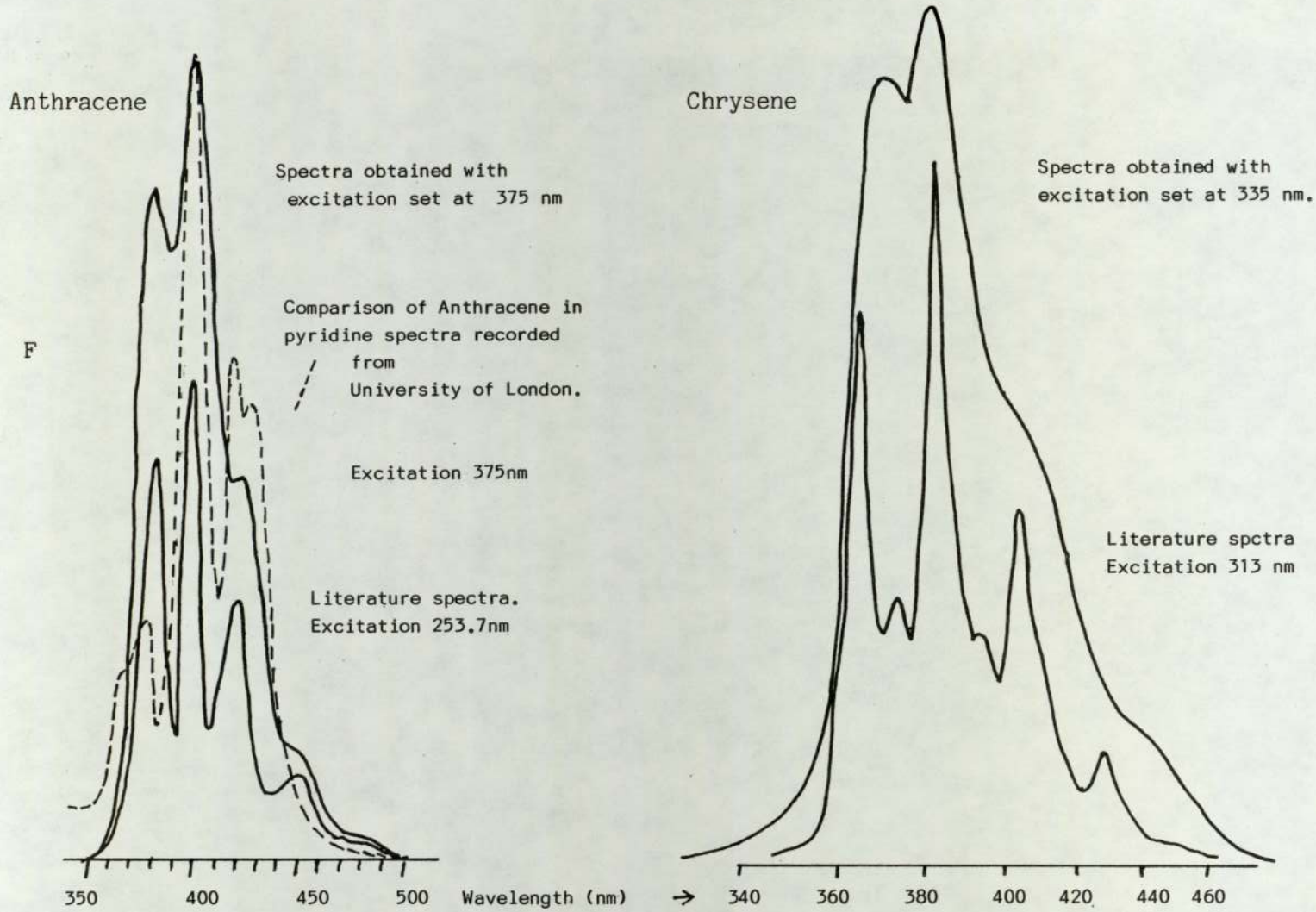


Figure 4.1 Comparison of literature and experimental emission spectra of standards in cyclohexane

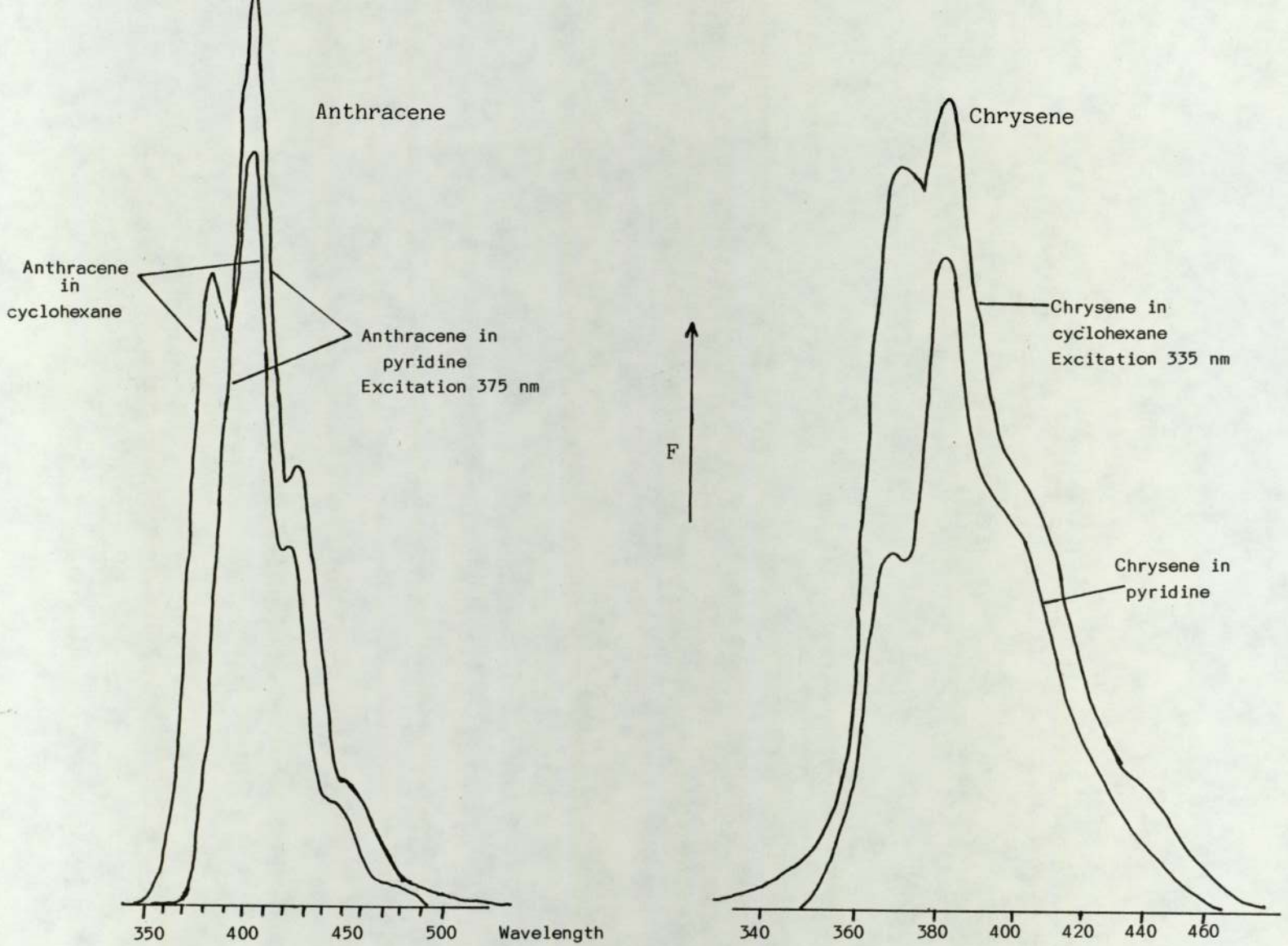


Figure 4.2 Comparison of standard spectra in cyclohexane and pyridine. Excitation set at 375 nm

From these spectra (figure 4.2.) it is seen that the spectra in cyclohexane are compatible with those in pyridine for anthracene and chrysene. The anthracene spectra was also confirmed in a fluorescence emission spectra of anthracene in pyridine received from Birkbeck College in London, (figure 4.1)

It is, therefore, possible to look at other compounds in cyclohexane to see which compounds might be present in coal causing fluorescence, which can be seen in the coal maceral spectra reported in this study.

Thus several spectra from the literature have been drawn, which could be causing the fluorescence of coal macerals (figure 4.3.).

As can be seen from these spectra none are identical to the spectra obtained from the coal maceral extracts. However, these spectra do exhibit one or more of the characterisitics of the coal maceral spectra. For example, 1.7 diphenyl naphthalene does have the right profile, with two shoulders, while 1 - naphthylamine and particularly 1,4,5,87 tetraphenyl naphthalene have their peak of maximum fluorescence at 430 nm and 435 nm respectively, which is in the same position as that of the coal macerals. Rubrene is included to show that some compounds do have their peak of maximum fluorescence at 520 nm or above, as in this case.

As seen later, (figure 4.8), this approach might provide indications to the reason and mechanisms behind the three different peaks of fluorescence, seen when the coal maceral fluorescence is quenched at high concentrations.

So far there has been no reference to the excitation spectra. The following diagram (figure 4.4.) shows three absorption spectra of standards, as compared to an approximation

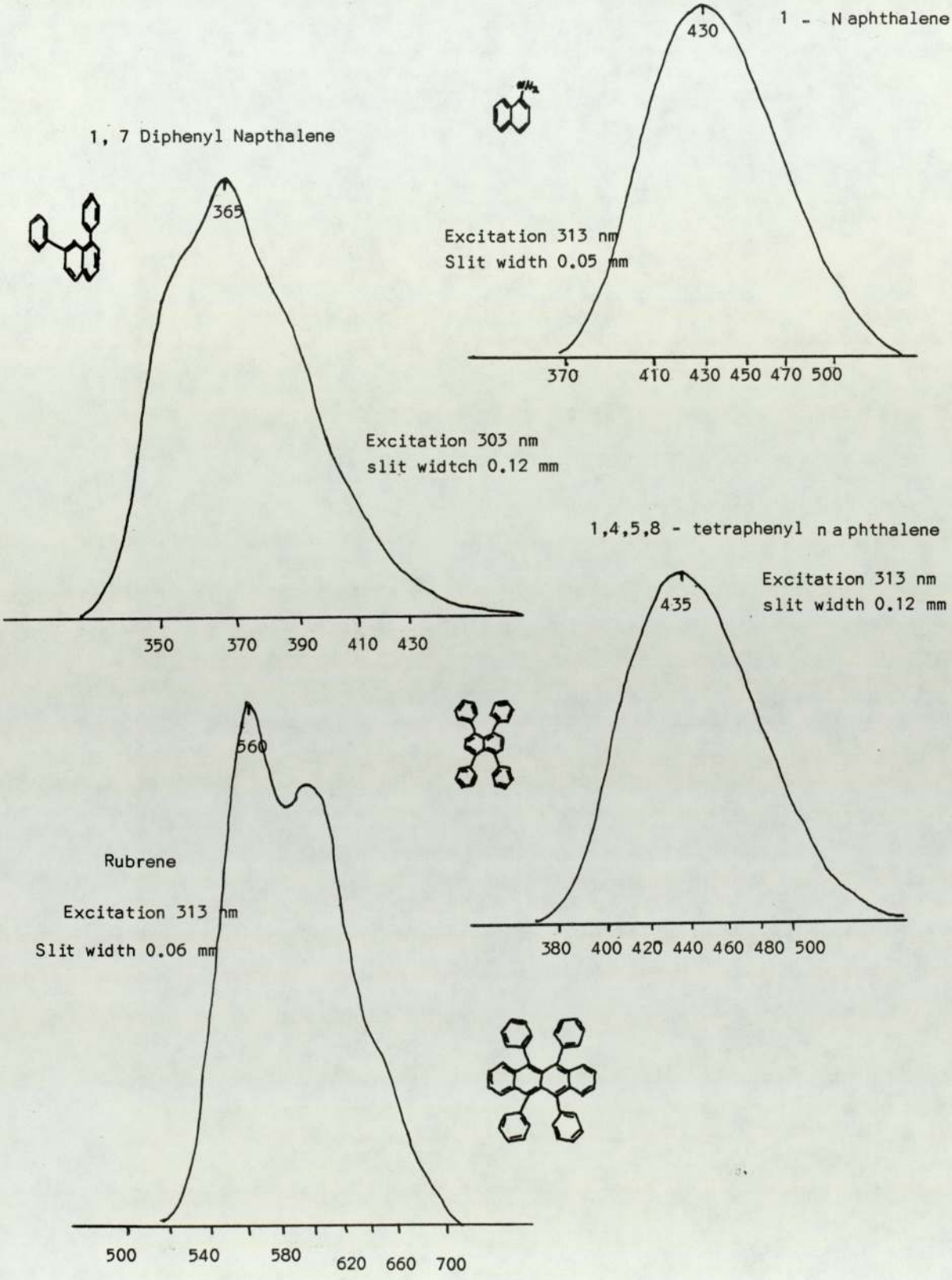
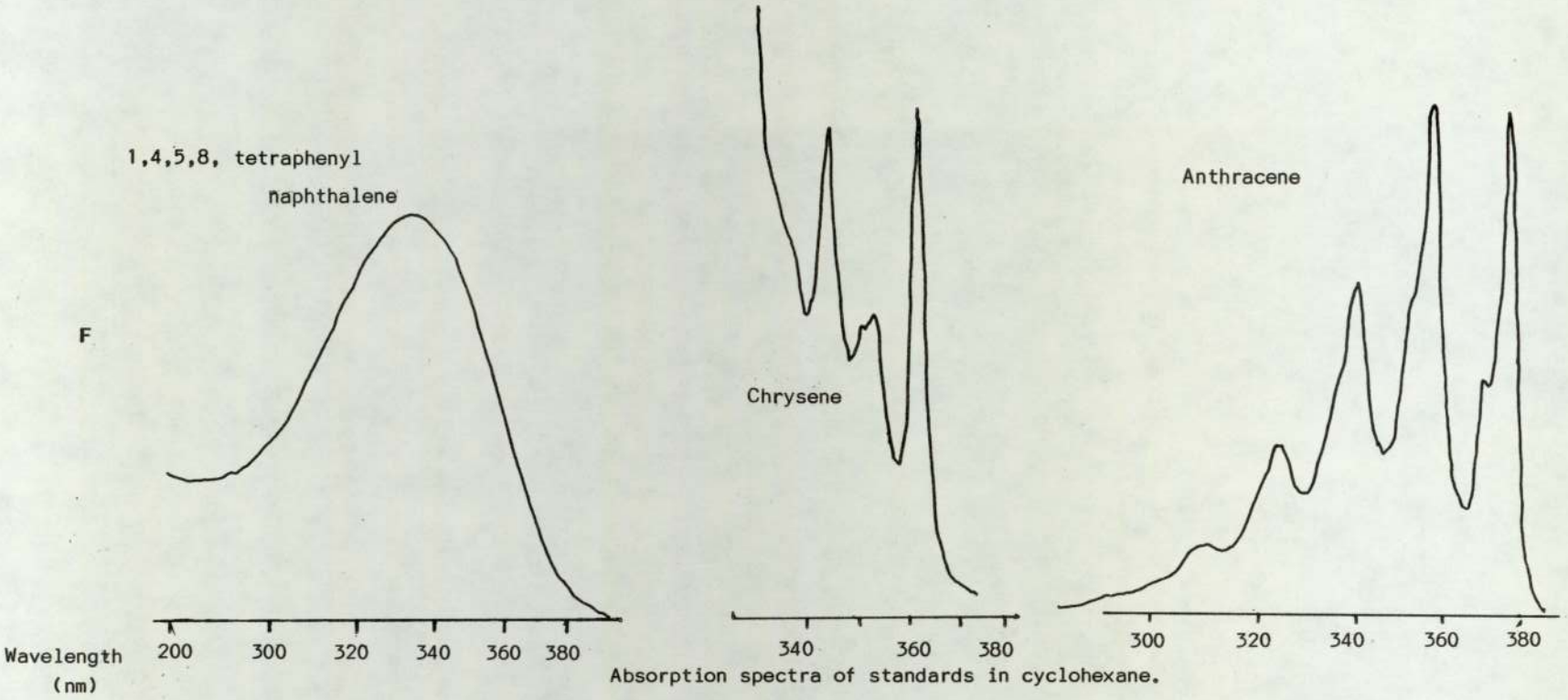


Figure 4.3 Emission spectra of aromatic molecules in cyclohexane.[30]



Absorption spectra of standards in cyclohexane.

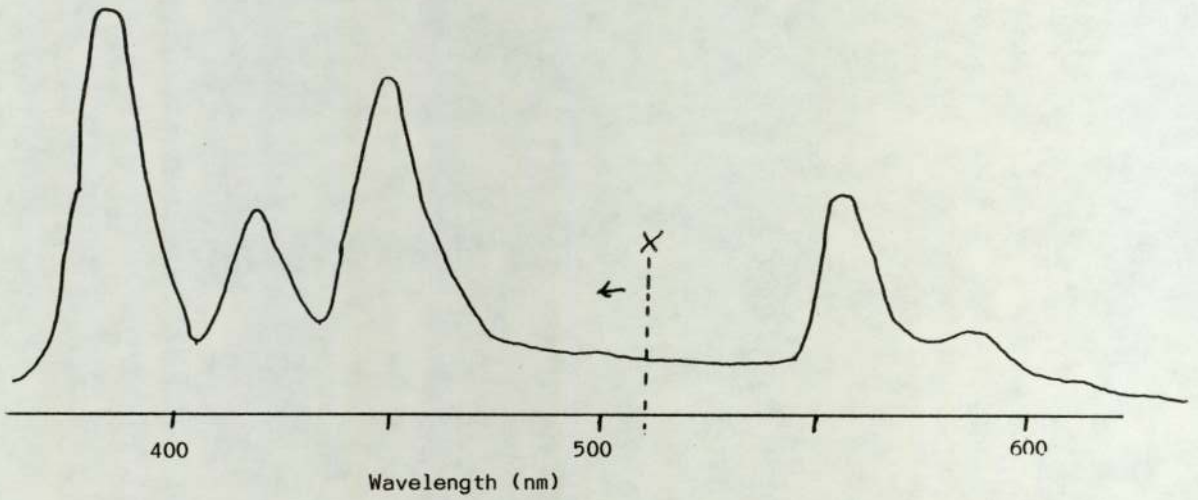


Figure 4.4 An approximation of the excitation spectra of a coal maceral Em. set 620 nm

of the excitation spectra of coal macerals.

As stated previously (page 104) the excitation spectra do not seem to be totally characteristic of the coal maceral solutions and further work needs to be carried out to ascertain the true nature of these spectra. Although as for the anthracene and Cortonwood vitrinite emission spectra several of the observations in this study are supported by spectra from Birkbeck College, University of London (figures 4.1, 4.7).

If the 555 nm and 590 nm peaks are ignored, and just the peaks at 375 nm, 420 nm and 450 nm are observed (see to the left of X, figure 4.4.) this suggests that these peaks could be the absorption characteristics of an anthracene of tetracene type compound, shifted to longer wavelengths. Statements such as this are difficult to prove catagorically because the exciatation spectra are an indirect measurement of the absorption spectra. Thus equipment errors may be included. Due to these problems the statements in the conclusion and discussion are mostly orientated towards the emission spectra.

The split in the excitation spectra was found in one of the standard spectra of 9,10 bis(phenyl-ethynyl) on page 370 in "Handbook of Fluorescence Spectra of Aromatic Compounds" [30]. The synchronous spectra of standards are shown in figure 4.5. and show how synchronous spectra are useful in the simplification of fluorescence spectra of aromatic compounds into one major, clean peak. This peak will have a characterisitic wavelength, thus making identification of certain aromatics in mixtures or organic materials possible[24, 25].

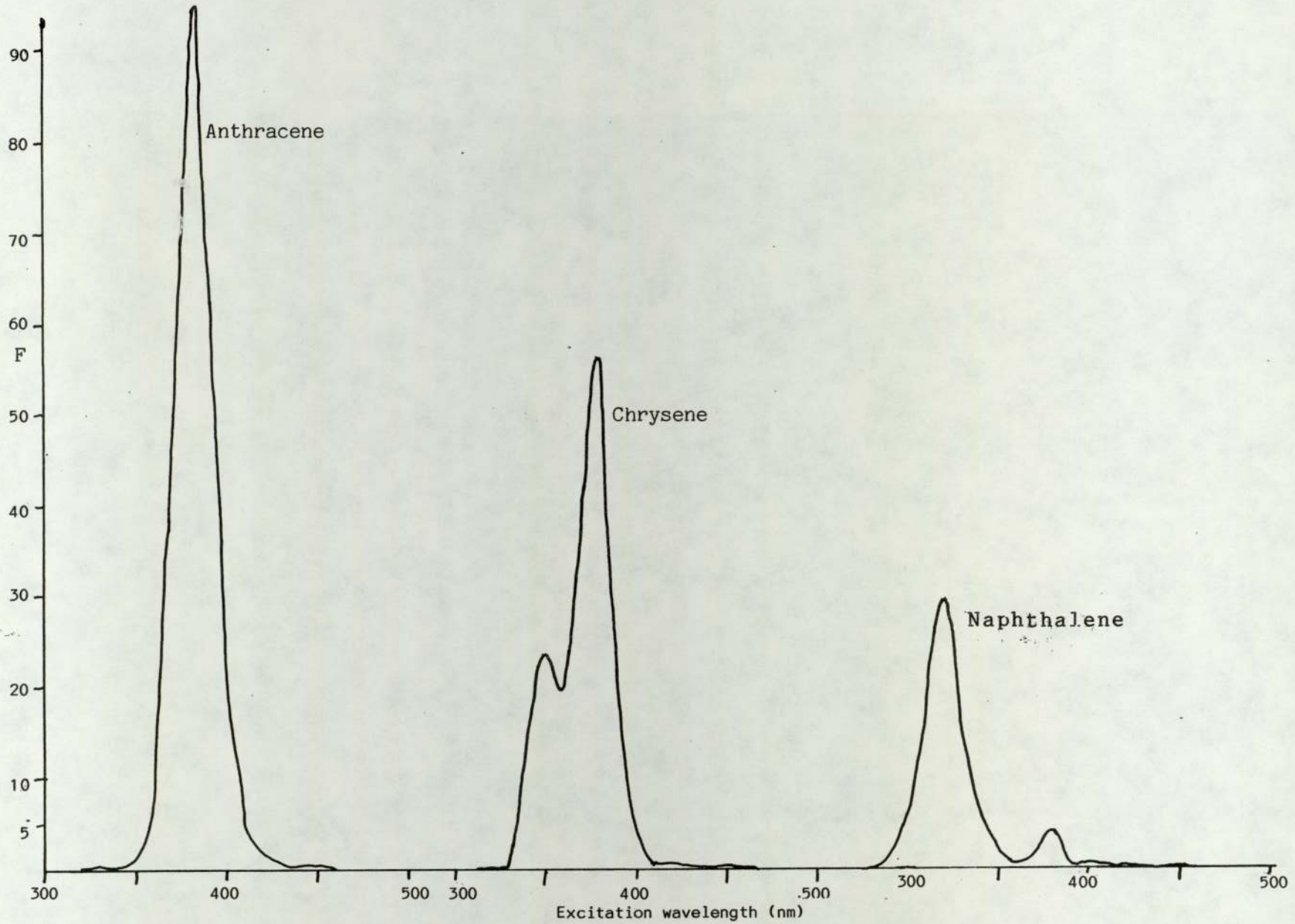


Figure 4.5 Synchronous Spectra of three 'standards' in Pyridine. Δ 30nm, Scale 1.0

The final results are now reported, which look at the effect of the cell, clear, dark and non-fluorescent solutions. Here internal reflections are eliminated in order that all the reported spectra can be studied.

The spectra in figure 4.6. show how the cell and cell housing conditions have no effect on the emission spectra which have been reported. Also, the effect of having no light passing through the cell was investigated by using a dark non-fluorescent solution, in this case coffee was used. As shown (figure 4.6.) there are three peaks in the spectra, all below the excitation wavelength and so can therefore be ignored. These peaks appear in the high concentration maceral spectra and some of the hypochlorite spectra.

The comparison in figure 4.7. shows that a typical spectrum from this study of a coal maceral is comparable to spectra obtained from Dr. A. F. Gaines at Birkbeck College in London. This figure shows that for Cortonwood vitrinite there is a good comparison between the spectra from two different spectro-fluorometers. The spectra in this study are more accurate due to the use of a narrower slit width and a slower scan.

The fluorescence spectra of pyridine was investigated and the cleaned substance was found to have a reduced level of background interference. For emission spectra, with excitation at 375 nm, there is no peak above the 375 nm peak, as for the water in figure 4.6., with a longer tail off back to zero level. So the effect of the impurities in pyridine on the emission spectra can be ignored.

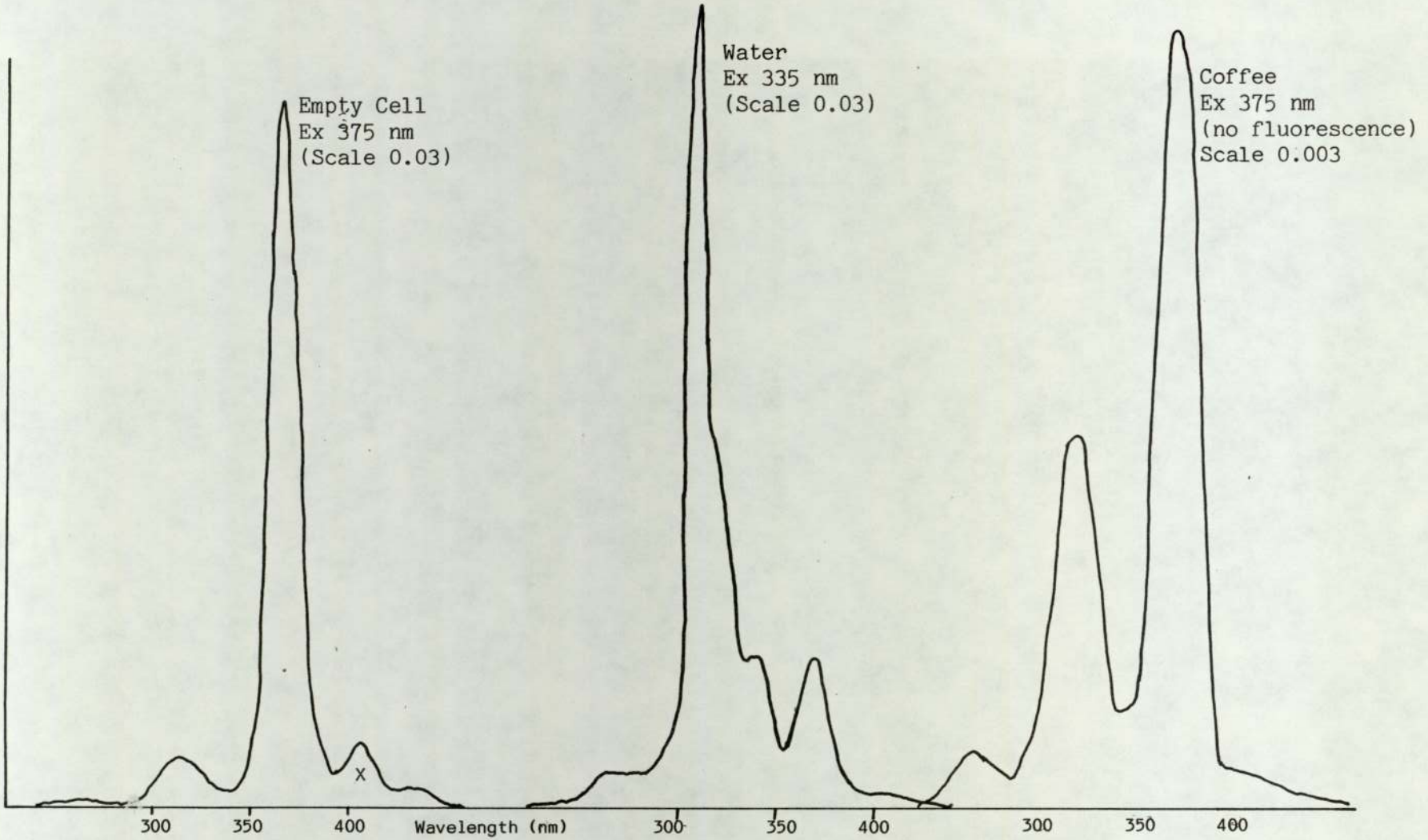


Figure 4.6 Emission Spectra of cell in basic non fluorescent conditions.

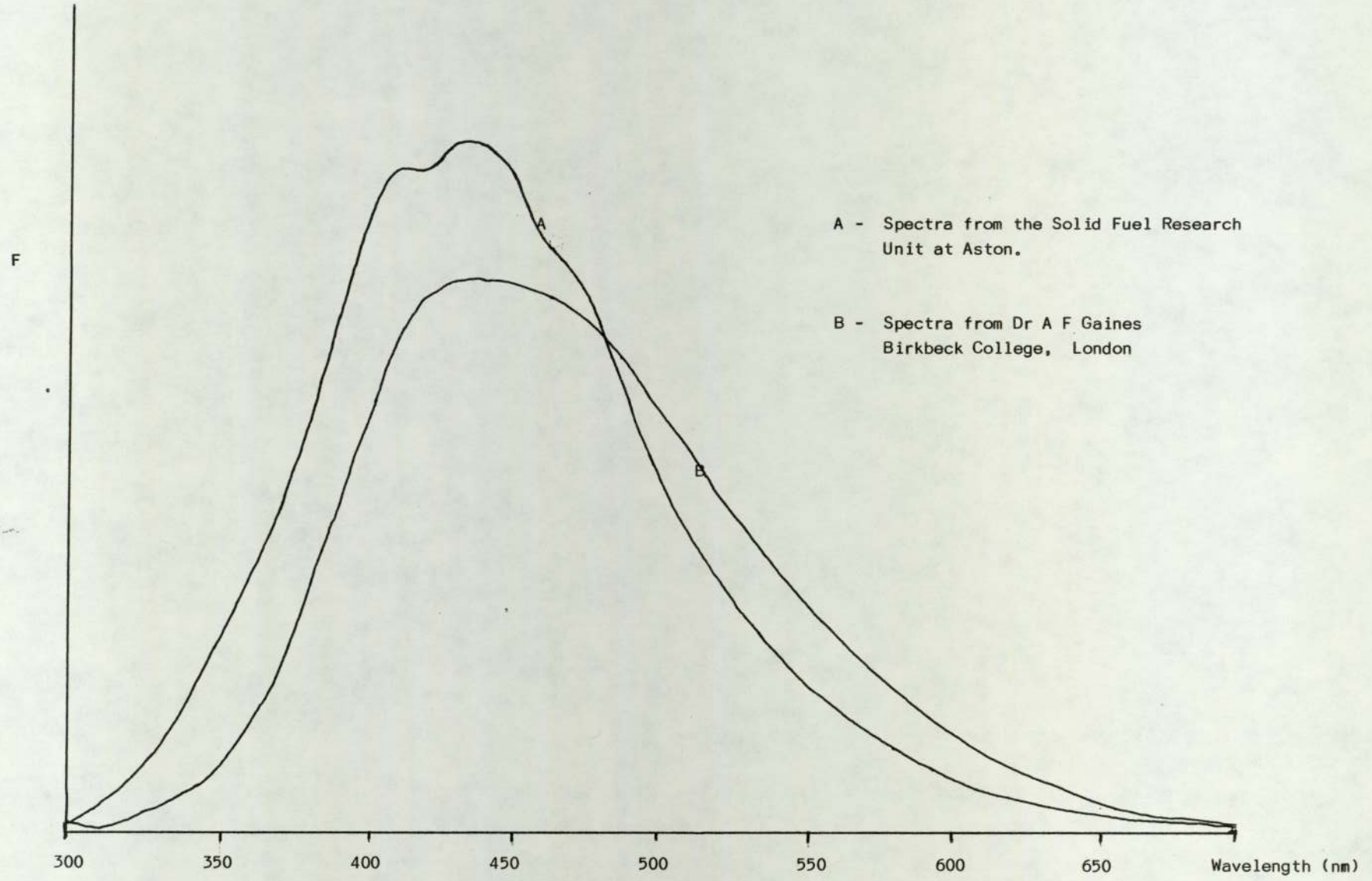


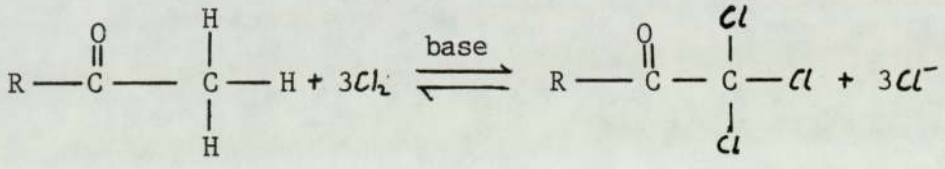
Figure 4.7 Comparison of spectra received from Birkbeck College and the spectra obtained in the study for Cortonwood vitrinite. Ex.335nm

From studying the standard spectra in figure 4.3., it can be seen that the primary fluorescing particle is most likely to be a tetraphenyl naphthalene. It is possible that there is the involvement of an attached nitrogen compound (NH_2). Also, from previous obsservations, and from the reported N.M.R.[29] spectra of these extracts, it is likely that there is a phenolic group to be considered. So by expanding figure 3.39 the possible structure of the primary, secondary and tertiary, particles are postulated in figure 4.8. It has to be noted that these structures are three dimensional so these approximate structures are not truly representative.

4.2. A study of the effect of sodium hypochlorite on the pyridine extracts of coal macerals

These results show the effect of mild oxidising conditions on the fluorescence of coal macerals in pyridine.

The oxidising reagent used is sodium hypochlorite in an alkali solution[8, 31], which has been used before when studying humic acids[17] . The oxidation reaction is as follows:-



Over several transition stages it produces carboxylic groups in equilibrium with carboxylate ions and Haloforms:-

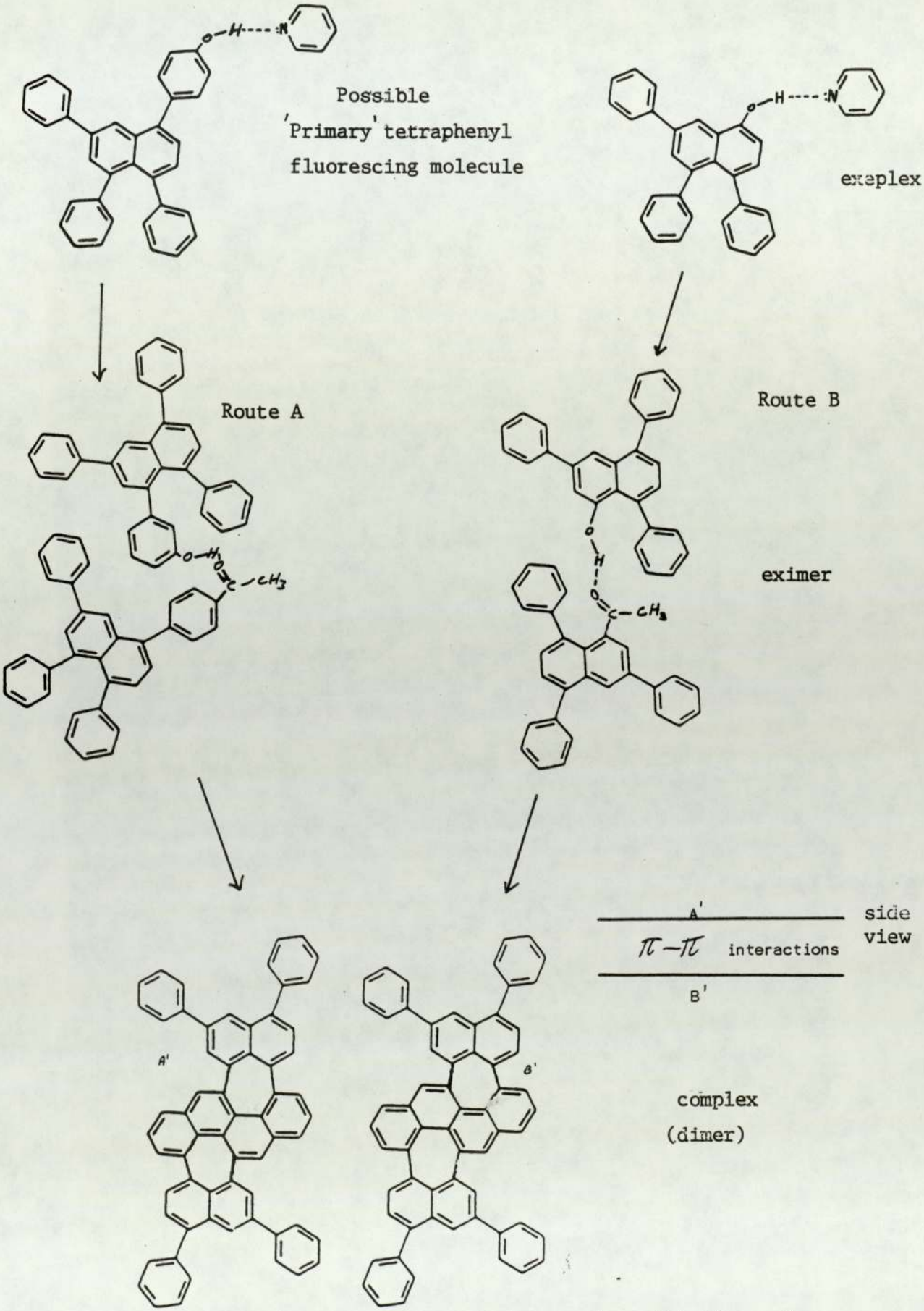


Figure 4.8 Postulated structures of the primary, secondary and tertiary coal particles causing fluorescent coal macerals.

carboxylate haloform

The sodium hypochlorite is formed as follows:-

$$Cl_2 + 2\ Na\ OH \rightleftharpoons Na\ O\ Cl + Na\ Cl$$

and oxidises any methyl groups present in the pyridine extract.

To investigate the oxidation of the extracted coal particles in pyridine four separate runs or sets of solutions were taken through the sodium hypochlorite oxidation procedure (page 42). For the first and fourth sets the oxidising conditions were more harsh than for the second and third runs. The solution of sodium hypochlorite mentioned is strongly alkali i.e. a 50/50 mix. For the second and third runs the solution was only just alkaline.The results of the first set of solutions are now reported in figures 4.9 - 4.14.

The resultant spectra were consistent once the original fluorescence had been quenched, with all the spectra showing a slight increase in fluorescence after one month. This also corresponds to colour changes occurring over this period.

However, the effects on the fluorescence within the first few hours varied in each case:-

1) The vitrinite emission spectra showed a marked increase in intensity and a peak shift from 485 nm to 435 nm (figure 4.8.).

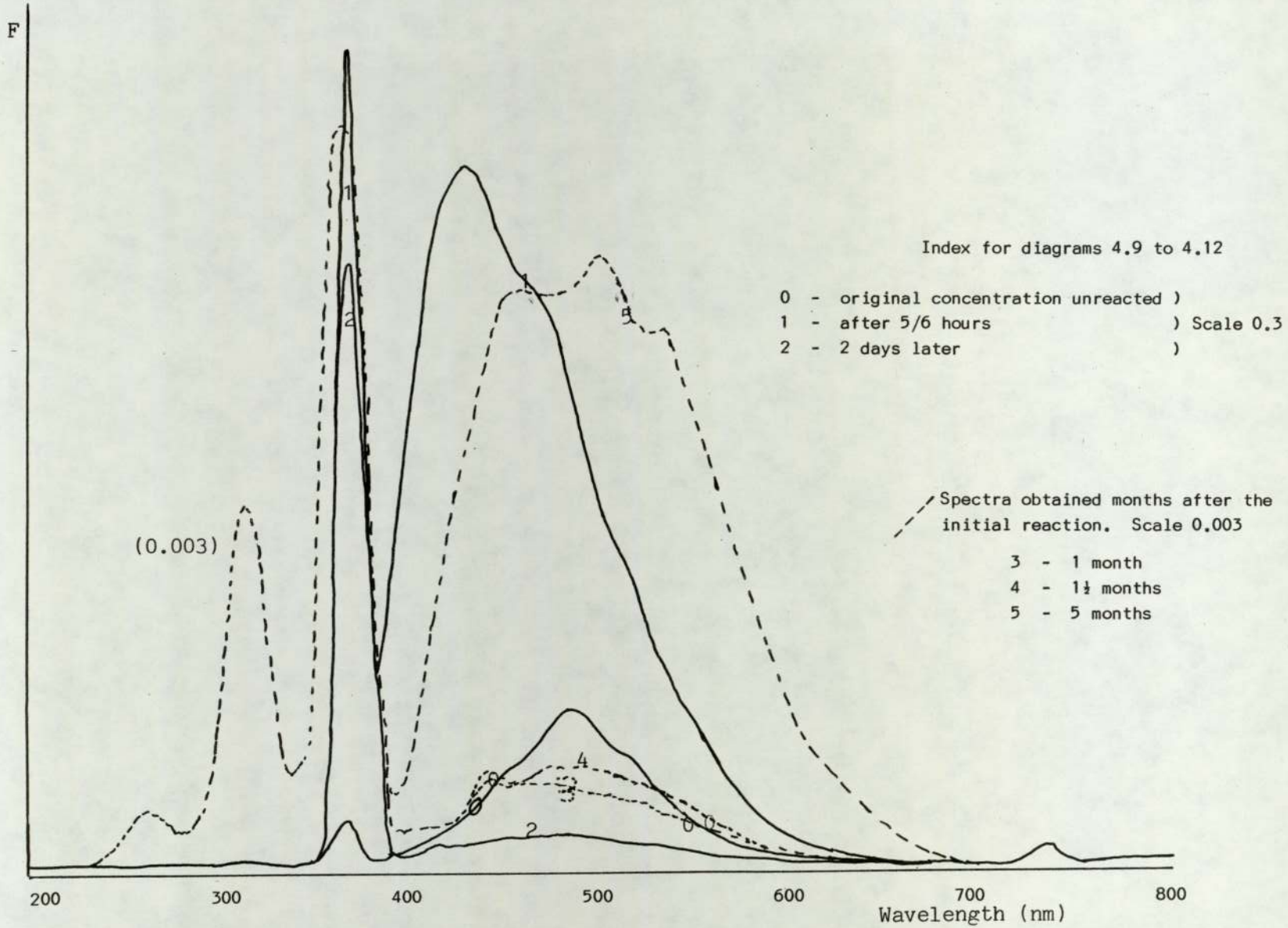


Figure 4.9 Cortonwood vitrinite + sodium hypochlorite. Excitation set 375 nm. Scale 0.3

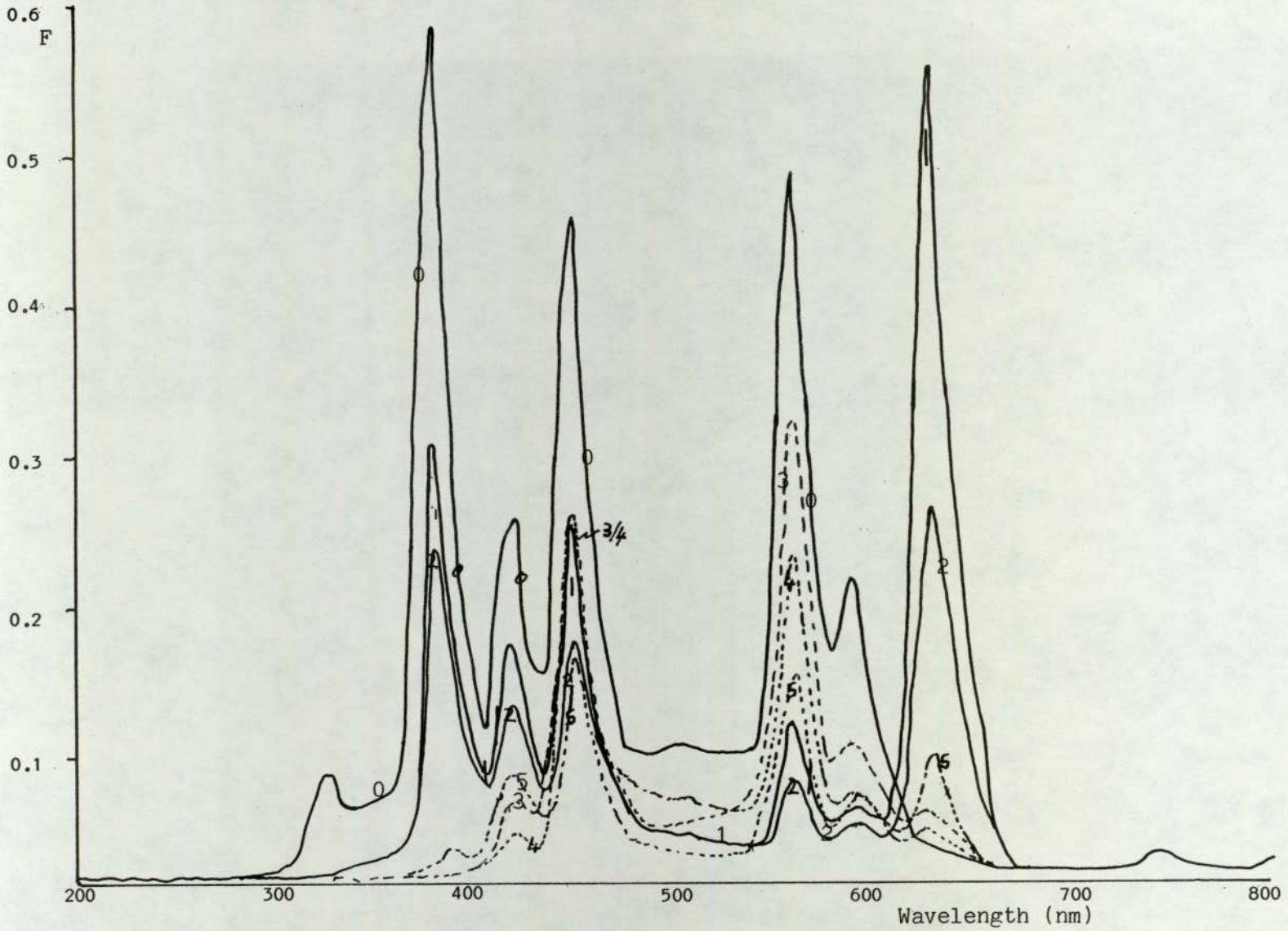


Figure 4.10 Cortonwood vitrinite + sodium hypochlorite. Emission 620 nm

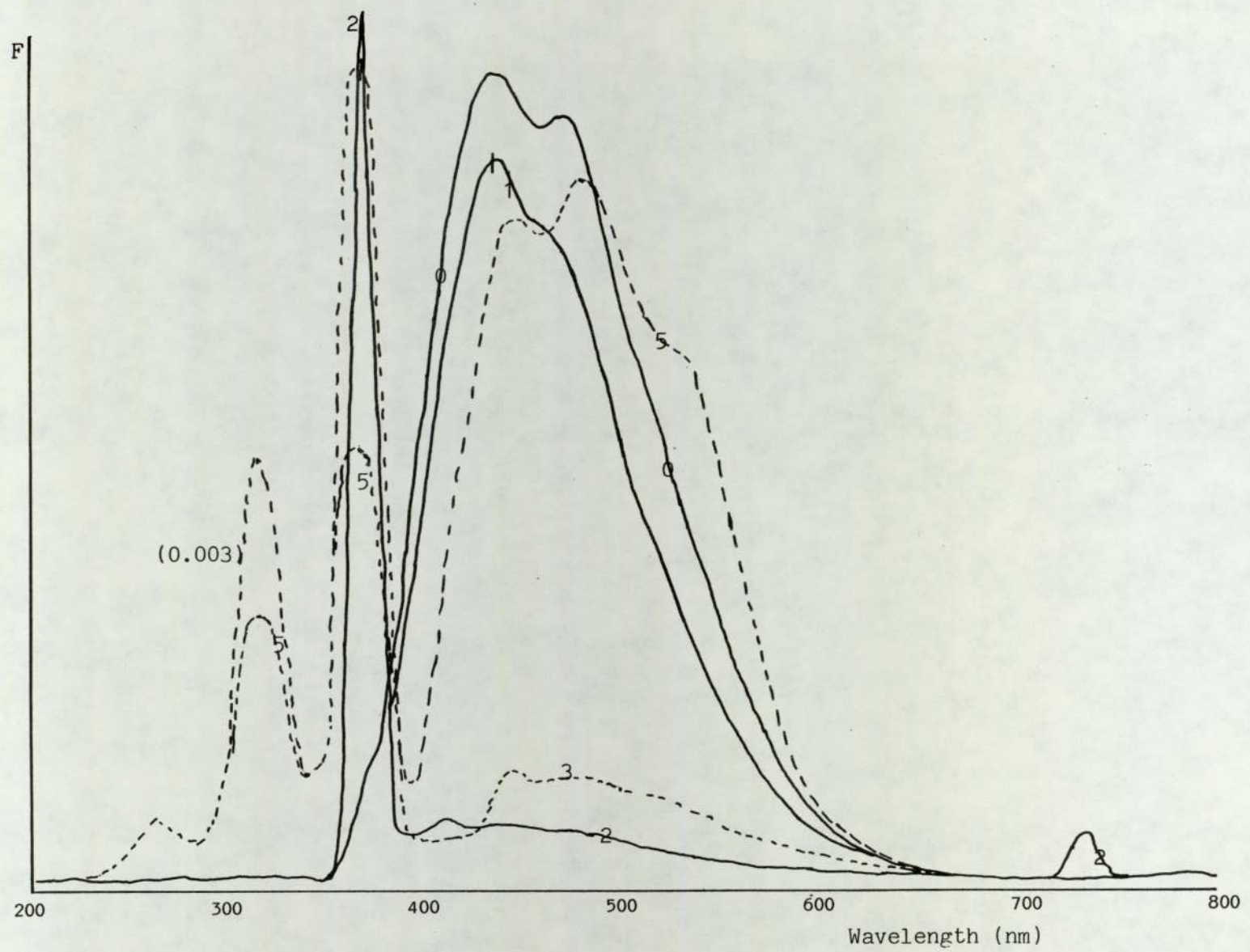


Figure 4.11 Cortonwood exinite + sodium hypochlorite. Excitation 375 nm. Scale 0.3

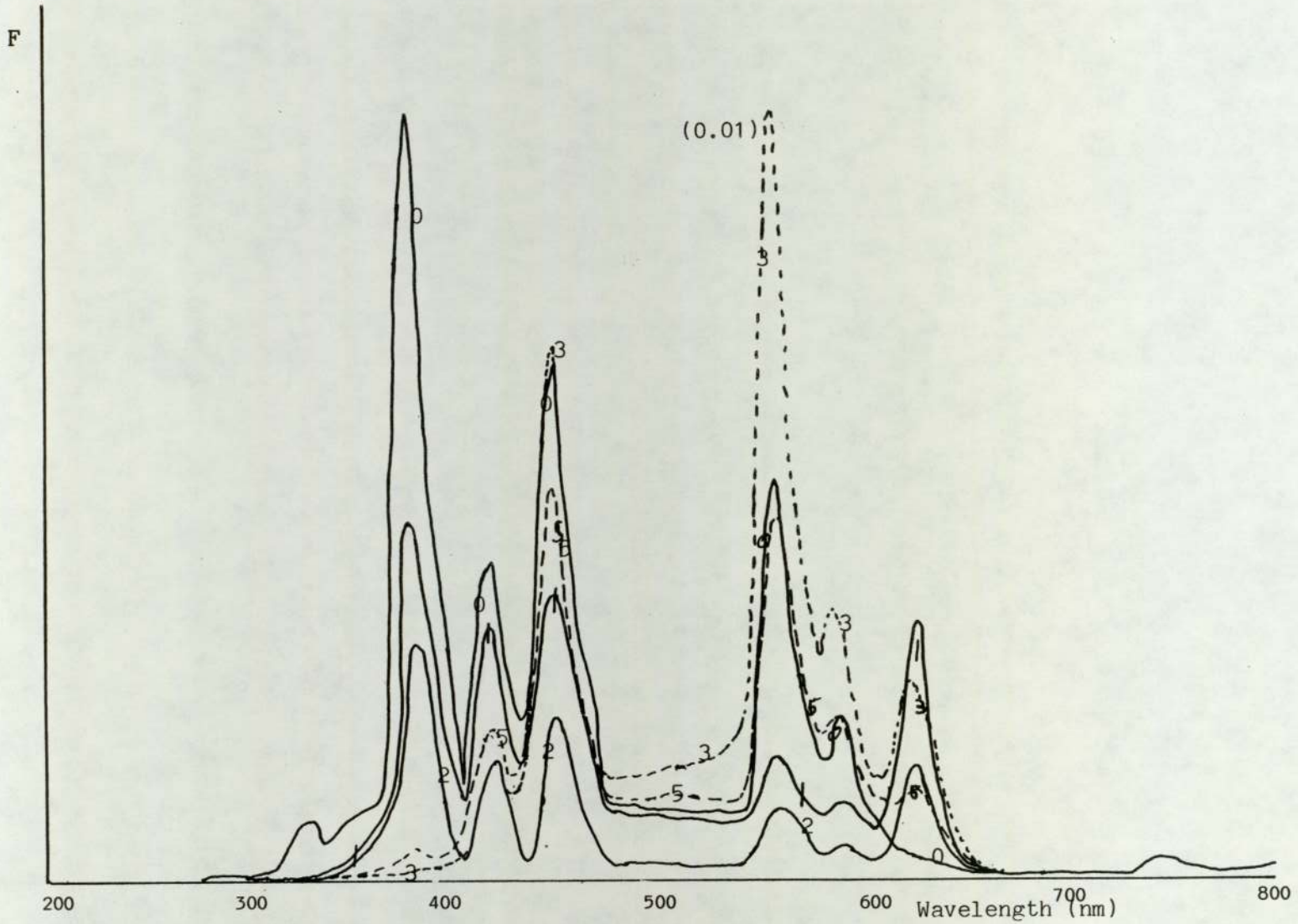


Figure 4.12 Cortonwood exinite ; sodium hypochlorite. Emission 620 nm. Scale 0.03

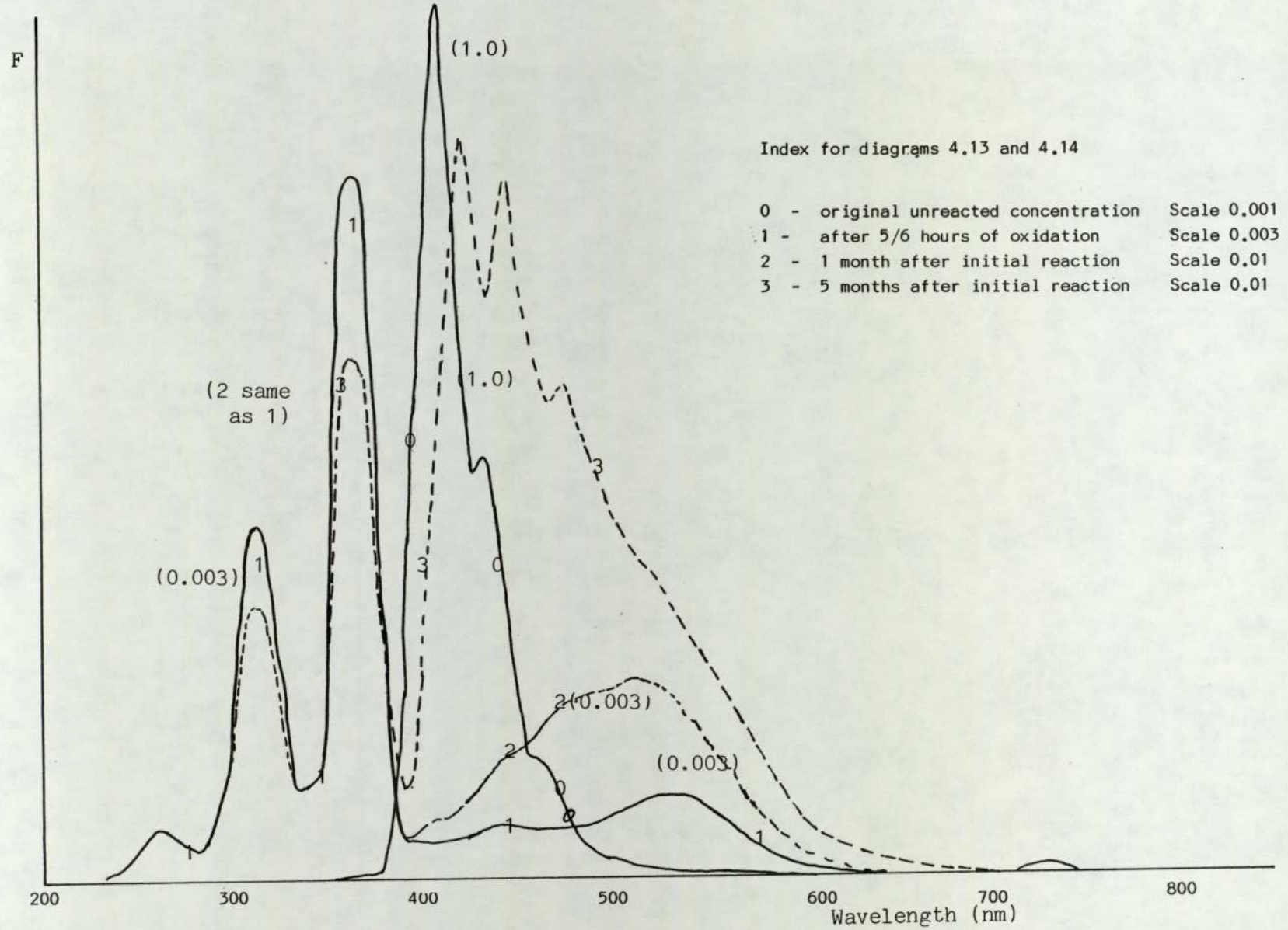


Figure 4.13 Anthracene with sodium hypochlorite. Excitation 375 nm.

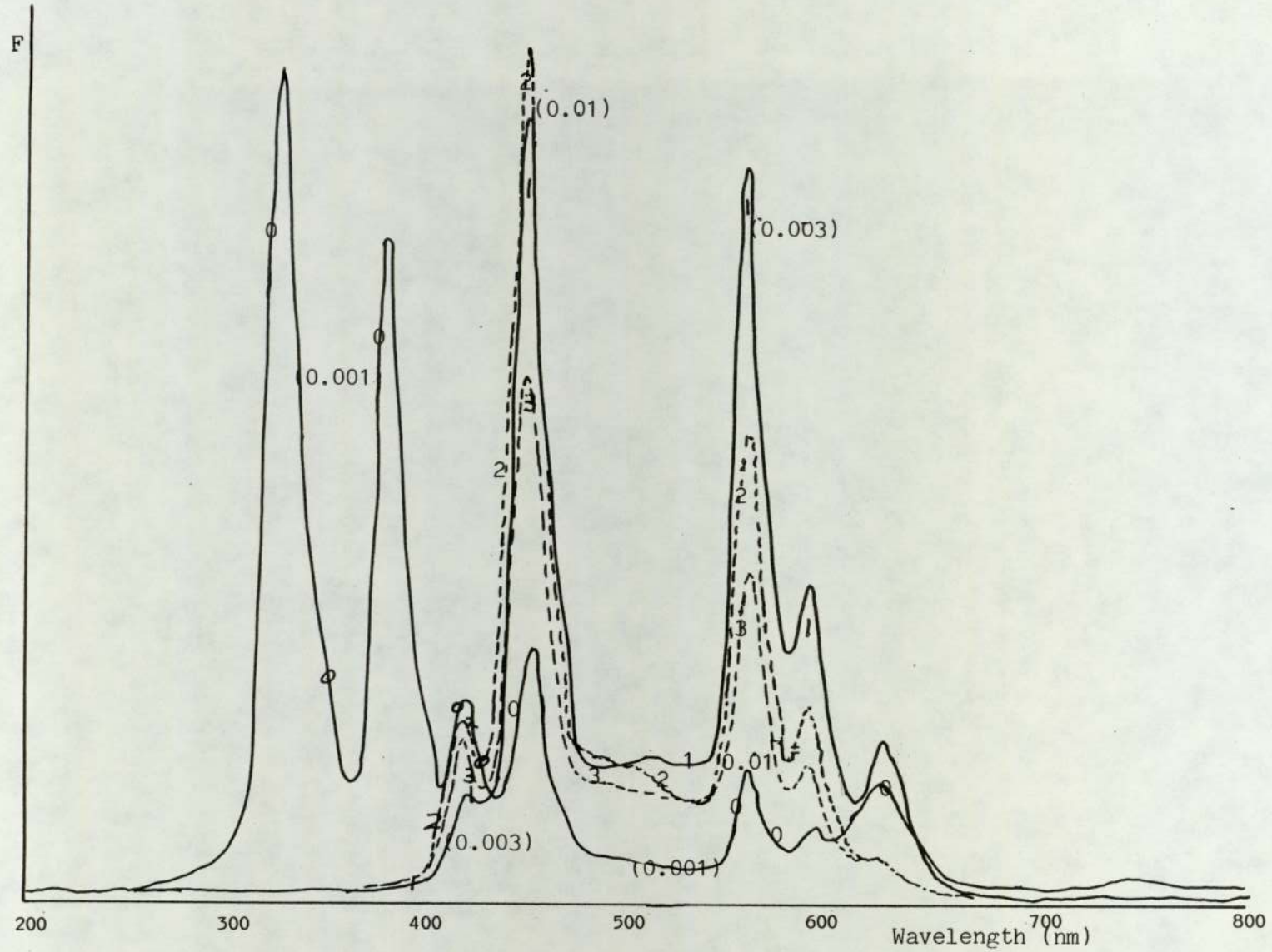


Figure 4.14 Anthracene + sodium hypochlorite. Emission 620 nm

2) The exinite showed little change in fluorescence intensity, but also displayed a shift towards the 435 nm peak (figure 4.11).

3) The anthracene was quenched almost totally within the first few hours (figure 4.13).

The excitation spectra (figures 4.10, 4.12., 4.14) all showed a general decrease in peak intensity, in particular the 375 nm peak was affected and eventually disappeared. Also, the emission peak at 620 nm could be seen to increase in comparison to the other peaks due to the solutions becoming cloudy. This increases the reflection from the source. For anthracene both the 325/330 nm and 375 nm peaks disappeared after the reaction.

To evaluate the consistency of these results, the exinite was rerun, this time running spectra ½ hour and 2½ hours after adding the sodium hypochlorite (see figure 4.5).

These spectra correspond more favourably with the vitrinite results, showing an increase in fluorescence intensity, as well as a peak shift to 435 nm. It could also be seen that three peaks in the excitation spectra, those at 375 nm, 420 nm and 450 nm, increased in relative intensity during the reaction (see excitation spectra on figure 4.15).

As stated previously, there were colour changes that correspond to alterations in the fluorescence spectra. These changes roughly followed the same route:-

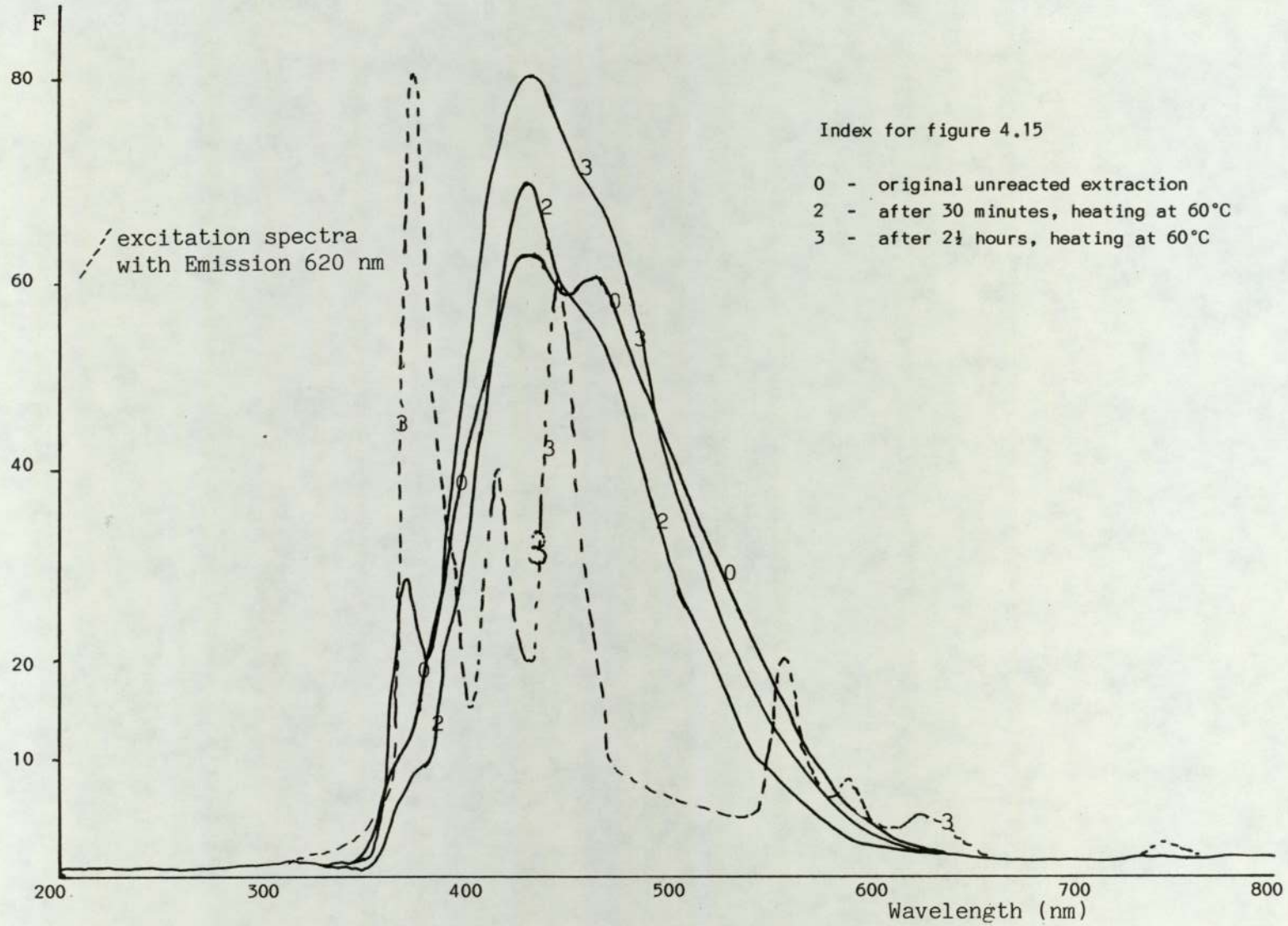


Figure 4.15 Cortonwood Exinite + sodium hypochlorite. Excitation 375 nm. Scale 0.3 (with heating).

1) A decrease in the brown colouring of the original maceral solution to a pale yellow. This occurred at varying times soon after adding the alkali hypochlorite and corresponded to maximum fluorescence intensity, at 435 nm.

2) Within a few hours red drops appeared on the vial caps, which seemed to signify a decrease in the fluorescence intensity.

Eventually, the pyridine solutions turned pink and then gradually changed to red from 12 hours to 3 days. Anthracene turned red far quicker than the maceral solutions, with the exinite changing slightly before the vitrinite.

In addition to these initial colour changes later changes also occurred. After the pink/red stage there is an orange stage and finally a dark yellow stage after which no further changes occurred. This final colour change was seen some 2 - 5 months after the initial reactions and in fact re-introduced some fluorescence, (figures 4.9 and 4.13).

One major problem is that this reaction is carried out in a two phase 'medium', where the aqueous sodium hypochlorite is under the coal maceral in pyridine solution. This two phase situation could explain the slow, sometimes gas rendering reaction and colour changes.

To follow the initial stages of this reaction, i.e. through the period that promotes fluorescence, two more sets of solutions were reacted in milder oxidizing conditions using less alkaline sodium hypochlorite. These runs used Frickley macerals and a chrysene solution (figures 4.16 -4.18).

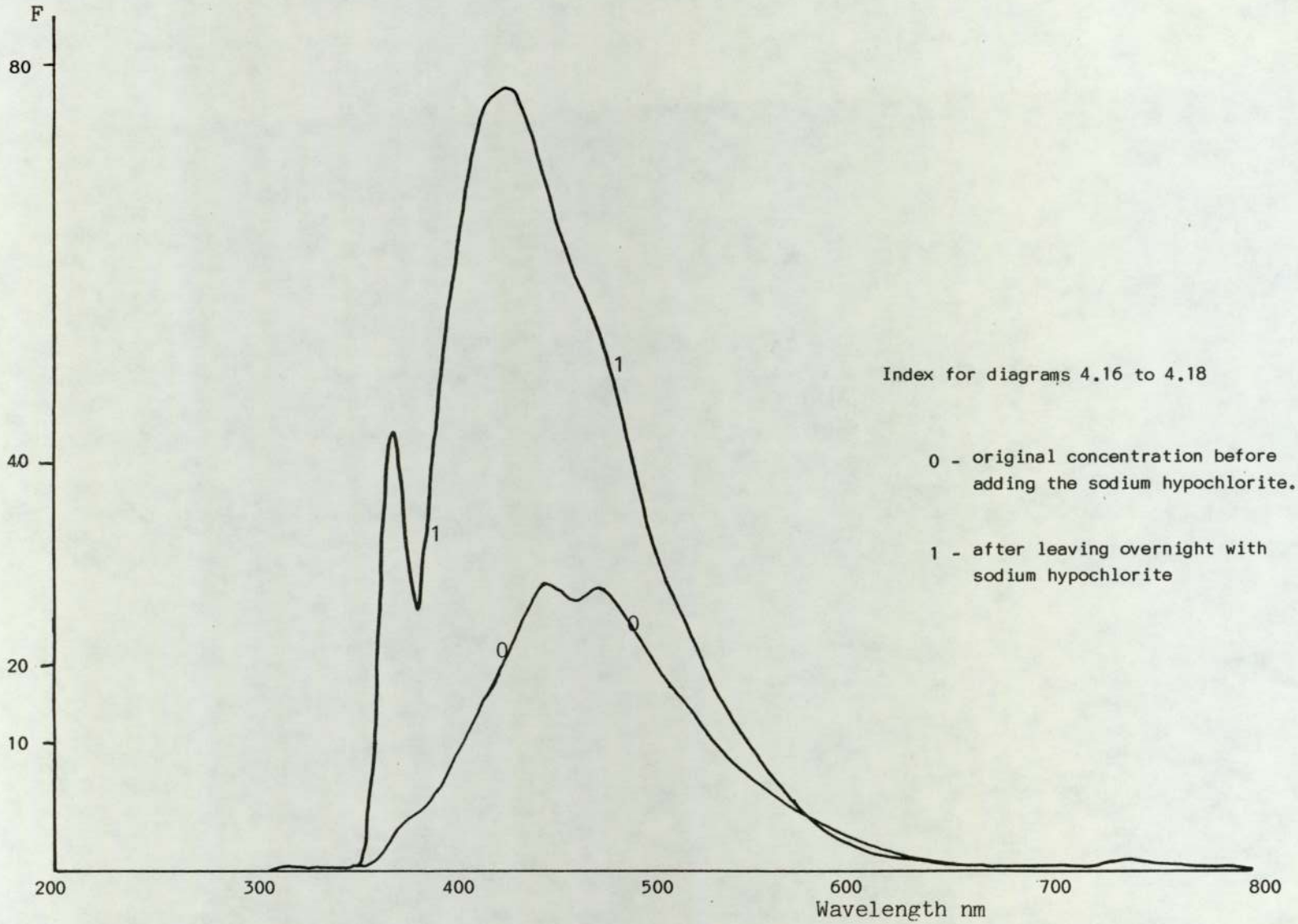


Figure 4.16 Frickley vitrinite with sodium hypochlorite. Excitation 375 nm. Scale 0.3

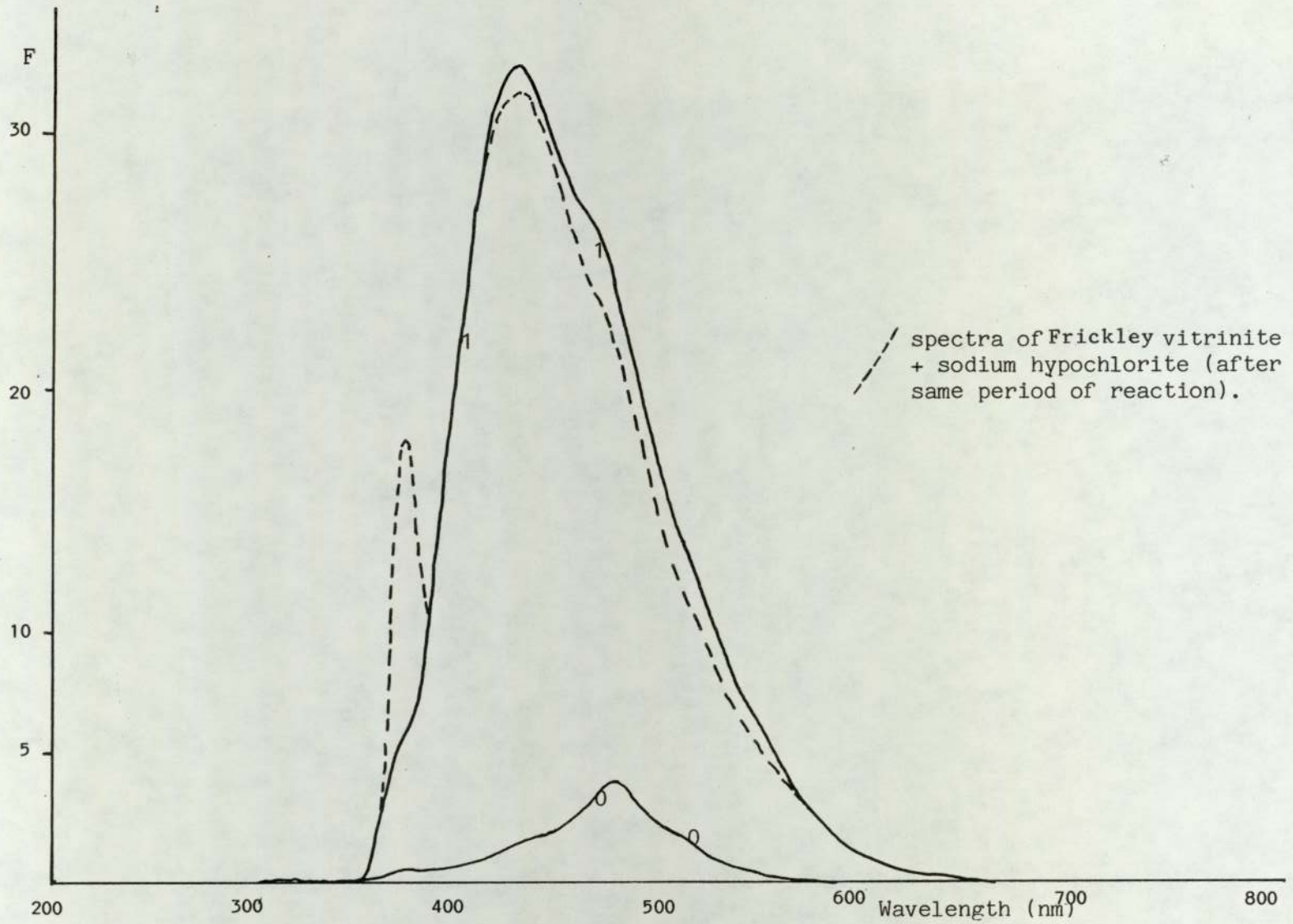


Figure 4.17 Frickley exinite with sodium hypochlorite. Excitation 375 nm. Scale 1.0

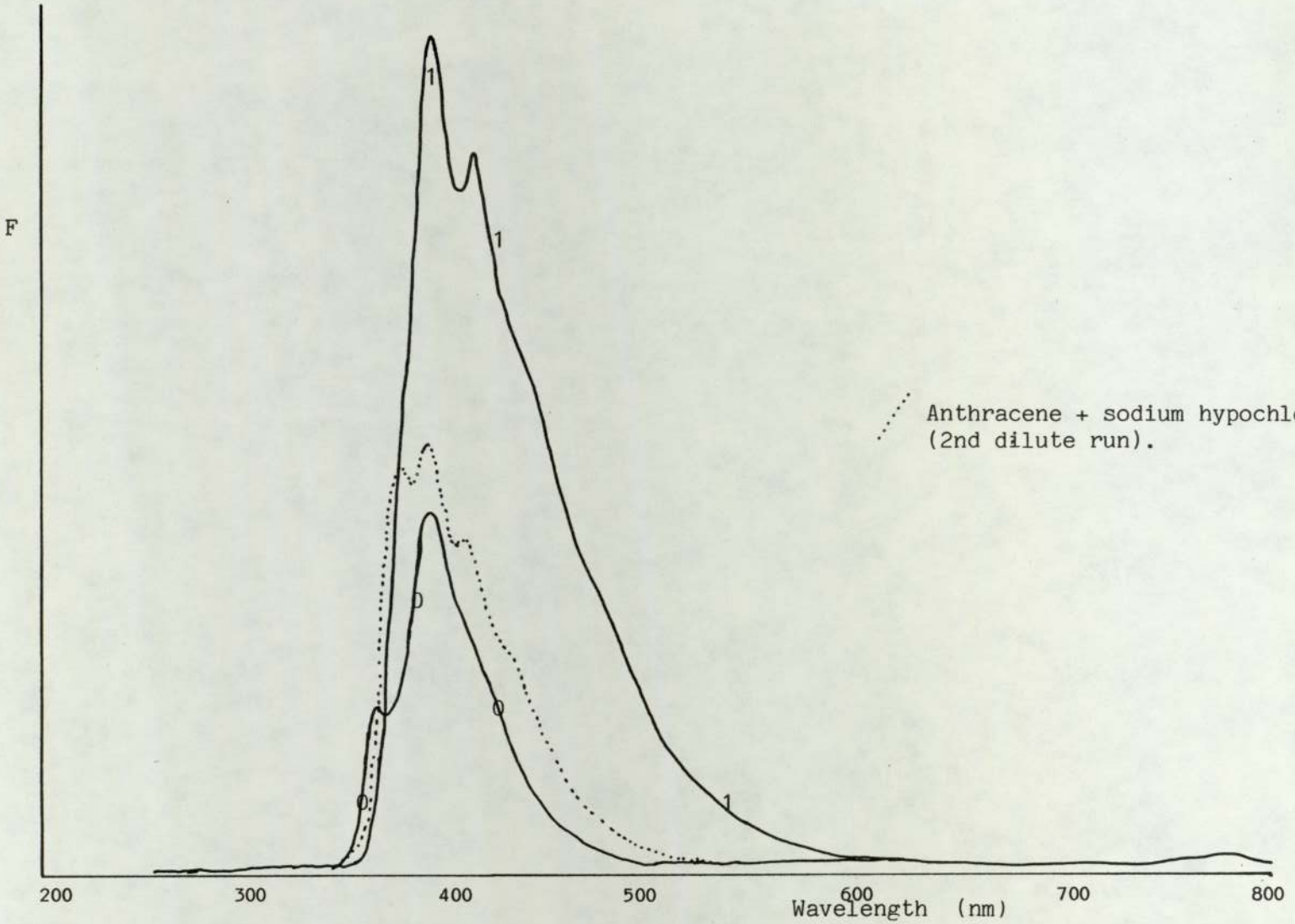


Figure 4.18 Chrysene in Pyridine + Sodium hypochlorite.
Excitation 375 nm. Scale 1.0

Both sets of solutions gave identical results, with the emission spectra of the first set being reported here (figures 4.16-4.18). As can be seen, the increase in fluorescence intensity is quite considerable in all cases. Again the resultant spectra, after the initial reaction, show the 435 nm peak to be the most intense.

In addition, it can be seen that both the vitrinite and exinite result in almost identical spectra in both intensity and profile, after the initial reaction (ie. when pale yellow) - see figure 4.17.

The chrysene emission shifts in the opposite direction, again towards the 435 nm peaks, and also increases in intensity (figure 4.18).

Lastly, a fourth set of solutions was investigated again using the Frickley maceral solutions. This time stronger oxidizing conditions were used, as in the first run, so the results of the first set of solutions could be confirmed (figures 4.19 - 4.25).

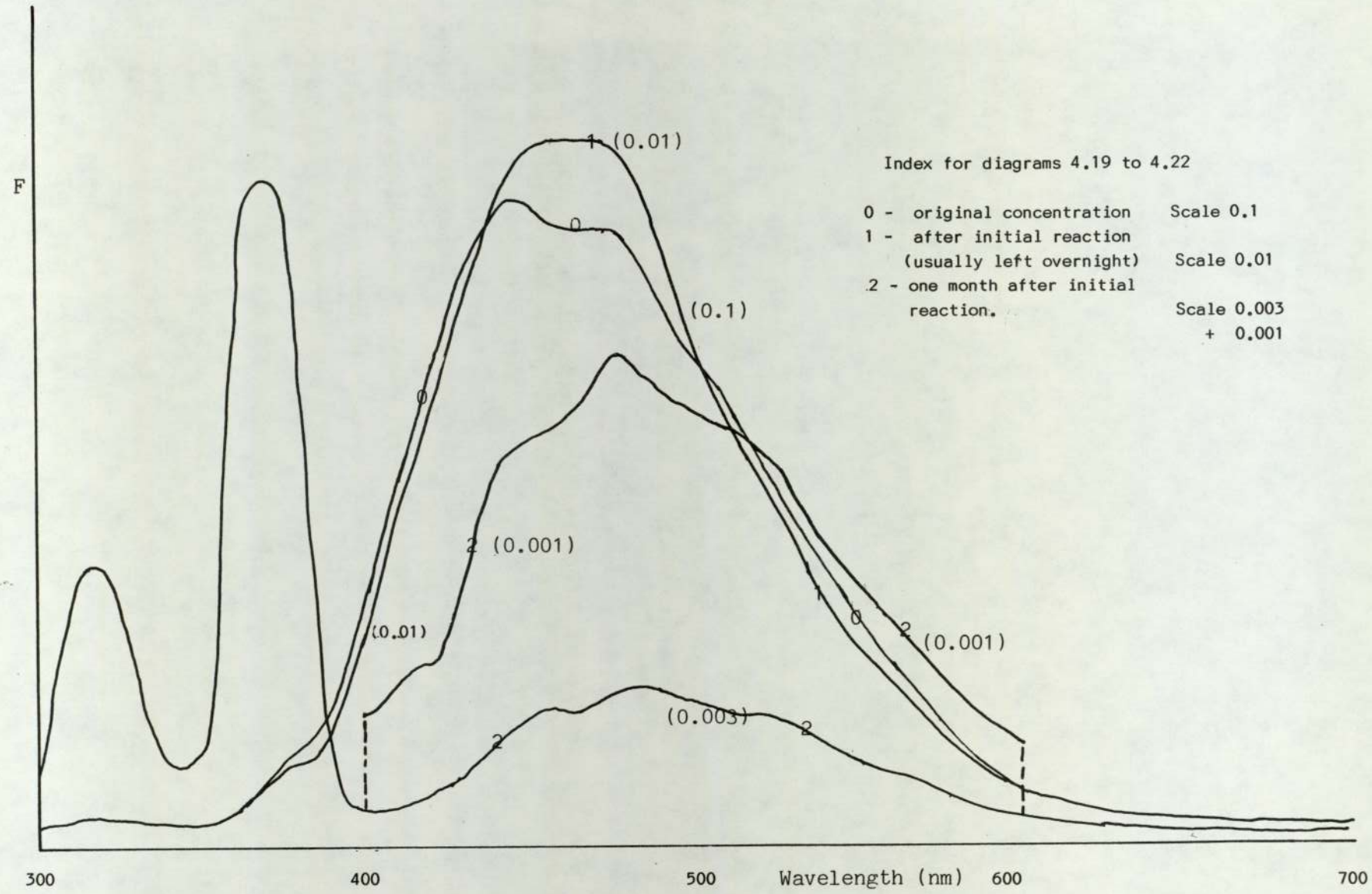


Figure 4.19 Frickley vitrinite + sodium hypochlorite. Excitation 375 nm. Scale 0.1 emission spectra

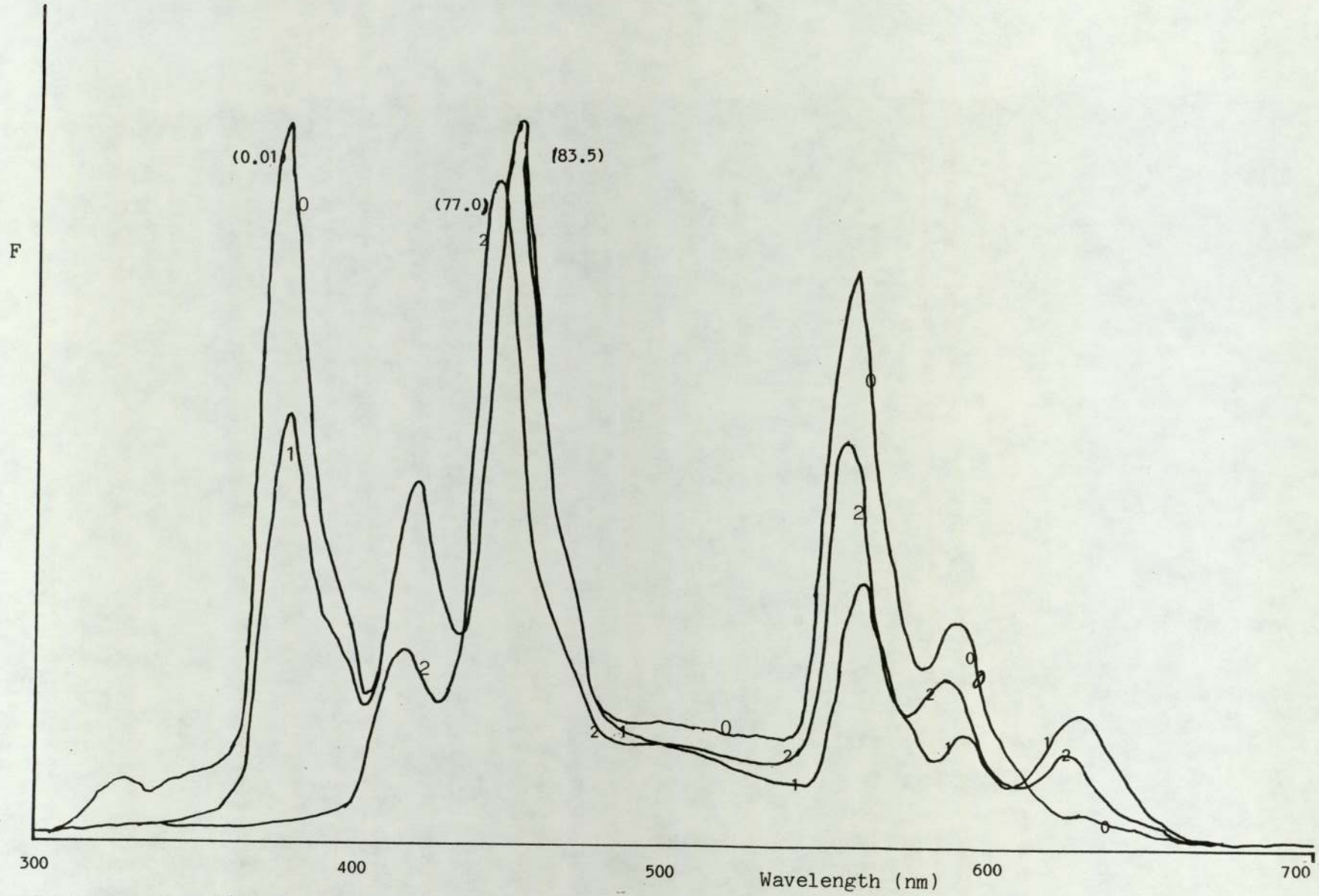


Figure 4.20 Frickley Vitrinite + Sodium Hypochlorite. Emission 620 nm. Scale 0.003

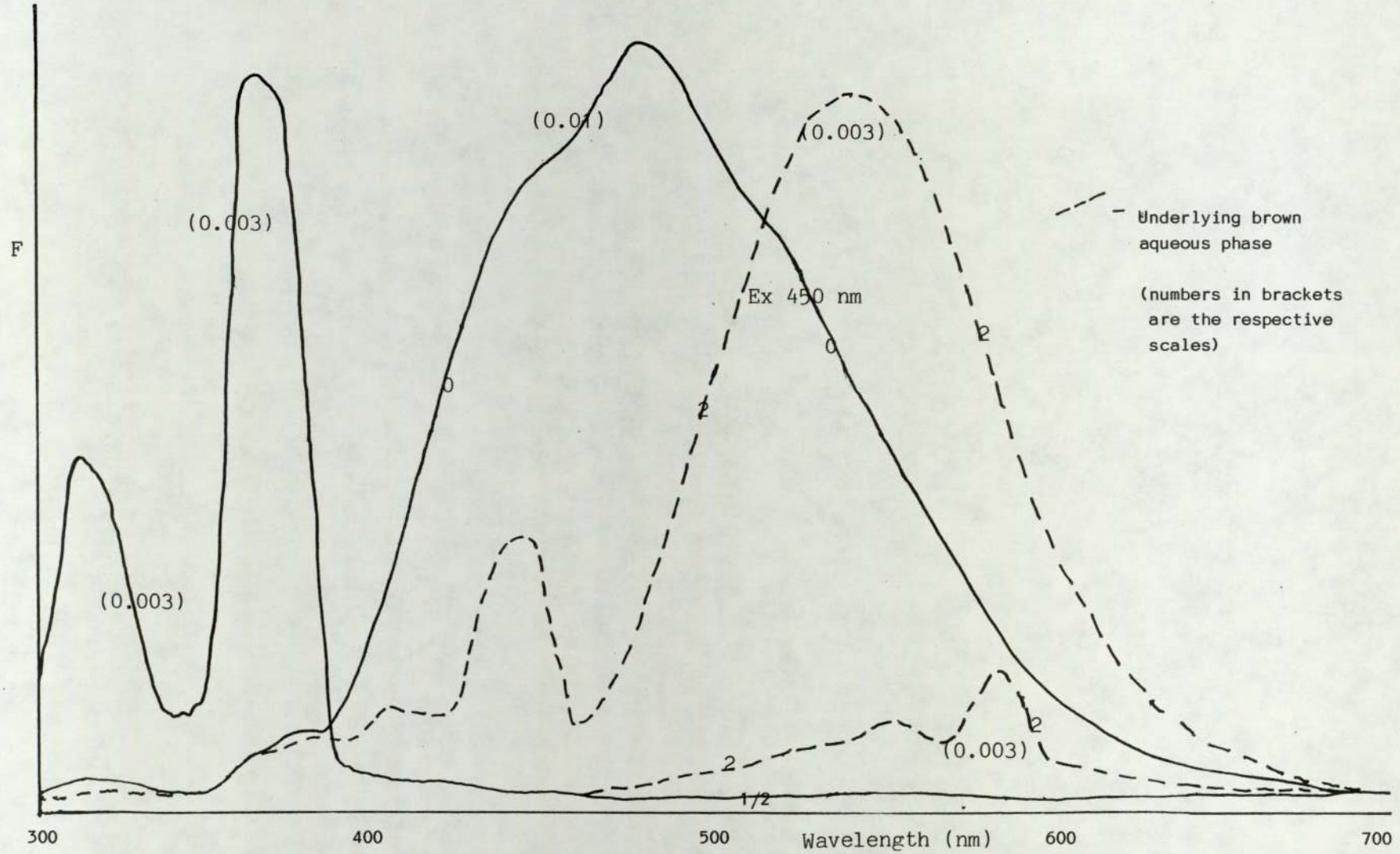


Figure 4.21 Frickley Exinite + Sodium hypochlorite. Excitation 375 nm

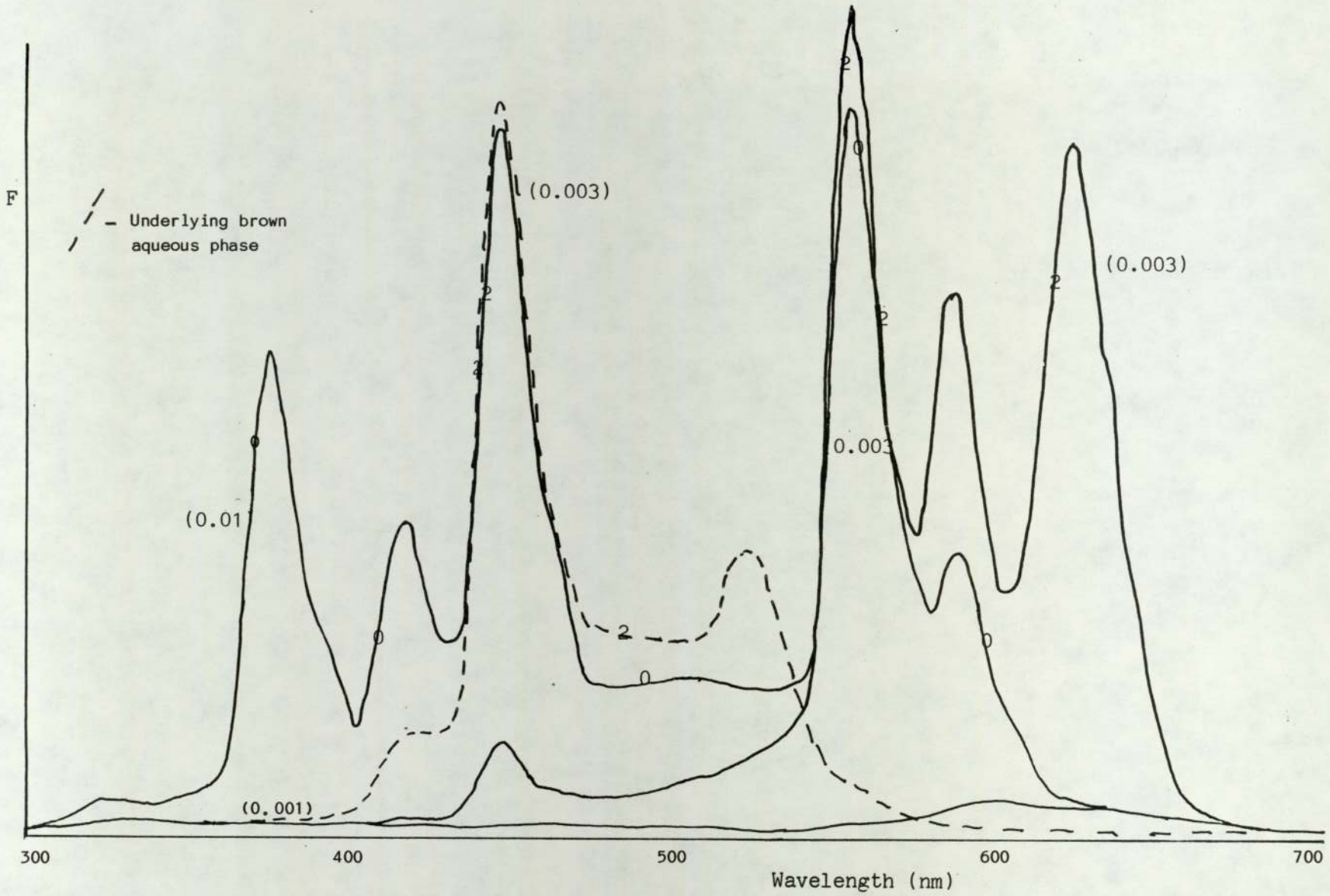


Figure 4.22 Frickley Exinite + Sodium hypochlorite. Emission set at 620 nm

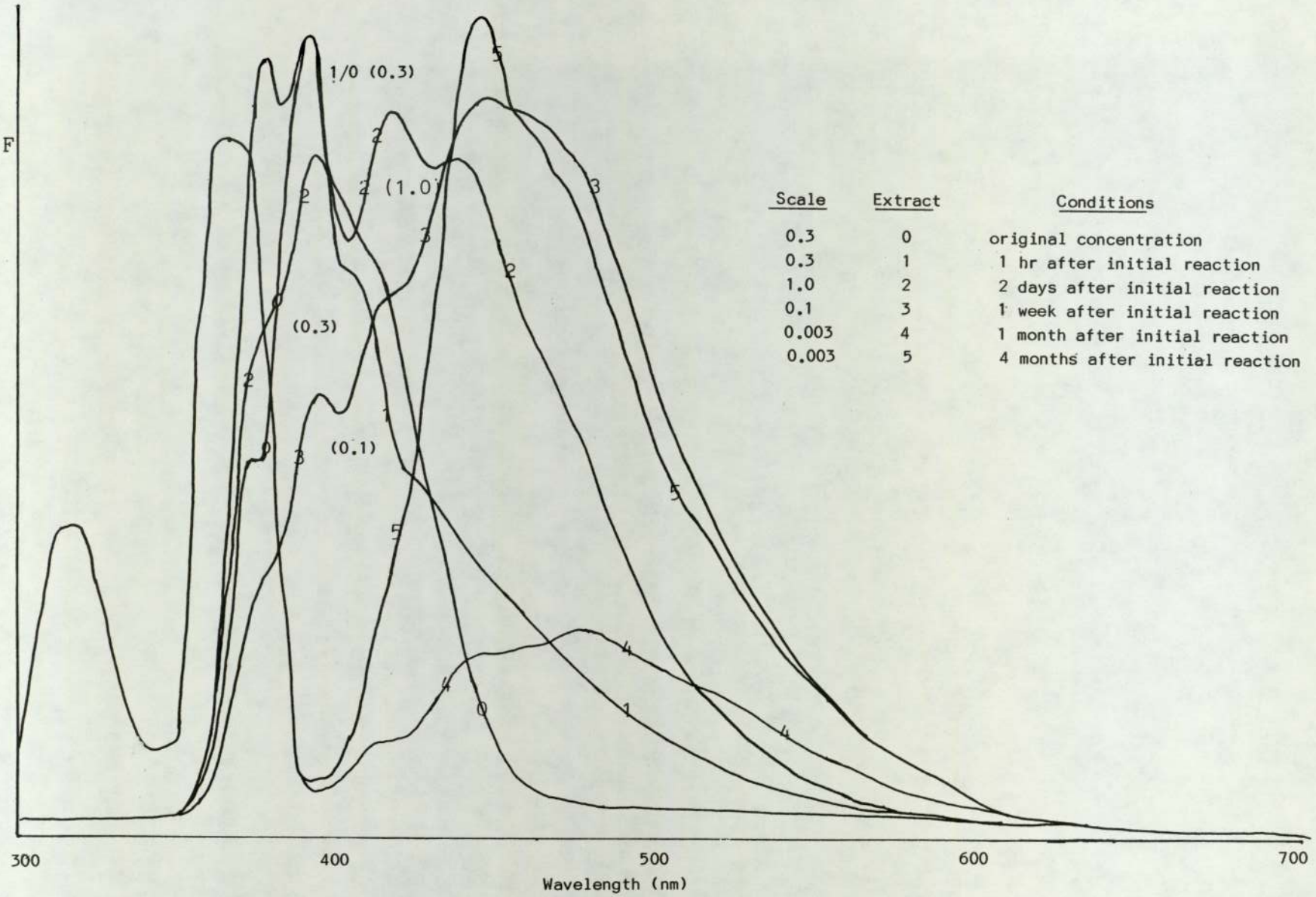


Figure 4.23 Chrysene + sodium hypochlorite. Excitation 375 nm. Scale 0.003.

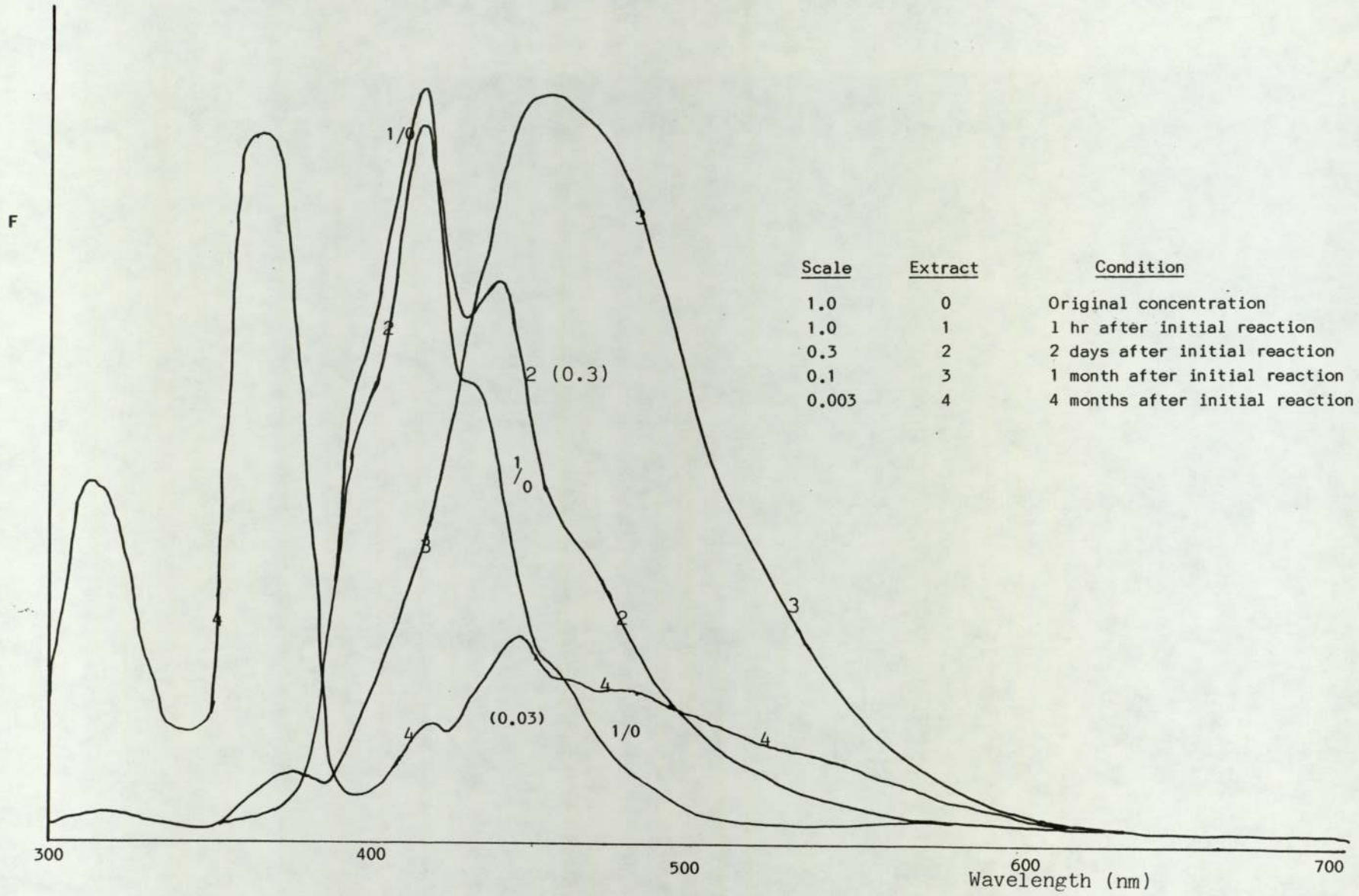


Figure 4.24 Anthracene + sodium hypochlorite. Excitation 375 nm

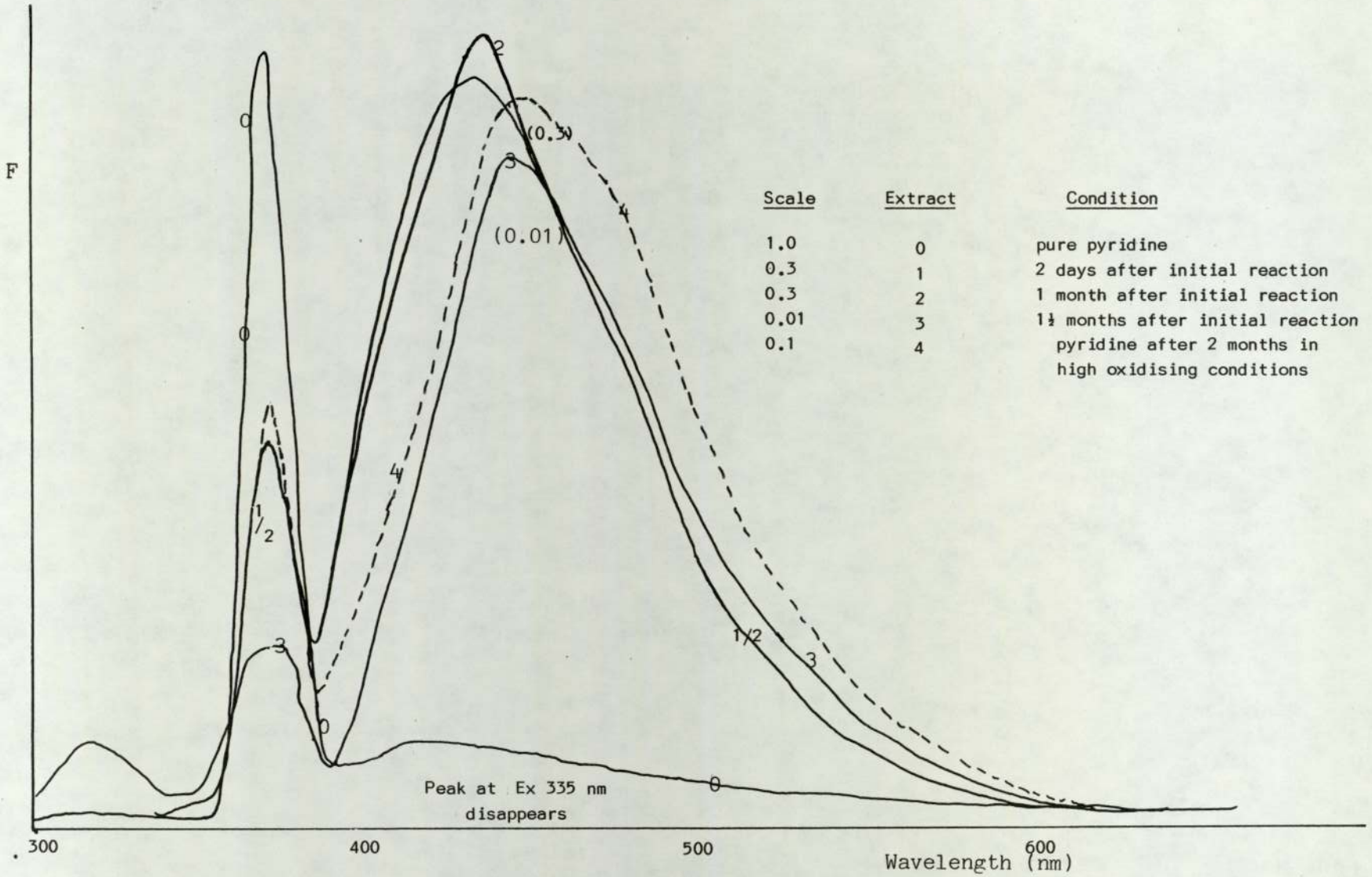


Figure 4.25 Naphthol + sodium hypochlorite. Excitation 375 nm. Scale 0.3.

These spectra (figures 4.19 - 4.25) show the same general characteristics as before, with an increase in intensity followed by a considerable reduction after the initial reaction. However, this time the reactions occurred far faster than before with the exinite reacting uncharacteristically. The exinite solution became dark red with no fluorescence in its emission spectra (figure 4.21) and for the first time the underlying aqueous phase became coloured (a light brown solution). It was later observed that this aqueous phase quite clearly fluoresced when excited at 450nm (see figure 4.21). Also, the excitation spectra appeared as if it had split into two halves between the phases (see figure 4.22).

In these results (figures 4.23 - 4.25) three standards were closely followed throughout the reaction. All showed a shift to longer wavelengths with only chrysene showing an increase in fluorescence intensity over the initial day of the reaction (figure 4.23). The naphthol was slow to react (ie. turn red) and, in fact, had the same profile as that of pure pyridine after 2 months under the same conditions (figure 4.25). Synchronous spectra of the initial stages of the sodium hypochlorite oxidation are now shown (figure 4.26 and 4.27).

These two spectra show in initial shift to lower wavelengths with an increase in intensity of the 375 nm and 420 nm peaks, while there is a reduction in intensity of the 450 nm peak.

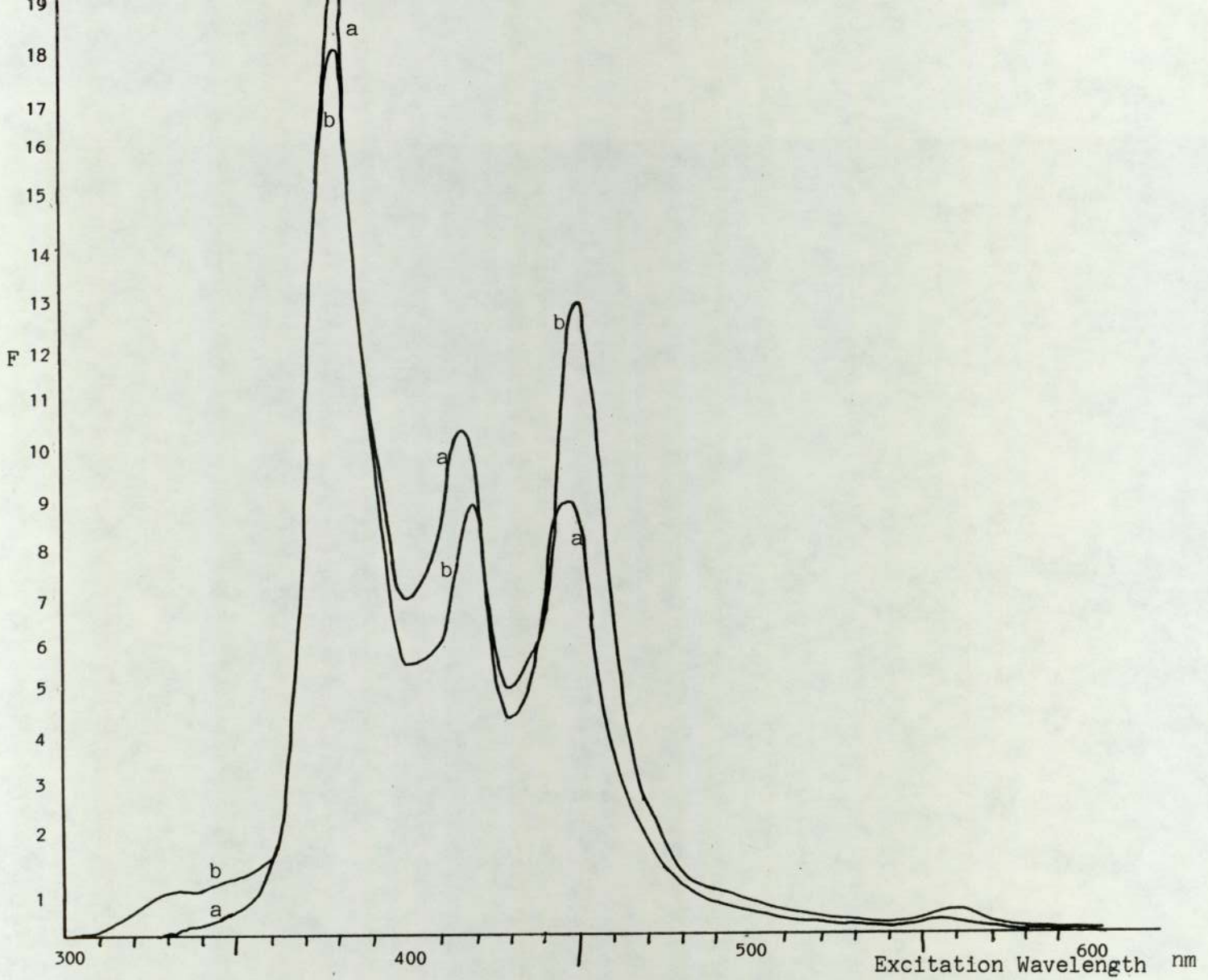


Figure 4.26 Comparison of Frickley Exinite Synchronous Spectra before and after reacting with Sodium hypochlorite. $\Delta\lambda$ 30 nm

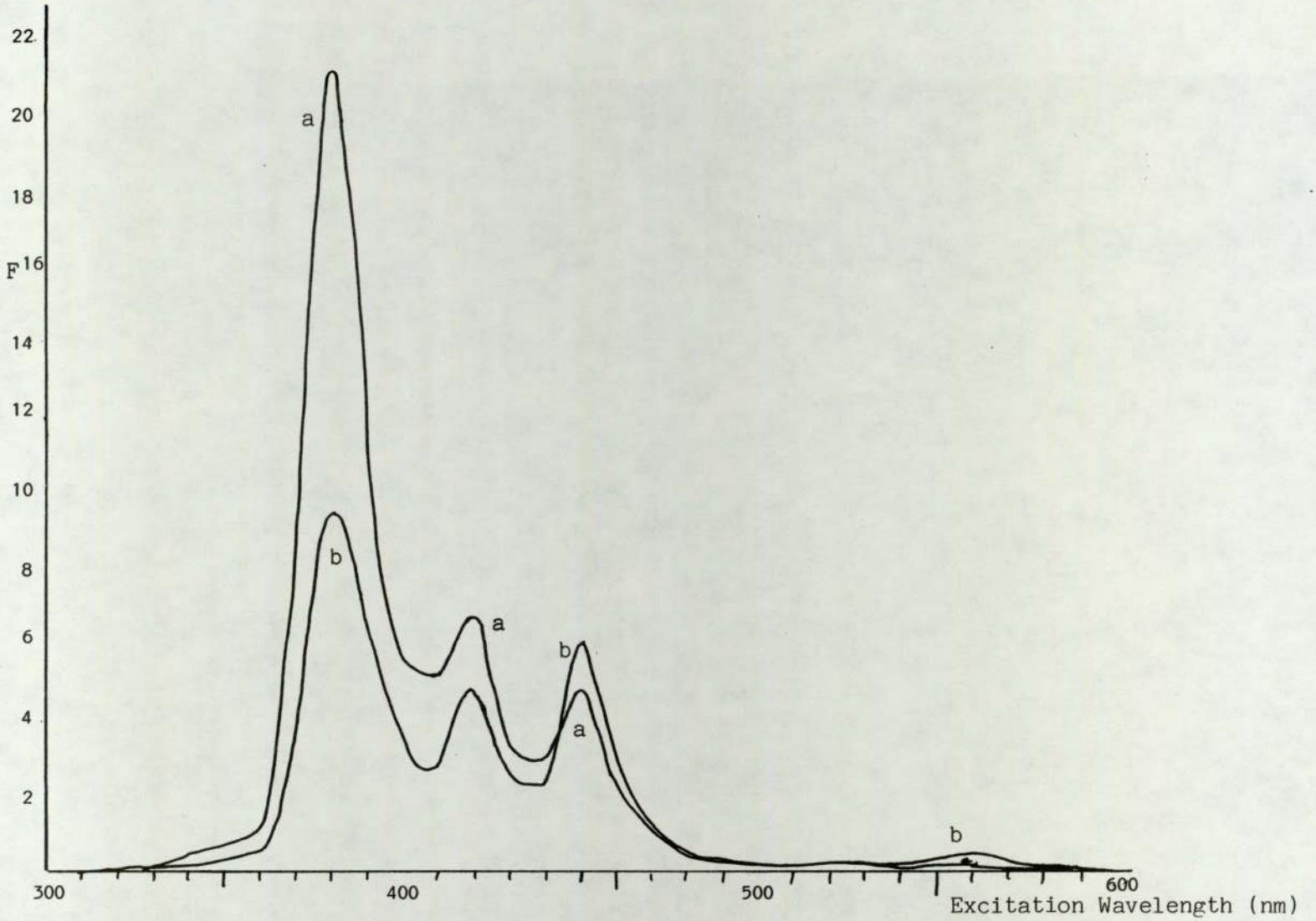
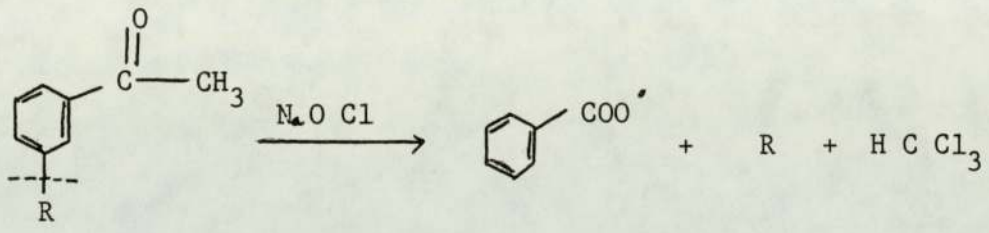


Figure 4.27 Comparison of the Frickley vitrinite synchronous spectra before(b) and after(a) reacting with alkali sodium hypochlorite. $\Delta\lambda$ 30 nm

Lastly, the Frickley exinite extraction which produced a coloured aqueous phase may show that the same part of the fluorescing molecule/particle causing the fluorescence of coal macerals is soluble in an aqueous phase. This effect may be produced from the harsh oxidizing conditions splitting and oxidizing the aromatic molecule producing a carboxyl group which may then be soluble in the aqueous phase:-



Perhaps this carboxyl ion may then form bonds with components in the aqueous phase. Thus producing a dark brown aqueous phase that was slightly fluorescent (fig. 4.2). Producing a maxima at the wavelength 550nm, when excited at 450nm.

4.3. U.V. Spectra

Ultra violet spectra were obrained for several different pyridine extracts of known concentration. Unfortunately none of the extracts produced any significant results.(fig. 4.28) In fact the results show a peak at 250nm, which is the absorption peak for pyridine. Then there was a gradual tail over the rest of the scan.

These results seem to confirm the view that these pyridine extracts are not solutions but in general are a colloidal suspension. Thus in this study the prepared extracts of coal macerals are not referred to as solutions.

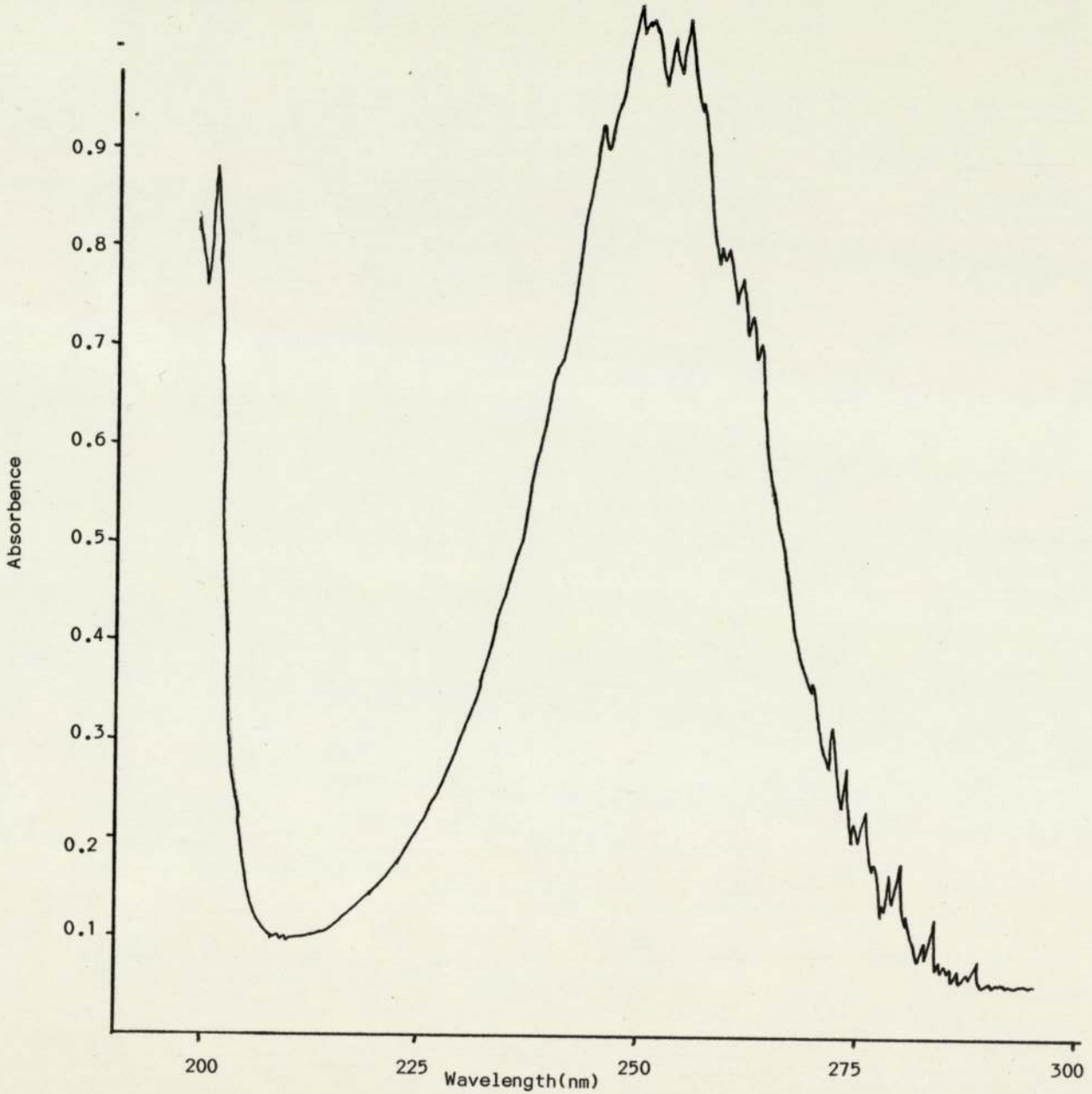


Figure 4.28 Ultraviolet Spectra of Cortonwood vitrinite original concentration (slow scan).

During the analysis of these spectra, it has been seen that the emission spectra have shown greatest alteration. Thus, it is these spectra that will be of most use when analysing the effect of sodium hypochlorite on the fluorescence of coal macerals.

4.2.1. Conclusion

From the four 'sets' of standard solutions and coal maceral extracts it has been observed that a reaction does occur. The results are non-repetitive and it is assumed that the alkalinity of the oxidising sodium hypochlorite solution is critical in this reaction. This is seen and was investigated by using fluorescence, which proved to be a sensitive technique for following this reaction and its effect on the fluorescence.

Whilst not being totally repetitive, most, if not all of the coal maceral extracts did behave along the following general path:-

1) In the early stages of the oxidation, for all the coal maceral extracts, the fluorescence spectra became sharper, with only the 435 nm peak remaining. In fact, in most cases, the fluorescence of the coal particle/molecule, fluorescing at 435 nm, was promoted. The reactant, organic phase was clearly fluorescing with increased intensity. The standard solution of chrysene also displayed a similar fluorescence promotion. This promoted fluorescence was

accompanied by a colour change from the brown colour of the original extract to a light yellow at maximum intensity.

2) After a few hours, or several days, depending on the alkalinity of the sodium hypochlorite solution, the promoted fluorescence of the 435 nm peak would reduce and the organic phase would change colour from light yellow to pink.

3) After continuing the oxidation process still further other colour changes occurred. During the period a week to two months, depending on the alkalinity of the sodium hypochlorite solution, the colour changed from pink to green and finally to dark red.

4) Finally, this red colour changed into a dark yellow which re-introduced slight fluorescence after three to five months.

Two other observations that are interesting, are the 'cloudy' effect, which was seen in many of the samples while obtaining the spectra, and the sample which produced an aqueous coloured solution.

In addition to becoming 'cloudy' it was also noted that the speed of the colour change was increased, and at times occurred while the sample was in the fluorometer. These observations, along with the spectra obtained in this chapter show that it was possible to follow the photo-chemical reactions of coal extracts and fine coal suspensions using fluorescence.

4.4 Conclusion

Although there were no absorption characterisitcs seen in the ultra-violet spectra produced from the pyridine extracts of coal macerals in this study, these spectra support the view that the extracts are a fine colloidal suspension.

From the comparison with standard spectra and those spectra received from Birbeck College, University ofLondon it is seen that the spectra reported in this study are supported by existing literature [16] . These spectra are also compatible to the spectra received from Birkbeck College of pyridine extracts of the identical separated coal maceral material used in this study. Thus, the results reported in this study can be used for direct comparisons and have minimal errors. This is particularily true for the emission spectra.

Looking at the results in the reaction of the pyridine extracts with alkali sodium hypochlorite, it is seen that over initial stages of the reaction the fluorescence intensity increases, the peak becomes narrower and other peaks, such as 485nm, are quenched. This promotion of the 435nm fluorescing peak for coal macerals is probably due to the ease of breaking the possible π interactions and phenolic bridging bonds. These bonds are easily broken as the hypohalite oxidization specifically attacks these 'types' of bonds [31] . Also, under these conditions the alkaline hypohalite may oxidize other loosely held component groupings which may be present in these maceral extracts. Thus initially promoting the fluorescence of the

basic molecular structure as the π electrons will have less molecular forces acting upon them which will allow them to be more easily excited. Once excited there is less chance of intersystem conversion so the energy is more likely to be admitted as light causing fluorescence. The removal, by oxidization, of the stabilising components, which interfere with fluorescence would also allow the lone pair present in pyridine molecules to have maximum effect. This promotes the fluorescence of the basic molecular unit still further. However, in time more oxidation occurs producing complex structures which quench the fluorescence. This process occurs in several stages causing the organic phase to change colour.

CHAPTER FIVE

5. CONCLUSION

From the study of known concentrations of pyridine extracts of two British bituminous coals, obtained from Frickley and Cortonwood collieries the nature and effect of the concentration of five individual pyridine extracts of the exinite and vitrinite maceral groups of these coals were investigated. Inertinite was not investigated as past studies have proved this fraction is non-fluorescent[5].

This study produced the first direct observations of the absorption of light by the aromatic nuclei of coal extracts. The excitation spectra, along with the emission spectra were investigated in order to examine the effect of the concentration of the extracts on their fluorescence.

Synchronous spectra produced in this study were far clearer than the emission spectra. These synchronous spectra could be used along with emission and excitation spectra to produce a three dimensional fluorescent schematic diagram. This fluorescent "fingerprinting" has been investigated in a recent paper and has been proved to be possible [23].

Direct comparison can be made between the vitrinite and exinite of each coal due to the high purity obtained when separating the coal maceral groups. The fluorescence characteristics of coal macerals can also be observed due to the high sensitivity of the methods used. From comparison of vitrinite and exinite spectra of two coals, it can be seen that there are slight differences in emission spectra, where, in general, the exinites fluoresce more strongly

than vitrinites.

Another observation from both vitrinites and exinites was that there were three fluorescent peaks (λ max) clearly visible and distinct but over different concentration ranges. Perhaps this phenomena, with specific concentration peaks, could also be used to characterise coals (see Table 1.1). From observing the three concentration peaks, three separate concentration curves could be drawn (see figure 3.23). From these concentration curves, general concentration parameters for the fluorescence of coal macerals could be evaluated. Perhaps, these concentration parameters (see Table 1.1), along with the "fingerprinting" profile could be used as a more accurate method for characterising coals and their macerals.

Due to the high solubility of the coal macerals in pyridine a general theory was formulated involving exeplexe and excimer formation. It was postulated that perhaps the pyridine promoted the natural fluorescence of the suspended coal particles. Proof of this colloidal suspension was supported by ultra-violet spectra in this study and by Drayden's findings[26] . Thus, a general theoretical equation, involving exeplex formations were considered most suitable for describing the fluorescence phenomena of the three λ max's.

The involvement of pyridine in the fluorescence of coal maceral extracts is supported by Larsen[27] , who stated that pyridine broke the hydrogen bonds present in

the structure of coal. This produces the high solubility of coal in pyridine.

From the report by Ms M R Davis[11] it is noted that the hydrogen/carbon ratio is higher in the exinites, which have lower aromaticity than vitrinites. Also, in this report, the N.M.R. spectra of pyridine extracts of the identical separated coal macerals produced evidence of aromatic and phenolic content in all the extracts used in this study.

Also, from another paper[29], the relative abundance of aromatic phenyls in benzine and methanol extracts of the same separated coal maceral groups was reported to be higher for the exinites than the vitrinites, used in this study.

Finally, the sodium hypochlorite oxidation also supports the idea of exeplex promotion as the bridging phenolic bonds are broken, thus allowing the re-coupling to pyridine molecules and again the fluorescence intensity increases with the 435 nm peak being pronounced in the early stages of oxidation.

The comparison to standard spectra led to the conclusion of a basic tetraphenyl structure being the main source of fluorescence. Although the nitrogen in the pyridine molecule may be behaving in a similar fashion to that in 1 - naphthylamine thus also promoting fluorescence in the 435 nm region.

The three separate fluorescence peaks can be explained from the relative abundance of phenolic groups available to form an exeplex with the pyridine solution. This theory, that the availability of phenolic groups to form bonds with the pyridine molecules is directly related to the fluorescence intensity, was seen in this study. Thus exinites, with a higher phenolic content and lower aromaticity generally have a higher fluorescence intensity (see figure 3.16).

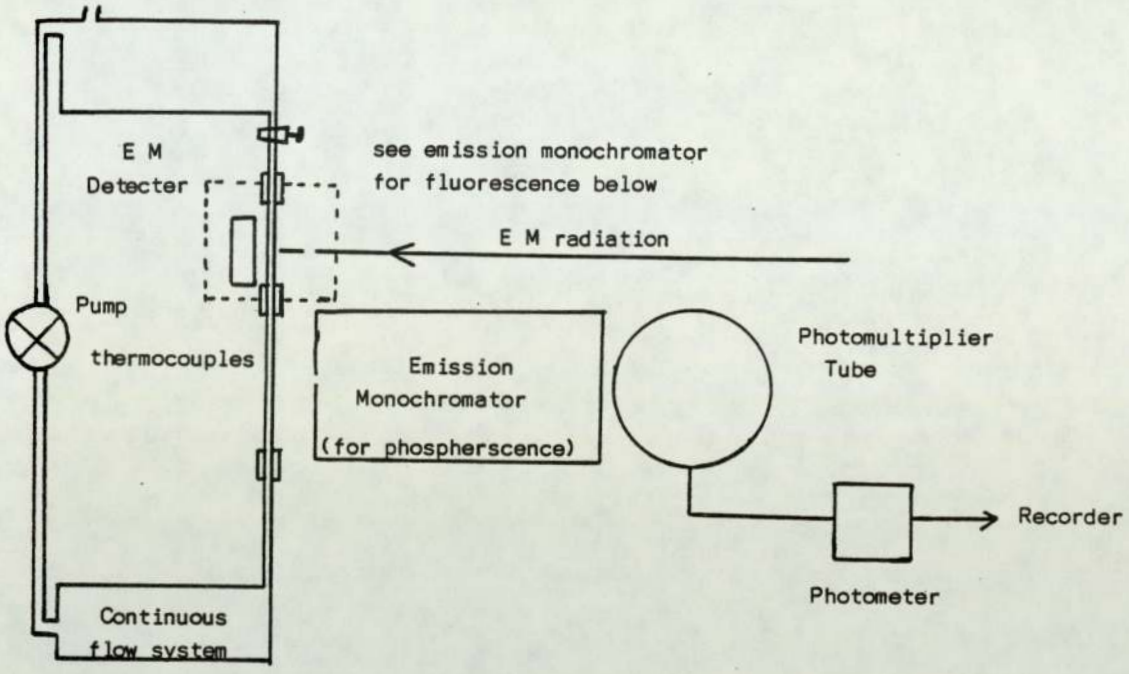
So the fluorescence is at its most intense at 435 nm, prior to the formation of a bridging phenolic bond creating 'excimers'. This reduces the quantity of phenols available for the 'lone pair' in pyridine to promote the fluorescence of this excimer with a resultant reduction in fluorescence intensity at 485 nm. As the concentration of the excimers increase, the Van-der-Waal's bonds are formed, to produce 'dimers', there is still further reduction in the phenol substituent groups available. So for the fluorescence peak at 520 nm the fluorescence intensity is reduced still further.

Thus, from the information obtained from this study, the fluorescence of coal macerals is best explained by equations 1 - 5 and 7 on page 99 (section 3.51). This possibly relates to the structures in route B on figure 4.8.

The observations and results in this report suggest that further studies in this area may prove to be beneficial

with recent studies showing that the fluorescence of coal particles in other colloidal suspensions can be examined.[23] Figure 3.14 has been published in a journal (see Appendix 1).

It is suggested that future studies into the fluorescent properties of coals may involve the use of equipment as laid out in figure 5.1. The fluorescence and phoshorescence of suspended coal particles can be studied using various electro-magnetic radiation sources.



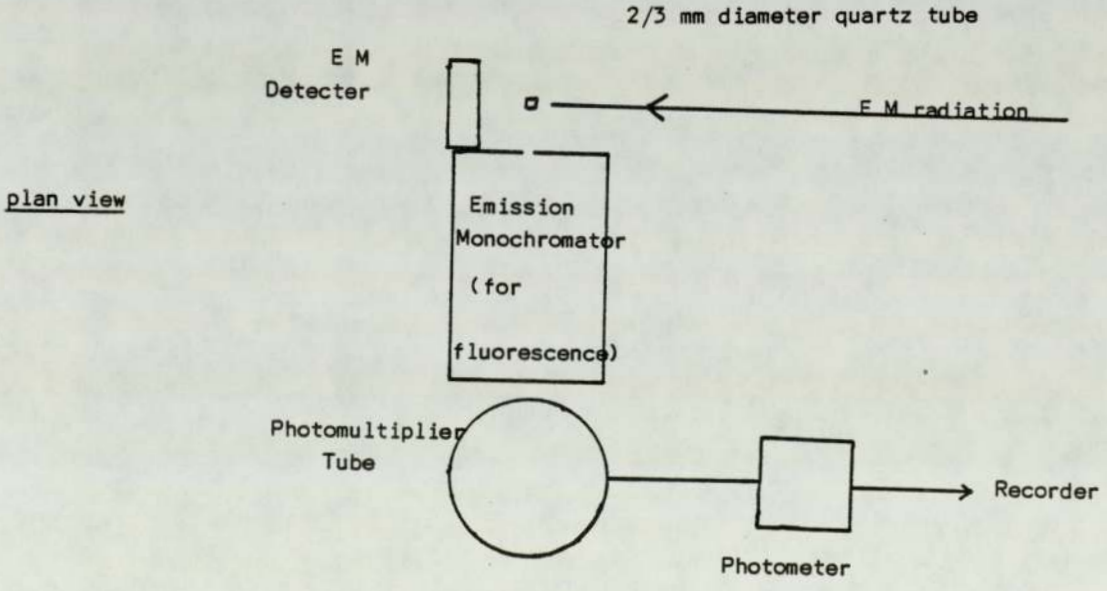


Figure 5.1 Equipment for future studies into fluorescence properties of coal

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