

## **VI. PAPERS**

### **OPTICAL TECHNIQUES FOR WATER MONITORING**

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#### **1. Abstract**

A review of optical techniques used for water monitoring is presented, including sensors based on optical fibres, waveguide and integrated optics technology. The impact of the optoelectronics revolution in reducing cost of optical components and stimulating new materials and devices, is discussed, along with new concepts in sensor technology such as biosensors and immunosensors based on optical techniques. The effect of legislation versus cost of new technology is considered. Finally, examples of optical sensors suitable for water monitoring are described, including commercially available sensors.

#### **2. Introduction**

Classic optical techniques for chemical analysis have been traditionally used for water quality monitoring and trace chemical analysis; e.g. UV-Visible spectrophotometry, IR-spectrometry and spectrofluorimetry. The characteristic transmission, absorption or fluorescence spectrum of a chemical species is measured in order to determine its concentration or identity. In addition, techniques such as Microtox for toxicity measurement, exploit bioluminescent bacteria affected by toxins, to generate light. Such instruments are big and bulky, cost in the region of Stg 20 K, and require the sample to be taken to the instrument, which is operated by a highly skilled technician.

The burgeoning, multi-billion dollar optical fibre communications market, expanding throughout the Eighties, with associated mass production of optical and optoelectronic devices, has lowered the cost of existing optoelectronic devices, and enhanced R&D interest in new optoelectronics, light sources, detectors and new optical materials. This has paved the way for a new generation of optical sensors and measurement techniques, which exploit the new, low cost and compact light sources, detectors and devices, arising from the optical communications revolution. An excellent example of the fruits of the Optical Era, is the Compact Disc player, which has spiralled in price over a decade from 100s of Stg, to 10s of Stg. This consumer item, owned by every European teenager is as much a symbol of the Optical Age, as the Transistor Radio was of the Electronics Age of the 1960s.

Existing optical and spectroscopic techniques can be adapted, using new optical components, to form new, miniaturised, low-cost and portable sensors and optical instruments for applications in medicine, process control and for the water industry. New optical techniques, materials and devices are continually evolving due to the optical telecomms market driven research, enabling generation of new optical measurement and sensing systems.

### 3. Optical sensor and measurement systems

Due to the diversity of techniques and technologies available both commercially and in research labs and reported in the literature, it is difficult to classify optical sensing and measurements. Different classification schemes have been used, ranging from those based on the physical or chemical quantities measured by the system, to those based either on the physics of the sensing mechanism, or the detection system, or the modulation of the light [1,2,3,4,5].

An optoelectronic system can be divided into its component parts :

- The light source
- The light detector
- Coupling optics

The coupling optics can either be based on conventional lenses, optical fibres or waveguides. By using integrated optics, all three components can be placed on the same chip or substrate.

#### 3. 1. *Optical fibre sensors*

Optical fibre sensors form a large sub-set of the family of optical sensing and measurement techniques, and are particularly relevant to the water industry because of the ability to perform point and distributed measurements remotely from the interrogating electronics.

Work on optical fibres was initiated in the 1960s, and optical fibre sensors was one of the spin-off technologies. The technology is sufficiently mature to be the subject of several review books [2,3,4,5].

In an optical fibre sensor, the fibre forms the coupling optics, and transmits the light from the light source, to the modulation zone, where the properties of the light are modulated in response to a change in an external parameter, which can be physical, chemical or biological. The light is then transferred to the detector, where the perturbation in the light characteristics is converted into an electrical signal.

The advantages of optical fibre sensor systems over conventional sensor systems have been well documented and are summarised as follows :

- Immunity to electromagnetic interference.
- Electrical isolation compatible with intrinsic safety requirement, rendering such sensors to be useful in wet environments.

- Passive operation, ensuring no power or electrical circuits are required at the sensing point.
- Transmission of light over long distances, enabling remote or distributed sensing due to the low losses achievable in optical fibres.
- Integration of sensing and telemetry in intrinsic optical fibre sensors.
- Chemical immunity to corrosion enabling use in hostile environments.

Optical fibre sensors can be categorised as [6] :

- Intrinsic sensors in which there is no break in the fibre, and the characteristics of light carried within the fibre are modified by the measurand acting upon the physical properties of the fibre.
- Extrinsic sensors in which the light leaves the fibre and enters a physically separate modulator, where the light characteristic are changed by the measurand.

The advantages of extrinsic sensors are that the modulator can be specially designed to maximise the modulation of the light signal. The disadvantage is that the number of optical interfaces is increased, with a resultant loss of optical power and the danger of contamination of optical surfaces.

Optical fibre sensors can also be classified according to the characteristic of light that is modulated by the measurand: intensity, wavelength, polarisation and phase.

### *3. 2. Optical fibre for optical sensing*

Optical fibre sensors came into being because of the development of optical fibres in the 60s. Several types of optical fibres are currently available, based on silica glass, which can be manufactured in the form of single mode and multimode step index and graded index fibre. These fibres are now cheap due to large scale manufacture, resulting from the optical telecomms industry.

#### *3.2.1. Optical fibre may be classified as*

*Single Mode fibre*, which allows the propagation of one or few modes in the fibre, and which require coherent laser light sources to excite the fibre. Polarisation maintaining fibre are a subset of monomode fibres, and such fibres form the basis for intrinsic optical fibre sensors using phase, polarisation and evanescent field modulation. The problem with such fibres is that they do not carry much light.

*Multimode fibres* allow propagation of 100s or 1000s of modes and therefore are much better at coupling light from broad band incoherent light sources such as tungsten halogen lamps, LEDs and multimode laser diodes, to the modulation zone, and then back to the detector. Such fibres form the basis for extrinsic sensors, and in particular for fibre optic chemical sensors (FOCS), which are primarily of interest to the water industry, because they exploit chemical reactions sensed in the visible and UV part of the spectrum.

### 3.2.2. Optical fibres made of materials other than silica are now available and can be used for sensing

*Plastic Optical Fibres (POF)* are thought to be the poor cousin of silica based glass fibre in terms of their poor transmission properties (20 dB/km instead of 2 dB/km) making them only suitable for Local Area Networks (LANS) and crude sensor applications. However, recent advances in polymer materials in Japan [7,9], leading to low loss and high bandwidth, graded index POF, with improved attenuation characteristics and increased temperature tolerance, is posing a serious challenge to glass fibre. Such fibres are far easier and cheaper to terminate than silica glass based fibres, being easy to cut and polish. They usually have 1 mm diameter core, which are easy to couple light into, and requiring low tolerance, injection moulded plastic couplers. Fluorescence doped plastic optical fibres are a new venture in POF, in which the core is doped with fluorescent dyes. When such fibres are excited by a suitable wavelength, fluorescence occurs at a longer wavelength, and the fluorescent light is guided within the fibre core. Such fibres act as light detectors, amplifiers and wavelength shifters and their applications in sensing are becoming apparent [7].

*Polymer clad silica fibres (PCS)* are large diameter, step-index, multimode silica fibres, with a polymeric coating that can be chemically removed, exposing the cladding. Such fibres form the basis for multimode evanescent sensors, widely used as Optical Fibre Chemical Sensors [8].

*UV and IR transmitting optical fibres* :Conventional silica fibres are damaged by, and are highly attenuating at UV wavelengths, and their use is restricted to the 300 to 1800 nm wavelength region, which limits their use in sensors based on UV or IR spectroscopy. Fibres transmitting below 230 nm have been developed, with a transmission of 0.3 dB/m at 210 nm, enabling UV light sources such as deuterium lamp, to be used for fibre based spectroscopic applications [11,12]. Fibres have also been developed for the mid-IR region, based on fluoride (0.5 to 5  $\mu\text{m}$ ), chalcogenide (1 to 6  $\mu\text{m}$ ) and silver halide (3 to 15  $\mu\text{m}$ ).

### 3.3. Light sources for optical sensing

A major development, also driven by the optical telecommunication industry, is the semiconductor laser diode or injection laser, producing monochromatic, coherent light at infra-red and red wavelengths. These were initially developed to match the transmission windows in optical fibres at 1.3 and 1.55  $\mu\text{m}$ , but are now commercially available at near infrared (950, 850, 780 nm) and red wavelengths (660, 630 nm). Together with new developments in LEDs, such light sources have been mass produced at low price and are optimised for optical fibre coupling (pigtailed lasers etc.). They have the advantages of low power consumption, high stability and long lifetime, as well as being compact, robust and easily intensity modulated.

The availability of cheap laser diodes have fuelled interest in associated laser diode driven light sources, such as fibre lasers, and diode driven solid state lasers, giving an even greater range of wavelengths and intensities, and the possibility of using new optical materials and crystals for frequency doubling, and frequency mixing. Advances in semiconductor technology have led to

green and blue LEDs and laser diodes being commercially available, as well as the possibility of compact, cheap UV lasers [13,14].

Such light sources would be of great importance to the water industry, which relies on laboratory based UV-visible and fluorescence spectrometers and colourimetric tests, with inherent bulky, heat generating incandescent filament bulbs, interference filters and monochromators, or bulky, expensive, cooled, three phase driven visible and UV lasers (Argon-Ion, eximer), because they would enable compact, on-line fibre based spectroscopy systems to be developed. LEDs are both longer lived and more efficient than incandescent bulbs, with a lifetime of up to 15 years, but a power consumption of just a tenth.

Tuneable lasers over the range 200 to 10,000 nm, can be constructed using optical parametric converters and difference frequency generation, and have important applications in spectroscopy. Diode pumped solid state lasers (DSP) and frequency doubled DSPs are replacing helium neon and argon ion lasers [15,16].

Electroluminescent films (ELF), usually used for backlighting of displays, are available in a range of wavelengths, with high stability, and can be used to excite fluorescence in optical sensors. ELFs emit a diffuse pattern of light over their surface, and can be wrapped round glass vessels, to excite fluorescence of a measurand liquid. [17]

#### *3. 4. Light detectors for optical sensing*

Once again, the range of light sources is driven by the optical telecomms applications. Light detectors include silicon or germanium based pin photodiodes, APDs and photomultipliers. For sensor applications based on absorption or fluorescence spectroscopy, a dispersing element is required. Compact scanning monochromators, can be used, but an exciting recent development has been fibre compatible CCD linear array spectrometers, which are now commercially available from companies such as Zeiss, Ocean Optics and Microparts, with resolution of a few nm. Such devices provide spectral information in real time, have no moving parts and are compact in size.

Formation of a grating on the end of an optical fibre, negates the requirement for a separate diffractive element, thus avoiding alignment and contamination problems, and such gratings can be formed on the distal ends of plastic optical fibres using a phase mask and 248nm eximer laser light, and interrogated using a CCD linear array. Applications of fibre end gratings are numerous, including wavelength sensing and referencing and wavelength division multiplexing (WDM) [18].

#### *3. 5. Integrated optical systems and new materials*

Optical light sources, devices and detectors all on the same chip or substrate enable further miniaturisation of optical systems, including devices such as waveguides, gratings, couplers. Several sensor components have been integrated on a chip, by Texas Instruments, combining light sources, waveguides, detectors and coupling optics in a single device, compatible with a printed circuit board [15,62].

The optoelectronics industry has stimulated interest in new optical materials, such as optical polymers and photorefractive materials. Sol-gel is a material which is of particular interest for sensor applications.

A porous glass matrix produced at low temperatures (<100°C), enables chemical molecules, usually analyte sensitive dyes, to be trapped in the pores. Sol-gels were initially used to make a chemically porous glass tip for silica based fibres, but are now being used as chemically sensitive coatings for a variety of optical systems, such as thin film coatings on substrates and waveguides, and as alternative cladding materials for evanescent wave planar sensors and surface plasmon mode systems [11,20,21,22,23].

#### **4. Water quality monitoring**

The water industry has traditionally used laboratory based analytical techniques such as AAS (atomic absorption spectroscopy), GC (gas chromatography), HPLC (high performance liquid chromatography), MS (mass spectroscopy) and GCMS (gas chromatograph mass spectrometer). Optical techniques include UV-visible and IR spectrophotometry and fluorescence spectrophotometry. Such instruments are used for diagnostic measurements, in order to determine contaminants, sources of contamination, and toxic effects.

Monitoring measurements have a different philosophy, and require frequent, preselected, repetitive sampling. The use of expensive, time consuming diagnostic methodologies is not appropriate here; analytical versatility must be sacrificed for dedicated, faster and more economical systems [24].

##### *4.1. Legislation versus cost and realistic technology*

Legalisation determines what parameters are monitored; in Europe, recent EU laws address the chemical and micro biological quality of drinking water, composition of industrial discharges, bathing water quality, waste disposal and many other issues[25].

Once a substance is implicated by legislation, sensors will be required to monitor it. However, species in water can often be determined accurately and cost-effectively by existing laboratory analytical methods. Sensors are only required if it is necessary to monitor the species at the point of discharge, or in the external environment [25]. In addition, legislators only stipulate continuous monitoring if realistic technologies exist. A very large number of chemical and other quantities are implicated by legislation, but no generic measurement techniques, sensing principles or technologies are available for their determination. Thus there are a number of barriers to be overcome, before optical techniques, developed in the research laboratories, are accepted as necessary by the water industry, and become commercially viable.

**Table 1 : Parameters for in-land water, implicated by environmental legislation: After Bogue [25].**

Ammonia	Nitrates
Phosphates	Metals
Halogenated organics	Suspended solids
Cyanide	Pesticides
Fuels and oils	Biochemical oxygen demand (BOD)
Chemical oxygen demand	Total organic carbon (COD)
Algae and algal blooms	Bacteria and viruses
Phenols	Chlorine
Dissolved oxygen	pH

An example of slow uptake of new monitoring technologies is illustrated by the National Rivers Authority (NRA) in the UK, which samples river water in order to measure 200 to 300 different analytes. Over 4.3 million determinations are made annually, and 95% are achieved by traditional sampling and laboratory analysis. Techniques such as AAS, GC, HPLC, MS and GCMS are widely used, and even taking into account new sensor and instrument developments, the NRA estimates that field measurements with sensors will not exceed 10% of the total [25]. This is because laboratory analysis can be very cost effective, when large numbers of samples are involved.

Trace level determinations are required (sub ppb), which exceed the detection limits of most chemical sensors.

For compliance monitoring, approved high accuracy analytical methods are stipulated by legislation.

In addition, sensors are not available for most of the analytes involved, and commercially available sensor based field measurements in the aquatic environment are presently restricted to parameters such as pH, DO, ammonia, conductivity, some metals, turbidity etc.

#### *4. 2. The impact of new optical technology on water quality measurement*

The replacement of existing sensors and monitoring instruments and techniques with new optical techniques, depends on the following factors:

The technical benefits of optical sensors over existing sensors: i.e. will they work better and be more reliable and accurate with improved sensitivity, specificity, response time and capability of measuring new parameters?

Will they offer economical benefits over existing techniques: i.e. are they cheaper.

Reducing ownership costs (5-year life costs: consumable, reagents and purchase price can total Stg 10 to 20 K). Multiparameter sensors, disposable sensors, on-line sensors also reduce cost.

Situations where sampling and laboratory analysis is too slow and/or costly.

Where legislation stipulates new monitoring regimes: i.e. species, applications etc.

One of the most obvious places to start, is to replace, simplify and reduce the size of existing optical instruments using current spectrometric and chemical techniques, to make them cheaper, more compact, and remove them from the laboratory, to the test site. The largest and oldest class of optical sensors, Optical Fibre Chemical Sensors (OFCS), were developed in this way, and are now available commercially.

Limitations of existing on-line water quality analysers for ammonia, TOC, metals and nitrates include high cost of ownership and limited field reliability.

These limitations can be overcome by new optical techniques, which will enable species to be determined that are at present, difficult or impossible to measure on-line. Such techniques include ultra-violet absorption, fluorescence spectroscopy, as well as immunoassay, enzyme reactions and live cell biosensing effects, which can be configured to produce or modulate light. Such sensors are made possible by the new light sources, fibres detectors and integrated waveguide technologies described in Section 2 [26].

To date, no on-line analysers yet exist for pesticides, biochemical oxygen demand (BOD), halogenated and other organics (TCE, phenols etc) and toxicity. Problems include the use of sensing techniques that require wet reagents, the requirement for frequent calibration, the need for often complex sampling systems, and the lack of availability of suitable sensing methods. These can be overcome by remote fibre coupled optical sensors, reagent free techniques and disposable sensors. Many of the most promising sensor principles and technologies are already being exploited commercially in medical and process control fields [26].

## **5. Fibre optic chemical sensors (FOCs)**

Due to their exploitation of traditional spectrometric and standard colourimetric chemical techniques, FOCs form the oldest, and most well developed class of optical sensors, and can be classified into two categories [11].

Direct spectroscopic, where the spectral power distribution of the light is modulated by the spectral properties of the analyte. Using the Beer-Lambert law, concentration of a chemical species can be measured by traditional analytical techniques such as fluorescence or absorption. Reagent mediated, where an intermediate chemical reagent reacts with the target analyte to cause light modulation such as an absorption change, fluorescence etc.

The reagent may be in a liquid form or immobilised in a solid matrix such as sol-gel. FOCs are fibre sensors with preselected chemical and/or physical properties attached to the distal end and/or sides, so that sensitive specific in-situ remote real-time analyses can be made. FOCs can be based on fluorescence, absorption, Raman effects, refraction or reflection. Interaction of the analytes with the sensing reagents produces a change in one of the mentioned spectroscopic parameters [19,27].

FOCs enable inexpensive spectroscopic sensors for specific chemicals, simplifying the spectrometer back end, and reducing the price. They consist of a light source, the sensitised fibre, a spectral sorter/disperser/filter, and signal processing and display electronics.

The wavelength or spectral modulation technique is usually derived from traditional wet chemistry analysis and absorption or colourimetric and fluorometric techniques. The appropriate chemical reaction is chosen to have the specificity, sensitivity and stability required, and a FOCs design is matched to the optical modulation properties of the reaction.

FOCs designs are as follows [24] :

- *Tip coated FOCs*

A reagent is immobilised on the tip of the fibre, usually large diameter multimode fibre. The reagent may be contained within a membrane or polymer, attaching large diameter, porous fibre coatings (sol-gels) [11], or porous glass beads, or using highly sensitive reagents.

- *Evanescent Wave FOCs*

Removing the lower refractive index cladding from an optical fibre, exposes the core to the analyte. Light propagating within the core of the fibre, creates an evanescent wave in the cladding, which interacts with the analytes at the core-cladding interface, causing spectral attenuation of light within the core, or fluorescence excitation generating guided waves at fluorescent wavelength within the core. Fibres can be tapered to increase the evanescent field interaction [29].

- *Side coated FOCs*

Multilayered FOCs in which the reacting analyte is sandwiched between the core and the cladding, forming an intermediate porous layer of higher refractive index than both the core and the cladding. The light rays interact with the sensitive intermediate cladding many times, amplifying the spectral modulation more than with a tip coated or evanescent wave FOCs.

- *Refractive index FOCs*

A bare fibre core, with a thin extra cladding layer of an organic or inorganic compound near the distal end. A change in the refractive index of the analyte surrounding the fibre end alters the transmission properties of the fibre and thus modulates the light reaching the detector. The extra outer cladding must have a refractive index that matches the refractive index of the analyte.

FOCs often use membranes or sol-gels, to contain the reaction chemistry or fluorescent dyes, to protect the chemistry from undesirable species in the environment being monitored, or to allow selective permeation of analytes. Many FOCs use sol-gels as a porous glass tip for silica based fibres. sol-gel provides a solid, inert and porous support rigidly attached to an optical fibre, giving a large, chemically inert surface area [11,20,21,22,23], that enables containment of a wide range of chemically sensitive molecules. Chemicals immobilised in sol-gels for sensing purposes include: fluorescein isothiocyanate dye, which changes its absorption as a function of pH [23], as well as various colourimetric pH indicators, anions, cations, heavy metals, acids, ammonia and enzymes.

Since FOCs were the first optical fibre sensors, based on well-known chemical reactions, they are well developed, widely accepted, and thus are being commercialised [19].

A FOCs has been developed for multicontaminant monitoring of environmental systems such as ground water systems, using an indicator, PRODAN, bound chemically to the cladding on the optical fibre. When excited in the UV, PRODAN fluoresces at various wavelengths, in response to an array of antropogenic organics including acetone, cyclohexane, chloroform, toluene and cyclohexane [28].

## **6. Optical biosensors**

An optical biosensor incorporates a biologically active material, which alters its optical properties, reversibly and selectively in response to the analyte, usually a chemical species. Biosensors form a new and rapidly expanding field of sensors, using isolated enzymes, intact bacterial cells, mammalian and plant tissue, antibodies and bioreceptor proteins. To date, biosensors have generally used physical transduction processes involving charge transfer such as amperometric and potentiometric electrodes, field effect transistors, or solid-state devices such as peizo electric crystals and surface acoustic waves (SAW) devices [30].

Recently, optical biosensors have been developed, in which the biologically active material is a catalyst which is immobilised at the surface of a single fibre, waveguide or fibre bundle, and the detected species is measured by absorbance, fluorescence or chemiluminescence. An analyte consuming reaction is catalysed by the immobilised biocatalyst and a product of this reaction is monitored. The biocatalyst mediates between the analyte of interest and the transducer by converting the analyte to a detectable species. [ 32,33,34]

Another class of optical biosensors include fibre optic immunosensors (FIS) [35,36], which offer excellent selectivity via anti-body-antigen recognition, enabling measurement of important compounds at trace levels in complex biological samples. FIS for detection of human and environmental exposure to toxic chemical and biological materials, are based on various spectrochemical mechanisms such as absorption, total internal reflection, fluorescence, evanescent field and surface plasmon resonance.

## **7. Waveguide and integrated optics sensors**

Waveguide and integrated optics technology has given rise to a number of clever designs for sensors, including the deposition of sensing layers on waveguides, using a hollow capillary to act as waveguide and sample holder, and devices such as grating couplers adapted for sensing purposes.

Planar waveguides have advantages over optical fibres and are often used for biosensors [37], in applications where the flexibility and remote capability of an optical fibre are not essential.

These advantages include the following :

Total internal reflection fluorescence (TIRF) can be used with lipid membrane structures stabilised onto optical surfaces in planar waveguides.

Planar waveguides allow control over incident reflection angle, enabling control of penetration depth of evanescent field. Langmuir Blodgett deposition of membranes onto planar substrates is well characterised, but difficult onto cylindrical surfaces.

Polarisation information is lost in multimode optical fibres, but retained in planar waveguides. Interferometric measurements possible. Single mode optical fibres would allow polarisation maintenance and interferometry but are not yet available at short wavelengths required for fluorescence in terms of fibre diameter or fibre material. Planar waveguide structures can be placed in flow cell modules.

An optical sensor using inhomogeneous waveguiding in the walls of capillary tubes (capillary waveguide optrodes) [37], also has several advantages over an optical fibre based sensor. The capillary has a chemically sensitive coating on its inner surface which measures analytes in gaseous and liquid samples. Light from a laser or LED is coupled into and out of the capillary, which acts as a waveguide. Light is absorbed in the chemically sensitive coating as a function of the concentration of the analyte.

Advantages include :

- The capillary acts as a sample cavity or flow cell for the gas or liquid and holds a well defined volume.
- Suitable for direct or on-line sampling.
- Optical path length is much longer than other optrode designs and can be optimised for the particular analyte.
- The sensor is not affected by colour and turbidity of the sample.
- Cheap LED light sources and detectors can be used.

Optical devices such as grating couplers are used in integrated optics to couple light into and out of waveguides. Such a device can be used to measure refractive index. The angle at which light couples into a waveguide is a function of the refractive index of the waveguide; if the refractive index changes in response to an ambient medium, then a sensor for refractive index measurement of fluids, humidity or gas concentrations can be constructed. Advantages include small size of sensing head and no moving parts [38].

Optical surface plasmon resonance (SPR) sensors measure the refractive index of a sample near the sensor surface. SPR is an optical effect, in which incident light excites a charge density wave at the interface between a metal and a dielectric. Reflected light decreases in intensity at a certain angle or wavelength, corresponding to a resonant wave vector, whose location depends on the optical characteristics of the medium surrounding the sensor surface. SPR has been used to detect concentrations of 10 ppm Cu and 13.76 ppm Pb [39].

## 8. Examples of optical sensors for the water industry

Here an attempt is made to match optical sensors and techniques reported in the literature, to the parameters shown in Table 1. Often, sensors have been developed to measure parameters for other applications, such as medical, biotechnology or process control, which can be adapted to the water industry :

- *Multiparameter Water Monitor based on LEDs and colourimetric tests*

A LED based portable sensor system using standard colourimetric tests uses a multipurpose flow cell with an array of LED sources of different colours, to enable measurement to be made of aluminium, iron, manganese and phosphate levels, as well as sample colour and turbidity [11].

- *Ammonia*

A fibre optic LED based fluorescence based sensor for ammonium ions uses a pvc membrane containing nonactin, a plasticiser and a proton carrier (lipophilic Nile blue). The ammonium ions are extracted into the pvc membrane and protons are released by the dye, contained in the pvc membrane, into the sample solution. Upon deprotonation, the dye undergoes a colour change from red to blue, which is detected fluorescence intensity measurement. A detection limit of 0.03 to 10 mM is achieved with a response times of 1 minute. [40].

- *Nitrates*

Commercial nitrate analysers use ion specific electrodes, colourimetry and UV absorption. A study of their specifications, as provided by the manufacturer, and their response to waste water and laboratory samples, indicated that the UV based systems were simpler and quicker to use and required less sample conditioning than colourimetric methods. The ion specific electrode analysers were affected by contamination [55].

- *Metal ions and chloride*

"Optodes" use highly selective ion sensing films to detect ions such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ , and  $\text{Cl}^-$ , by optical absorption, fluorescence or reflection mechanisms. In this case, the optical response is generated using ion-pair extraction of the ion-ionophore complex and a deprotonated or protonated lipophilic anionic dye, contained within plasticised PVC membranes. The optodes are designed for disposable use and detect ions by immersion in a glass vessel containing the sample solution, and measurement of the absorption change associated with the lipophilic anionic dyes [59]. Such a sensor is designed for use with serum, but could be adapted for water.

- *Toxicity*

Microbial toxicity can be measured using a respirometer to measure oxygen consumption. Luminescence quenching by molecular oxygen is the light modulation process, using a luminescent ruthenium complex adsorbed on amorphous fumed silica

and immobilised inside silicone rubber. Luminescent intensity depends on the oxygen concentration of the sample in contact with the sensing film. This sensor was evaluated by measuring the inhibition effect of heavy metals on the respiration rate of micro-organisms in activated sludge, and indicated that IC<sub>50</sub> (concentration of a toxicant producing 50% respiration inhibition), could be measured [43].

An optical fibre toxicity biosensor, for point or on-line monitoring of toxic effluents, measures the rate of hydrolysis of fluorescein diacetate (FDA) by micro-organisms, which is proportional to their metabolic rate. Rate of increase of fluorescence is proportional to the metabolic rate of the organisms, thus indicating the toxicity of their environment. The organisms are contained within a glass tube, round which is wrapped an electroluminescent film, emitting at the excitation wavelength. Fluorescent light is detected by scattered coupling of light into the walls of the glass tube, in which are embedded an array of fluorescent-core polymer fibres, forming a detecting bundle. The light coupled into the walls of the tube is preferentially detected and amplified by the fluorescent fibre, which is insensitive to the excitation light. The sensor can detect concentrations of fluorescein down to ppb [44].

- *Metals*

Surface plasmon resonance (SPR) techniques can be used to measure metal ions; concentrations down to 500 nM lead and copper[45], and 10ppm copper and 13.76 ppm lead [39] have been measured.

- *Organic solvents*

An optical fibre dipping sensor was developed for detection of organic solvents in waste water, using changes in the optical absorbance of triphenylmethane dyes, measured in the visible part of the spectrum. The sensor layer was separated from the water by a gas permeable membrane. Organic solvents in water were measured down to 30ppm [46].

Chlorinated hydrocarbons such as chloroform and trichloroethylene, can be detected by colourimetry at 560nm, monitored by optical fibres. Pyridine, exposed to chlorinated hydrocarbons, become red, absorbing in the green part of the spectrum. Incandescent lamp and bandpass filter or 555 nm LED and Silicon photodetector was used [47].

- *Suspended solids*

A particle concentration sensor uses two, parallel, plastic 1mm diameter fibre with an extra layer of higher refractive index optical cladding, to make the fibres "leaky". Light in the transmitting fibre, leaks out and undergoes multiple scattering by measuring particles in aqueous suspension, before entering the receiving fibre, which is similarly sensitised. The sensor can be used in point or distributed mode and has been used to measure yeast concentration in the range 0 to 16 g/l. It has been calibrated in turbidity units (FAU) over a range from 0 to 400 FAU, and optimised for the 0 to 20 FAU range. It is presently being optimised for the 0 to 4 FAU range, and also to measure activated sludge concentration [48,49].

- *Cyanide*

A FOCS for cyanide detection, exploits the reaction of metalloporphyrins with cyanide. A membrane was used to trap the reagent solution at the common end of a bifurcated fibre-optic bundle.

The cyanide in the sample solution is buffered at a pH low enough to convert to hydrogen cyanide, which diffuses through the membrane and reacts with the reagent. The changes in the optical properties of the reagent can be related to the concentration of cyanide in the sample solution [50].

- *Pesticides*

An immunosensor configured as a waveguide Mach Zehnder Interferometer (MZI), can detect a layer of pesticide of  $2 \times 10^{-3}$  nm, using a well known antibody/antigen system ( $\alpha$ -hSA/hSA). The waveguide, contained within a flow cell, uses its evanescent field, associated with guided light within the waveguide, to detect binding processes close to the surface. An immunoreaction at the surface causes a change in the refractive index profile, altering the waveguiding properties of the sensor. The analyte molecules are specified by the immunochemical reaction which takes place at the antibody coated sensor surface [56].

A fibre-optic system based on solid-state, optoelectronic components, including yellow LEDs and photodiodes, detects pesticides because they inhibit the enzyme acetylcholine esterase. A yellow synthetic enzyme substrate is hydrolysed by the enzyme to give a blue product, whose rate of production is reduced by the presence of an inhibitor [57].

- *Fuels and oils*

Near infra-red photoacoustic spectroscopy can be used to detect analytes. In weakly absorbing liquids, the conversion of a pulse of optical energy into acoustic energy, is affected by the composition of the liquid. The properties of the acoustic wave generated enable oil contaminated water to be measured from 0 to 900 mg l<sup>-1</sup> [58].

- *Dissolved oxygen (DO) and Biological Oxygen Demand (BOD)*

The advantage of optical oxygen sensors over conventional amperometric devices, are that they do not consume oxygen, and are not easily poisoned, small size, no requirement for reference, and inertness against sample flow rates and stirring. Fluorescence quenching of Ruthenium complexes in the presence of oxygen appear to be the sensing mechanism in reported sensors.

One configuration of a DO sensor uses a Ruthenium complex immobilised in a thin film sol-gel, which has strong absorption in the blue-green region of the spectrum, compatible with blue LEDs [11]. A second type of optical oxygen sensor also uses a Ruthenium complex as an oxygen sensitive fluorescent dye, circulated through a loop of oxygen permeable silicone tubing immersed in test medium. The intensity of fluorescence is related to oxygen tension [41]. A third type of sensor for measurement of both dissolved oxygen and BOD, also uses a Ruthenium complex, embedded in a

silicone rubber film, which is attached to the inner surface of a transparent vessel in which dissolved oxygen is measured. An optical scanner provides the excitation light and measures the emitted light from the sensing surface and can monitor oxygen in many vessels, simultaneously [42].

- *Total organic carbon*

A comparison of different methods of measuring TOC, examined UV absorption spectroscopy at 254 nm, optical fluorescence with excitation at 340 nm, emission at 420 nm, and established chemical methods of measuring TOC in water samples, together with a commercial UV on-line absorption monitor. The study indicated that such techniques could be adapted for field based instruments using optoelectronic devices. [51]

- *Algae and algal blooms*

Chlorophyll fluorescence of algae can be used to measure presence of algae, these has been performed remotely using satellite imaging systems, as well laboratory based spectrofluorimetry [52]. Time dependent fluorescence techniques, using laser excitation can be used to monitor the effects of pollutants on algae [53].

- *Bacteria and viruses*

Fluorimetric sensors were used to sense CO<sub>2</sub> produced by bacterial metabolism, based on fluorescence [54].

- *pH*

Two pH indicators dyes were co-immobilised in a sol-gel film, coated on the core of an optical fibre, so that the pH dependent changes in the cladding could be monitored by evanescent field absorption. Indicators included bromophenol blue, and bromocresol purple. A pH range of 3 to 10 pH units was measured, using a tungsten halogen lamp as the light source, and an Ocean Optics spectrometer for detection [11].

An example of a non-colourimetric indicator pH sensor exploits the surfacic adsorption of positively charged methylene blue dye, chromophores onto the negatively charged surface of a stripped core 200  $\mu\text{m}$  PCS fibre. The adsorbed chromophores interact with the evanescent field and affect the absorption of light guided through the fibre, as the pH of the solution increases. The methylene blue solution is encapsulated within a semipermeable membrane. The linear range of operation is 2 to 10 pH units with a sensitivity of 0.75dB/pH, and the sensor performs well at low and high ionic strengths, since its sensing mechanism directly exploits OH<sup>-</sup> ions activity [8].

- *Flow*

An optical fibre based flowmeter, uses two optical fibre strain sensors to measure the strain generated in two orthogonal directions, when placed on adjacent sides of a beam deflected by fluid flow. Strain magnitude is proportional to the square of fluid velocity magnitude. Vectorial addition of the orthogonal strain components give the strain magnitude and direction [60].

## 9. Commercial optical measurement systems

A survey of commercially available optical sensors [1] indicates that spectrometer and spectrophotometer based sensors, for measuring chemical fluorescence and absorption dominate the market. A selection of commercial optical sensors and measurement techniques measuring parameters useful to the water industry, are briefly described, as follows :

- *Polytec in-line process measurement using a diode array photometer*

Polytec [61] have an X-DAP fibre optic based system, with a series of light sources illuminating samples, and being split into component wavelengths, by a dispersing prism and detected by a diode array. Polytec Procell DAS allows in-line measurement and control of concentrations and colours, continuous monitoring of production process, monitoring of output of waste materials. The complete source, flow cell and detection package is intended for integration into pipes and other parts of process systems, and has no moving parts. The diode array signal is interfaced to a PC.

- *Fibrechem FOCS systems*

Several FOCS systems available, developed by Fibrechem Inc, USA, in collaboration other companies including Texas Instruments (USA) [19]; These included Petrosense CMS (continuously monitoring permanent installation) and Petrosense, Aquasense and Aersense, which are all portable devices. All four systems have the ability for performing on-site, in-situ monitoring of vapour or water samples. Petrosense monitors hydrocarbons, detects leaks smaller than required by legislation (0.2 gal h<sup>-1</sup> ). The lower limit of detection of vapour is 10ppm for xylene petroleum hydrocarbons, and 0.1 ppm for hydrocarbons in water [62]. The Aquasense unit can be used with solid state or reservoir probes, can operate in absorption, reflection or refractive modes and can handle 19 different sensors [19]. Small, low cost sensors, using 4 to 16 individual sensors on a chip on 2.5 mm<sup>2</sup> in size, and to house electronics in a second chip of a similar size, are under development. Parameters to be sensed include hydrocarbons, trichloroethylene, carbon dioxide, carbon monoxide, oxygen, ammonia, cyanide, phosphate, sulphate, nitrate and nitrite, trichloroethane, chloroform, carbon tetrachloride and other organics, arsenic, selenium, ferrous iron, manganese, zinc, cadmium, lead, total heavy metals, total iron, mercury and silver.

- *Toxicity Measurement with Eclox, Aquanox and Microtox*

Both the Eclox (Aztec Environmental & Control Ltd) and Aquanox (Randox Laboratories) hand held monitors uses an enhanced chemiluminescent reaction; free radical reaction of the oxidation of luminol in the presence of horse radish peroxidase enzyme, using p-iodophenol as an enhancer and to stabilise the reaction [63, 64] . Any substance, such as an antioxidant pollutant, that inhibits the enzyme reaction, causes a reduction in light emission which is measured on a portable luminometer. The advantage of these units is that they are relatively cheap (Stg 1-4K), portable and can be used by inexperienced operators. Disadvantages include insensitivity to some toxins. Microtox uses a freeze dried marine bacteria; *Photobacterium phosphoreum*, stored in a cooled storage area within the instrument. In use, a standard amount is rehydrated and

mixed with the water sample. The bacteria emit light under favourable conditions and reduce their emission when exposed to toxins. Microtox is widely used in the water industry but it is large, expensive (>Stg 20K) and laboratory based, though an on-line monitor and a hand-held version are under development [65, 66].

- *EauxSys portable turbidity monitor*

A battery powered, portable turbidity meter is designed for low turbidity range of 0.00 to 50.00 NTU. It can be configured for batch or for flow measurement. Light scattered by the particles in aqueous suspension, is measured at 90° to the incident light, giving a true nephelometric measurement [67].

- *Ocean Optics Fibre Optics Sensors for pH, Toxic Metals and Oxygen*

Ocean Optics [68] has a range of optical fibre sensors, coupled to miniature spectrometers to monitor colour changes in immobilised dyes. They form an excellent example of commercialised OFCS, using well-known colourimetric or fluorescent chemical reactions. A tungsten halogen light source and a fibre optic film probe is used with a choice of reactive films. The pH sensitive films are solid state versions of traditional dissolved pH indicators, and each dye has a 3 to 4 pH range, with a precision of  $\pm 0.001$  pH units. The sensors can be PC interfaced, using custom made Windows compatible software for data acquisition and full spectral analysis. The toxic metal films are immobilised complexing agents, which bind metals in a irreversible reaction, to give a unique spectrum for a particular metal. ppm levels can be detected in 30 minutes.

The oxygen sensor uses a well-known fluorescence quenching reaction to measure oxygen concentration. An optical fibre probe has a proprietary thin film coating on its tip, and a blue LED is the excitation source, with a miniature spectrometer as the detector. Fluorescence detected at the probe is reflected back to the detector, where a 550 nm cut-off filter blocks the excitation light.

- *MetriCor*

MetriCor optical fibre sensors use thin film interference as a sensing mechanism. A miniaturised interferometric cavity is placed at the end of a multimode fibre. The optical thickness of the cavity is modified by the measurand, causing a spectral shift. The parameter of most interest to the water industry is refractive index, which can be used to monitor fluids. The optically resonant cavity is exposed to the measurand fluid, causing a change in optical path, and thus a spectral shift that can be measured [69].

## **10. Conclusion**

The range of optical sensors and measurement techniques continue to expand, as new optoelectronic devices and materials become available, driven by the massive optical fibre communications and optoelectronics market. Optical fibre based sensors have been in existence for over two decades and researchers are moving towards novel sensors based on waveguides, integrated optics and new materials.

However, the water industry, driven by legislation and relying on traditional analytical methods, is slow to take up new monitoring technology, and this is indicated by the fact that optical sensors and techniques which have reached the market place, are based on well known colourimetric and fluorescence reactions, measured by spectrophotometric techniques and using optical fibres. Medical, biotechnology and process control industries are adventurous in exploiting new optical technology and many promising sensor principles and techniques are being encouraged by this sector, and will eventually filter through to more conservative industries. The review of new developments and sensors at the research stages indicate that optical techniques can be used to measure all the parameters indicated in Table 1, and that optical techniques can offer advantages over existing diagnostic and monitoring techniques. Problems to be overcome by the optical designer include biofouling, calibration stability and selectivity.

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