Development of a Fibre Optic Based System for the Measurement of Organic Pollutants in Water

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A thesis submitted to Dublin City University
in candidacy for the Degree of Master of Science

I hereby certify that this material, which I now submit for assessment on the programme of study leading to the award of the Degree of Master of Science is entirely my own work and has not been taken from the work of others save and to the extent that such work has been cited and acknowledged within the text of my work.

Signed: David Connolly Date: 1/10/93
Candidate

September 1993

Declaration

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Signed: David Connolly Date: 1/10/93
Candidate

Date: _____

Dedication

To my Mum and Dad for never doubting me

Acknowledgements

I would like to thank everybody who helped me in any way throughout the course of this work In particular, I wish to thank my Supervisor Dr Brian MacCraith for his continous help and encouragement during the course of this project

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Abstract

The development of a fibre optic based system for the measurement of organic pollution in natural waters is reported This system was designed to monitor organic pollution levels to warn of possible threats to the health of natural waters used as amenities and sources of drinking water

An experimental system was constructed to investigate fluorescence as a possible basis for an organic pollutant sensor A systematic study was performed on laboratory prepared polluted water samples in order to identify the appropriate excitation and detection wavelengths These measurements were compared and correlated with standard methods of analysis for gross organic pollution Excitation and emission spectra were recorded on standard laboratory spectrofluorimeters In addition measurements were made on a fibre optic based sensor characterization system It was found that a linear relationship existed between organic pollution concentration and detected fluorescence when excited and detected at appropriate wavelengths Fluorescence detection was identified as a method for the measurement of Total Organic Carbon (TOC) concentration in water A correlation co-efficient of 0 994 was achieved between TOC concentration and detected fluorescence signal for excitation at 340nm and collection at 420nm Limitations in the experimental system such as the expense and nature of the equipment meant that the experimental system was not suitable as a basis for a portable organic pollutant detection system

On the basis of this systematic study a dedicated optical fibre pollutant sensor for monitoring natural waters was constructed This system used a higher power lamp, filters of appropriate wavelengths instead of a monochromator and high quality UV transmitting fibre The performance of the prototype system was characterised in terms of range, resolution and response time

Chapter 1

Introduction

1 1 Introduction

Optical fibres have had a large impact on the telecommunications industry in recent years In addition they have found applications in sensors A sensor is defined in this context as a device that is able to determine continuously and reversibly the value of a measurand which may be a physical or chemical parameter There has been considerable research activity in the area of optical fibre based sensors [1-10,29-32] These sensors exploit different types of optical fibres, detectors, light sources, couplers and other components developed for the fibre optic telecommunications industry Optical fibres have been used to measure concentrations of various chemicals and physical parameters such as temperature, pressure, acceleration and flow [1] The work reported here is concerned with the development of of an optical fibre based sensor for the detection and concentration determination of total organic carbon (TOC) in water

1 2 Optical Fibres

Optical fibres consist of a transparent waveguiding cylindrical core surrounded by a transparent cladding of slightly lower refractive index which in turn is often surrounded by an outer protective layer A typical step index multi-mode fibre structure is shown in Fig 1 1

The core diameter ranges from a few microns to a few millimetres in diameter depending on the application The core material is generally silica or plastic but developments in glass technology have enabled enhanced transmission in the I R and U V regions

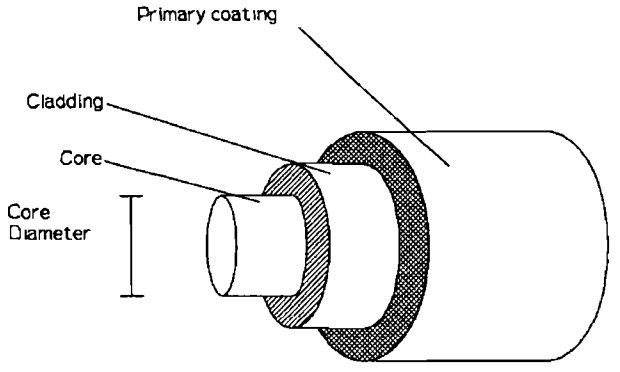

Figure 1.1 A diagram of a typical step index multimode optical fibre

1 3 Optical Fibre Chemical Sensors

An optical fibre chemical sensor is considered in this work as a device that can continuously and reversibly monitor the concentration of a desired chemical parameter and has an optical fibre or fibres as an integral part of the sensing process In general, two distinct approaches are employed (i) Optical Fibre Optrodes and (ii) Remote Fibre Spectroscopy

(i) Optical Fibre Optrodes

In this category a reagent whose optical properties (absorbance, fluorescence etc) vary in proportion to the concentration of the chemical of interest is attached to, or located close to, the optical fibre in such a way that the analyte can interact with it but cannot leach it away Reagents are chosen to react sensitively and specifically to a particular analyte

(ii) Remote Fibre Spectroscopy

Here the fibre acts as a simple light guide which separates the sensing location from the monitoring instrumentation and allows conventional spectroscopic measurements to be made at a distance Such sensors have been developed for a wide range of applications such as biomedical [6,7,8], and environmental monitoring [1-6,9,10] In particular sensors have been developed to monitor specific water quality parameters such as organochlorides [2,3,4] and nitrate [5] concentration

1 4 Environmental monitoring

Effective enviromental monitoring requires frequent repetitive measurements of specific environmental parameters or chemical species rather than complete analysis

of the sample A wide variety of different approaches are presently in use Specialised electrochemical, solid state, biosensing and optical techniques have been developed to measure specific environmental parameters Environmental monitoring is generally performed in one of two ways grab sampling followed by a laboratory analysis or in-situ continuous or semi-continuous sensing

While grab sampling followed by laboratory analysis can boast great sensitivity and accuracy, it is expensive in terms of personnel, transportation and equipment Furthermore there may be doubts about sample integrity due to the possibility of sample degradation during storage and transportation This is especially true for volatile samples More importantly, however, this approach incurs a delay of hours or maybe days before the result of the analysis is known Clearly signifigant pollution events may have transpired during this time and sample integrity cannot be guaranteed

In-situ monitoring is not as costly and can provide real-time information Furthermore, the high sensitivity of the laboratory methods is often unnecessary as detection of the prescence or introduction of a pollutant health hazard is a sufficient indication that prompt action is required Thus in-situ monitoring can offer many advantages for enviromental monitoring

The use of optical fibre sensors has many advantages over other methods of in-situ monitoring The nature of optical fibres makes possible sensors which are very small, light in weight, rugged and corrosion resistant Furthermore, the fibres are relatively inexpensive, with low attenuation, geometrically flexible and offer the capability of multiplexing All these factors make optical fibre sensors excellent in-situ environmental monitoring devices

1 5 Numerical Aperture

In this work the approach used is based on remote fibre spectroscopy and as such the fibres were used as light transmission and collection channels to and from the sensing location respectively In particular the approach was based on the inherent fluorescent properties of the analyte For the most effective use of fibres in this role certain parameters of the fibres must be taken into consideration In particular a knowledge of the influence of numerical aperture on the fluorescence collection efffiency was

critical

From a ray optics point of view the propagation of light in multimode optical fibres can be described by total internal reflection Total internal reflection occurs when light impinges on the the core-cladding interface at an angle of incidence greater than a critical angle θ_c Propagation is achieved by multiple total internal reflections at the core-cladding interface along the length of the fibre

The critical angle θ_c is given by

$$\sin \theta_c = \frac{n_{cladding}}{n_{core}}$$

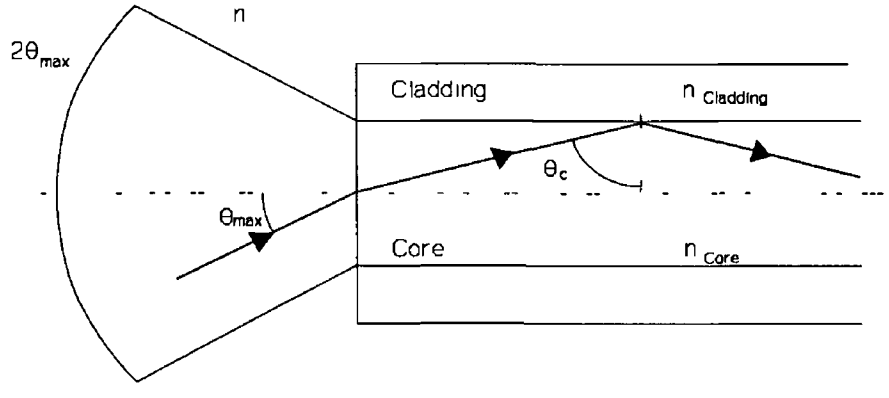

Figure 1 2 A diagram of the cross-section of an optical fibre showing the maximum acceptance angle θ_{max} and the critical angle θ_c

Any light striking the core-cladding interface at an angle less than the critical angle will be lost to the cladding and not propagated Therefore the critical angle determines the maximum acceptable angle θ_{max} for the light entering the fibre Furthermore the numerical aperture, N A, is a critical parameter in determining how much light can be collected by an optical fibre The numerical aperture helps to determine the conditions for light entering or leaving the fibre It can be shown that N A is given by the following equivalent expressions

$$N A = n_i (n_{core}^2 - n_{clad}^2)^{1/2}$$

$$N A = n_1 \text{ Sin } \theta_{max}$$

where n_1 is the refractive index of the incident medium

The relevance of the numerical aperture in determining the most efficient method for the collection of fluorescence from the sample solution in this project is discussed in detail in Chapter 3

1 6 Conclusion

Optical fibres have proved themselves in many applications since their development The technology developed for their use has led to still more applications The combination of optical methods for chemical analysis with the advantage of optical fibres for light transmission has led to a wide range of sensors with particular advantages in environmental monitoring

Chapter 2

Total Organic Carbon in Natural Waters

2 1 Introduction

This work is concerned with the detection and concentration determination of total organic carbon (TOC) in natural waters The total organic carbon content of a sample may be defined as the difference between the total carbon concentration and the total inorganic carbon concentration in a sample Organic molecules are made up of relatively few elements, carbon and hydrogen occur in all compounds, oxygen in a great many, and nitrogen, the halogens and sulphur are often present too The vast majority of organic compounds do not contain any of the other elements In the context of the typical methods of analysis for the determination of TOC, organic carbon may be defmed as carbon that is bonded chemically to carbon, oxygen, hydrogen, nitrogen, sulphur or a halogen and was present in an organic compound before analysis The total is comprised of volatile, particulate (or undissolved) and dissolved fractions [11]

Volatile organic carbon (VOC) is that fraction of the total which is susceptible to evaporation Particulate organic carbon (POC) is that fraction of the total which is matter and does not dissolve in the liquid and takes the form of suspended solids Dissolved organic carbon (DOC) is that fraction of the total present in the liquid phase after filtration

The determination of TOC concentration in a sample typically involves sample acidification followed by purging to remove inorganic carbon During the purging process the VOC fraction and some of the POC fraction may be lost and so the TOC measurement is based on the residual or non-purgable total organic carbon Analytical results are expressed in terms of the equivalent mass of organic carbon per

litre of water (mg/L) and include the sum of all organic compounds with no indication as to the concentration or types of individual compounds [12]

2 2 Total organic carbon in the environment

The TOC concentration of natural waters is composed of naturally occurring and man-made organic substances Naturally occuring organic substances found in natural waters are due to the metabolic processes and decomposition of the indigenous flora and fauna and also due to matter leached from the surrounding land during drainage of water to lakes, rivers or streams Among these naturally occuring organic substances are the decomposition intermediates and products of proteins, lipids, carbohydrates, porphyrins, plant pigments, complex substances formed from breakdown intermediates as well as humic and fulvic substances [13] Compounds such as these form a background to any attempt to detect TOC change due to external pollutant sources

Pollution found in natural water could be due to deliberate or accidental dumping into lakes, rivers and streams Sources of organic substance pollution can be runoff of agrichemicals, silage effluent or slurry from farms, petrochemical runoff from roads, seepage from landfills, faulty domestic sewage equipment (e g septic tanks) or leaks from industry Standard methods of TOC analysis are incapable of differentiating naturally occurring from pollutant organic substances and so other methods of analysis are necessary when determination of the specific type of organic substances in water is required

2 3 Total organic carbon in relation to health hazards

Many of the naturally occurring organic compounds found m natural waters are not hazardous to human health In contrast, many man-made compounds have serious health implications at low concentrations for the use of natural waters as amenities and as sources of drinking water A high TOC concentration, particularly in surface waters, is not necessarily an indication of pollution as background levels of TOC can be quite high However any increase in the TOC concentration should be investigated as it may indicate the introduction of a pollutant The nature of the potential hazard depends on the source of the polluting material e g influxes of slurry or silage effluent can lead

to potential health problems and/or eutrophication of natural waterways whereas influxes of agrichemicals or fuel oils can lead to poisoning. Determination of increase in TOC concentration alone would not indicate the presence of a health hazard but would indicate that further analysis would be prudent. For these reasons European Community has not set a maximum admissible concentration for TOC concentration but comments that " the reason for any increase in the usual concentration should be investigated" [14].

2.4 Current methods for the determination of TOC concentration in water

There are a number of methods used for the determination of TOC concentration in both laboratory and field situations. In general all the laboratory methods are based on the same principle: the organic carbon is converted by oxidation to a gas which is then detected and quantified as a measure of TOC content. Oxidation is performed by high temperature catalytic, chemical or photochemical methods and produces carbon dioxide. Some systems are designed to detect carbon dioxide and others reduce the carbon dioxide to methane which is then detected. Detection of the gas is performed by flame ionization, non-dispersive infra red, titrimetric, nephelometric, electrical conductivity or spectrophotometric methods [12].

A field-based instrument for TOC monitoring is based on UV absorption of a water sample at 254nm [15]. This method, however, has certain limitations. Some organic compounds, such as sugars, simple aliphatic acids, alcohols, paraffines and simpler amino acids which might be found in natural and waste waters do not absorb in the ultra-violet and hence cannot be detected by this method. However, these compounds are those that will be most rapidly consumed as food by microorganisms in open water and in biological treatment plants. The correlation between the absorbance at 254nm and TOC will be adversely affected by turbidity beyond certain limits. The instrument was designed to compensate for turbidity. High concentrations of inorganic UV absorbers or organics which do not absorb in the UV may also affect the correlation between absorbance at 254nm and TOC. Generally, these conditions represent a problem in monitoring certain industrial wastes or mixed municipal-industrial wastes and not in natural water systems [16].

The advantages and disadvantages of laboratory based systems and field

based systems for effective environmental monitoring are discussed in Chapter 1 The shortcomings of field based systems are not of critical importance as TOC concentration is used only as a gross monitor of water quality and rapid detection of potential pollution by continuous monitoring is more important than comprehensive analysis in terms of effecting remedial action

The aim of this work was to build a low cost on-line, field based method of determining TOC and detecting gross pollution events using fibre optic technology

2 5 Conclusion

The wide range of compounds present in a natural water makes a comprehensive detailed analysis a time-consuming and complex process As the TOC concentration represents the total organic chemical content of the water any change in TOC concentration represents a change in the chemical composition of the water Thus TOC concentration is most useful as a gross monitor of the health of a water and indicates the need for more specific investigation

Chapter 3

The Laboratory Based System

3 1 Introduction

In this work it was necessary to construct an instrument capable of stimulating fluorescence in the sample under examination, collecting the fluorescence produced and then quantifying the fluorescence for sensing applications

A system was designed using the standard principles of quantitative fluorimetry but taking into account the use of optical fibres for the delivery of the exciting light and the collection of the fluorescence produced This system was used to establish whether the detection and quantification of total organic carbon (TOC) would be feasible using a fluorescence-based approach This system was intended as a purely laboratory based system using sophisticated equipment (e g a double monochromator) unsuitable for field applications It was intended that in a field based system a more dedicated approach would be taken in which the more expensive and versatile components be replaced by more rugged, specific equivalent components A schematic diagram of the experimental system is shown in Figure 3 1 The system comprises a light source with an excitation filter, an optical fibre carrying the light to the probe head, nine collection fibres, a double monochromator, a photomultiplier tube, a photon counting unit and a personal computer

The system operates as follows the preferred excitation wavelength is isolated from the light from a deuterium lamp using a bandpass filter The light is then focused into a one metre length of optical fibre The distal end of this fibre is located along the central axis of the probe head and produces fluorescence in the sample The design of the probe head is discussed in more detail in section 3 3 The fluorescence is then collected by nine one metre lengths of the same type of optical fibre used for excitation At the detection end these collection fibres are configured in a rectangular shape to match the profile of the slit of the double monochromator This provides the

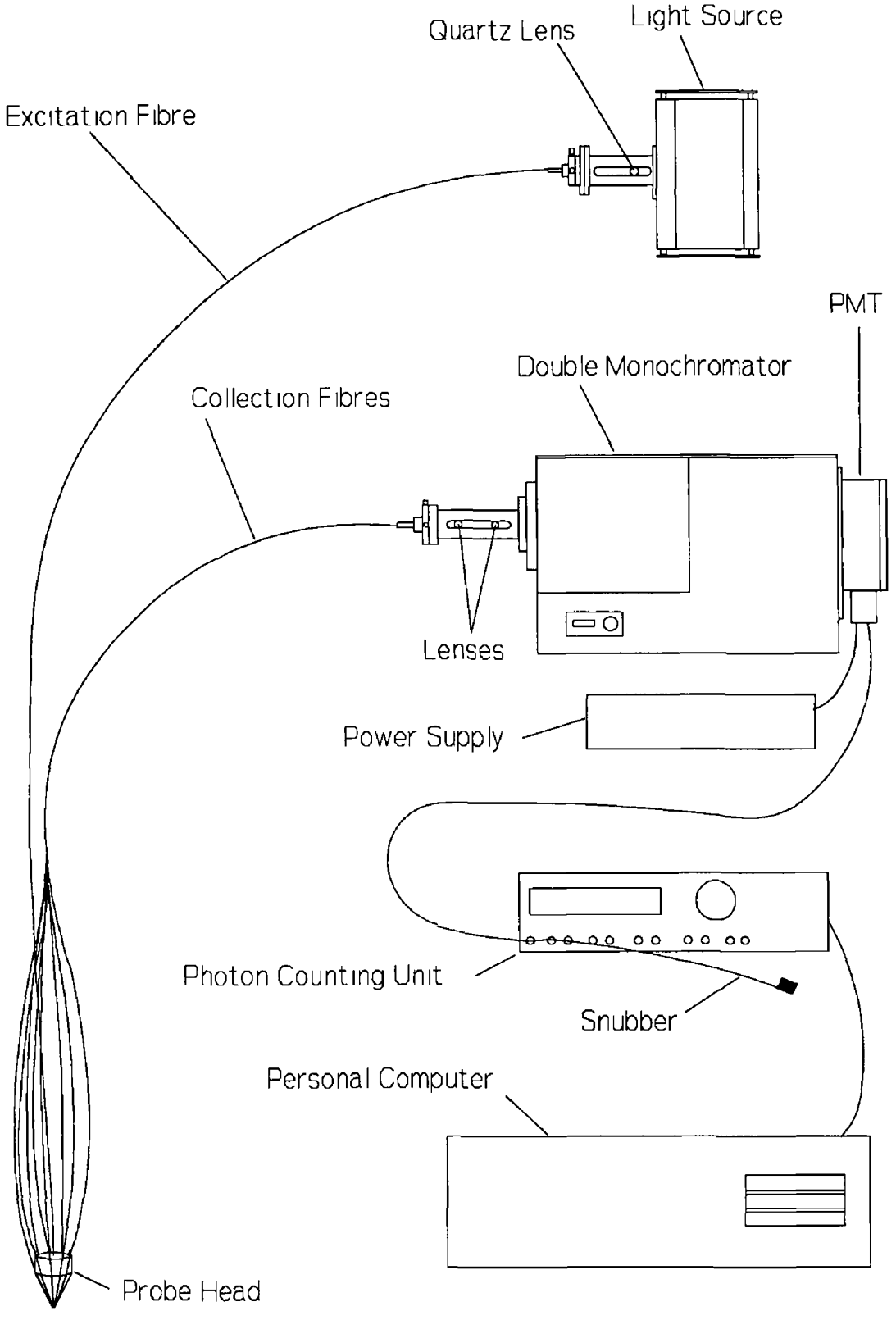

Figure 3 1 The laboratory based system

most efficient delivery of the collected fluorescence for the detection system The collected fluorescence is collimated by a convex lens and then focused into the entrance slit of the double monochromator by a second convex lens The use of a double monochromator is important as it provides a high rejection of scattered light and allows low levels of light to be detected The double monochromator is used to identify the wavelength of the maximum fluorescence signal and intensity measurements are made at this wavelength The collected fluorescence is detected at the exit slit of the double monochromator by a photomultiplier tube with a special photon counting base The signal is quantified by a photon counter whose operation is controlled by a personal computer The performance of the system may be divided into three sections fluorescence production, fluorescence collection and fluorescence detection

3 2 Fluorescence Production

The first part of the system is dedicated to the production of fluorescence in the sample under examination This part of the system includes a light source, launch optics and the fibre that carries this exciting light to the sample

3 2 1 The Light Source

The light source is a 30 Watt Cathodeon R36 deuterium lamp in a Bentham 1L5 housing A deuterium lamp is used because it provides adequate spectral coverage in the region of interest The preferred excitation wavelength is isolated by a Corion bandpass filter with a peak transmission at 360nm and a full width half maximum bandpass of 10nm This wavelength was selected on the basis of data presented in a paper by G Lakshman [17] and is in broad agreement with other papers dealing with optical methods for examining dissolved organic matter in waters [18-28] Subsequent measurements detailed m Chapter 4 led to the selection of a different excitation wavelength for the dedicated system The filter and a quartz lens of focal length 40mm are both placed in a carriage inside the lamp housing The position of both can be adjusted along the carriage axis The light is focused mto the exciting fibre by the convex quartz lens The couplmg of the light into the fibre is optimised by adjusting the fibre position using an X-Y-Z positioner The fibre used is a one metre length of

Fibreguide Industries, Superguide G, Tefzel coated, plastic clad silica fibre with a core diameter of 400μm The fibres were hand polished at both ends to achieve good launch effiency and the distal end is located along the central axis of the probe head

3.3 Fluorescence Collection

This section of the system is dedicated to the collection of the fluorescence produced at the probe head This section consisted of the probe head, the collection fibres and the double monochromator A novel sensor head was designed to optimise fluorescence collection efficiency and this a particular feature of the system design

3.3.1 Design of the Probe Head

The sensitivity and limit of detection of the system are dependent critically on the fluorescence collection efficiency For this reason considerable attention was paid to this part of the system

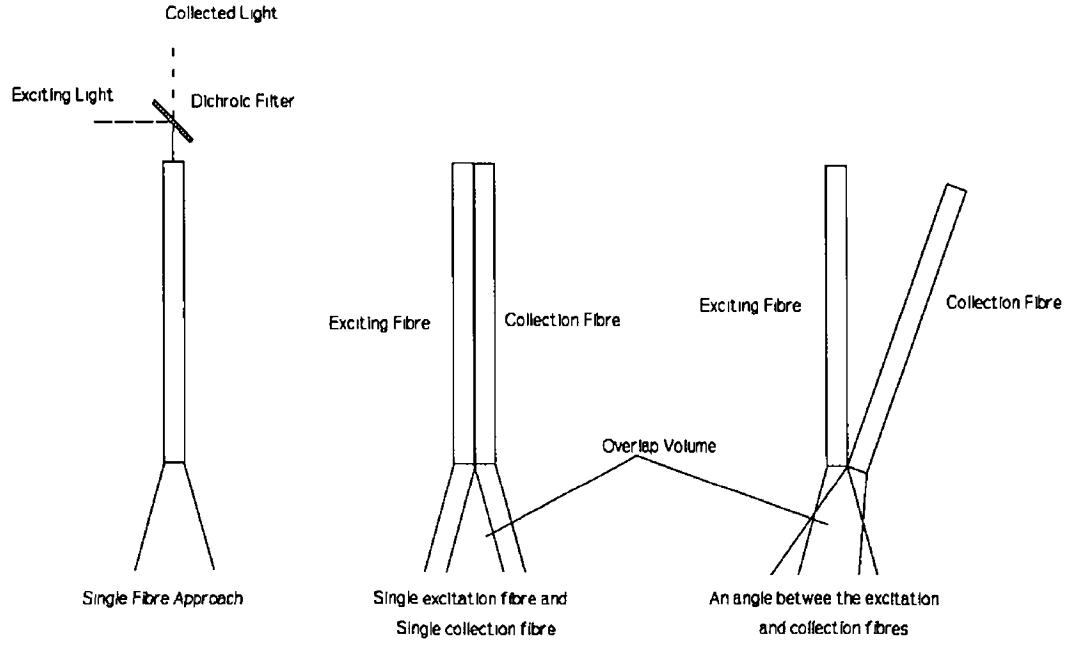

Figure 3 2 Different approaches to fluorescence collection using fibres

Previous attempts to use optical fibres and fluorescence for remote sensing applications have used either a single fibre for exciting and collecting fluorescence [29,30] or a single fibre to excite and one or more fibres to collect

fluorescence [31,32] (Fig 3 2) For this work the single fibre approach was rejected because it necessitates the use of a dichroic filter which can lead to alignment difficulties and a loss of light signal in transmission Dichroic filters are expensive components which would need to be replaced if there was signifigant change in the selected excitation or collection wavelengths It was decided to use a single fibre for excitation and multiple collection fibres to maximise collection efficiency

Previous work [33] had suggested that collection efficiency could be improved by positioning collection fibres at an angle (rather than parallel) to the exciting fibre An experimental approach was adopted to determine the optimum angle for fluorescence collection effiency between the exciting fibre and each of the collection fibres The fibre used in this experimental approach was the same type as that used in the laboratory based system The experimental determination was performed by constructing an apparatus (Fig 3 3) that allowed the exciting fibre and the collection fibre to be positioned at a selected angle to each other The apparatus was placed into a solution in which suitable fluorescence could be produced The resulting graph of fluorescent signal against angle between the exciting and collection fibres is shown in Fig 3 4 and indicated that the optimum minimum angle for the most efficient collection of fluorescence is 22°

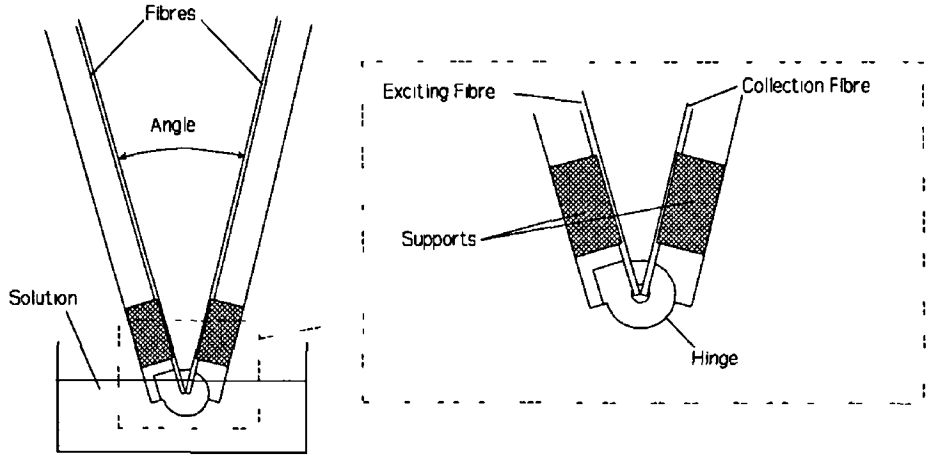

Figure 3 3 The apparatus used to determine the optimum angle between the excitation and collection fibres

A computer model of the experimental determination was designed by another member of the group working on a similar project [34] The aim of this model was to predict the angle for maximum collection effiency The basis of the model was to characterise the overlap volume of the excitation and the collection cones in three dimensions and its dependence on the angle between the two fibres The dimensions of the excitation and collection cones are defined by the numerical aperture and the core diameter of the fibres used The predicted angle from the model for the fibres used in the experimental determination was 24° which was close to the result of the experimental determination

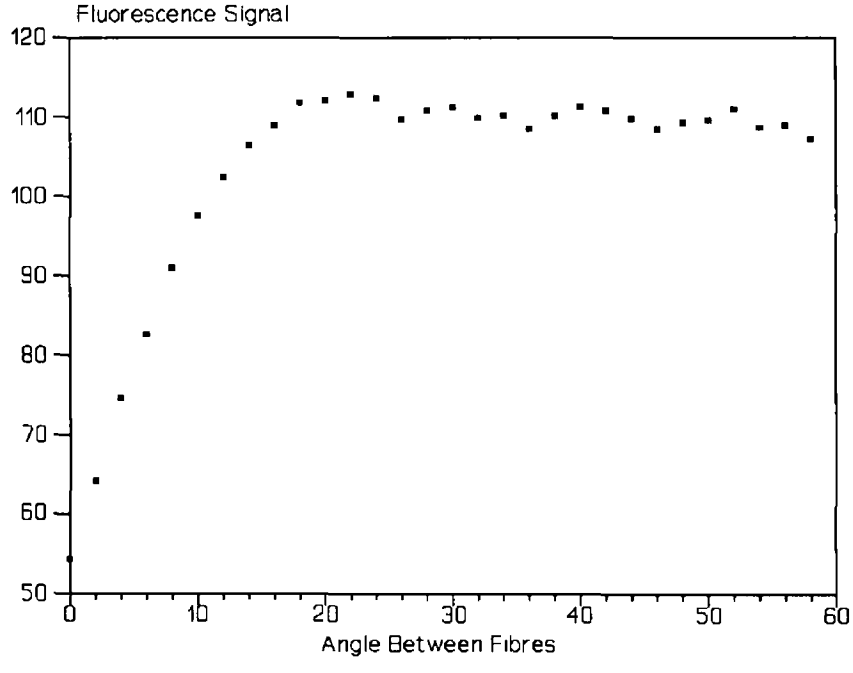

Figure 3 4 An experimental plot of fluorescence signal against angle between an excitation and a collection fibre

The probe head (Fig 3 5) constructed on the basis of the experimental results is a novel design It consists of a metal cylinder with a cone at one end and a hole of suitable diameter through its centre for the exciting fibre The half-angle of the cone was machined to be 22° in order to maximise collection efficiency The maximum number of collection fibres which can be arrayed around the exciting fibre is governed by the diameter of the fibre used In the case of the fibres used here nine fibres could

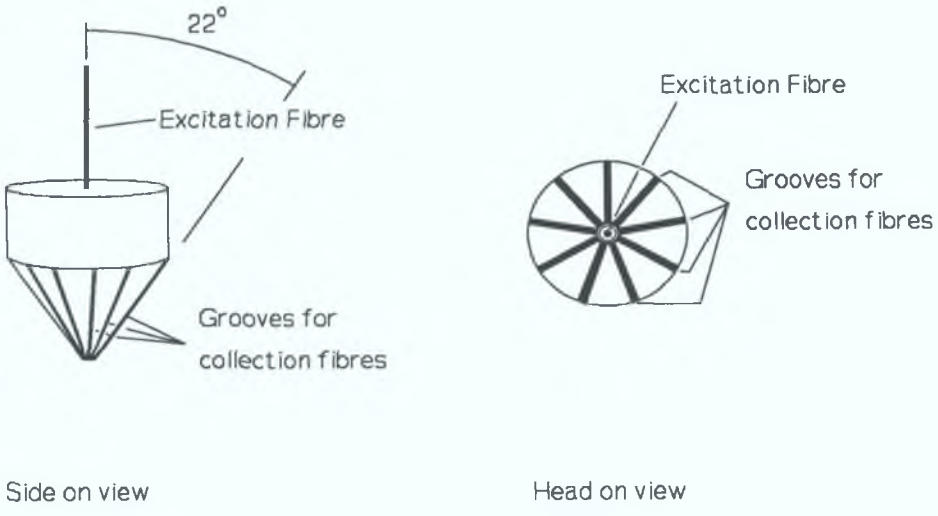

Figure 3.5 The probe head

be accommodated. Nine grooves were cut symmetrically into the side of the cone to guide the collection fibres. The collection fibres were fixed into the grooves of the probe head and their collecting ends positioned as close as possible to the end of the exciting fibre. This probe head arrangement was used in all experiments using the laboratory-based system.

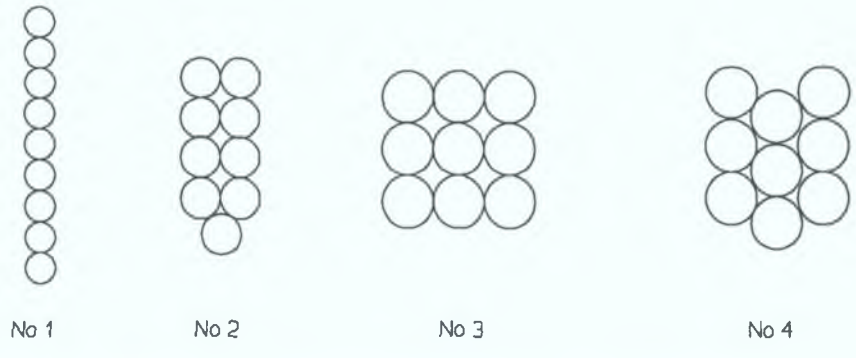

Figure 3.6 Possible configurations for the nine collection fibres

3.3.2 The Double Monochromator

A number of different configurations (Fig. 3.6) for the nine collection fibres were examined for the most efficient delivery of fluorescence into the double monochromator. The most efficient configuration would match the profile of the entrance slit of the double monochromator and take into account the physical constraints of the system. Configurations 1 and 2 were rejected because they were not

compact enough and too large for the X-Y-Z fibre positioner Configuration no 4 was preferred over no 3 because it matched the rectangular profile of the slit more closely The collection fibre bundle was optically matched to an f/2 lens The subsequent collimated beam was focussed into the double monochromator by an f/4 lens This lens matches well with the double monochromator which has a focal length of 300mm and f/# of 4 2

The double monochromator consists of two Czerny-Turner grating monochromators in series, with an in-built stepper motor for wavelength scanning The double monochromator has two 69mm x 69mm kinematically mounted plain diffraction gratings with 1200 lines/mm The instrument is fitted with continuously variable, 20 mm high, bilateral slits, variable between 10μm and 5mm by a direct reading micrometer screw gauge The dispersion is 2 7nm per mm of slit width The use of a double monochromator is important because it is very efficient at rejecting scattered light and therefore allows detection of very low signals

3 4 Fluorescence Detection

This detection system for the collected fluorescence consists of a photomultiplier tube, a photon counter, a personal computer and the associated software

3 4 1 The Photomutiplier Tube

The detector used is a Hamamatsu R1527P photomultiplier tube (PMT) which is specifically designed for photon counting This tube has a low noise bialkali (Sb-Rb-Cs) photocathode, with a spectral range of 185nm to 680nm, a peak sensitivity at 375nm and a UV glass window It has a gain of 5 x 10^6, a rise time of 2 2ns and a dark count of 3 counts per second at room temperature This last feature makes it particularly suitable for photon counting The PMT has a Hamamatsu C956-06 base with a built-in voltage divider also designed specifically for photon counting The PMT is located in a light tight housing which is attached to the rear of the double monochromator so that the collected fluorescence can strike it through the exit slit Because of its sensitivity great care had to be taken to ensure no stray light could reach the PMT and cause interference for detection of low count rates

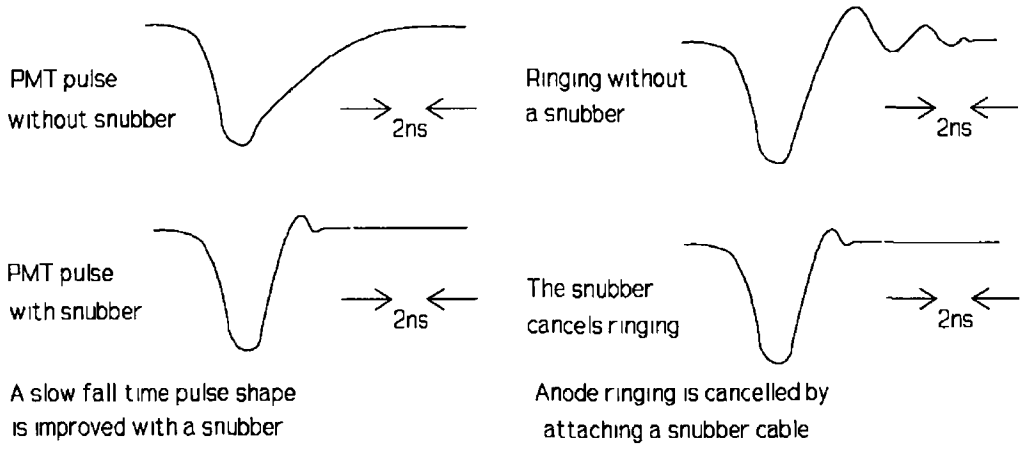

Figure 3 7 The effects of using a snubber cable

3 4 2 The Photon Counting Unit

The photon counting unit is a SR400 Stanford Research Systems Gated Photon Counter The photon counter is controlled by a personal computer with the appropriate software The PMT is connected to the photon counter with a snubbing device connected in parallel Snubbing refers to the practice of adding a network to the anode of the PMT to improve the shape of the output pulse for photon counting applications The 'network' in this case is a ten inch length of fifty ohm coaxial cable terminated with a variable resistor of maximum resistance of 50Ω If the variable resistor is adjusted to a value of below 50Ω some portion of the signal will be inverted, reflected back toward the anode and delayed by the round trip in the snubber cable This reflected signal will cancel out some of the signal from the PMT Snubbing prevents the build-up of charge on the signal cable from the PMT and hence damage to the photon counter, improves the resolution of the signal pulse by reducing its fall-time and cancels out 'ringing' that can cause multiple counts from a single photon (Fig 3 7)

The system was set up for photon counting by first adjusting the fifty ohm variable resistor of the 'snubber' to give the sharpest signal pulse The magnitude (in mV) of the pulses caused by noise and the photons detected was examined and this pulse height distribution (Fig 3 8) was used to set the discrimination level on the

photon counter so as to exclude noise pulses from being counted.

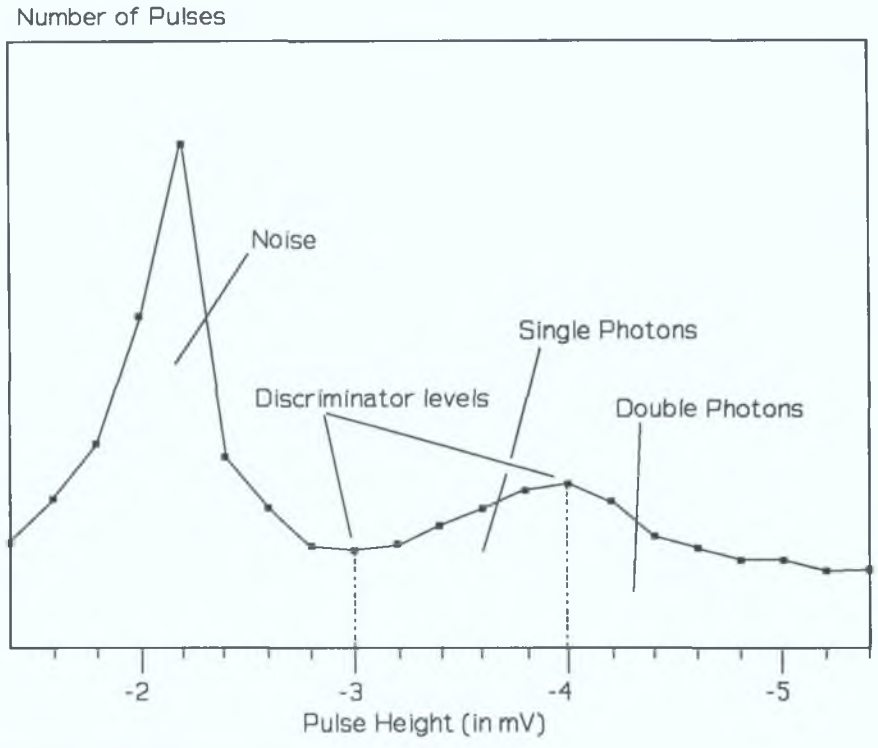

Figure 3.8 The PMT pulse height distribution

This discriminator level resulted in an average dark count of three counts per second. The average dark count is susceptible to some mild fluctuations due to temperature and was never observed to go above an average of five counts per second.

3.4.3 The Personal Computer

A Quattro 8088, 12MHz, IBM-compatible personal computer was used to control the photon counter and to store data from it. It was also used for recording the pulse height distribution and emission spectra.

3.5 Conclusion

This laboratory system is capable of versatile spectroscopic examination of a sample using fluorescence at a distance from the instrumentation. The wavelength of the exciting light may be changed by using a different bandpass filter with the deuterium lamp. The probe head was designed specifically for the most efficient collection of fluorescence. The fluorescence detection section of this system has been specifically designed for the detection of low fluorescence levels with good noise reduction. The

system is capable of recording emission spectra or can be used for quantative measurements with excitation and collection at specific wavelengths

Chapter 4

Preliminary Results

4.1 Introduction

In this chapter the fluorescent properties of slurries are reported The relationship between the concentration of three types of slurry (poultry, pig and cattle) and the resultant fluorescence signal was examined using the laboratory based system described in chapter 3 A detailed investigation of the excitation and emission characteristics of each of the types of slurry was undertaken in order to identify the optimum wavelengths for measuring concentration using fluorescence

4 2 Samples

As animal slurries represent perhaps the single most important problem this work could address in the Irish context it was decided to tailor the instrument specifically for their detection and the determination of their concentration Therefore samples of raw slurries of different origin were obtained from the Teagasc agricultural research station at Johnstown Castle, Wexford These samples were used as a means of characterising the instrument and investigating the fluorescence properties of slurries Samples of the other varieties of waste products were also obtained to investigate if this work could be beneficial in determining new methods for their detection In addition water industry calibrated samples of known TOC concentration but of unknown origin were investigated

4 3 Experimental Results

It was decided to confirm that slurries exhibit fluorescence and that a strong correlation exists between fluorescence and slurry concentration as suggested by Lakshman [17] The experimental system used was that described in Chapter 3

The optimum excitation wavelength suggested by Lakshman was 360nm

and this was isolated using a bandpass filter of full width half maximum of 10nm Measurements were made in a darkened room and background light was eliminated by covering the sample and probe head with a black cloth The probe head was placed in a sample of tap water and the double monochromator scanned across the relevant spectral region The probe head was then placed in a mixture of water and slurry and the double monochromator scanned across the same region A comparison of two typical spectra is shown in Fig 4 1 and these results indicated the strong slurry fluorescence in the 400nm to 600nm region The wavelength of maximum fluorescence is 425nm

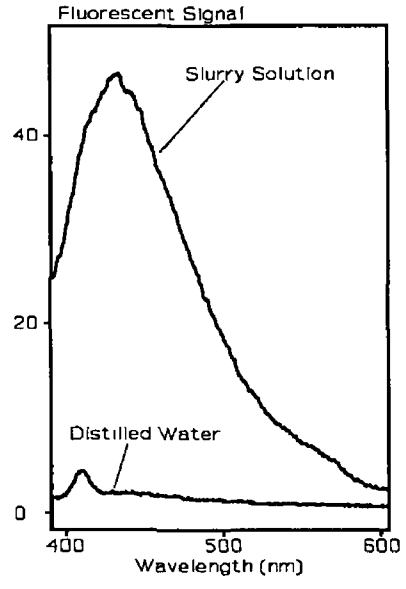

Figure 4 1

It was decided to investigate the relationship between fluorescence signal and slurry concentration for pig, poultry and cattle slurries respectively The procedure for taking measurements was as follows a stock solution of a slurry was made up in distilled water and from this stock solution a series of samples of known slurry concentration were made up in distilled water Each solution was placed in a glass beaker and the probe head placed with the tip below the surface of the liquid Background light contributions were minimised The double monochromator was set at 425nm with a slit width of 2mm giving a bandpass of 5 4nm The fluorescence signal for each concentration in the series was measured by taking twelve 100 second scans The fluorescence signal of a sample of water was taken before and after each slurry solution in order to take account of interferences such as background light and

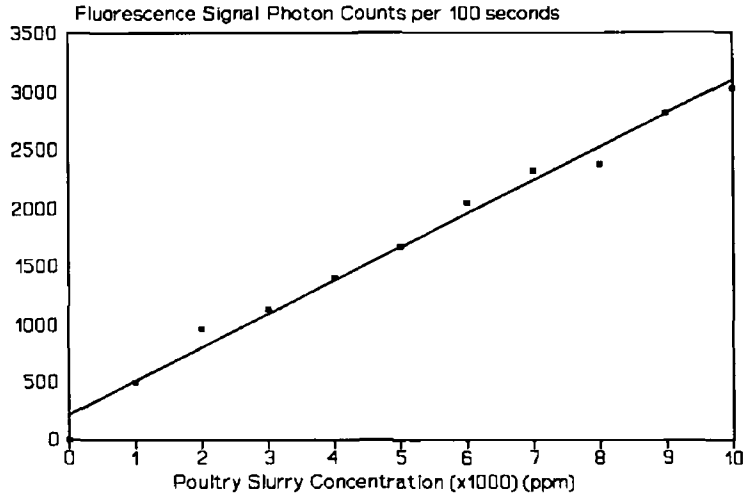

Figure 4 2 Fluorescence signal vs pig slurry solution concentration

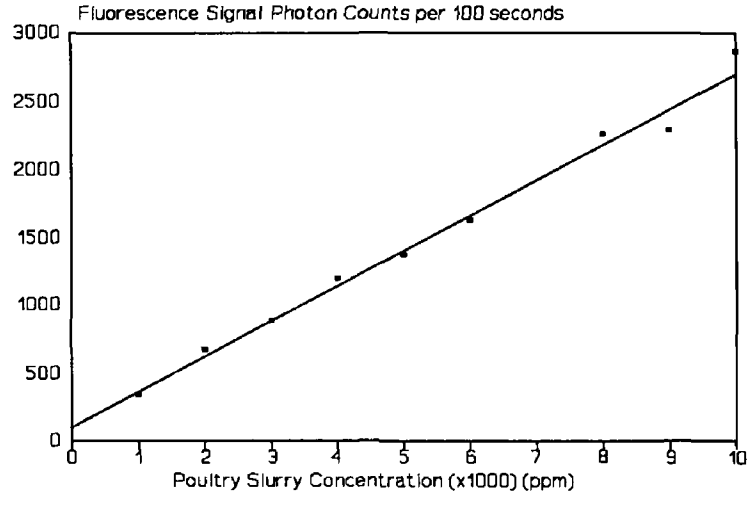

Figure 4 3 Fluorescence signal vs poultry slurry solution concentration

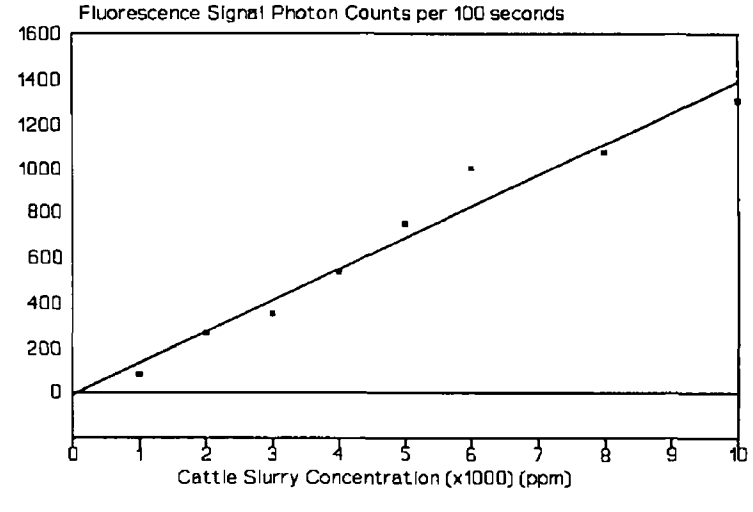

Figure 4 4 Fluorescence signal vs cattle slurry solution concentration

temperature induced fluctuations in signal from the PMT The fluorescent signal plotted was the averaged solution signal minus the average of the water signal before and after This procedure was repeated for each type of slurry A plot of fluorescence signal against slurry concentration as shown in Figures 4 2, 4 3 and 4 4 indicates a linear relationship over the range of the concentrations examined for each sample type which does not change sigmfigantly over time

4.4 Excitation and Emission Spectra

While the above data indicated the potential of monitoring animal waste contaminants via fluorescence using the excitation wavelength reported by Lakshman [17] it was decided to investigate the excitation and emission spectra of the slurries to see if more efficient excitation and emission wavelengths for the spectrofluorimetric concentration determination of slurries could be identified

The excitation and emission spectra of the slurries were obtained using a Perkin Elmer LS-50 Spectrofluorimeter Dilutions of the raw slurries in water were used in this study to imitate the addition of slurries to river water and also because raw slurry is essentially opaque These dilutions were not filtered or treated in any other manner as the instrument is intended for field type examinations of natural waterways where no such pre-treatment would be performed For each type of slurry a dilution to 10g of slurry per litre of water was used All spectra were recorded under the same conditions Quartz cuvettes were used as excitation and emission spectra extended into the ultra-violet region

Excitation spectra for emission wavelengths from 320nm to 440nm at intervals of 20nm and emission spectra for excitation wavelengths from 200nm to 380nm at 20nm intervals were obtained for each type of slurry These spectra indicated that there was a number of excitation wavelengths for which useful levels of fluorescence could be observed

Poultry and pig slurries exhibited similar excitation and emission spectra with poultry slurry yielding more fluorescence Excitation spectra for both types of slurries indicated that fluorescence could be obtained for excitation wavelengths in the regions of 220nm (Fig 4 5), 280nm (Fig 4 5) and 340nm (Fig 4 6) Emission spectra for both type of slurries confirmed that 220nm, 280nm and

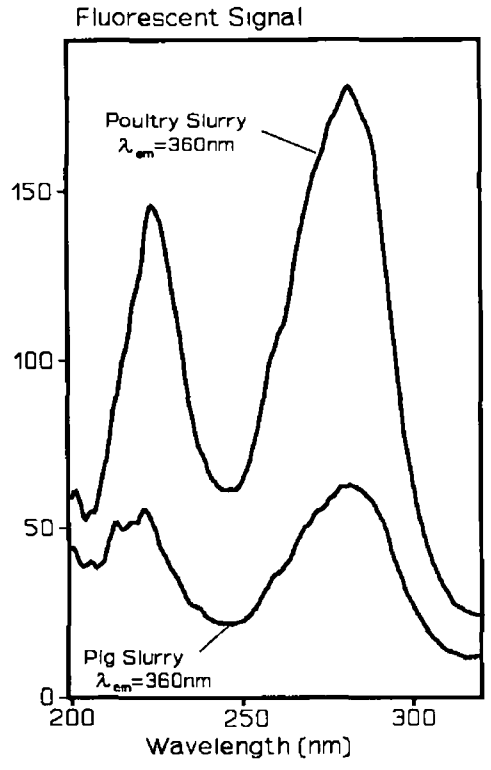

Figure 4 5 Excitation spectra of pig and poultry slurries

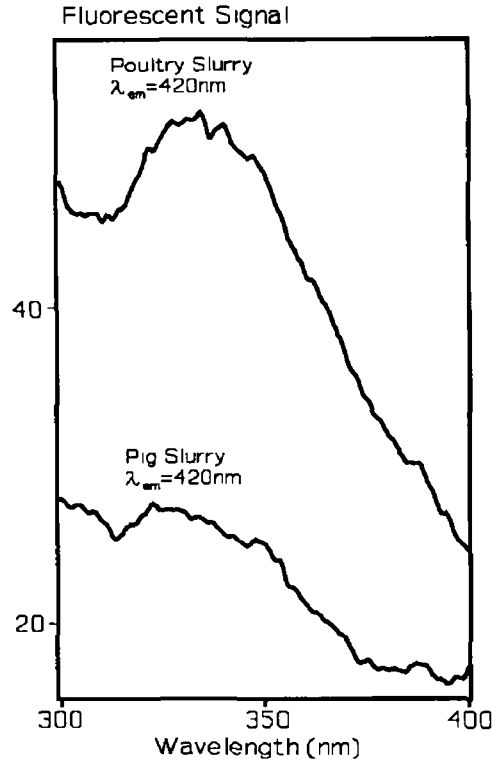

Figure 4 6 Excitation spectra of pig and poultry slurries

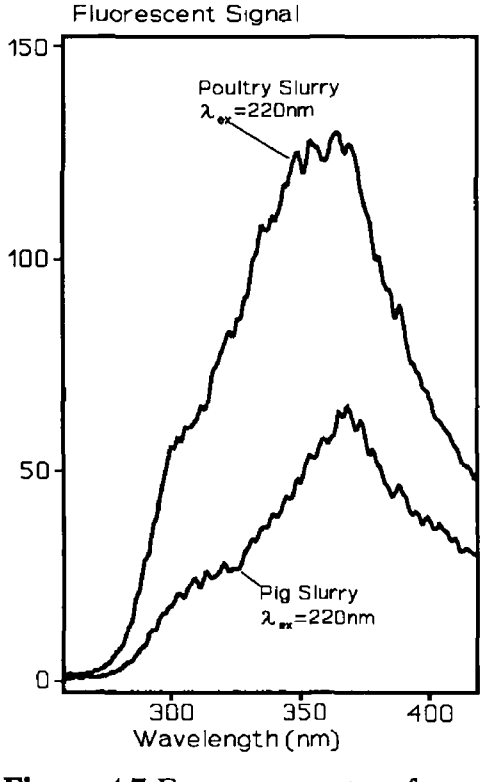

Figure 4 7 Emission spectra of pig and poultry slurries

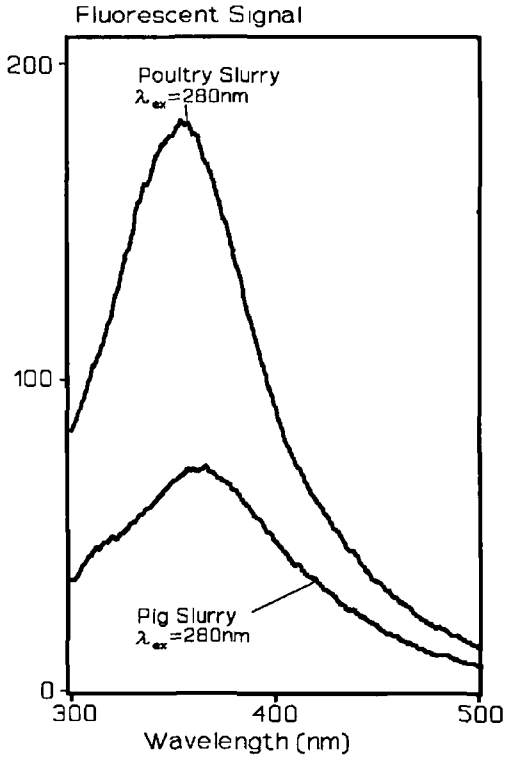

Figure 4 8 Emission spectra of pig and poultry slurries

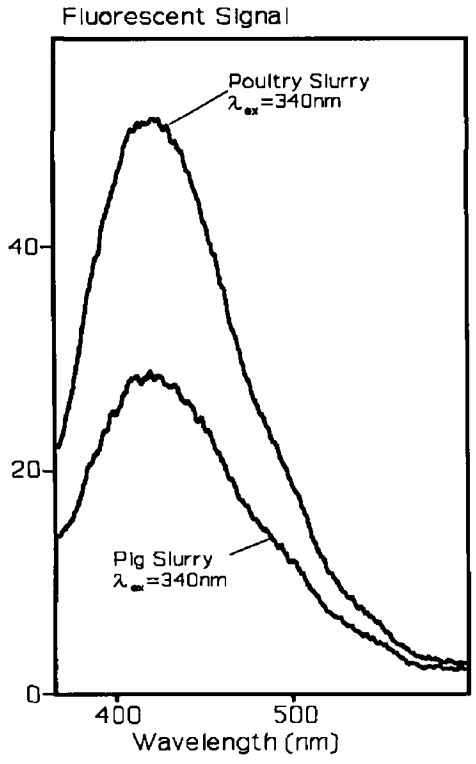

Figure 4.9 Emission spectra of pig and poultry slurries

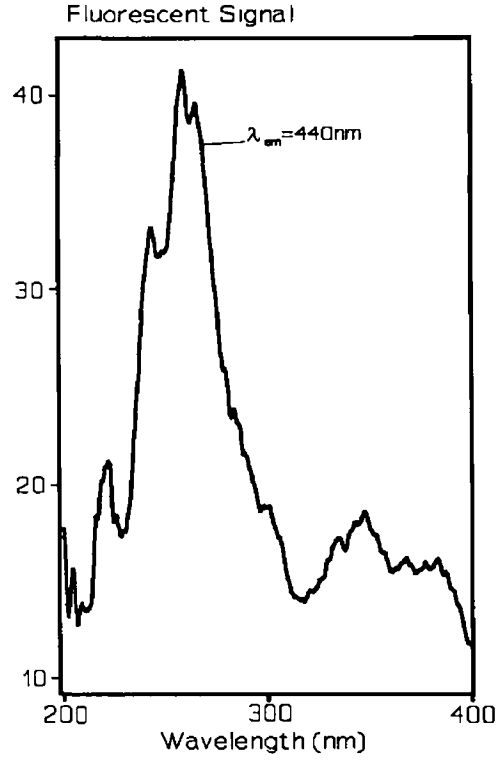

Figure 4 10 Excitation spectrum of a cattle slurry

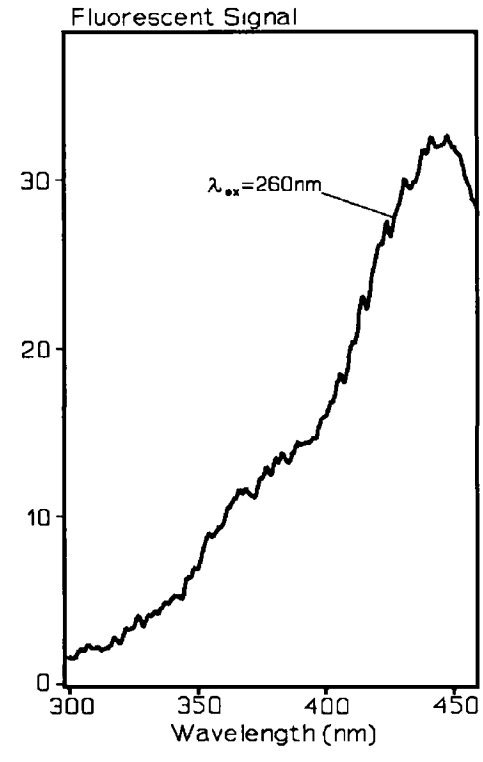

Figure 4 11 Emission spectrum of a cattle slurry

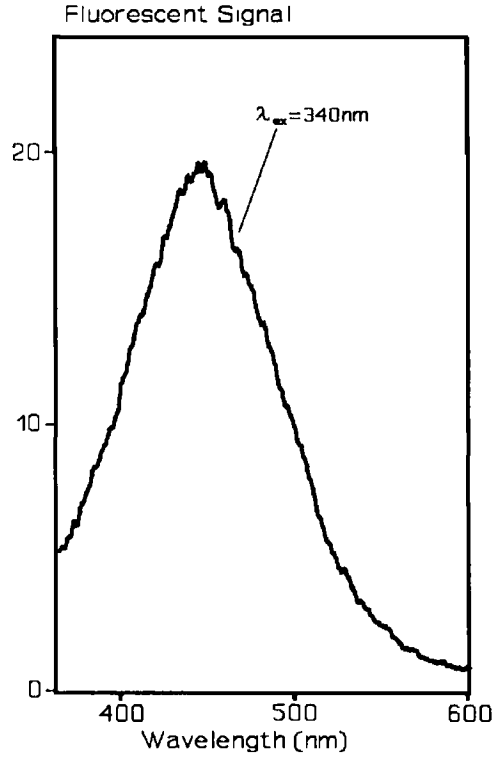

Figure 4 12 Emission spectrum of a cattle slurry

340nm were the regions of most interest and indicated that excitation at these wavelengths led to fluorescence with maximum emission in the regions of 360nm (Fig 4 7), 360nm (Fig 4 8)and 420nm (Fig 4 9), respectively A comparison of the relative intensities of the fluorescent signals indicates that excitation at 280nm and fluorescence collection at 360nm (Fig 4 8) would be the most efficient method for measuring slurry concentration Excitation at 220nm generates slightly less fluorescence at 360nm but both generate considerably more fluorescence signal than excitation at 340nm with collection at 420nm

Excitation and emission spectra for cattle slurries were obtained by the same procedures Excitation spectra indicated that useful levels of fluorescence could be obtained for excitation at 260nm and 340nm (Fig 4 10) Emission spectra indicated maximum emission in the region of 440nm for excitation wavelengths of 260nm (Fig 4 11) and 340nm (Fig 4 12) with excitation at 260nm yielding greater fluorescence

4 4 1 Other Potential Applications

Although the main focus of this work was animal slurries other organically produced waste products that could be found in natural waters and constitute a health hazard (such as silage and sewage) were investigated

Samples of silage effluent and sewage influent and effluent from a treatment plant were obtained Excitation and emission spectra were obtained for these samples using the same procedures and instruments as for the slurries These spectra indicated that these substances are capable of fluorescence and suggested that fluorescence could be used as a means of detecting their presence and determining their concentration

Excitation spectra for the silage effluent (Fig 4 13) suggested a number of different excitation wavelengths which were in the regions of 220nm, 280nm, 330-360nm and 390nm Emission spectra (Fig 4 14) suggested that excitation at 280nm and 340nm with maximum emission in the regions of 390nm and 440nm respectively would be most useful with excitation at 340nm yielding the most fluorescence

Sewage influent and effluent exhibited very similar excitation and emission spectra with only slight differences in intensity Excitation spectra indicated

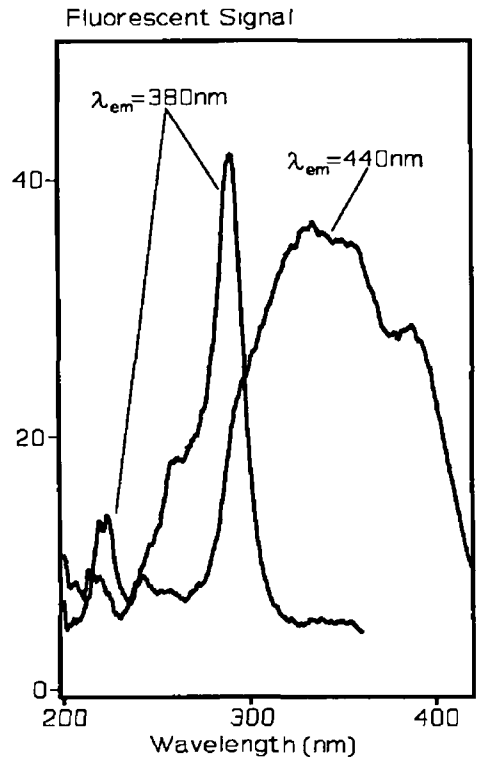

Figure 4 13 Excitation spectra for a silage effluent

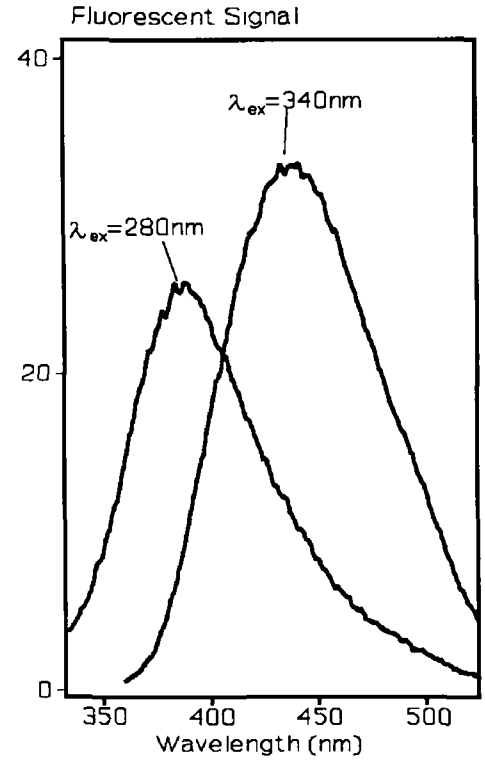

Figure 4 14 Emission spectra of a silage effluent

Figure 4 15 Excitation spectrum of a sewage effluent

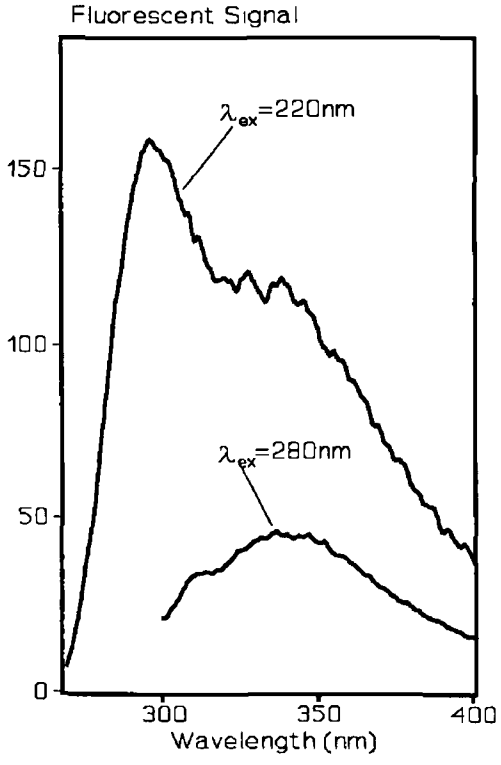

Figure 4 16 Emission spectra of a sewage effluent

that fluorescence could be obtained for excitation in the regions of 220nm and 280nm (Fig 4 15) Emission spectra (Fig 4 16) indicated that excitation at 220nm had maximum emission in the regions of 300nm and 340nm and excitation at 280nm had maximum emission in the region of 340nm with excitation at 220nm yielding greater fluorescence

This information suggests that the dedicated system could be utilised in the detection and concentration determination of these substances if the excitation and collection wavelengths were suitably chosen Indeed this system could be adapted for the detection of any substance in a non-opaque liquid that exhibits sufficient levels of fluorescence and for which suitable excitation and collection wavelengths could be identified

4 5 Total Organic Carbon

As the original work by Lakshman [17] had suggested a correlation between the fluorescence of organic waste and TOC it was decided to investigate this in our system A series of solutions of known TOC concentration but of unknown origin was obtained via City University London from Resource Consultants Cambridge Using the information gained from the excitation and emission spectra the fluorescent signal was measured for each of the concentrations The fluorescent signal for each of the concentrations was measured for each pair of excitation and collection wavelengths shown in the table below

Excitation Wavelength (nm)	Collection Wavelength (nm)
280	360
340	420
360	425

A Perkin-Elmer LS-50 Spectrofluorimeter was used for excitation at 280nm and 340nm For excitation at 360nm the laboratory based system detailed in Chapter 3 was

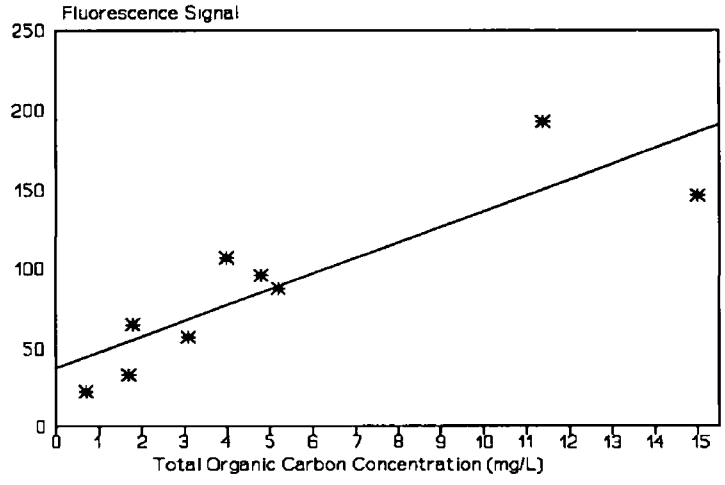

Figure 4 17 Fluorescence signal vs TOC concentration for excitation at 280nm and collection at 360nm

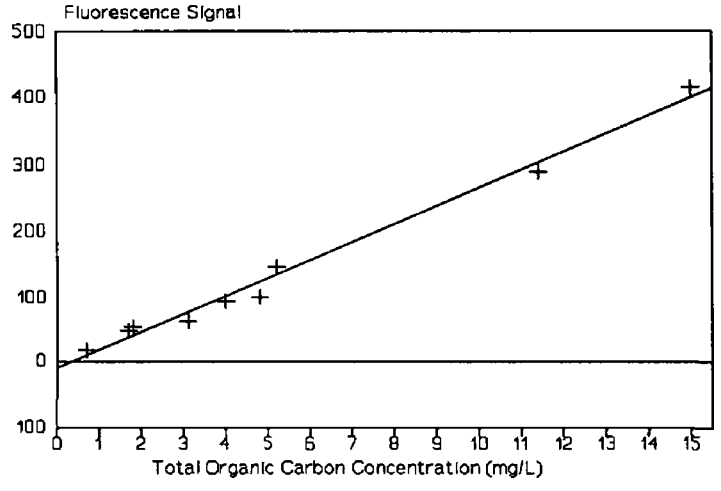

Figure 4 18 Fluorescence signal vs TOC concentration for excitation at 340nm and collection at 420nm

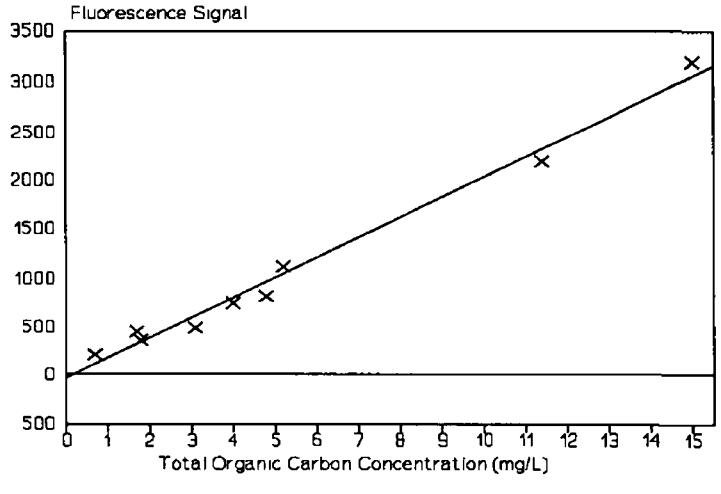

Figure 4 19 Fluorescence signal vs TOC concentration for excitation at 360nm and collection at 425nm

used Plots of fluorescent signal against TOC concentration for each of the excitation and emission pairs are shown in Figures 4 17, 4 18 and 4 19 These plots indicate that an approximate linear relationship exists between the two, with the degree of correlation dependent critically on the pair of wavelengths used An examination of these plots showed that the plots for excitation in the regions of 280nm, 340nm and 360nm had correlation co-efficients of 0 876, 0 994 and 0 993, respectively This indicated that excitation in the 340nm or 360nm region would be more appropriate for the measurement of TOC concentration than excitation in the region of 280nm

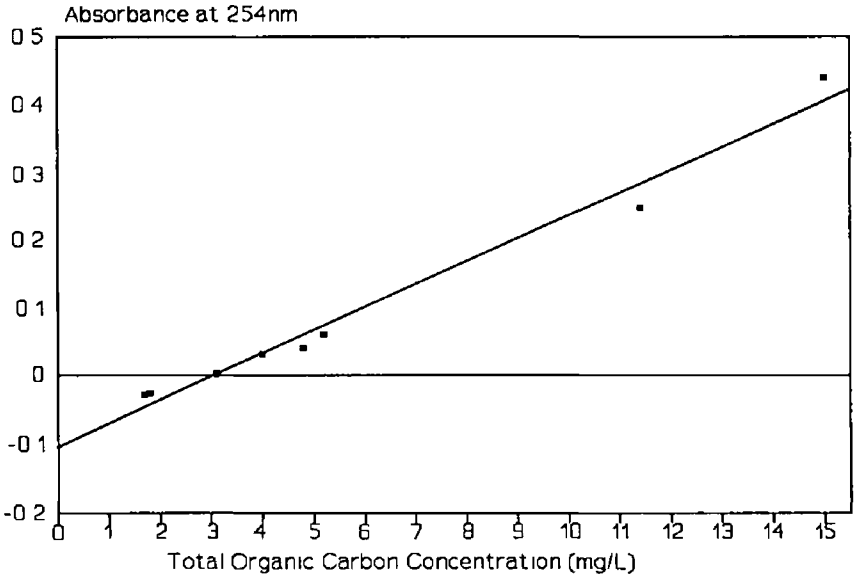

Figure 4 20 Absorbance at 254nm vs TOC cencentration

4.6 Absorbance at 254nm

A field based optical instrument for the determination of TOC concentration presently in use is the OPM 500, manufactured by pHox Systems Ltd, U K This instrument is based on the measurement of absorbance at 254nm corrected for scattering at a nonabsorbing visible wavelength In order to investigate if determination of TOC concentration by fluorescence displayed a correlation with this field based method the absorbance at 254nm was measured on a Hewlett-Packard 8452A Spectrophotometer for each of the solutions of known TOC A plot of the absorbance at 254nm against TOC concentration shown in Fig 4 14 confirmed the relationship between absorbance at 254nm and TOC concentration A plot of fluorescence signal against the corresponding absorbance at 254nm as shown in Fig 4 15 indicated a strong

correlation (correlation co-efficient 0 995) between fluorescence signal and absorbance at 254nm

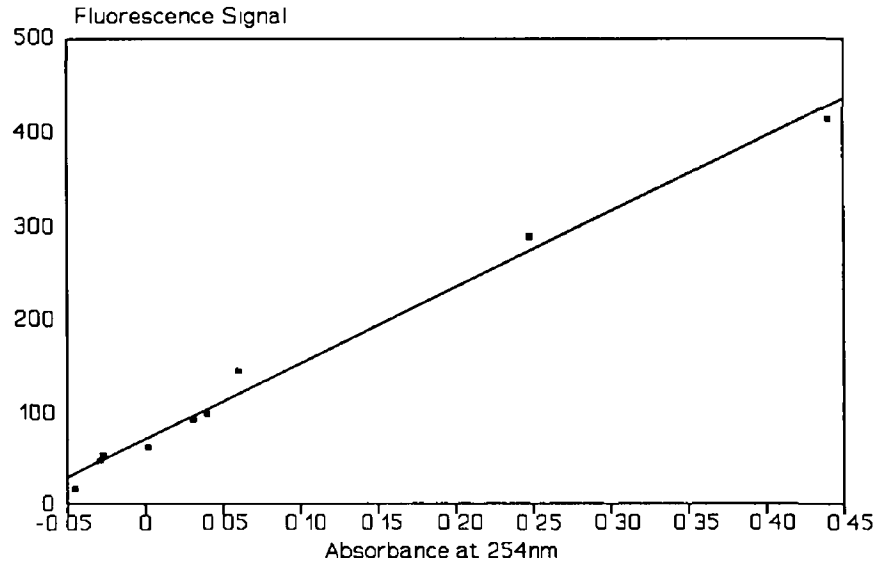

Figure 4 21 Fluorescence signal for excitation at 340nm and collection at 420nm vs absorbance at 254nm

4.7 Conclusions

The results presented in this chapter indicate that fluorescence can be reliably and repeatedly produced from slurries and that this fluorescence can be used to determine the concentration of a slurry in water A linear relationship exists between fluorescence signal and slurry concentration over the concentrations examined The excitation and emission spectra recorded for the slurries indicate that there is more than one excitation wavelength for which useful levels of fluorescence can be obtained From the plot of fluorescence signal against TOC concentration it is clear that TOC concentration can be measured using fluorescence The strong correlation between absorbance at 254nm and fluorescence suggests agreement with an established field based method of determining TOC concentration Based on the information presented here it was decided that the optimum wavelengths for a dedicated TOC monitoring system would be an excitation wavelength of 340nm and a collection wavelength of 420nm

Chapter 5

The Dedicated System

5 1 Introduction

As a result of the work outlined in Chapters 3 and 4 it was decided to construct a more dedicated version of the laboratory-based system described in Chapter 3 The principal objectives of constucting a more dedicated system were to increase sensitivity and make the system more portable

It was intended that this dedicated system would be closer to a system that could be used for field applications than was the laboratory based system Therefore the number and size of the components was reduced with the more expensive and versatile components being replaced by more rugged, specific equivalent components A schematic diagram of the dedicated system is shown in Figure 5 1 The system comprises a light source with an excitation filter, launch optics, an optical fibre carrying the light to the probe head, six collection fibres, fluorescence collection optics with an emission filter, a photomultiplier tube, a photon counting unit, and a personal computer

The system essentially operates identically to the laboratory based system, the appropriate excitation wavelength band is isolated from the light from a Xenon lamp using a narrow band filter The light is then focused into a 1 5m length of optical fibre The distal end of this fibre is located along the central axis of the probe head and produces fluorescence in the sample The design of the probe head is discussed in more detail in section 5 3 The fluorescence is then collected by six 1 5m lengths of optical fibre The collected fluorescence is collimated by a convex lens, the preferred collection wavelength band is isolated by a bandpass filter and a second convex lens focuses the fluorescence into the photomultiplier tube (P M T) The signal is quantified by a photon counting unit whose operation is controlled by a personal computer

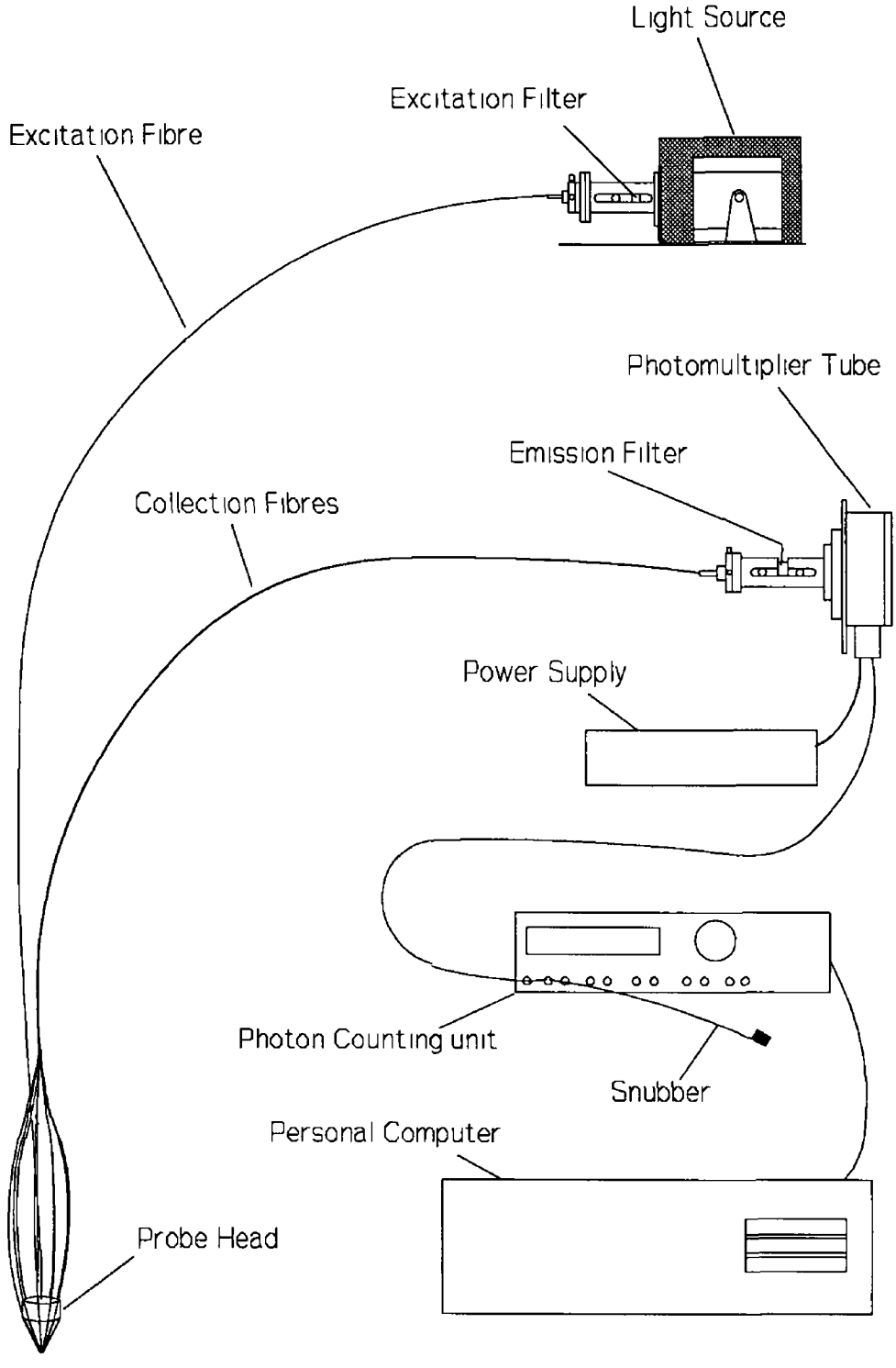

Figure 5 1 A schematic diagram of the dedicated system

The performance of the system may be divided into three sections fluorescence production, fluoresence collection and fluorescence detection

5 2 Fluorescence Production

The first part of the system is dedicated to the production of fluorescence in the sample under examination This part of the system includes a light source, launch optics and the fibre that carries the exciting light to the sample

5.2.1 Light Source

The light source is a Cermax Compact Source 75W Xenon Arc Lamp in its own air cooled housing This light source was chosen to replace the one used in the laboratory-based system because of its higher total output power and because its spectrum (Fig 5 2) is more suitable for the preferred excitation wavelengths A feature of the lamp housing is that it is specially designed to collimate the light from the lamp The light was launched into the exciting fibre by a quartz lens of focal length 40mm The preferred excitation wavelength is isolated by an appropriate bandpass

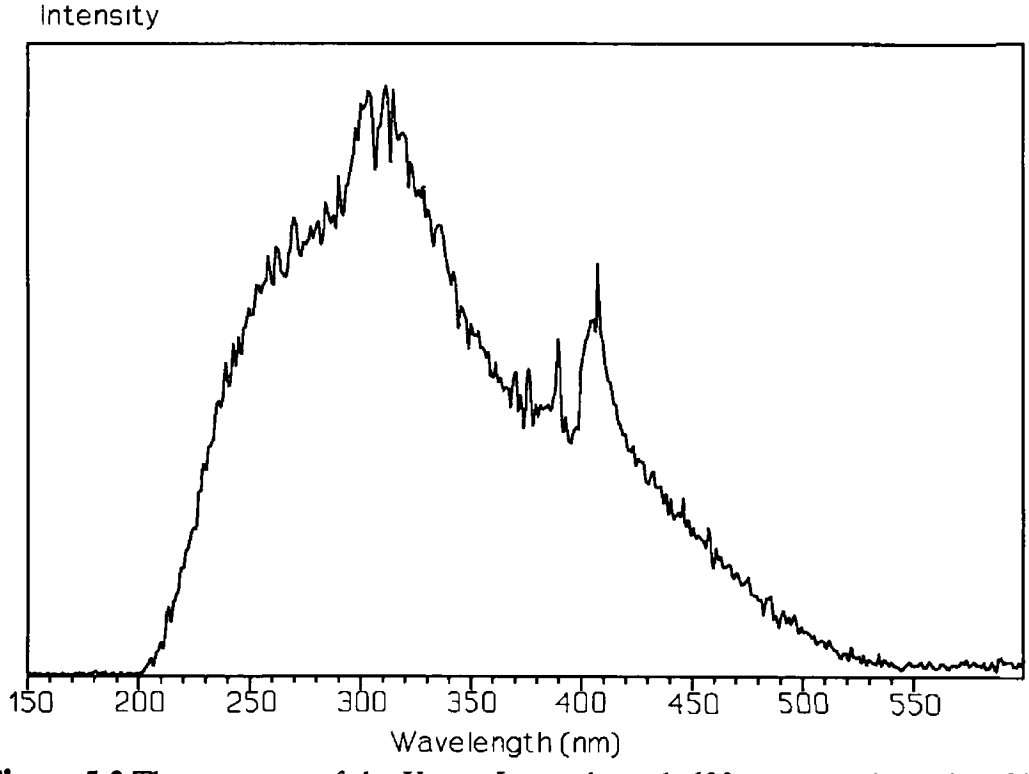

Figure 5 2 The spectrum of the Xenon Lamp through 600μm core silica silica fibre

filter between the housing and the lens The bandpass filter and the quartz lens were both placed in a carriage in an attachment to the lamp housing The position can be adjusted along the carriage axis The coupling of the light is optimised by adjusting the fibre position using an X-Y-Z positioner The fibre used for excitation is a 1 5m length of Fibreguide Industries, Superguide G, Tefzel coated, all-silica fibre (silica core, silica cladding) with a core diameter of 600μm The exciting fibre is located along the central axis of the probe head

5 3 Fluorescence Collection

This section of the system is dedicated to the collection of the fluorescence produced at the probe head This section of the system consists of the probe head, the collection fibres, two convex lenses and a bandpass filter

5 3.1 Design of the Probe Head

The reasons for the design of the novel sensor head used here are detailed in Chapter 3 The probe head design was adapted for use with the fibres used in this dedicated

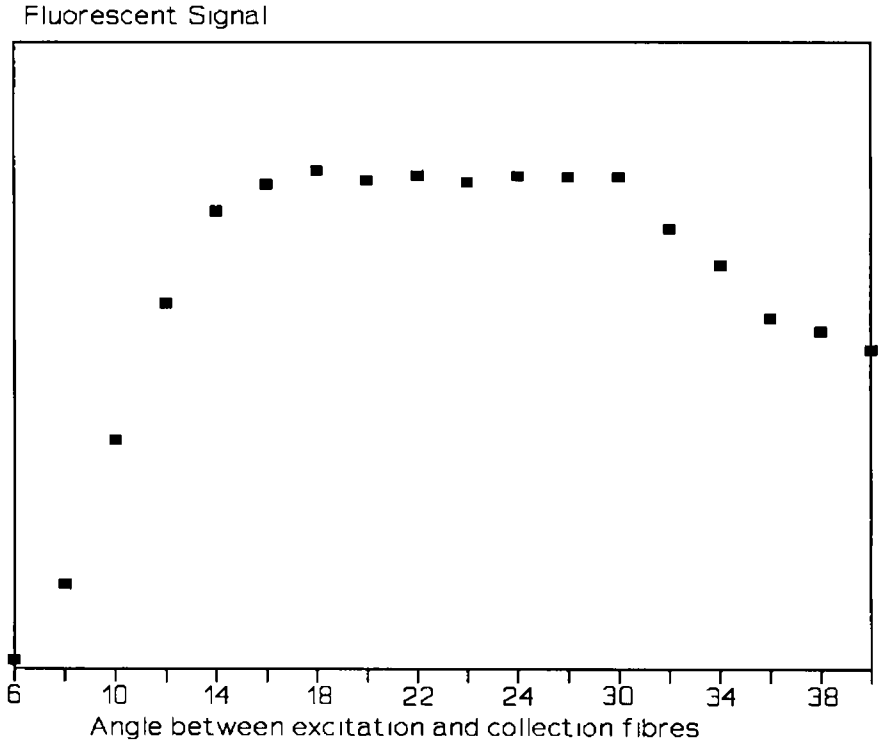

Figure 5 3 Fluorescence signal vs the angle between excitation and emission fibres

system and is very similiar to the one used in the laboratory-based system. The optimum angle between the excitation fibre and the collection fibre is different because the core diameters and numerical apertures of the fibres used are different. The procedure described earlier in Chapter 3 was used to determine the optimum angle for the probe head for the dedicated system. A plot of the measured fluorescence signal versus the angle between an exciting fibre and a collection fibre is shown in Fig.5.3 and indicates that an interfibre angle of between 16° and 30° would maximise the collection effiency with the optimum angle being 18°. The probe head was constructed on the basis of these experimental results. It consists of a metal cylinder with a cone at one end and a hole of suitable diameter through its centre for the exciting fibre. The half-angle of the cone was machined to be 18° to the central axis of the cylinder in order to maximise collection effiency. The maximum number of collection fibres which can be arrayed around the exciting fibre is governed by the diameter of the fibre used. In the case of the fibres used here six fibres could be accommodated. Six grooves were cut symmetrically into the side of the cone to guide the collection fibres. The collection fibres are fixed into the grooves of the probe head and their collecting ends positioned as close as possible to the end of the exciting fibre. This probe head arrangement was used in all experiments using the dedicated system.

5.3.2 Fibres

Two different types of fibre were used in the dedicated system. All-silica fibre of core diameter 600μm was used to transmit the exciting light to the probe head. This fibre was used because the preferred excitation wavelengths are in the ultra-violet region and it has excellent transmission characteristics in that region (approximately 0.5dB/m attenuation for the preferred excitation wavelengths). The fibre used for the collection fibres was plastic clad silica of core diameter 600μm. Although this fibre does not have the high UV transmission of the all-silica fibre it was used because it has low attenuation in the region of the fluorescence and it is less expensive than all-silica fibre. Both the exciting and the collection fibres have larger core diameters than those used in the laboratory based system. This was to increase the overall fluorescence signal and the overall fluorescence collection efficiency.

5 3 3 Fluorescence delivery

The six collection fibres from the probe head were arrayed in a rectangular format to match the profile of the entrance window to the photomultiplier tube (P M T) housing The light from the collection fibres was collimated by a convex lens of focal length 20mm The wavelength of maximum intensity from the collected fluorescence was then isolated by a bandpass filter with a full-width half maximum of 10nm The resultant light was then focussed into the P M T housing by a second convex lens of focal length 40mm The housing containing the two lenses and the bandpass filter was designed so that the bandpass filter can be changed easily if necessary

5.4 Fluorescence Detection

This detection system for the collected fluorescence is identical to the one used in the laboratory based system which is described in detail in Chapter 3 It consisted of a photomultiplier tube (P M T), a photon counting unit, a personal computer and the associated software to control the photon counting unit

5 5 Performance of the system

It was necessary to characterise the dedicated system in order to establish that it could carry out the function for which it was constructed and to identify the advantages it offers over the laboratory based system

It was decided to duplicate an experiment performed with the laboratory based system to compare the performance of the two systems The excitation wavelength used was 340nm and the collection wavelength was 420nm as suggested by the results in Chapter 4 The fluorescence signal from a series of solutions of known slurry concentration was measured The resulting graph of fluorescence signal vs slurry concentration is shown in Fig 5 4

Initial measurements indicated that the level of fluorescence signal was such that adequate measurements for differentiation between solutions could be made over smaller time intervals than were necessary for the laboratory based system The fluorescence signal graphed in Fig 5 4 is the average of one hundred 1 second scans From this graph the average increase in fluorescence signal for an addition of 1000ppm of poultry slurry was approximately 15000 photon counts per second This

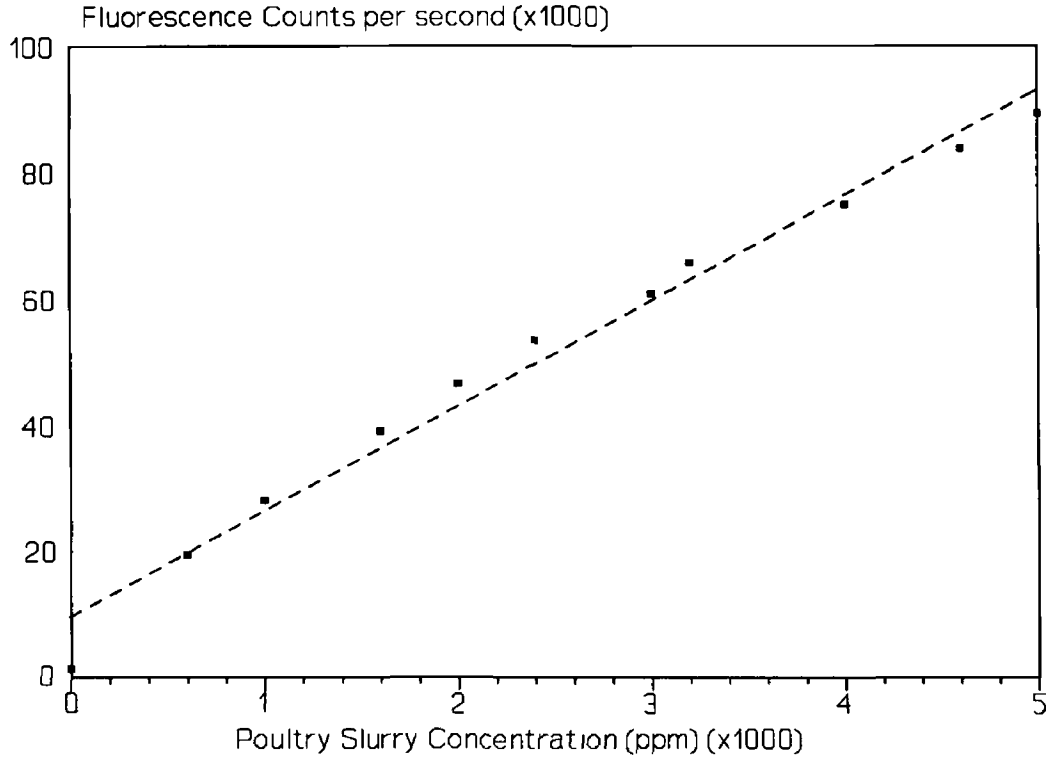

Figure 5 4 Fluorescence signal vs poultry slurry concentration

represents a signifigant improvement in the level of fluorescence signal as compared with the laboratory based system In that case, for an identical series of solutions, the average of six 100 second scans was required for adequate differentiation between solutions and the average increase in fluorescence signal for an addition of 1000ppm of poultry slurry was approximately 250 photon counts per hundred seconds

It was decided to investigate if this increase in fluorescence signal leads to a corresponding improvement in system performance parameters (such as the limit of detection and resolution) relative to the laboratory based system The probe head of the dedicated system was placed in 1 5 L of ultrapure water which was constantly stirred Consecutive additions of 1 5ml of a stock 10,000ppm(w/v) poultry slurry to the ultrapure water were made, each addition representing an increment of 10ppm in the slurry concentration For each addition fifty 1 second scans were made The resulting graph of fluorescence signal vs time is shown in Fig 5 5 A plot of the averaged fluorescent signal versus the poultry slurry concentration for the same measurements is shown in Fig 5 6 These graphs indicated that an addition of 10ppm of poultry slurry to distilled water can be easily detected This represents a signifigant improvement over the laboratory based system whose lower limit of detection was

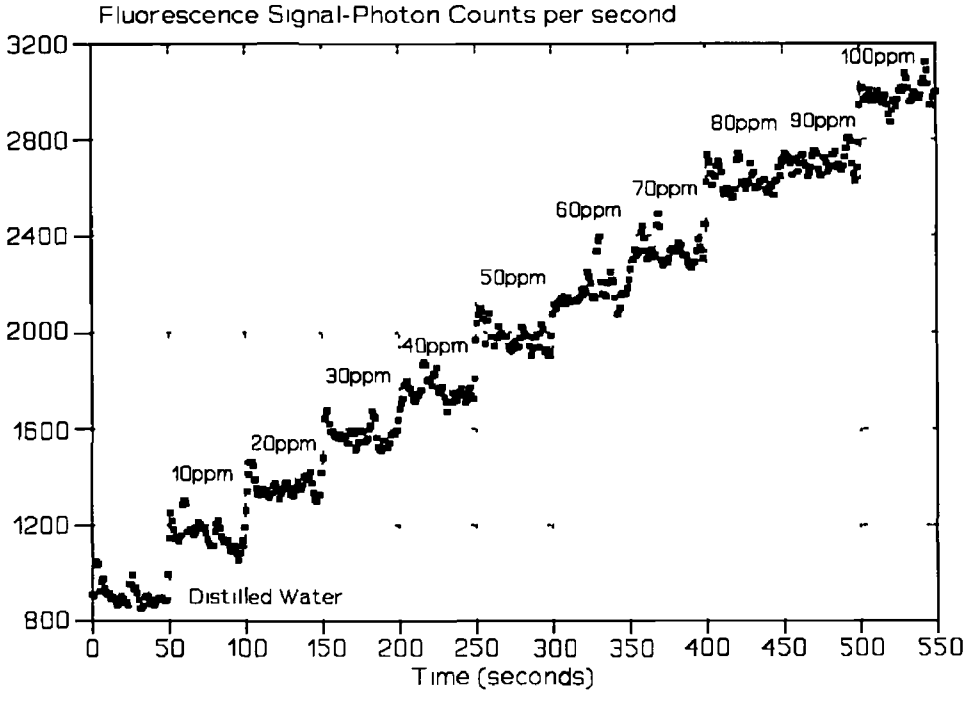

Figure 5 5 Fluorescence signal vs time for additions of 10ppm poultry slurry to distilled water every 50 seconds

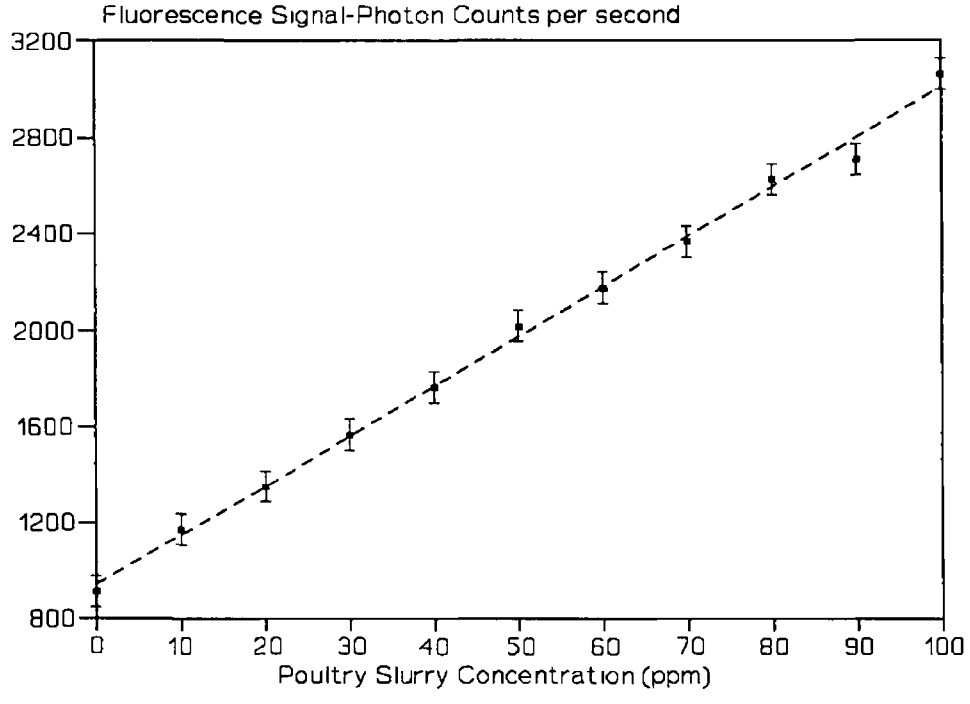

Figure 5 6 Average fluorescence signal vs poultry slurry concentration in ultrapure water

approximately 200ppm of poultry slurry in distilled water

It was decided to investigate if the system could detect the addition of slurry to a sample of actual river water and to determine the smallest addition that could be detected Water from a nearby river was collected The probe head was placed in 1 5 L of the river water which was constantly stirred The river water was not filtered or chemically treated in any way Additions of known quantities of a 10,000ppm(w/v) poultry slurry solution to the water were made until an adequate differentiation between additions could be made Two hundred 1 second scans were made for each addition The lower limit of detection was determined to be an addition of 100ppm of poultry slurry (Fig 5 7)

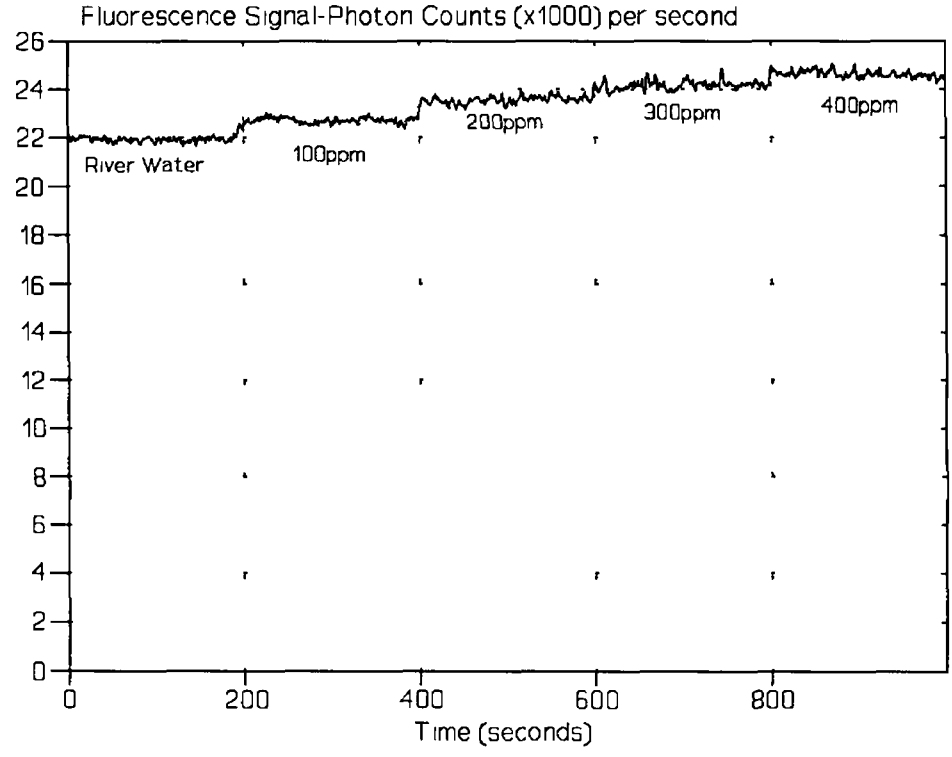

Figure 5.7 Fluorescence signal vs time for additions of 10ppm poultry slurry to river water every 50 seconds

The increase in the lower limit of detection observed for additions of poultry slurry to the river water sample was due to the high background count from the sample (approximately 21000 counts per second) and the slight opacity of the water

It was decided to investigate if a lower limit of detection could be achieved if the excitation and collection wavelengths were changed to yield more fluorescence specifically from a poultry slurry solution The excitation wavelength was

changed to 280nm and the collection wavelength was changed to 360nm as determined in Chapter 4 Additions of known quantities were added until adequate differentiation between additions could be made Fifty 1 second scans were made for each addition The lower limit of detection was determined to be an addition of 10ppm of poultry slurry (Fig 5 8)

These graphs indicated that the dedicated system has signifigant advantages over the laboratory based system in terms of lower limit of detection and the rate at measurements could be made They also indicated that the lower limit of detection for the system is dependent on the properties of the water in which the measurements are to be carried out This information also suggested that the sensitivity of the system to a specific pollutant could be improved if the excitation and collection wavelengths are chosen only for that pollutant

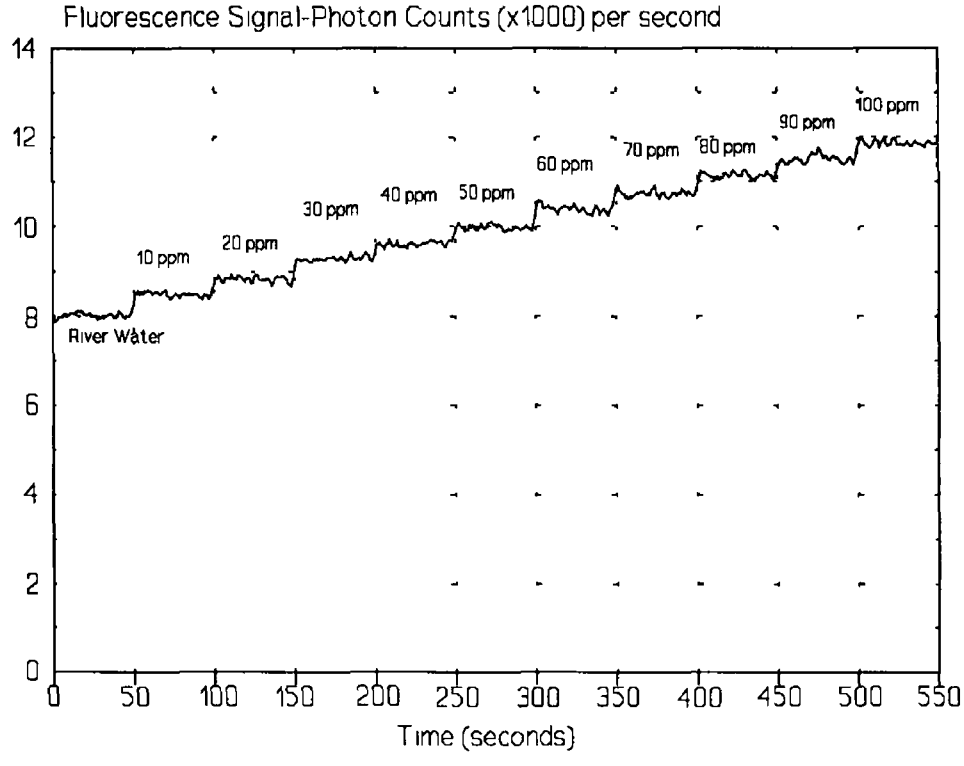

Figure 5 8 Averaged fluorescence signal vs poultry slurry concentration in river water

5 6 Conclusion

This dedicated system does not have the versatility of the laboratory based system for

spectroscopic examination of a sample using fluorescence at a distance from the instrumentation However, as specific excitation and emission wavelengths have already been identified this versatility is unnecessary It was felt that some flexibility in the dedicated system would be useful so it was designed so that the excitation and emission bandpass filters could be easily changed if required The dedicated system is more sensitive and allows more rapid measurement than the laboratory based system The superior performance of the dedicated system over the laboratory based system is due to the higher total output power of the Xenon lamp and the higher core diameter of the fibres used Thus the dedicated system is able to perform the quantative analysis performed by the laboratory based system but with improved speed and sensitivity Although the dedicated system could not be considered portable at this stage a number of its elements (e g the personal computer and photon counting unit) could be replaced by components which are considerably smaller and lighter In this manner an easily transportable system could be accomplished

Chapter 6

Conclusions/Future Work

6.1 Introduction

The ability to determine remotely the concentration of three types of slurry using an optical fibre based fluorescence measurement system has been demonstrated A laboratory based system based on the standard principles of fluorimetry and using a novel design for the probe head was designed, constructed and tested Experiments with this system to determine the dependence of fluorescence signal on slurry concentration indicated a linear relationship between the two and that fluorescence could be used to determine TOC concentration A table of the correlation co-efficients achieved for fluorescence signal against slurry concentration for each of the three types of slurries is presented below

Type of Slurry	Correlation Co-efficient
Pig	0 9959
Poultry	0 9906
Cattle	0 9817

A detailed investigation of the fluorescent properties of the slurries was undertaken using standard laboratory instruments This investigation suggested a number of possible pairs of excitation and collection wavelengths Experiments using these pairs of excitation and collection wavelengths and water industry calibrated water samples of known TOC concentration indicated that excitation at 340nm and collection at 420nm would be the most suitable for TOC determination A table of the correlation

co-efficients achieved for the fluorescence signal, obtained using these pairs of excitation and collection wavlengths, against TOC concentration is presented below

Excitation Wavelength (nm)	Collection Wavelength (nm)	Correlation Co-efficient
280	360	0 876
340	420	0 994

Based on the information gained from the laboratory based system and the investigation of the fluorescent properties of the slurries a more dedicated system was designed, constructed and tested The dedicated system is capable of high sensitivity, resolution and repeatability Experiments indicated that it could detect additions of 10ppm of a poultry slurry into water with a correlation co-efficient for fluorescence signal against slurry concentration of 0 999 The dedicated system is capable of detecting small changes m the TOC concentration which is in line with the relevant EC directive [14]

Characterisation of the dedicated system revealed areas where the design would need modification before a more portable, versatile and perhaps commercial sensor is obtained

(1) The light source The light source in the dedicated system is a 75W xenon lamp whose spectrum extends from approximately 230nm to 460nm A light source of a lower total output power could be used to replace the xenon lamp Although there be a loss of some sensitivity such a lamp would probably be more compact, more portable, less expensive and require less power than the present lamp

(2) The probe head The present probe head design might be susceptible to interference by daylight as the preferred collection wavelength is in the visible and lock-in techniques would have to be used to take account of the background Modulation of the source and the detection system at that modulated frequency is also a possibility

(3) The photomultiplier tube The PMT in use at present is specially designed for the purpose of photon counting and is extremely sensitive Smaller and more robust

PMTs are available One of these could be used to replace the existing one at the loss of some sensitivity though this would not be a serious problem in light of the E C directive [14]

(4) The photon counting unit The photon counting unit in use in the dedicated system is a highly versatile and expensive photon counter and only a limited use of its capabilites is made Simpler, modular photon counting units are available (e g Hamamatsu) which could be used to perform the functions of the present photon counting unit

(5) The personal computer At present the personal computer is only used as a data logging device for the photon counting unit and this function could be performed by a single board computer

All characterisation of the dedicated system has been done in the laboratory and if its potential for field use is to be properly assessed field trials would have to be carried out These would investigate problems such as stability and surface fouling of immersed fibre surfaces during prolonged exposure The stability of the system might be addressed by temperature control and surface fouling might be solved by systematic maintenance or some automated form of cleaning

6 2 An On-line Version of the Dedicated System

If an on-line approach is more appropriate for TOC concentration determination the dedicated system could be easily adapted to accommodate the situation The major changes from the present dedicated system would be in the launch of the exciting light into a sample or flow cell and the collection of the resultant fluorescence The launch optics required for delivering light into the excitation fibre could be replaced with a lens capable of providing a collimated beam of excited light The preferred excitation wavelength would be isolated by a bandpass filter as before This collimated beam of exciting light would be delivered into a sample or flow cell through an aperture of suitable diameter Another aperture of suitable diameter could be placed in the flow cell at 90° to the direction of the exciting light The present fluorescence collection section of the dedicated system could be adapted by removing the X-Y-Z fibre optic positioner and replacing the first convex lens with a concave lens to collect and collimate the fluorescence produced The preferred collection wavelength would be

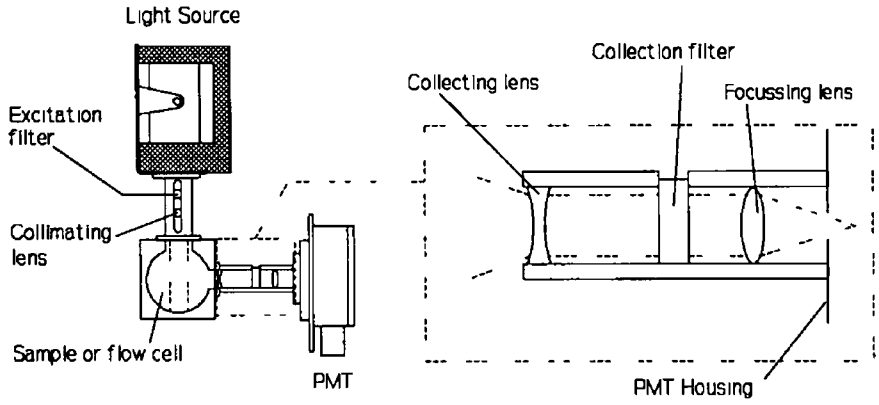

Figure 6 1 A diagram of a proposed on-line version of the dedicated system for TOC concentration determination

isolated by a bandpass filter The second convex lens which currently focuses the filtered collected light into the PMT housing would remain The housing already in use in the dedicated system could be used to contain these lenses and the collection bandpass filter The fluorescence detection section of the dedicated system could be used as it stands The improvements suggested in section 6 1 could also be adopted for making the system more suitable for specific on-line functions A diagram of this proposed on-line version of the dedicated system is shown in Fig 6 1

The proposed system changes should give an on-line system a lower limit of detection than the dedicated system There would be no attenuation of exciting light or fluorescence signal due to the optical fibres in the proposed on-line system The proposed on-line system should produce more fluorescence signal than the dedicated system in a given sample because its launch optics would deliver a uniform collimated beam of exciting light instead of the cone of exciting light delivered by the dedicated system The proposed on-line system should be able to accept more of the available fluorescence signal than the dedicated system because of the configuration of the optics in its fluorescence detection system

There are economic advantages in using the proposed on-line system instead of a standard laboratory instrument While the cost of a typical automatic TOC analysing instrument is approximately £12,500 the cost of the proposed on-line

system, even on a once off basis, would be less than £4000 and mass production of such a system would make the cost lower The proposed on-line system also has the advantage that the expenses associated with grab sampling are not incurred

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