RECENT DEVELOPMENTS IN MONITORING WATER QUALITY

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ABSTRACT

This paper provides a discussion on current attitudes in the UK to the need for improved water quality monitoring instruments and support systems, both for process control in water, wastewater treatment and transport and in environmental monitoring generally. Existing and further requirements are discussed as are inadequacies in existing technology and the research needed to bring about desired improvements.

Particular requirements within the Industrial Sector as a whole, the recently privatised Water Authorities and the newly constituted National Rivers Authority are examined and the pressures brought about by recent European Community (EC) legislation discussed.

Effects in terms of economics and on research impetus are discussed, particularly the impact of recent developments of relevance in fibre and electro-optic technology, solid state sensors and biosensors.

KEY WORDS

Water Quality, Instrumentation, Evaluation, Specifications, Legislation, Solid State, Fibre Optic and Biosensors.

INTRODUCTION

The use of instrumentation, control and automation (ICA) at sewage and water treatment plants and within sewerage and water distribution systems has increased considerably during the past decade. So too has the use of on-line systems for monitoring natural water courses and effluents discharging into them.

In general however the performance of ICA equipment in the Water Industry has not been regarded as satisfactory, the faults being attributable both to suppliers and users. The Water Industry Steering Group on ICA identified in its policy statement in 1981 that in order to advance the use of ICA within the industry there was a need to develop user specifications for all aspects of the required ICA systems, particularly sensors and instruments since their performance has been the subject of much criticism within the industry. Additionally the need to develop methods for instrument evaluation was highlighted.

Over the past few years considerable effort has been expended by both the Water Industry as a whole and the Water Research Centre (WRC) in the UK in particular to produce the required specifications and also evaluate as rapidly as possible currently available equipment. Hence the setting up in recent years of two evaluation and demonstration facilities (EDFs). Additionally much effort has been directed by the WRC and elsewhere (Briggs and Grattan 1989) in the identification of Water Industry and Water Users needs and to studying recent developments in relevant sensor and system technology.

This paper provides details of progress to date in all the above areas.

WATER INDUSTRY AND WATER USERS' NEEDS

The requirement for water quality data has been assessed with consideration of the following topics:

    (i) Proof of compliance with relevant legislation

    (ii) Measurements needed for the operation and maintenance of water and waste water treatment and transport facilities

    (iii) Control of industrial effluent treatment.

(a) Sampling Requirements

These are detailed in the joint circular from the Department of the Environment and the Welsh Office (1982). This document draws attention to the EC Directive relating to the quality of water intended for Human Consumption (80/778/EEC) the text of which is reproduced in the document and also gives guidance on the way in which the directive is to be implemented in England and Wales. The document contains a list of the required determinands especially the following topics:

-   Organoleptic
-   Physio-chemical
-   Toxic Substances
-   Microbiological

Proof of compliance is achieved in most case by means of a programme of sampling and subsequent laboratory analysis and there appears to be ample instrumentation available to carry out reference methods of analysis at the present time. However, most Water Authority Scientists are of the opinion that far lower limits of detection will be required in the future, particularly for monitoring toxic substances. There are certain determinands that are better measured on site including microbiological variables and labile determinands such as dissolved oxygen, nitrate ions and ammonia. Additionally there is a need in some cases for continuous monitoring, for intake protection for example, and this implies a need for field-based staff unless the required instrumentation and telemetry equipment are available in a robust and reliable form.

If portable battery powered versions of the required instruments could readily be plugged into existing and future telemetry networks (e.g. PTSN, private wire, UHF radio or satellite) then the results of field analysis and field calibration could be automatically loaded into a central data file, with obvious savings in time and man hours. This also would appear to be a promising area for the application of new sensor technologies.

In the above context it is of interest that UK Water Authorities currently spend of the order of £ 35M p.a. on sampling and laboratory analysis. This can be divided into the following categories:-

    Collection of samples - £ 10M p.a.
    Laboratory Analysis - £ 25M p.a.

At the present time staff costs account for the bulk of the £10M p.a. spent on sample collection whereas in the case of analysis, costs include staff time costs, and capital equipment costs (including the cost of up-rating or replacement) and an overhead element which is significantly reduced by minimizing the number of laboratories deployed. Assuming an average equipment life of 5 years, the likely spend on capital equipment will be about £ 5M p.a. unless further major re-organisations occur.

(b) Operational Needs

Most Water Authorities, Public Utilities and other relevant government agencies are committed to a policy of continued improvement to the environment and this implies better process control and in consequence an increased need for reliable process control instrumentation.
The matters to be considered in this context are:-

(i) The likelihood of the existence, in developing countries, of increasing surpluses of unskilled labour, permanent shortages of capital for public works and ever increasing costs.

(ii) The ability to treat wastewater to the minimum standard required to maintain the quality of the receiving waters downstream of the discharge at a level adequate for the use to which the water is to be put. Clearly this will be different for different rivers and different sections of rivers.

Comprehensible details of measurement requirements in both water and wastewater treatment areas have been published recently. This information is based on reports received from Canadian, West German, Swedish and United Kingdom representatives and the contained data have been combined in the form of a listing of variables of most significance in treatment process control, measurement priorities and equipment availability (Drake 1985, D.O.E./NWC 1981 and I.A.W.P.R.C. 1978 and 1981).

A list of variables of most significance and ranked according to priority has recently been produced by the Process Instrumentation Specification and Evaluation Group (PISEG) and the ICA Policy Group of the Association of Water Authorities and their Liaison Engineers have been utilised by WRC in the writing of user specifications. However, because of the impending impact of EC legislation this list has been extended by the authors to include heavy metals and trace organics thought to be potentially harmful to health (Briggs and Grattan, 1989) and is provided in tabular form below (Table 1)

TABLE 1: Variables of Greatest Significance in the Operation of Water and Waste Water Treatment and Transport Systems

Water Treatment and Distribution	Sewage Treatment	Sludge Disposal	Source and Receiving Waters
Ozone	Dissolved Oxygen		Dissolved Oxygen
Organic Matter	Suspended Solids	Heavy	Suspended Solids
pH value	Sludge Solids	Metals	Nitrate ion
Colour	Organic Matter		Trace Organics
Turbidity	Ammonia	Pathogens	pH value
Aluminium	Nitrate		Algae
Iron	Toxicity		Organic Matter
Manganese	Treatability		Ammonia
	BOD		Heavy Metals
	TOC		Conductivity
	UV Absorption		Oil
			Gross Pollution

(c) Instrument and System Requirements

It is now evident that complete instrumentation systems will be required, capable of interfacing to existing and proposed telemetry systems. In general these systems should comprise three major components or building blocks. These are:

(i) A sample conditioning system, in most applications

(ii) A robust, reliable and comparatively inexpensive sensor system

(iii) A microprocessor based electronic system capable of operating and controlling the sensor and sample conditioning units, providing additional control outputs and providing alarms and data outputs to telemetry systems (e.g. RS232).

Such a system would be particularly useful in the protection of intakes to water treatment plants since in the UK about 30% of the required drinking water comes from lowland rivers, other major sources being ground water and reservoirs. Although lowland rivers are a comparatively cheap source of water they are more prone to pollution than are other sources.
Pollutants involved in closure of lowland intakes, according to Dobbs and Briers (1988), have been reproduced in Table 2.

TABLE 2 : Pollutants Affecting Lowland Intakes

Pollutant	Percentage Occurrence
Fuel Oils	40
Farm Waste	10
Sewage	10
Plating Effluent	5
Phenols	5
Other Chemicals from Industry or Road Accident	30

About half of the major intakes have bankside storage with residence times, in the absence of short circuiting, of between 1 and 60 days. The remainder have none and water typically passes through the treatment works and into distribution within 4 hours. Recent work in France (Philipot et al 1988) has gone much further than elsewhere but even so there appears to be a requirement for sensors of adequate sensitivity and reliability for determining low level concentrations of toxic metals, oils and other hydrocarbons, low levels of pesticide and herbicide residues as well as other carcinogenic species. Recent advances in sensor technology of relevance is provided in a subsequent section.

SPECIFICATIONS

In the writing of user specifications WRC has taken into account the following:-

a) the need to meet user requirements precisely and not to over specify
b) the need to avoid directing the specification towards a particular technology
c) the need to avoid basing the specification on instrument qualities which can be met by existing instruments rather than to address the requirement objectively.

The aims of the specifications were said to be threefold. (Elvidge 1989). Firstly, to specify the instruments that are required to measure and control a particular part of the treatment process. This is clearly the prime aim of the specification. Having identified the qualities the instrument needs for these tasks, it should then enable the instrument manufacturer to develop instruments which are specific to the Water Industry requirements. This could be done by modifying the existing product ranges or by developing new instruments to meet the more exacting aspects of the specification. The third aim of the work is to enable the Water Industry to purchase to a common industry-wide standard. The specifications have been written to identify the requirements of an instrument to satisfy a particular control task without stifling the instrument manufacturer's choice of technology.

The first few specifications are now available and have been produced in the same form as other Water Industry Specifications Information and Guidance Notes. These have been collated in the 7-00-00 series and are known as Water Industry Specification for Process Control Instruments. The full series is shown in Table 3 below with projected publication dates.

Each section is made up of further subsections covering the basic specification, the appropriate applications and other general guidance documents. As an example the subsections for pH are shown in Table 4 below; subsequent specifications will follow a similar format.

tables 3 and 4.

WATER INDUSTRY SPECIFICATIONS FOR PROCESS CONTROL INSTRUMENTS

7-00-00	Requirements common to all control and monitoring instruments	June '89
7-01-00	pH	June '89
7-02-00	Residual Chlorine	July '89
7-03-00	Flow Meters	July '89
7-04-00	Aluminium and and Iron	September '89
7-05-00	Dissolved Oxygen	October '89
7-06-00	Colour	June '90
7-07-00	Suspended Solids	December '89
7-08-00	Ammonia	March '90
7-09-00	Turbidity	March '90
7-10-00	Total Organic Carbon	June '90
7-11-00	Nitrate	June '91

WATER INDUSTRY SPECIFICATIONS FOR PROCESS CONTROL GENERAL SUBSECTIONS

-01-01	Specification for pH Analysers
-01-02	Method for the Evaluation of pH Analysers
-01-03	pH Analyser Evaluation Results - Summary
-01-04	Applications for pH Analysers
-01-05	Present pH Sensor Techniques
-01-06	General Control Techniques
-01-07	Sensor Choice and Installation

EVALUATION AND DEMONSTRATION FACILITY (EDF)

Details of the evaluation work carried out to date by WRC have been published by Elvidge (1989) and are reproduced in part below.

During the early 1980's, EDFs were established to provide the manufacturer and the Water Industry with a site where the value of ICA could be demonstrated. As part of this project evaluation facilities have been set up to assess the performance of process stream control instruments when operating in the process stream. Two sites have been set up, one at a sewage treatment works, at Witney within Thames Water and a second at a water treatment works at Eccup, within Yorkshire Water. A further site at Chorleywood within Rickmansworth Water Company is used to assess potable water flow meters. The evaluations carried out enable the assessment of the performance of instruments over a 12 month period and in general the consideration of the instruments's accuracy, response time (if appropriate), construction and ease of use as well as the overall cost of ownership.

A wide range of instruments have been tested and are indicated in table 5 below along with the date of report production.

TABLE 5:

INSTRUMENTS ASSESSED AT THE EDFs

INSTRUMENT TYPE		REPORT DATE
pH		September '88
Chlorine		July '89
Turbidity		August '89
Flow - closed pipe	- water	Rolling programme
	- sewage	December '86
	- sludge	December '86
- open channel	- sewage	November '88
Dissolved Oxygen		September '89
Ammonia		November '89

The approach adopted in most of the evaluations for accuracy and related parameters was to select an instrument and use that as the master instrument against which others may be compared. This master instrument was calibrated using techniques traceable back to national standards, often at the appropriate standards house, and maintained to a high degree by careful and regular cleaning and calibration.

In general the procedure, once a test rig had been set up and verified, was to mount the instruments in the test rig according to manufacturer's instructions, making note of any problems, lack of detailed instructions etc. and then set the rig running. There was usually a 'burn in' period of about a month, followed by an evaluation period. Routine maintenance, calibration, etc were carried out according to the manufacturer's schedules and readings taken of the instrument output, master output and any other relevant information. At the end of the evaluation further tests were carried out and individual reports written for each instrument. The manufacturer was allowed to comment on the report on his instrument and the reports are then published. A summary report is also produced to enable users quickly assess to the merits of each instrument.

Further details of the results, to date, are available in the literature (Elvidge 1989) and these and the specifications in the form of a single loose leaf document are available from (WRC, Swindon, UK).

EXISTING MEASUREMENT TECHNIQUES

Existing measurement techniques and their limitations in terms of accuracy, and reproducibility of results, overall reliability and ease of maintenance and repair of the equipment utilised are discussed below.

(a) Sensor Logistics

Prolonged exposure of sensors to industrial and domestic wastewaters and to the products of the various treatment processes inevitably leads to a degradation in performance and reliability, particularly in the case of those sensors which have evolved from laboratory instruments which were designed to measure the same or a related variable but under favourable environmental conditions. Such sensors are frequently unreliable when deployed in situations that are not climatically well controlled, where gross fouling and/or growth of biological films and slimes occurs and where skilled human supervision is not readily available.

Various remedies exist but in general they add considerably to the cost and complexity of the instrumentation. A dual sensor system has been developed, initially to protect intakes to water treatment plants where the maximum reliability is required (Briggs 1981). With this system, two identical sensors are deployed, one on stream and the other on standby (immersed in a calibrating solution containing a biocide).

By transposing automatically the functions of the sensors, both on a time basis and on receipt of data indicating that a sensor reading has deviated significantly from past data trends, it is possible to detect a sudden and serious change in sample quality on the one hand or a sensor failure on the other.

(b) Existing Sensors

State of the art data in respect of the performance of commercially available sensors for monitoring flow and quality have been published previously (Briggs and Grattan 1989, Briggs 1981). Nevertheless it seems appropriate to provide in this paper brief details of the performance of some of the more frequently utilised sensors (e.g. sensors for monitoring flow, dissolved oxygen and temperature, oxidised nitrogen, ammonia, suspended matter, organic matter and pH value).

(i) Flow

Since in many applications, such as consent for effluent discharge and treatment plant design it is the mass flow of pollutants that is of greatest significance rather than actual concentrations, the current situation with respect to flow measurement technology is indicated below.

In open channels, conventional techniques based on level measurement are common but have limitations in unattended operation when applied to liquids containing high concentrations of suspended and/or floating matter. Remote level sensing using pressure or ultrasonic transducers gives better results for some applications but temperature variations can cause significant errors, and both ultrasonic and optical devices have been used successfully for measurement of sludge blanket level. Magnetic flow meters are being used increasingly to measure flow of heavily polluted liquids and slurries in pipes. There are instances, however, where large variations occur, and the accuracy of measurement at the lower end of the scale suffers because of zero drift. It has been suggested that magnetic flow meters with smaller internal diameters than the adjoining pipework could be used for the following reasons: (a) less susceptibility to zero drift, (b) during periods where the main pipework may not be completely full, adequate measurements could still be made in the reduced section, provided the meter was correctly located and (c) since the throughput would necessarily be higher, self-cleaning of the electrodes mounted on the inner wall would be more effective. However, these advantages must be carefully weighed against the increase in line pressure and the possibility of blockage under high flow conditions. A technique based on measurement of turbulence-induced electrical noise at on-line ultrasonic sensors has been shown to give data proportional to the solids concentration. Mass and volumetric flow rates can therefore be determined simultaneously on sludges at various stages in process (Balachandran and Briggs 1981).

(ii) <u>Dissolved oxygen</u>   (0 to 100% $\pm$ 1% or 0-200% $\pm$ 2% of the air saturation value)

Dissolved oxygen is perhaps the most important overall indicator of pollution and is measured utilising galvanic or polarographic probes which will work reliably in flowing samples. However, both rely on the diffusion of gaseous oxygen through a hydrophobic membrane (usually polythene or Teflon), and in polluted waters it is necessary to inhibit the formation of algal growths and bacterial slimes on the membrane and to calibrate the probes regularly. To avoid interferences from gaseous hydrogen sulphide it is possible to deploy a silver/silver sulphide salt as an electrolyte and thus avoid the possibility of sensitivity loss by poisoning.

A recent innovation developed by Leeds and Northrup Limited which is claimed to be maintenance free is based on a coulometric principle. The probe contains three electrodes; an anode or oxygen generator, a cathode at which oxygen reduction occurs and a reference electrode. The electrolyte is contained by a polythene or Teflon membrane but this is protected by a second robust silicone rubber membrane which is far more permeable to oxygen. However, it still seems vital to provide automatic cleaning daily and some form of automatic calibration

(iii) <u>Temperature</u> (-10 to $+40^\circ$, 0.5°C)

Temperature measurement is seldom a problem. Platinum resistance thermometers give the best results, but in many cases the long-term stability of thermistors is adequate.

(iv) <u>Oxidised nitrogen</u> (0 to 50 mg N $^{-1}$, $+^-$ 5% of reading)

Apart from the automatic wet-chemistry analyser approach, which is not generally recommended for unattended monitoring, the only technique known to be in common usage is the deployment of a 'specific ion monitor' fitted with a nitrate ion-selective liquid ion-exchange electrode. The electrode performance is affected by interference from other ions in solution, in particular perchlorate, iodide, permanganate, thiocyanate and zinc. In addition, the algicide Panacide, which could in other circumstances be used to inhibit algal growth, also has an adverse effect on electrode performance.

However, the specific ion monitor has the facility for mixing the sample with a reagent, in this case a total ionic strength adjustment buffer (TISAB) to stabilise the ionic strength and to reduce the pH value below 4.5 to eliminate carbonate and bicarbonate interference. The means of thermal stabilization of the sample and electrode assembly, the automatic calibration and standardisation are also built into the monitor and, provided that the sample does not contain a high concentration of suspended solids, the 3 mm bore pipework and peristaltic pumps will operate effectively for up to a week unattended, thus providing a measure of nitrate ion concentration in the sample in the range 1.4 - 140 mg N l^{-1} with a precision of approximately $\pm$ 10% of reading.

(v) <u>Ammoniacal nitrogen</u> (0 to 5, 10 or 50 mg N^{-1} $+^-$ 5% of reading)

A specific ion monitor similar to that described for the measurement of nitrate ion may be used for the determination of total ammonia (as NH_3) in the sample. In this case the electrode consists of a glass pH electrode situated behind a thin gas- permeable hydrophobic membrane, with a small quantity of ammonium chloride solution in contact with the electrode tip and the membrane. When the probe is immersed in a sample containing free ammonia, the latter diffuses through the membrane until the partial pressure of ammonia is equalized on both sides. Thus, as the ammonia concentration in the sample changes, the pH electrode detects the change in hydrogen ion concentration and the probe as a whole has a Nernstian response to ammonia. The probe exhibits considerable resistance to contamination by dissolved ions and gases. Carbon dioxide, hydrogen sulphide and sulphur dioxide which might be expected to interfere do not affect the performance at the high pH value at which measurement of free ammonia is made. In practice the reagent added to the sample consists of a mixture of sodium hydroxide solution to increase the pH value to 11-12 and ethyldiamine tetra acetic acid (EDTA) to minimise the deposition of hardness.

The response time of the probe varies from a few seconds at concentrations about 1 mg l^{-1} to several minutes at concentration about 0.1mg l^{-1}. When used in the specific ion monitor it will operate unattended in samples containing low concentrations in the range 0.4-140 mg N l^{-1} with a precision of approximately $\pm$ 10% of reading.

(vi) <u>Organic matter</u> (0 - 10 or 0 -100 mg l^{-1} $+^-$ 5% of reading)

Ultraviolet absorption at 254 nm has been shown to correlate well with total organic carbon (TOC) for a wide variety of samples ranging from settled sewage and effluents to raw and treated river water and an instrument has been developed for water quality monitoring applications and for control of water and wastewater treatment processes. When the 'Organic Pollution Monitor' (Briggs et al 1976) first became commercially available, difficulties were encountered because of drifts in the intensities of light emitted in the ultraviolet and visible parts of the spectrum (the latter is used to correct for suspended solids which may be present in the sample). This drawback has now been overcome by the provision of a thermal stablization unit around the base of the UV lamp. After settling down, which usually takes several hours after initial switch on, the monitor will operate satisfactorily for at least a week without any attention.

(vii)<u>Suspended solids</u> (0 to 0.1, 0 to 1, 5 to 500, 500 to 5000 mgl^{-1} +$^-$ 5% of reading)

Strictly speaking, this variable can only be determined gravimetrically by filtration or centrifugation of a known volume of sample followed by drying and weighing the residue. However, optical techniques have been used for some time to measure turbidity which may be related to the suspended solids concentration provided that variations in the nature of the particulates in suspension, their shape and size distribution are known (Briggs et al 1967). Turbidimeters fall into two basic categories, i.e. absorptiometers, which measure the amount of light transmitted through sample and nephelometers which measure the amount of light scattered at one or more angles to the incident beam. There is now a very wide range of absorptiometers and nephelometers commercially available; these satisfy most operational requirements including the monitoring of ultra-pure waters, river waters, effluents, sludges and slurries, whose concentration is measured in per cent solids (weight/volume) rather than mgl^{-1}. It should be possible therefore, by careful selection, to find a turbidimeter suitable for almost any river water quality monitoring application. Some of the better turbidimeters have built-in compensation for fouling of optical surfaces and/or mechanical means of cleaning these surfaces, and in some instances the optical elements are not in contact with the sample at all. These can be calibrated by means of the Formazin standard which has been shown to be reproducible between samples and stable after several months of storage in recommended conditions.

When obtaining a practical correlation, however, it is necessary to take into account the effect of flow on particle size distribution since this will in general cause a reduction in sensitivity at higher solids concentration. Provided adequate cleaning and calibration procedures are used and the hydraulic circuit is designed to avoid trapping gas bubbles and sediment settlement, data of the required precision can be obtained.

(viii) <u>pH value</u>

A large selection of glass sensing and reference electrodes is now commercially available. To be effective, the reference electrode, which ideally should be of the double-junction type should not be electrically grounded or present a low impedance to ground. An earthed guard electrode would be placed around the pH probe, and the glass/reference electrodes connected to a dual input stage-balanced differential amplifier with a very high input impedance (10^{13} ohms). This overcomes the drift problems and provided that periodic mechanical (brush), ultrasonic or chemical (algicide and bacteriocide) cleaning techniques are also used, it is possible to monitor pH in the range 1-12 with a precision of 0.2 pH units for periods of up to one week in unattended operation. The interval between servicing may be extended considerably if low and high calibration solutions are fed to the probe on a daily basis and used to correct the calibration of the instrument automatically.

Novel optical techniques are being developed to measure pH by monitoring colour changes in indicator dyes used to sense this variable. For example, simple devices for use in titration work have been developed (Benaim, Grattan and Palmer 1986) with low cost LED sources, and work is progressing on systems where dyes are immoblized or bonded to a subtrate, yet free to react with the pH sensitive medium (Narayanaswamy 1988). Problems of speed of response and lifetime of the probes remain, although they may well be suitable for 'one-shot' operation.

(ix) <u>Gases</u>

Gases which need to be monitored include oxygen, chlorine, carbon monoxide, carbon dioxide, hydrogen sulphide, methane and other flammable gases both for process control and to ensure health and safety at work.

Existing sensors are mainly electrochemical in nature and in general work satisfactorily provided they are maintained properly. However a non-contact optically based sensor could offer considerable advantages here (Briggs and Grattan 1989).

RECENT DEVELOPMENTS IN SENSOR TECHNOLOGY

In spite of the well published advances in microelectronics and the consequential reductions in the costs of computer and micro-processor hardware, progress with the implementation of control and automation projects in the water industry has, in many cases, been disappointingly slow. The reason often put forward for this lack of progress is the absence of sufficiently robust and reliable sensors for the measurement of those variables of significance in the monitoring and control of the particular process or plant in question. In many cases this view is only partially true and recently developed techniques such as the use of dual sensors, one on-line and one on standby, majority polling, automatic cleaning and calibration have enabled many existing sensors to be utilised successfully in a wide range of process control applications.

Frequently, however, environmental or process stream conditions are such that the requirement is for non-contact sensors or, at the very least, intrinsically safe sensors such as those deploying fibre optics for measurement of a range of physical variables.

Unfortunately, non-contact sensing techniques are not yet practicable when monitoring such variables as treatability, toxicity and concentrations of nutrient/substrate, heavy metal ions and trace organics as would be required, for example, in certain water, fermentation, pharmaceutical and medical applications. Here the development of low cost multiple sensor arrays based on semiconductor technology is of distinct relevance (Briggs, Meredith and Solman 1985).

(i) Flow Measurement

Since a wealth of information on methods of flow measurement is readily available, particularly in respect of turbine meters, vortex meters and methods utilising ventures, flumes and weirs (Medlock 1982) this aspect will not be discussed further. However two aspects are worthy of brief mention, these being:-

1. Measurements where intrinsic safety is a serious problem and/or where the environment is particularly hostile and as in sewers.

2. New technological developments may well have a significant impact on flow measurements generally; these include cross-correlation techniques and measurement of flow and/or pressure utilising fibre or electro-optically based sensors.

A significant application of lasers and fibre optics is to flow measurement through the use of the laser (Doppler) anemometer which has been commercially available for some years, but at significant cost.

Laser anemometers are non-contact optical instruments for the investigation of fluid flow structure in gases and liquids. These instruments can also measure surface velocities of solids or in a slightly different implementation, surface vibrations. All these instruments owe their existence to the invention of the gas laser in the early sixties. Some earlier attempts to measure fluid velocities by optical methods had been made, but it was not until the advent of laser light wit its unique properties of spatial and temporal coherence that it became possible to design on efficient optical anemometer. A commercial device is shown in Figure 1.
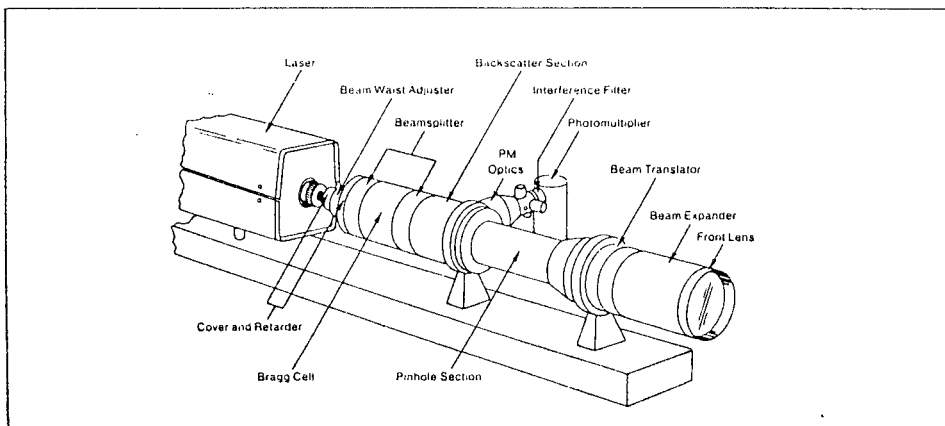

Fig. 1. Laser doppler anemometer (from Dantec 1985)

Laser anemometers offer unique advantages in comparison with other fluid flow instrumentation, as reported by Dantec Instrumentation (1983), a major European manufacturer:

- non contact optical measurement
- no calibration (no drift)
- well defined directional response
- High spatial and temporal resolution
- Multi-component directional measurements

However the conditions under which laser anemometer measurements are carried out vary considerably. It is essential that the optical system can be adopted to the mode and configuration most suited for a particular measurement, e.g. the use of "seeding particles" which must be small enough to track the flow accurately yet large enough to scatter sufficient light for the proper operation of the instrument.

Other fibre optic analogues of "conventional" flow metering devices e.g. vortex shedding devices, have been proposed and discussed (Medlock 1986) and may be valuable where intrinsic safety aspects are important e.g. the monitoring of flammable fluids.

(ii) Sensors for Monitoring Specific Pollutants

Summary descriptions are provided in subsequent paragraphs of sensing systems based either on solid state sensors or electro- optic techniques (Webb 1985 and Williams et al 1987). In principle these are cheaper to fabricate and install, frequently more useful and of more general applicability than conventional sensors.

One of the most attractive possibilities for monitoring such variables as heavy metals and trace organics is the deposition of appropriate sensitive materials on the gates of an array of metal oxide field effect transistors (MOSFETS) which are integrated with a microprocessor on to a single chip. Clear advantages are low cost if the market allows volume production, miniaturisation, the ability to use a good deal of redundancy and thus obtain better reliability and in some cases the ability to deploy in situ cleaning and calibration. Additionally if trend and/or ratio measurements are satisfactory then these devices would be particularly useful and certainly less expensive than those in use at the present time (Briggs, Meredith and Solman 1985).

(iii) Heavy Metals

An attractive approach to the problem of monitoring toxic metal concentrations has been investigated by STL, Harlow, under sponsorship by WRC. The principle of the method is to deposit soluble phrophate and/or borate glasses containing oxides of the heavy metals of interest on to the gate of a MOSFET thus forming an ion-selective electrode. An example is shown in Figure 2.
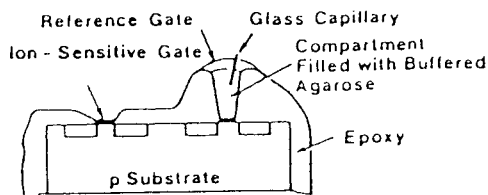

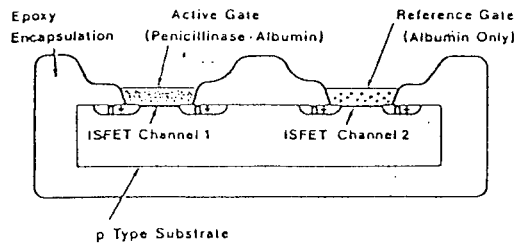Fig. 2. Sectional diagram of an ISFET with an integral reference gate (from Sibbald, 1986).

Fig. 3. Simplified sectional diagram of an enzyme modified FET sensor pair (from Sibbald 1986)

Using a MOSFET array a number of ion-selective electrodes responsive to a number of different metal ions could be fabricated on a single chip. If one of the ion-selective electrodes was made predominantly sensitive to a non-toxic metal of little interest then the concentrations of the other ions could be determined as a ratio of a known concentration of the reference ion.

By this means, the concentrations of a large number of metal ions can be monitored utilising a single probe incorporating the MOSFET array and the microprocessor element needed to solve the resulting simultaneous Nernstian type equations relating ionic activities to gate potential. Clearly for this to be practicable each gate must be considerable more sensitive to one ion than to the others and the device as a whole must be waterproof; achieving adequate sealing proved to be a problem initially but has since been largely overcome firstly by using silicon nitride for the devices and secondly to encapsulate all areas other than the gates themselves in silicon rubber. Initial work indicated that lead, copper, mercury, cadmium, zinc, iron, aluminium and manganese in this way but not yet with sufficient sensitivity in all cases.

An alternative, developed initially for measurement of pH value sodium potassium, calcium and chloride ions for use in medical applications is the use of chalcogenate glasses. However the technique is essentially the same as that described above, only the sensitive material applied to the gate being different.

(iv) Measurement of treatability, toxicity and trace organics

At the present time (and indeed for the foreseeable future) there are limits to the scope and range of information that can be obtained at reasonable cost form monitors based on physical and chemical sensors. Therefore attention has been directed to the use of biological monitoring techniques. These have included the use of nitrifying bacteria (Holland 1977), the use of non-contact electrodes to measure potentials resulting from muscular activity in rainbow trout using a non-contact electrode system (Miller 1977, Morgan 1977 and Sloof 1979).

Alternatives developed more recently have included immobilisation of enzymes in MOSFET gates, the work being carried out at Case Weston University (Neuman et al 1980), Utah (Cares and Janata 1980) and at a number of centres in the UK (Sibbald 1986, 1985 and Sibbald et al 1984) and in Continental Europe (Bergveld 1970). A simplified diagram of an enzyme modified FET sensor pair is shown in Figure 3.

Also of considerable interest is the work being carried out in England under the auspices of WRC at Luton College of Higher Education with assistance from Cranfield Institute of Technology and reported by Rawson and Willmer (1987). Basically the method comprises the use of mediator assisted whole cell biosensors for monitoring photosynthetic electron transfer at an electrochemical cell. To date useful measurements have been made of concentrations of herbicide residues up stream of intakes to water treatment works.

An interesting alternative is that described by Mosbach and Dannielson (1987). In this case enzymes are immobilised on thermistors which are then utilised to measure heats of reaction. An indication of the sensitivity and selectivity of the approach is provided in Table 6.

TABLE 6:

Achievable Selectivity and Sensitivity of Detection of Technique
Based on Measurement of Heat of Reaction Utilising Enzymes Immobilised on Thermistors or Similar Devices

Application area	Substance	Immobilised biocatalyst	Conc range (mmole/l)
Environmental	heavy metal ions (eg PB^{++})	Urease	10^{-6} (detection limit)
	insecticides (eg parathion)	Acetyl- cholinesterase	5×10^{-3} (detection limit)
	Cyanide (substrate)	Rhodanese	0.02 - 1
	Phenol (substrate)		0.01 - 1

(v) Optical Methods of Measurement

The use of electro-optics and optical fibres coupled with microprocessors offers an attractive solution to many water industry problems, particularly those associated with measurement in or communication from hazardous areas where intrinsic safety considerations are paramount. Additionally the use of fibre optics, and multiple light sensor arrays coupled with pattern recognition techniques can be particularly useful as a means of monitoring plant and equipment status.

Optical sensors may be defined as those devices which use ir/visible/uv radiation to detect a change in a variable to be measured, regardless of the nature of the interaction of the light with the measurand. "Open-air" (free space propagation) of the radiation is equally relevant, though current emphasis is on the utilisation of fibre optics in sensors for convenience of measurement. In certain cases the primary interaction between the measurand and the sensor need not be an optical interaction, but the sensor must produce an optical output after further transduction, as in the so-called "hybrid" devices or optically powered electronic sensors.

Extrinsic fibre sensors use the fibre primarily as a means of guiding light through the fibre to the measurement region, where its polarisation, wavelength, phase or intensity is modulated by the measurand, and guided to a receiver where signal processing occurs. Within this class are some systems (eg time-division- multiplexed, shaft-encoders, and "frequency-out" sensors) where the information transfer is non-intensity dependent. In an intrinsic fibre optic sensor, the fibre itself acts as the sensor, and the propagation of light within the fibre is disturbed in a measurable way; distributed or quasi-distributed sensors are important special cases within this class. There are only very limited applications of the latter class of sensors to chemical variables, although work in the field is being undertaken.

The development of optical sensors is being stimulated by advances in optical fibre technology arising primarily through telecommunications requirements. The advantages of the use of fibre optic sensors are summarised below and slowly this new technology is becoming accepted for measurement applications.

There is a vast wealth of optical phenomena which can be utilised to measure both physical and chemical variables. Research into most of these areas is being carried out on a worldwide basis and includes research into the development of robust easy to install and maintain fibres for data transmission purposes.

The advantages and applications of Fibre Optic Techniques these may be summarised as: inherent electrical safety and freedom from interference from electromagnetic "noise". Additionally fibre optics are light, small and largely free from cross-talk. With the development of powerful solid state laser sources and detectors, there is considerable potential for cost reduction and high performance from small, compact systems, rather than using lasers or lamp sources, which are fragile.

It is beyond the scope of a paper of this nature to discuss the very wide range of optical phenomena used in optical sensors and the many experimental schemes suggested to utilise these effects. Several sensor schemes are shown in Figure 4. A number of reviews exist in the literature, often focusing upon recent trends (Culshaw 1986), specific measurands (Grattan 1987) or techniques (Pitt et al 1985). In 1989 a text book will be available (Wolfbeis 1989) to which a large number of experts in the field of Fibre Optic Chemical Sensors have contributed. This will represent the most comprehensive review of this very wide field and below is an illustration of the breadth of the subject. For example the following extrinsic sensor schemes may be applied: absorptiometry, reflectometry,

fluorimetry, phosphorimetry, infrared and Raman spectoscopy, evanescent wave techniques, chemi- and bio-luminescence. In addition there are the use of ground state and excited state optical sensing processes.
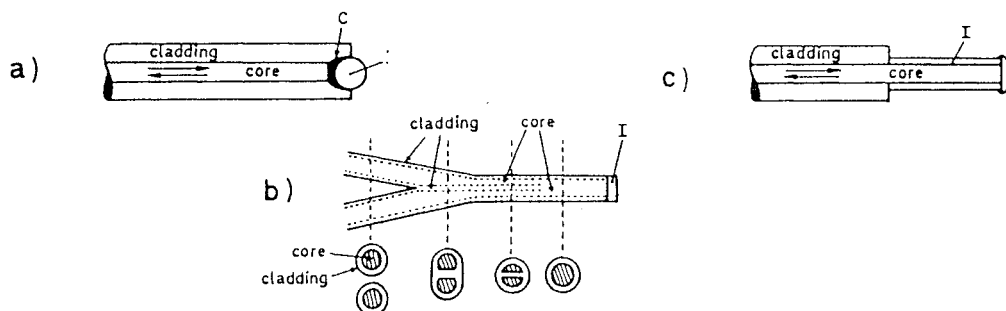

Figure 4: Types of indicator phase sensors. (a) A glass ball is cemented onto the end of a single fibre, with an indicator layer immoblized on the ball. Fluorescence is guided back through the same fibre through which exciting light is guided to the ball. (b) an indicator phase is attached to the common end of a bifurcated fibre. (c) The indicator is immobilized directly onto the fibre core. (From: Wolfbeis, 1988).

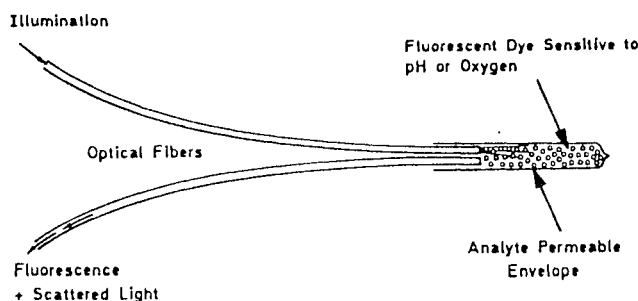An early and relatively simple pH sensor is shown in Figure 5 below.

Figure 5: Schematic of a thin fibre optical catheter suitable for invasive sensing. for measurement of pH, the fluorescent dye was replaced by an absorption indicator and the ratio of reflected light at two different wavelengths measured. (From: Wolfbeis, 1988).

There is much research in the chemistry of sensor materials needed to make them suitable for incorporation in fibre optic devices. The use of immobilisation techniques and fluorescent labelling have been discussed. pH sensors are widely needed and a number of fluorescence and absorption based schemes proposed (Narayanaswamy and Sevilla, 1988). Again, considerable work will be required before systems meeting the acceptable quality criteria of response time, use of solid state optoelectronics and avoidance of loss of the sensor material are available. Processes using changes in the characteristics of materials e.g. cation detection using ion-selective binding with optical readout or conversion of non-fluorescent ligands to fluorescent complexes or the synthesis of compounds which undergo colour changes upon ion-binding can be used. Dissolved oxygen is known to quench fluorescence and this may be utilised as the basis of a sensor. Chemo-retention techniques may be used where selective binding events associated with receptors located within liquid matrices can change the electrostatic and physical structure of such liquid membranes. These perturbations can be detected optically be the use of fluorescently-labelled receptors and also by incorporation of fluorescent probes in liquid membranes. Hence devices using wavelength, intensity or lifetime data can be devised.

CONCLUSIONS

There is a sizeable market area within the Water Industry and Water User sectors for new technologies which either give rise to more robust, reliable and easily maintainable instruments to replace those currently in use in on-line monitoring and control applications, hopefully at lower cost or for sensors and support systems for monitoring those variables which can not be monitored reliably on-line at the present time.

The continuing work on the provision of user specifications coupled with the instrument evaluations at present being carried out provided guidance both to those in research and to instrument and system manufacturers.

It is hoped that the considerable impetus that has been provided in the ICA area will lead both to increased efficiency, in process control and environmental monitoring applications and to the production by the Instrument Industry of equipment tailored more specifically to user needs.

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