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# MONITORING OF NITRATES AND PHOSPHATES IN WASTEWATER: CURRENT TECHNOLOGIES AND FURTHER CHALLENGES

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***Abstract- Consumers expect water supply companies to deliver safe drinking water that meets both health quality standards and aesthetic requirements such as colour, turbidity, taste and odour. Current water quality assessment methods of these parameters, which form the basis for sound water resources management, are mainly laboratory based, require fresh supply of chemicals, trained staff and are time consuming. Real-time water quality monitoring is essential for National and International Health and Safety, as it can significantly reduce the level of damage and also the cost to remedy the problem. This paper critically analyses both commercially available and state-of-the-art research methods and devices suitable for real-time wastewater quality monitoring and suggests further developments in this area. In particular, the focus is made on the monitoring of nitrates and phosphates in wastewater and a novel microwave based method for instantaneous water quality assessment is suggested.***

**Index terms*:* water quality monitoring, *in situ* analysis, optical methods, industry, nitrates and phosphates, lab on chip sensors, microwave sensors, solid-state sensors.**

# I. INTRODUCTION

Potable water is one of the most valuable natural resources that our planet has. The European Water Framework Directive (WFD) requires the monitoring of water systems in the European Community with the goal of maintaining and improving these systems [1]. Rapid and confident assessments of aquatic resources using a variety of sensors form the basis for sound environmental management, as it is vital to assess source waters and the aquatic systems that receive inputs from industrial waste and sewage treatment plants, storm water systems, and runoff from urban and agricultural lands.

Water quality assessments are based on the analysis of the physical, chemical and bacteriological parameters and require customised apparatus and trained staff. Environmental water monitoring includes measurements of physical characteristics (e.g. pH, temperature, conductivity), chemical parameters (e.g. oxygen, alkalinity, nitrogen and phosphorus compounds), and abundance of certain biological taxa. Monitoring could also include assays of biological activity such as alkaline phosphatase, tests for toxins and direct measurements of pollutants such as heavy metals or hydrocarbons. In May 2007, the European Parliament proposed increasing from 33 to 61 the toxic products covered by European legislation on water quality. Forty five of these were classified as priority substances and should no longer be used by 2015.

Consumers expect water supply companies to deliver safe drinking water that meets health quality standards, and aesthetic requirements such as colour, turbidity, taste and odour. To this end water supply companies have developed quality management systems and monitoring strategies, using well-established laboratory techniques. The quality of treated wastewater is primarily defined by the measurement of global parameters such as Biological Oxygen Demand (BOD), Chemical Oxygen Demand (COD), Total Organic Carbon (TOC) and Total Suspended Solids (TSS) [2].

In daily use there are up to 70,000 known [3] and emerging [4, 5] chemicals that might be present in various water resources, including for drinking water production. Therefore, on-line monitors should be able to detect the excess of pollutants established by the official water quality regulations. This requires sensitive sensors as standards are often close to the limits of detection, e.g. the EU pesticide standard of 0.1 μg/L [1].

Multi-parameter water quality monitors, or sensor panels, are mainly used in finished water, i.e. in water which has been treated and is ready for consumption. Typical parameters and techniques used in these monitors are listed in Table 1. Single probes or combinations of sensors are commercially available, enabling water utilities to monitor the quality of processed water. There are difficulties with independent validation of these systems as the methods and algorithms employed are commercially sensitive.

Table 1. Most commonly measured water parameters and associated sensing technologies.

| **Parameter being measured** | **Sensing technology** |
|---|---|
| Aluminium | Colorimetry; Atomic Absorption Spectrometry |
| Antimony | Atomic Absorption Spectrometry |
| Ammonia | Colorimetric (Manual; Nessler's Reagent; Automated; Berthelot Reaction) |
| Chlorine | Colorimetric; Membrane electrode |
| Conductance | Conductivity cell |
| Dissolved oxygen | Membrane electrode; Optical sensor |
| Oxidation-Reduction Potential | Potentiometric |
| pH | Titration with Sodium Hydroxide; Glass bulb electrode; Ion Sensitive Field Effect Transistor (ISFET) |
| Phosphates | Manual or Automated Colorimetry |
| Temperature | Thermistor |
| Turbidity | Optical sensor; Nephelometric |
| Ions ($Cl^-$, $NO_3^-$, $NH_4^+$) | Ion-selective electrodes |

In accordance with EC directives, wastewater treatment facilities are obliged to meet discharge consents of phosphate into the environment. High levels of nutrients such as phosphates from wastewater treatment plants are released into the environment and are the main cause of eutrophication, which occurs in oceans, lakes and rivers when water quality is impaired due to nutrient pollution. Algal and plankton growth increases greatly (algal bloom) and this results in oxygen depletion for other aquatic life in the ecosystem. In order to combat the release of phosphate into the environment a group of microorganisms are added to wastewater that have the ability to accumulate and metabolise phosphate intracellularly. They can also store phosphate thus reducing the amount of phosphate released into the environment. This process called Enhanced Biological Phosphate Removal or EBPR is still in the early stages of development and is difficult to maintain especially when the influent in treatment plants varies so greatly.

This paper provides a critical review of the currently available sensor technologies for monitoring of nitrates and phosphates in water, and in wastewater in particular. This includes the untreated and treated wastewater from sewerage systems, agricultural sources such as fertilisers and animal waste [6]. The presence of nutrients and heavy metals in water is a serious threat to human health.

Human activity is the main source of excessive phosphate and other nutrients in water. Phosphorus is widely used as an agricultural fertiliser and within domestic detergents. Phosphates can exist in wastewater in several forms depending on the source/nature of the discharge but are generally grouped within three broad classes: orthophosphates, condensed phosphates (pyro-, meta- and poly-) and organic phosphorus. Approximately 50-70% of the phosphate in wastewater exists as orthophosphate ($PO_4$) [7], which could be in the form of phosphoric acid ($H_3PO_4$), dihydrogen phosphate ($H_2PO_4^-$), hydrogenophosphate ($HPO_4^{2-}$) and phosphate ion ($PO_4^{3-}$).

From an environmental perspective, the concentration of phosphate in water is crucial due to its role in eutrophication [8]. Traditionally phosphate was monitored manually by collecting and filtering samples which were later analyzed in a laboratory. Various detection strategies for phosphate include phosphate ion selective electrodes based on potentiometric techniques, indirect voltammetric detection based on the reaction of phosphate with various metals and associated complexes, and the development of sensors exploiting enzymatic reactions [9].

Nitrate is a key element in the nitrogen cycle as it is the link between the nitrification and denitrification processes. As nitrate fertilisers are increasingly used in agriculture, the quantity of nitrate leaching from fields into rivers and ground waters is increasing cumulatively. Nitrate is a permitted food additive for use in curing meat, since it is not toxic to humans [10]. However, once nitrate has entered the body it can be reduced to nitrite by bacteria in the stomach and further incorporated into carcinogenic N-nitrosamine compounds. Nitrate is also an important analyte for environmental, food and human health monitoring and thus its detection and quantification is essential.

Current measurements of nutrients, such as phosphorous, ammonia and volatile fatty acids in water are mostly based on off-line monitoring and imply low frequency data sampling and delay between sampling and availability of the results. However, in past years there has been a growing interest in the use of on-line monitoring systems able to distinguish abnormal changes from normal variations [11, 12] for reasons of:

- lower costs;
- response time;
- security concerns.

Real-time monitoring of wastewater quality remains an unresolved problem to the wastewater treatment industry [13]. Advanced autonomous platforms capable of performing complex analytical measurements at remote locations still require individual power, wireless communication, processor and electronic transducer units, along with regular maintenance visits. Therefore, there is a need to develop an automated cost-effective method of wastewater quality monitoring, in particular for the measurement of nutrients and phosphates.

An overview of the state-of-the-art in the real time monitoring of nitrates and phosphates in water is given below. It reveals that it is not possible to achieve adequate simultaneous detection of different water parameters by using only one type of sensor. The solution could be in merging various technologies into a single system that would employ the best available methods for the detection of specific water contaminants, providing overall superior sensitivity, selectivity and long-term stability, while at the same time enabling real-time wireless data collection for enhanced cost-effectiveness. This approach is commonly known as sensor fusion, which refers to the acquisition, processing and synergistic combination of information gathered by various knowledge sources and sensors to provide a better understanding of a phenomenon [14].

Critical analysis of the available technologies suggests that to date sustainable sensor fusion for autonomous long-term monitoring of water quality was not possible due to the fact that most methods of pollutant detection are labour-intensive, either lab based and/or require expensive chemicals, maintenance and degrade over time. It is shown that a novel approach to wastewater monitoring, namely using specially designed microwave cavity sensors, could serve as the missing puzzle piece to a successful multi-sensor fusion to provide a platform for a real-time detection of water content with superior sensitivity (Figure 1).

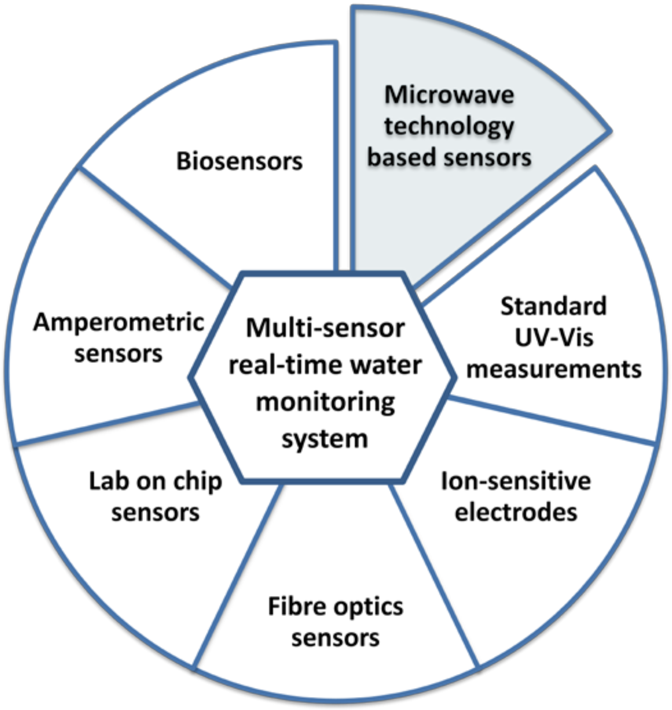

Figure 1. Components of an ideal multi-sensor real-time water monitoring system.

## II. CURRENT TECHNOLOGIES: STANDARD UV-VIS OPTICAL METHODS

The main method for phosphorus detection is using a photo sensor which measures the wavelength of a distinct colour (e.g. blue or yellow) that results from a chemical reaction between phosphorus and special reagent [7]. The concentration of the resultant dye indicates the concentration of phosphorus in the sample. Figure 2 shows conceptual diagram of the two standard UV-Vis optical methods, namely the molybdenum blue method and the vanadate / molydate yellow method.

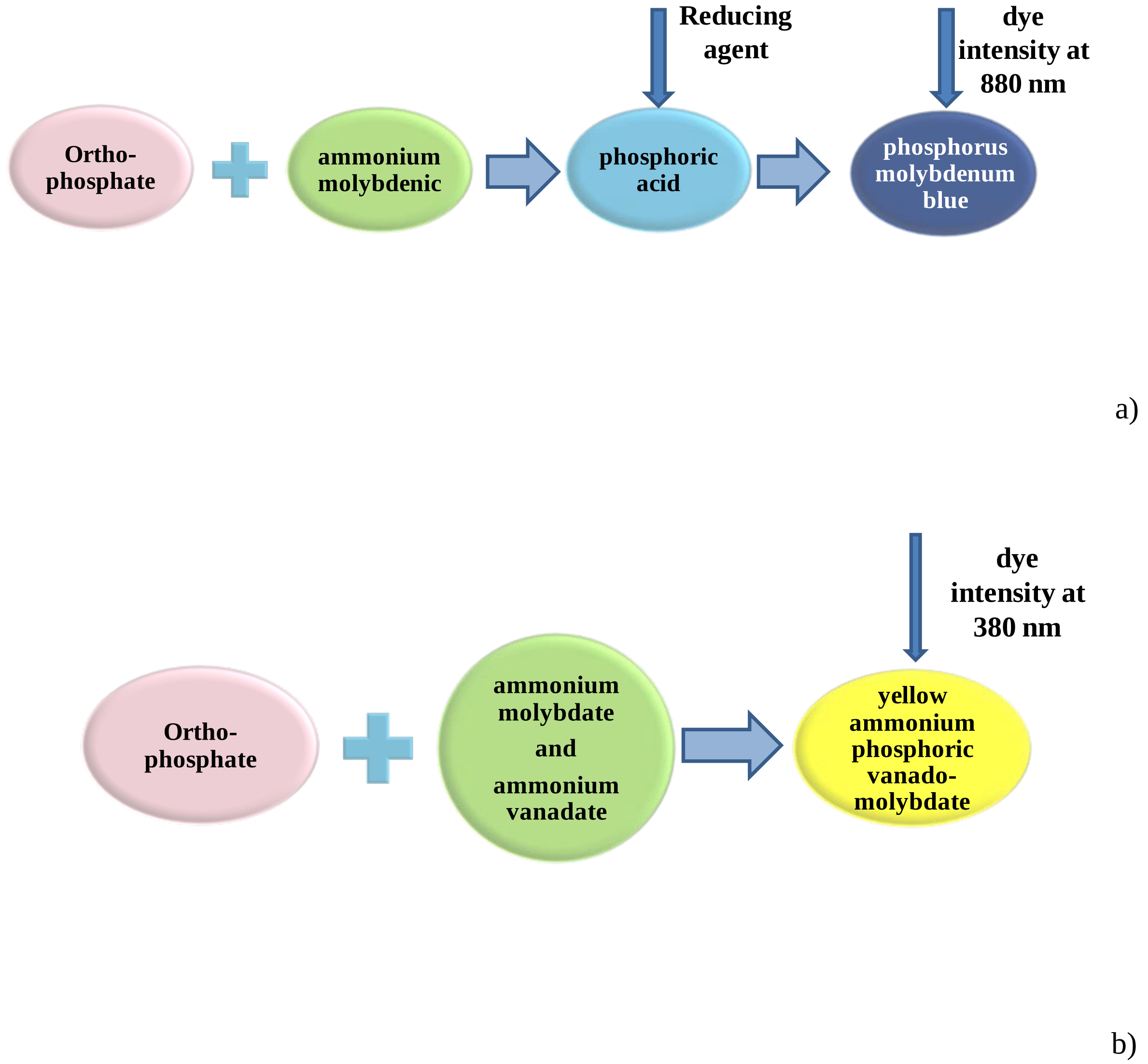

Figure 2. Conceptual diagram of standard UV-Vis optical methods: a) Molybdenum blue method, b) Vanadate / molydate yellow method.

In the molybdenum blue method, in an acidic medium, orthophosphate bonds with ammonium molybdenic to form phosphoric acid. With the aid of reducing agents this forms phosphorus molybdenum blue and photometric measurement then determines the dye intensity at 880 nm for the blue colour.

The vanadate / molydate yellow method is as follows: in acids, orthophosphate ions react with ammonium molybdate and ammonium vanadate to form yellow ammonium phosphoric vanadomolybdate, which can be analysed at 380 nm using a photometric sensor [7].

Most of the reported wastewater UV-Vis spectrometric applications are based on visual observation and direct comparison of the UV-Vis spectra. A few examples of commercially available systems are given below.

### i. Hach Lange instruments for water analysis

Hach Lange is probably one of the most known and reputable suppliers of equipment and chemicals for various lab based measurements, and especially for screening of water parameters. They provide a broad spectrum of analytical techniques that are considered as a standard by many industrial and utilities companies, and full details can be found at www.hach-lange.com.

### ii. EnviroTech Instruments

EnviroTech Instruments company offers, for example, a field-deployable nutrient analyser system available in single or dual channel configurations that may be "daisy-chained" to provide up to six channels of simultaneous chemical analysis. Parameters include nitrate, phosphate, ammonia, silicate, chloride, iron and urea. Sampling pump control and a cellular modem interface for real-time / on-line data are built-in. AutoLAB 4 has a very low maintenance requirement, incorporates easy-load reagent storage for maximum up-time and onsite service.

Figure 3. AutoLAB 4 – Remote Station Nutrient/Chemical Analyzer [15].

The AutoLAB 4 system, illustrated in Figure 3, employs well established wet-chemistry to determine nutrient concentrations via standard analytical techniques. This allows direct comparison with laboratory data and avoids interferences and fouling problems intrinsic with optical systems. AutoLAB is a discrete (not flow-type) analyser and so avoids problems with clogging and tube wear. The discrete analysis methods allow short sampling times, in-situ self-calibration and automatic maintenance. Beam attenuation from the colour reaction is recorded. It detects nitrate at a range of 0-5 mg/l at 543 nm wavelength and a phosphate in 0-0.8 mg/l range at 880 nm, both with 0.003 mg/l sensitivity.

### iii. TresCon

TresCon on-line water analysis systems, offered by WTW Measurement Systems Inc., in Ft. Myers, Florida, allow for the continuous determination of ammonia, phosphate, nitrate, or nitrite in most water and wastewater processes. TresCon is a modular device that can be configured to monitor one, two, or three of the parameters mentioned simultaneously.

To operate the TresCon system, a continuous supply of water to be analysed is required. A flow rate of 2-3 litres/hour is sufficient. The analyzer continuously "sips" from this sample stream, and feeds the sample to the measurement modules installed. In the ammonia module, the sample is mixed with a basic reagent to raise the pH. This converts ammonium compounds to gaseous ammonia which is sensed by an ammonia-sensitive electrode. In the nitrate module, a UV light source is used and absorption at two wavelengths determines the nitrate concentration. Phosphate is determined photometrically: the sample is mixed with a molybdate-vanadate reagent. The intensity of the yellow colour developed is directly proportional to the concentration of ortho-phosphate. Nitrite is also determined photometrically by mixing the sample with a dye that will turn pink in the presence of nitrite ions. However, the data on sensitivity and range are not available.

### iv. ChemScan UV-6100 Analyser System

Another example of a commercially available system for water quality measurement is the ChemScan UV-6100 Analyser, manufactured by Applied Spectrometry Associates (ASA) Inc., Waukesha, WI. USA, which was considered by The City of Calgary's Sewer Divisions as the most economical system for 20-year operation. The UV-6100 analyser system is an on-line UV spectrometer capable of measuring the concentration of multiple dissolved chemical constituents of an aqueous sample with a single analyser. It works by transmitting UV light through the sample. A portion of the light is absorbed by the chemical constituents and the analyser splits the resulting light into 256 individual wavelengths from 200 to 450 nm. The spectral signature is analysed using Chemometrics, a pattern recognition technique, to calculate the concentration parameters.

Parameters that absorb light naturally, such as nitrate, can be analys/ed without the addition of reagents. Parameters that do not have adequate natural light absorbing characteristics must be conditioned through the addition of chemical reagents. Orthophosphate is determined using a secondary chemical method. The orthophosphate is combined with ferric at a low pH in the sample conditioning unit. The analyzer measures the resulting combined spectra and uses the Chemometric algorithm to determine the orthophosphate concentration. The reported phosphate operating range is from 0.01 mg/l to 5.0 mg/l, while nitrate can be measured in a range from 0.5 mg/l to 20.0 mg/l.

### v. Research type Autonomous Phosphate Analyser (DCU and EpiSensor)

An autonomous platform for the measurement of phosphate levels in river water was developed by the Clarity Centre in Dublin City University (DCU) and is being commercialised with EpiSensor, a Limerick based Irish company. This device is designed to operate unassisted for one year, taking a measurement every hour and relaying the result to a laptop computer [6]. The phosphate measurement is based around a microfluidic chip that mixes (at a 1:1 ratio) the water with the reagent containing ammonium molybdate and ammonium metavanadate in an acidic medium [16]. After the reaction takes place the solution will absorb below 400 nm and its absorbance is proportional to the concentration of phosphate in the original sample. A photodiode and UV LED are used to make an absorbance measurement.

The system contains the sampling, chemical storage, fluid handing, colorimetric data acquisition and waste storage capabilities necessary to perform the phosphate measurement. In addition to this, the device has the embedded control, wireless chemical sensor platform, power supply to allow independent operation and operates via the Global System for Mobile Communications (GSM). This system reportedly has the following performance parameters: 0.1mg/l limit of detection with 20 minutes minimum sample interval and provides linear response range of 0-50 mg/l for orthophosphate.

### vi. Limitations of the optical methods of detection

Sensors based on colorimetric UV spectral measurements are widely used in commercially available systems [17], but they all suffer from a number of limitations. In particular, sample handling is problematic, and the acquisition of a reference spectra and calibration process are necessary for samples of different origin.

From the above discussion, it follows that methods for the determination of phosphate such as colourimetry or spectrophotometry are still predominant in a standard utilities operation [5, 17]. However, they do not lend themselves particularly well to in-situ analysis due to the use of potentially toxic agents and lengthy preparation and analysis times. There are two main drawbacks:

- Linearity between the concentration of a compound and its absorbance performance differs from compound to compound. Therefore it is hard to identify a compound based on a single spectral wavelength. Only the ratio between different wavelengths can assist identification.
- Secondly, only a small fraction of the potential compound array in water absorbs light with wavelengths from 190 to 850 nm.

This means that UV-Vis spectroscopy must be combined with other techniques to cover a larger compound spectrum. IR, Raman and X-ray fluorescence spectroscopy are new techniques for on-line chemical water quality monitoring, but many challenges must be overcome before these techniques can be used routinely. An alternative approach is to develop fibre optic, potentiometric or electrochemical biosensors [18] as they have the potential to be used in-situ, and when combined with hand-held instrumentation [9], offer a high degree of selectivity and specificity and may be operated by lay personnel.

## III. FIBRE OPTIC SENSORS FOR REAL-TIME WATER QUALITY MONITORING

Fibre optic sensors are used in combination with the UV-Vis methods of water contaminants detection discussed above. Normally an optic fibre is suitably doped to produce luminescence when exposed to an excitation light source. Glass fibres are either doped with a rare earth metal or activated with a transition metal. Polymeric fibres are doped with a dye. The fibres have fast response and decay times and can achieve high efficiency through the design of appropriate delivery optics. Fibre optic systems are particularly suitable for harsh and difficult to reach places. The design and selection of the fibre determines the peak wavelength of the output illumination; options exist to span the UV–Vis–NIR spectrum. A detailed review of the recently reported fibre optics based systems provides in-depth analysis of these systems for various water contaminants monitoring [19]. Notably, the coating of the fibre determines the sensitivity and selectivity of the sensor and research is continuing to develop novel materials that would suit the need of a particular sensing task [20, 21].

## IV. POLLUTANT MONITORING USING AMPEROMETRIC, POTENTIOMETRIC AND CONDUCTIMETRIC SENSORS

Amperometric, potentiometric and conductometric sensing approaches are widely used in the measurement of pollution in water [22]. These sensors change their properties as a result of interaction with the component being measured. The species of interest are either oxidised or reduced at the working electrode causing a transfer of electrons, thus generating a measureable signal. This change can be recorded as a change in the output signal, i.e. output voltage, current, change in conductivity, capacitance or dielectric constant – whatever parameter gives the most pronounced sensor response [23].

For example, a portable amperometric three-electrode immunosensor for screening of polycyclic aromatic hydrocarbons (PAHs) in water was recently reported [22]. In particular, amperometric detection is based on the measurement of current when a potential is applied to the working and reference electrodes of the system.

Potentiometric detection is the earliest direct electrochemical approach taken to the detection of phosphate. It is attractive since it possesses numerous advantages when considering the development of real-time sensing technologies, as the recording instrumentation is cost-effective and highly portable. However, the acquisition of sufficient selectivity and sensitivity to operate at the concentrations below 0.1 ppm remains problematic for these sensors.

Various potentiometric approaches to detect phosphate typically fall within one of five main categories [9], as illustrated in Figure 4.

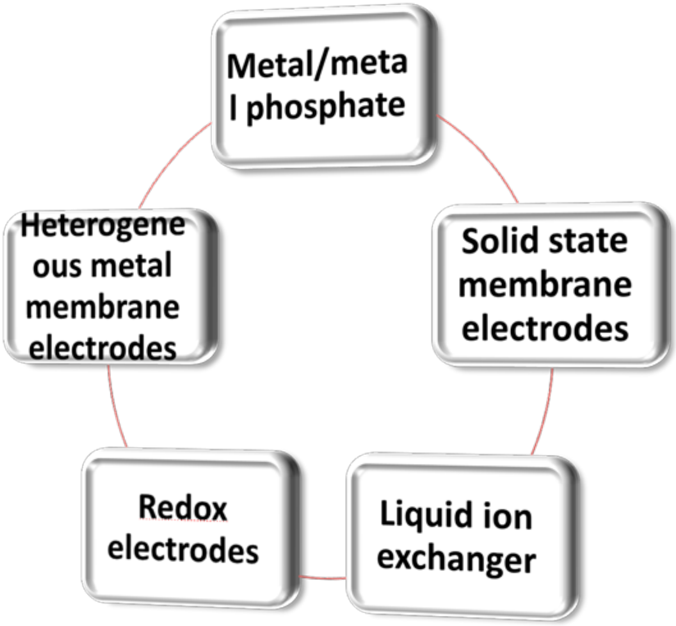

Figure 4. Potentiometric detection methods.

Although amperometric and conductimetric sensors are widely employed for various sensor systems, their use for monitoring of nitrates and phosphates in wastewater is in its infancy not least due to the limited research to find suitable materials that would provide not only desired sensitivity and selectivity, but also long-term stability and reusability of sensors.

## V. BIOSENSORS

Biosensors have been widely applied to a variety of analytical problems in medicine, food, process industries, security, defence and for environmental monitoring including water quality assessment. A biosensor is an analytical device which converts a biological response into an electrical signal. It consists of two main components: a bioreceptor or biorecognition element, which recognises the target analyte and a transducer, for converting the recognition event into a measurable electrical signal [24]. A bioreceptor can be a tissue, microorganism, organelle, cell, enzyme, antibody, nucleic acid and biomimic etc. and the transduction may be optical, electrochemical, thermometric, piezoelectric, magnetic and micromechanical or combinations of one or more of the above techniques.

Figure 5 shows schematic diagram of a biosensor. The bioreceptor recognises the target analyte and the corresponding biological responses are then converted into equivalent electrical signals by the transducer. The bioreceptor-protein interactions can be visualised with biosensors at μg/l levels (or even the sub-μg/l level). The amplifier in the biosensor responds to the small input signal from the transducer and delivers a large output signal that contains the essential waveform features of an input signal. The amplified signal is then processed by the signal processor where it can later be stored, displayed and analysed.

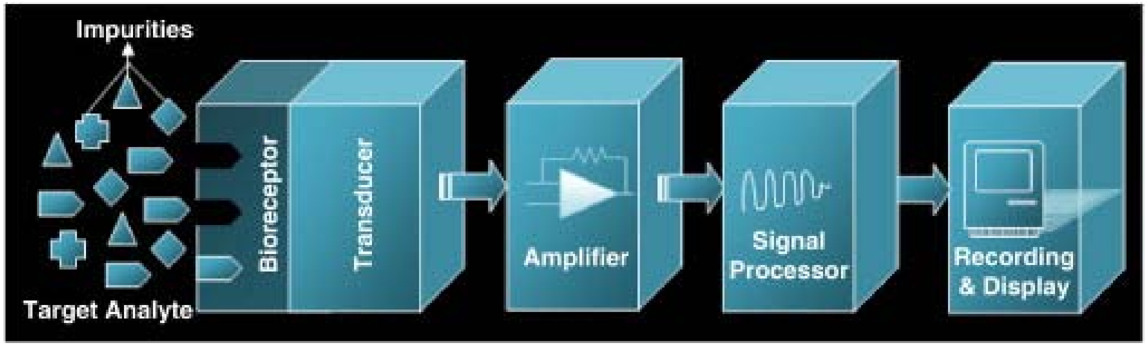

Figure 5. Schematic diagram of a biosensor [24], © Elsevier 2010.

Protein based biosensors have been developed for a series of chemical pollutants, but their sensitivity depends on the physical detection principle used and the affinity of the protein-analyte interaction. Their robustness is influenced by the selectivity of the interaction. Matrix effects can influence the binding between analyte and protein. Since water quality is variable, matrix effects are inevitable and result in a high rate of false positives and negatives, so regeneration or replacement of disposable reagents is needed between measurements.

Examples of analytes measured with biosensors are: propanil, atrazine, isoproturon, sulphamethizole, bisphenol A, estrone, 17ß-estradiol equivalents, nonylphenol, benzene, toluene, xylene, prometryn, trichloroetylene, ametryn, terbuthylazine, simazine, benzenesulfonamide, caffeine and so forth.

Biosensors for the determination of phosphate are normally based on mono- or multi-enzymatic reactions where phosphate acts as an inhibitor or substrate [10]. For example, an amperometric phosphate biosensor, based on a cobalt phthalocyanine screen-printed carbon electrode (CoPC-SPCE) was recently reported [8] to be successfully applied to the measurement of phosphate in pond water samples and a linear range of 2.5–130 μM with a limit of detection of 2 μM was obtained under optimal conditions, exhibiting a response time of ~13 s.

Also, a highly selective and sensitive monohydrogen phosphate membrane sensor based on a molybdenum bis(2-hydroxyanil) acetylacetonate complex (MAA) was reported in [25]. This sensor showed a linear dynamic range between $1.0\times10^{-1}$ and $1.0\times10^{-7}$ M, with a detection limit of $6.0\times10^{-8}$ M (~6 ppb). The best performance was obtained with a membrane composition of 32% poly(vinyl chloride), 58% benzyl acetate, 2% hexadecyltrimethylammonium bromide and 8% MAA. The sensor reportedly possesses additional advantages of short response time, very good selectivity towards a large number of organic and inorganic anions and is claimed to be suitable for at least 10 weeks usage without any considerable divergence in its slope and detection limit [25].

Nitrate concentrations are routinely determined using a method whereby nitrate is reduced to nitrite with a copper activated cadmium catalyst and the nitrite concentration is determined colorimetrically by its reaction with sulphanilamide and N-1-naphthylendiamine [10]. However, this method requires careful control of acidity during each step of the process and as such cannot be directly used as a real-time water quality monitoring system.

It is beyond the scope of this paper to discuss in detail all the methods, but notably, the application of the electrochemical sensing devices to phosphate and nitrate detection has not always been successful. He most common problems encountered and possible approaches that may be taken to solve them were discussed in [9].

Importantly, testing of new biodevices with real wastewater samples is a must in the final stages of a real-time monitoring system development, but most literature overlooks this stage and only reports applications being tested in either distilled water or buffer solutions. Therefore, the study of matrix effects, stability issues and comparison with established methods are still crucial steps to be made.

## VI. SYSTEMS BASED ON SPECIFICALLY-SENSITIVE MICROELECTRODES

### i. Cobalt-based phosphate microelectrode

Due to the difficulty of miniaturising traditional phosphate detection facilities and the problems with the classical colorimetric methods, a new approach, using phosphate sensitive materials to make the electrodes and detecting the concentration of phosphate by an electrochemical method has attracted increasing attention [26]. The phosphate ion sensitive electrode is one of the most important parts in the sensing system. Most reports on Co-based phosphate sensors have used a bulk Co-wire as the working electrode and used another isolated cell as the reference electrode. Potential response originates from a mixed potential due to slow oxidation of Co and simultaneous reduction of oxygen, and this response is directly based on the formation of $Co_3(PO_4)_2$ precipitate on the surface of Co electrodes [27].

Reportedly, a microelectrode with a tip size ~10 μm fabricated with cobalt wire was designed for in-situ and in vivo environmental analysis of orthophosphate ions ($HPO_4^{2-}$ and $H_2PO_4^{-}$) that evaluates the wastewater phosphorus removal system and for biological applications [28]. Cobalt is known as a phosphate-sensitive electrode material, since oxidised surfaces of metallic cobalt could be used as a selective potentiometric sensor for phosphate [29]. General schematics of phosphate microelectrode is illustrated in Figure 6. It has a micro-sized tip, a cobalt wire enclosed in a lead glass micropipette, which also contains bismuth alloy and a copper wire for electrical connection.

The detection range of the phosphate microelectrode was in the range of $10^{-5}$ to $10^{-1}$ M and the detection limit of the phosphate microelectrode was $7.5\times10^{-5}$ M, while the response time during the evaluation was less than 1 min [28].

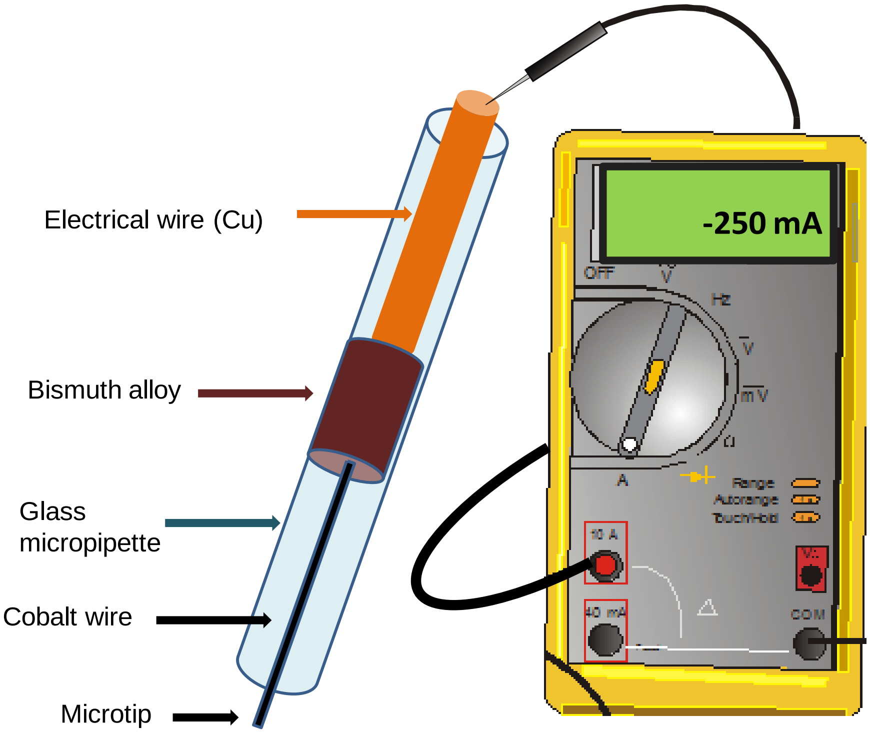

Figure 6. General schematics of phosphate microelectrode, after [28].

### ii. MEMs Microelectrode Array Sensors

The major advantages of the micro-electro mechanical systems (MEMs) microelectrode array sensors (Figure 7) include the ability to penetrate samples to perform measurements, small tip size for in situ measurements, array structure for higher robustness, and possibility of multi-analyte detection.

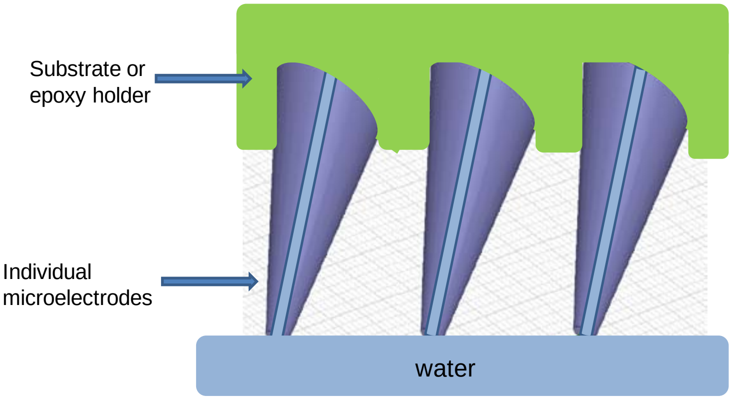

Figure 7. Microelectrode arrays.

For example, a cobalt-based MEMs microelectrode array sensors for direct measurement of phosphate in small environmental samples, such as microbial aggregates, has been introduced and applied for in situ measurement of phosphate within activated sludge floes in the enhanced biological phosphorus removal process as reported in [30]. These microelectrodes performed linearly and exhibited high sensitivity toward the phosphate ions in the range $10^{-5.0}$ to $10^{-25}$ M $KH_2PO_4$ solution at pH 7.5.

A similar MEMs type phosphorus microsensor with a microdigestion system (which converts various forms of phosphorus to phosphate) was reported in [26], where a cobalt metal film was introduced as the sensing material of the microelectrodes. The micro digestion chip is constructed with a silicon microfluidic device for the digestion of total phosphorus to phosphate. Three inlets are needed for digestion solution, water sample to be measured and cleaning solution that used to clean the channels and electrodes. Since the water sample to be measured need to be digested at 120°C for 30min under a pressure of 1.14~1.2 MPa before flow onto the micro phosphate sensitive electrodes, a micro heating electrode is placed under the digestion well, and a micro temperature sensor is coupled with the heating electrode. However, the presence of a micro digestion bioreactor can be seen as both advantage for enhanced sensitivity, but a drawback for a real-time unmanned water monitoring system.

Microfluidic technology is used to minimise the volumes of reagent and sample required. The sensor is based on the yellow method for phosphate determination, using a simple colorimetric technique involving the formation of vanado-molybdo-phosphoric acid when a phosphate-containing sample is mixed with an acidic reagent containing ammonium molybdate and ammonium meta-vanadate. A yellow-coloured compound is generated and the absorption of this compound is measured using a light emitting diode (LED) light source and a photodiode detector. The absorption is directly proportional to the phosphate concentration in the original sample.

However, due to the fragile nature of these sensors, they are capable of direct phosphate measurements only in small biological samples to enable in-situ analysis in many biological applications, but hardly for real-time long-term wastewater monitoring. A small volume of measured solution around the cobalt electrode is preferred, since the cobalt electrode deposited by sputtering [26] will dissolve when it is working as the sensing element. As a result, multiple long-term measurements with this system could be a challenge.

## VII. LAB-ON-CHIP SENSORS

Lab-on-chip and electrochemical sensing-based portable monitoring systems appear well suited to complement standard analytical methods for a number of environmental monitoring applications, including the water quality monitoring. The concept of a lab-on-chip type systems started from the integration of the various chemical operations involved in conventional analytical processes in a laboratory, such as sampling, preparation, mixing, reaction, and separation into a single unified system, requiring only a tiny volume of chemicals and sample and only a fraction of the time needed for the conventional approach.

Modern lab-on-chip is a complex system that combines amperometric/conductimetric sensor, microelectrodes and MEMs arrays, often along with microfluidics facilities. These techniques were discussed in previous sections. For a comprehensive review of a recent advances in the lab-on-chip systems one may refer to Jang et al [31], who recently reported on their efforts towards a lab-on-chip sensor for environmental water monitoring and gave a detailed review of the methods employed.

## VIII. THE MISSING PIECE OF THE PUZZLE TO POSSIBLE SOLUTION: MICROWAVE TECHNOLOGY BASED SENSORS

The use of the electromagnetic waves for sensing purposes is an actively researched approach [32-34] with considerable potential for commercialisation. In particular, microwave sensing is a developing technology which has been successfully used as a sensing method for various industrial applications including water solution concentrations [35] and water level measurements [36], material moisture content [37, 38], for continuous process monitoring for biogas plants [39] and of course in the healthcare industry, for example for non-invasive real-time monitoring of glucose in diabetic patients [40, 41].

Microwave sensors in the form of cavity resonators operate based upon the interaction of the electromagnetic waves and the material, i.e. water sample, being tested. Due to this interaction, the permittivity of the material changes and it manifests itself as a frequency change, attenuation or reflection of the signal. By considering how transmitted ($S_{21}$) and reflected ($S_{11}$) microwave powers vary at discrete frequency intervals, the change in the signal can be linked to the composition of the object under test.

Preliminary results for in-situ monitoring of phosphorus levels in the treated wastewater [7, 34] validate the potential of microwave sensors for a real-time water quality monitoring. Therefore, a combination of microwave technology based sensors with already developed and tested phosphate and nitrate sensing approaches discussed above to form a novel on-line multi-sensor monitoring platform could provide a solution to the puzzle that has so far been lacking a key component.

## IX. TOWARDS MULTI-SENSOR REAL-TIME WATER MONITORING SYSTEM

Even a brief overview of the state-of-the-art in the real time water monitoring given above reveals that it is not possible to achieve adequate detection of water parameters by using only one type of sensor. Accordingly, the solution is to merge various technologies into a single system that would employ the best available methods for the detection of specific water contaminants, so as to provide overall superior sensitivity, selectivity and long-term stability, while at the same time enabling real-time wireless data collection for enhanced cost-effectiveness. The feasible monitoring system might consist of a network of sensors deployed at key locations, capable of autonomous operation in the field for a year or more [42].

Such a system should be portable and would have to satisfy a broad range of requirements, including robustness and cost-effectiveness of the sensors; long battery life, which will depend on the sensors type and monitoring frequency [43]; data should be gathered in real-time from remote locations to a central server, where they will be processed, presented and communicated instantly, even by e-mail or SMS [42], if for example a set threshold of any water pollutant is exceeded. This will also help with mapping the spatial and temporal distribution of pollutants and may be of particular importance in identifying sources of water contamination [44, 45].

One such attempt, a multi-sensor system to monitor water quality parameters, namely pH, temperature, conductivity, turbidity and dissolved oxygen, is reported [43]. Here a group of water quality sensors were integrated into a distributed communication network, through interfacing them with the PSoC Plug and Play system, with Zigbee telemetry, capable of transmitting the data to the SmartCoast server, which processed the data for transmission to the web based on the IEEE 1451 standard.

The main problem, attributable to almost all water monitoring systems is biofouling, which can be defined as the undesirable accumulation of microorganisms, plants, algae, and/or animals on water-exposed surfaces [43]. This system also suffered from biofouling within days of deployment and the sensors required regular maintenance.

Biofouling can decrease the operating lifetime of sensors in the field and introduce a degree of error into the collected data. Frequently used mechanical methods of biofouling removal are not ideal for application in sensing where power consumption is a limiting factor in the deployment of devices for extended periods of time in the field [43].

A major advantage of physical techniques is the prospect of reduced analytical reagent use. Electronic-tongues are a group of sensors based on various physical detection principles such as ion-selectivity, mass balance, voltammetry and resistance. The water is sent through an array of sensors with different interface layers and the results are interpreted with multivariate analysis methods. This approach [46-51] attempts to provide an integral water quality assessment, but whether it can be realised in a commercially available system remains to be seen.

Currently available multi-sensor systems give only an approximate estimation of the water composition. Artificial neural networks, which are usually a part of such systems, require specially developed software. Various response times of each system component are also an issue, i.e. sensors for various pollutants could present a problem in case of sudden changes in wastewater composition. Though these systems are promising, they are reliable for a short period only and need further research and development.

The above analysis of the available technologies shows that due to the complex pollutant matrix and generally hostile environment [52], the lack of accurate, cost-effective and robust sensors, the automation of wastewater treatment and monitoring systems remains a challenge.

When developing a real-time water monitoring system, one needs to take into account that:

- monitoring equipment should better fit practical utility needs and should be easy to operate and maintain;

- verification schemes should sufficiently match utility practices;
- available sensor technologies should link to water quality regulations;
- technologies and practices should be developed to manage the large quantities of data and translate these into information for operational processes.

## CONCLUSIONS

It is demonstrated that at present, water quality control is still dominated by laboratory analysis of grab samples. Sensors are only available for a very limited number of parameters and frequently do not entirely meet the needs of the users. Thus, the water quality monitoring demands are not being met due to the infrastructure and maintenance costs of conventional sensing models. Advanced autonomous platforms capable of performing complex analytical measurements at remote locations still require individual power, wireless communication, processor and electronic transducer units, along with regular maintenance visits. Hence the cost base for these systems is prohibitively high, and the spatial density and frequency of measurements is insufficient to meet the requirements.

The interest in the use of field-based measurements stems from a need to provide quick on-site assessments that could cover a greater geographical spread while negating much of the cost, time delay and issues of sample integrity associated with traditional laboratory-based methods. Sensors and on-line monitoring systems may have clear and multiple benefits for water utilities. Possible applications are intake protection, control of operations, security, and providing information to customers.

Although sensors are increasingly appearing on the market, effective implementation in water utilities has not been realized particularly for those sensors based on chemical or biochemical detection processes. There are several reasons for the lack of implementation, not least due to sensors not being able to meet practical utility needs and mismatch in verification schemes. Also, poor links between available sensor technologies and water quality regulations can be a contributing factor.

On the other hand, there are rapid advances in various sensors, integrated components and microelectronics technology, which promise to make comprehensive on-line water quality control an increasingly realistic alternative. The most promising approaches for real-time nitrate and phosphate monitoring in water have been reviewed and it is concluded that since none of the methods alone can satisfy all of the above mentioned requirements, sensor fusion is required. Namely, multi-sensor platforms that utilise the best available methods combined into a single monitoring process are seen as the only way to achieve the ultimate monitoring capabilities. It is suggested that a special role in this development is reserved for microwave technology based sensors – a missing piece in the puzzle that is a possible solution of water quality control.

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