Monitoring Pollutants in Wastewater: Traditional Lab Based versus Modern Real-Time Approaches

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Abstract. Clean water – the most natural and yet the most precious natural resource that mankind needs. Current quality assessment methods of water parameters are mainly laboratory based, require fresh supplies of chemicals, trained staff and are time consuming. The ever-growing demand for simple, real-time and reliable techniques for the detection of pollutants and contaminants in the environment has sparked the development of remote detection and monitoring systems which include application specific sensors, instrumentation and signal processing. 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 book chapter critically compares the capabilities of traditional lab based and modern in situ methods for real-time wastewater quality monitoring and suggests further developments in this area.

Keywords: water quality monitoring, *in situ* analysis, optical methods, mass spectrometry, lab on chip sensors, electromagnetic waves, microwave sensors, solid-state sensors, amperometric detection.

1 Introduction

The increasing worldwide contamination of water sources with thousands of industrial and natural chemical compounds is one of the key environmental problems facing humanity. Approximately 3 billion people do not have access to safe drinking water, which is linked to over 35% of all deaths in developing countries. The World Health Organization (WHO) cites water borne illnesses as a major factor in 1.8 million deaths each year of which 88% are children in developing countries. Prediction models estimate that global consumption of water will double in the next 20 years, yet water quality assurance is singularly undervalued and poses a significant threat to global health. Water distribution systems are vulnerable to intentional and inadvertent contamination. Despite many technological advances, significant work remains to be accomplished for the purification of water.

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Consumers expect water supply companies to deliver safe drinking water that meets both health quality standards and aesthetic requirements such as color, turbidity, taste and odor. 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]. Continuous assessment of 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 is vital. The implementation of the WFD has triggered the need for new methods and systems which enable the monitoring of chemical and biological pollutants in real time.

Water quality assessments are based on the analysis of the physical, chemical and bacteriological parameters and require customized 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 daily use there are up to 70,000 known [2] and emerging [3, 4] chemicals that might be present in various water resources, including for drinking water production. Notably, approximately 860 active compounds are currently formulated in pesticide products, and these compounds belong to more than 100 substance classes, among them benzoylureas, carbamatea, organophosphorous compounds, pyrethroids, sulfonylureas and triazines are the most important groups [5]. The chemical and physical properties of the pesticides can differ significantly; for example, they might include heteroatoms such as halogens, phosphorous, sulfur or nitrogen. These properties are relevant for the detection of pesticides by various analytical methods. 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.

There is an acute need in on-line monitors that are able to detect the excess of pollutants established by the official water quality regulations. Ultra-sensitive sensors are required, as standards are often close to the modern 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.

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) [6]. However, wastewater is one of the most difficult sources of contaminants to deal with, as it carries micro-pollutants such as pharmaceuticals and hormonally active substances [7]. Table 2 lists current techniques in monitoring wastewater quality and their limitations [8].

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); Ion selective electrode
Chlorine	Colorimetric; Membrane electrode; Polarographic membrane; 3-electrode voltametric method
Conductance	Conductivity cell; annular ring electrode; nickel electrode; titanium or noble metal electrode
Dissolved oxygen	Membrane electrode; 3-electrode voltametric method; optical sensor
Ions (Cl-, NO3-, NH4+)	Ion-selective electrodes
Oxidation-Reduction Potential (ORP)	Potentiometric; platinum or noble metal electrode
pH	Titration with Sodium Hydroxide; proton selective glass bulb electrode, proton selective metal oxide; Ion Sensitive Field Effect Transistor (ISFET)
Phosphates	Manual or Automated Colorimetry
Temperature	Thermistor
Total Organic Carbon (TOC)	UV-persulfate digestion with near infrared detection or membrane conductometric detection of CO2
Turbidity	Optical sensor; Nephelometric (light scattering) method

Table 2. Status of current techniques in monitoring wastewater quality and their limitations

Parameter	**Technique**	**Limitations**
BOD	Non-specific sensor array (electronic nose)	Relationship is source/site specific and time dependent, further development needed
BOD, COD	Oxidation by hydrogen peroxide with UV light	Limited range and long (~55 min) measurement times, range and correlation are source dependent
OD, COD, TOC, TSS, Nitrates and anionic surfactants	UV spectral measurements and multivariate calibration	Sample handling is problematic, acquisition of reference spectra and calibration necessary for samples of different origin
BOD, nitrates, (TOC and COD)	Optical scattering (fluorescence)	Still in infancy, research needed, fluorescence affected by pH and temperature, correlation with BOD is plant sensitive.
BOD	UV adsorption (280 nm)	Poor sensitivity, uses only one wavelength, interferences from particles and toxic metals
COD, TOC	UV adsorption	Immerged sensor (fouling), influence of suspended particulate material
RQ value	Off-gas analysis (CO_2 and O_2)	Does not distinguish C-oxidation from N-removal, only big changes in nitrification activity can be monitored
COD, NH_4, NO_3	Artificial neural network + multi sensor (pH, temp, conductivity, redox potential DO, turbidity)	Approximate estimation, training needed, problems in case of sudden changes in wastewater composition, reliable for a short period only

This chapter provides a critical review of the currently available lab based and state-of-the-art real-time methods of water pollutants monitoring, in particular for monitoring of nitrates and phosphates. The presence of nutrients and heavy metals in water is a serious threat to human health [9]. Phosphorus is widely used as an agricultural fertilizer 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 [10].

From an environmental perspective, the concentration of phosphate in water is crucial due to its role in eutrophication [11]. Nitrate fertilizers are increasingly used in agriculture, the quantity of nitrate leaching from fields into rivers and ground waters is increasing cumulatively. 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 [12]. Nitrate is also an important analyte for environmental, food and human health monitoring and thus its detection and quantification is essential. Traditionally phosphates and nitrates were 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 [13]. These methods are also used for the detection of other water pollutants, as described further in the chapter.

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 [14, 15] for reasons of lower costs, faster response time and due to security concerns.

2 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 color (e.g. blue or yellow) that results from a chemical reaction between phosphorus and special reagent [10]. The concentration of the resultant dye indicates the concentration of phosphorus in the sample. Fig. 1 shows conceptual diagram of the two standard UV-Vis optical methods, namely the molybdenum blue method and the vanadate / molydate yellow method [16]. 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 color. 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 analyzed at 380 nm using a photometric sensor [10].

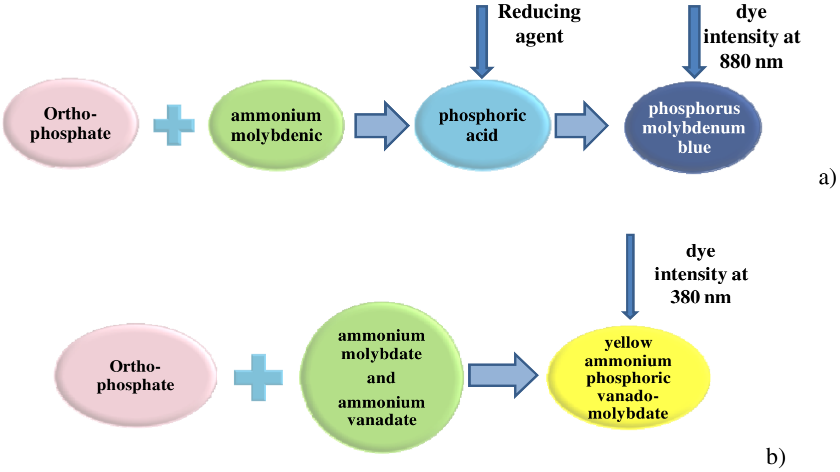

Fig. 1. Conceptual diagram of standard UV-Vis optical methods: a) Molybdenum blue method, b) Vanadate / molydate yellow method [16]

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.

2.1 Examples of Commercially Available Systems

Hach Lange[1] 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.

Hache Lange are not alone however; EnviroTech Instruments offers, for example, a field-deployable nutrient analyzer 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 and incorporates easy-load reagent storage for maximum up-time and onsite service.

The AutoLAB 4 system 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) analyzer and so avoids problems with clogging and tube wear. The discrete analysis methods allow short sampling times, in-situ self-calibration and automatic maintenance.

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[1] Full details can be found at `http://www.hach-lange.com/`

Beam attenuation from the color reaction is recorded. It detects nitrate at a range of 0-5 mg/L at 543 nm wavelength and phosphate in 0-0.8 mg/L range at 880 nm, both with 0.003 mg/L sensitivity.

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 analyzed is required. A flow rate of 2-3 liters/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. However, the data on sensitivity and range are not available.

Another example of a commercially available system for water quality measurement is the ChemScan UV-6100 Analyzer, 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 analyzer system is an on-line UV spectrometer capable of measuring the concentration of multiple dissolved chemical constituents of an aqueous sample with a single analyzer. It works by transmitting UV light through the sample. A portion of the light is absorbed by the chemical constituents and the analyzer splits the resulting light into 256 individual wavelengths from 200 to 450 nm. The spectral signature is analyzed using Chemometrics, a pattern recognition technique, to calculate the concentration parameters.

Parameters that absorb light naturally, such as nitrate, can be analyzed 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.

2.2 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. Although the methods for the determination of phosphate such as colorimetry or spectrophotometry are still predominant in a standard utilities operation [4, 17], 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 fiber 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.

3 Mass Spectrometry for Water Micro-Pollutants Control

Surface water reservoirs and aquifers are exposed to contamination by thousands of micropollutants from industrial, pharmaceutical, agricultural and natural origins. Traditionally, the monitoring of contaminant levels was based mainly on gas chromatography mass spectrometry (GC-MS and GC-MS/MS) a method that involves multistep sample preparation and has low specificity. Nowadays, liquid chromatography with UV/fluorescence tandem mass spectrometry (LC-MS/MS) has become a routine analytical tool and a key technique for environmental analysis, allowing the detection of a wide range of polar and nonvolatile compounds [19]. The use of this method has increased the specificity and confidence of identification, while reducing sample preparation to a minimum. Thus, one of the major challenges of water analysis is to reduce sample preparation to achieve direct analysis by LC-MS/MS detection; that is, analysis without the need to concentrate ultra-trace-level contaminants in the water sample.

3.1 Atmospheric Pressure Ionization

Liquid chromatography mass spectrometers can be equipped with several mass analyzers, each of which provides unique features able to identify, quantify, and resolve ambiguities by selecting appropriate ionization and acquisition parameters [19]. Despite the enormous variability in the chemical features of water pollutants, most can be ionized by atmospheric pressure ionization (API) methods. The most common ionization method for residue analysis by LC-MS/MS is electrospray ionization (ESI), which is suitable for the analysis of most of the compounds that pollute water. The use of LC-ESI-MS/MS for the detection of 500 pesticides in food and water samples was tested by Alder et al [5].

Less polar compounds, which can be separated using reverse phase chromatography, require higher ionization energy. For these compounds, atmospheric pressure chemical ionization (APCI) is usually the method of choice for LC-MS/MS analysis [19]. For example, APCI was used for the analysis of organochlorine pesticides in surface waters [20] and for the detection and identification of rotenone in lake and river waters [21].

3.2 Liquid Chromatography/Quadrupole Time-of-Flight Mass Spectrometry

The inherent characteristics of time-of-flight (TOF) mass analyzers — high resolution, mass accuracy and good sensitivity in scanning wide mass ranges — make these analysers well-suited to the analysis of pesticide residues in water samples, mainly for qualitative purposes [22]. The hybrid quadrupole-TOF (QqTOF) permits the pre-selection of a precursor ion in the quadrupole filter and the measurement of the full-scan product ion spectra with high mass accuracy, which makes it one of the most valuable modern lab-based technique for elucidating unknown compounds in environmental waters [23]. For example, the QqTOF system was used for the detection of 22 triazole compounds including parent fungicides and metabolites in water with a limit of detection of 0.5 ppb [24].

3.3 Triple Quadrupole and QTrap Technologies

Triple quadrupole instruments (QqQ) operating in multiple reaction monitoring mode (MRM) achieve the best absolute sensitivity for targeted compounds. QqQ instruments exhibit excellent quantitation abilities owing to their wide linear dynamic range. For these reasons, and because of the relative simplicity of the MRM analysis, this technology has become the most common method for environmental analysis for contaminant residues by LC-MS/MS [19]. The MRM analysis introduces high specificity as it is based on the detection of both a parent ion and one of its known fragments. Another dimension of specificity can be introduced with the unique combination of a linear ion trap in the third quadrupole (QTrap) and an online information-dependent driven workflow that provides a full scan linear ion trap spectrum to confirm of the identity of compounds detected by MRM.

For increased specificity, the European Union regulatory authorities require the identification of a residual compound in water samples using one of three approaches: a high accuracy MS spectra with a resolution of >10000 (e.g. as obtained with QqTOF instruments); an MRM identification based on two different MRM transitions and their ratios (e.g. using QqQ instruments); or a single MRM transition combined with a full scan MS/MS spectrum (e.g. QTrap instruments) [19].

4 Fiber Optic Sensors for Real-Time Water Quality Monitoring

Fiber optic sensors are used in combination with the UV-Vis methods of water contaminants detection discussed above. Normally an optic fiber is suitably doped to produce luminescence when exposed to an excitation light source. Glass fibers are either doped with a rare earth metal or activated with a transition metal. Polymeric fibers are doped with a dye. The fibers have fast response and decay times and can achieve high efficiency through the design of appropriate delivery optics. Fiber optic systems are particularly suitable for harsh and difficult to reach places. The design and selection of the fiber determines the peak wavelength of the output illumination; options exist to span the UV–Vis–NIR spectrum. A detailed review of the recently reported fiber optics based systems provides in-depth analysis of these systems for various water contaminants monitoring [25]. Notably, the coating of the fiber 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 [26, 27].

5 Pollutant Monitoring Using Amperometric, Potentiometric and Conductimetric Sensors

Amperometric, potentiometric and conductometric sensing approaches are widely used in the measurement of pollution in water [28]. These sensors change their properties as a result of interaction with the component being measured. The species of interest are either oxidized 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 [29].

For example, a portable amperometric three-electrode immunosensor for screening of polycyclic aromatic hydrocarbons (PAHs) in water was recently reported [28]. 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 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. Potentiometric DO detection is a better choice when dealing with fast changing large range of oxygen concentration, which cannot be accommodated by amperometric detection. A study on the performance of a Cu_2O-doped RuO_2 sensing electrode used in a solid-state potentiometric DO sensor in terms of both sensor capability and bio-fouling resistance for utilization in aqueous environments was recently conducted [30]. 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, as illustrated in Fig. 2.

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.

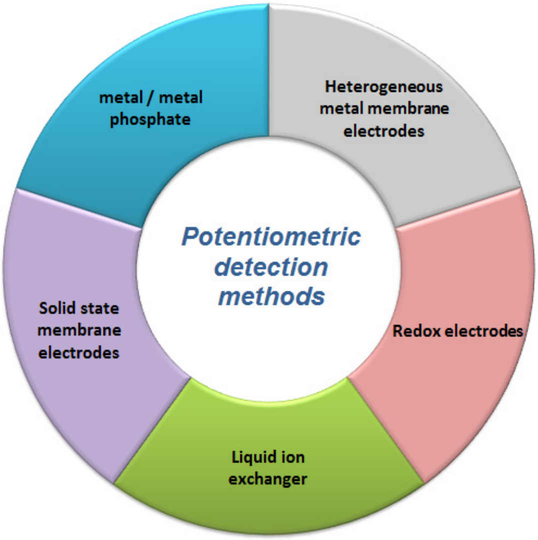

Fig. 2. Potentiometric detection methods

6 Biosensors

The presence of microorganisms in water is generally assessed with five indicators, such as total coliform, fecal coliform, fecal streptococcus, enterococcus, and Escherichia coli. To protect public health, microbiological standards have to be met at each individual treatment works and service reservoir. Notably, the presence of various microorganisms in water, including *salmonella, campylobacter, listeria, Bacillus cereus* and *Escherichia coli O157:h7* is a natural and unavoidable occurrence, but the level of these bacteria should be strictly monitored in real time. Infectious doses of these pathogens (as low as ~10 bacterial cells) increase the vulnerability of the elderly, infants, and people with immunological deficiencies or organ transplants [31]. In recent years, there has been greater recognition of the importance of biosecurity in relation to protection of the environment [32].

Examples of molecular methods used to identify specific microorganisms and to assess microbial community diversity using DNA sequences [33] are listed in Table 3. These methods are applicable for detecting and identifying microorganisms present in water (e.g. fecal indicators, pathogens) and examining community composition using microbial community DNA [34, 35].

Biosensors have been widely applied to a variety of analytical problems in medicine, food, process industries, security, defense 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 recognizes the target analyte and a transducer, for converting the recognition event into a measurable electrical signal [32]. 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.

Table 3. Status of current genomic tools that can be used to assess water quality [36]

Tool	Description	Current status
Direct hybridization	Detection of genes, gene expression	Requires sequence knowledge and DNA to label for probe
PCR, RT-PCR	Rapid, sensitive detection of specific taxa, genes, or gene expression (RT-PCR)	In wide use, requires DNA sequence information
RAPD, RFLP, AFLP, AP-PCR, DGGE, T-RFLP, RFLP, ARDA	PCR-based, provides “fingerprint” of microbial community or the genome of microbial strains. Useful for description of community composition and source tracking	Widely used
Q-PCR, real-time PCR	Rapid, sensitive, quantitative detection of target	Use increasing rapidly, requires sequence knowledge
Fluorescent in situ hybridization (FISH)	Allows detection, visualization of individual cells	Widely used, requires actively growing cells.

Fig. 3 shows schematic diagram of a biosensor. The bioreceptor recognizes the target analyte and the corresponding biological responses are then converted into equivalent electrical signals by the transducer. The bioreceptor-protein interactions can be visualized 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 analyzed.

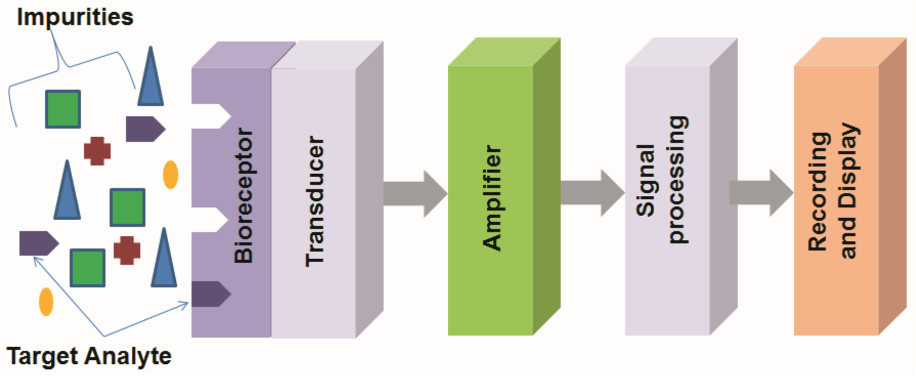

Fig. 3. Schematic diagram of a biosensor

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 [12]. For example, an amperometric phosphate biosensor, based on a cobalt phthalocyanine screen-printed carbon electrode (CoPC-SPCE) was recently reported [11] 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 [37]. This sensor showed a linear dynamic range between 1.0×10^{-1} and 1.0×10^{-7} M, with a detection limit of 6.0×10^{-8} M (~6 ppb). The best performance was obtained with a membrane composition of 32% poly(vinyl chloride), 58% benzyl acetate, 2% hexadecyltrimethyl-ammonium 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 [37].

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 [12]. 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 chapter 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 [13].

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.

7 Systems Based on Specifically-Sensitive Electrodes

7.1 Microelectrodes for Phosphate Detection

Due to the difficulty of miniaturizing 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 [38]. 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 [39].

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 [40]. Cobalt is known as a phosphate-sensitive electrode material, since oxidized surfaces of metallic cobalt could be used as a selective potentiometric sensor for phosphate [41]. General schematics of a phosphate microelectrode are illustrated in Fig. 4. 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 7.5×10^{-5} M, while the response time during the evaluation was less than 1 min [40].

Electrochemical sensors offer a suitable platform for the development of microsystems for the remote detection and monitoring of pollution in waters. These sensors can be mass fabricated using the manufacturing technologies available to the microelectronics industry and their miniaturization improves their performance.

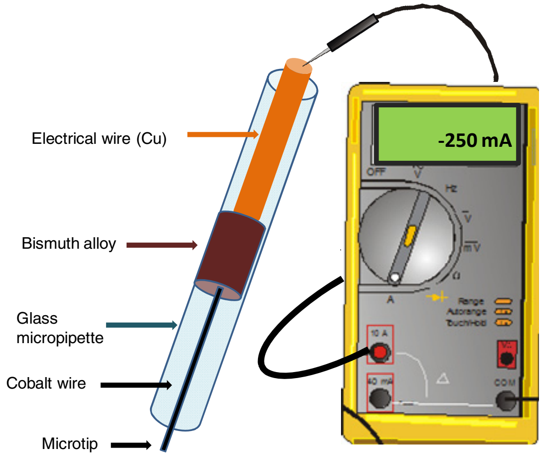

Fig. 4. General schematics of phosphate microelectrode [16]

7.2 MEMs Microelectrode Array Sensors

Microelectrode arrays have unique properties such as an improved mass-transport towards the microelectrode surface and a reduced ohmic drop, which both contribute to a higher sensitivity and hence, make them suitable for water-monitoring applications [42].

The major advantages of the micro-electro mechanical systems (MEMs) microelectrode array sensors (Fig. 5) 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.

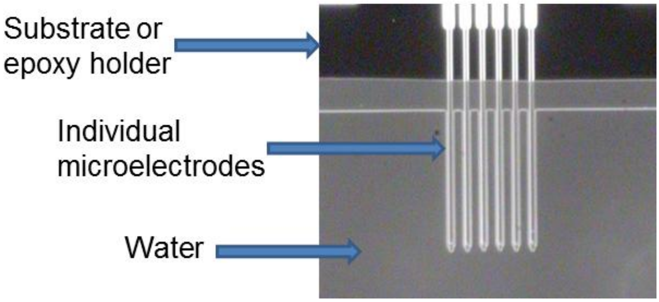

Fig. 5. Microelectrode arrays sampling water

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 [43]. 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 [38], 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 needs to be digested at 120 °C for 30 min 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 minimize 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-colored 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 [38] will dissolve when it is working as the sensing element. As a result, multiple long-term measurements with this system are a challenge.

7.3 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 water quality monitoring. The concept of a lab-on-chip type system 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.

The design, fabrication and characterization of four designs of microelectro-chemical systems on a silicon chip for the detection of pollutants in artificial seawater was reported in [42]. These systems were fabricated by photolithography and incorporate a Pt working microelectrode array, a Pt counter electrode and a Ag/AgCl reference electrode. They have been characterized by cyclic voltammetry of ferricyanide and behaved in good agreement with the theory. These systems were evaluated over 72 hours and showed good stability. Underpotential Deposition – Stripping Voltammetry experiments of measuring Cu^{2+} in artificial seawater have been carried out on an array of 35 micro-squares of 20 µm x 20 µm. The sensitivity achieved was (2.93 ± 0.14) $\mu A\ cm^{-2}\ \mu M^{-1}$, with 1 µM being the lowest Cu^{2+} concentration measured. These devices are believed to provide the basis for the development into sensor systems for remote analysis applications [42].

For a comprehensive review of a recent advances in the lab-on-chip systems one may refer to Jang et al [44], 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.

8 Sensors Based on Sound and Electromagnetic Field Interaction

8.1 Ultrasonic Measurement

Ultrasonic technique is non-destructive and non-invasive method capable of rapid characterization of systems which are concentrated and optically opaque. Ultrasonic technique is sensitive to particles with radius between about 10 nm and 1000 mm. The propagation of ultrasound in a fluid is affected by its density, compressibility, temperature and composition. Low-power ultrasound and infrared waves which are emitted from equipment isolated from the target material are well-studied candidates for water and food analysis applications, as they do not introduce extraneous contamination nor alter the properties of the substance [45]. Ultrasonic sensor coupled with chemometric techniques for discrimination of different water samples was recently reported [46].

8.2 Electromagnetic Wave Sensors

The use of the electromagnetic waves for sensing purposes is an actively researched approach [47-49] with considerable potential for commercialization. One of the most successful attempts to use the electromagnetic sensing as a method for the detection of nitrates and contamination in natural water sources have been recently reported [48], where sensors based on the combination of planar meander and interdigitated electromagnetic structure were used. The meander sensors part consisted of two coils. The exciting coil was driven by high-frequency sinusoidal current to create a high-frequency magnetic field. To increase the magnetic field strength, the number of meander turns was increased by introducing several spiral rectangular turns toward the inner section. When this sensor was placed near a material, an electromagnetic field was induced on it, which modified the created field, and the sensing coil, placed above the exciting coil, was used to pick up the resultant field. The operating principle behind the interdigitated sensor is as follows [48]. The positive electrodes are driven by an AC electric potential (same source as the meander) to create an AC electric field between the positive and negative electrodes. These fields pass through the material under test; thus, material dielectric properties as well as the electrode and material property affect the capacitance and the conductance between the two electrodes. The meander type of coil was connected in series with the interdigitated coil, and an AC voltage was applied across the combination of the coils. The sensor response was determined by measuring the total impedance of the sensor at different frequencies between 10 kHz and 100 MHz [48].

8.3 Microwave Sensing

Microwave sensing is a novel and upcoming technology which has been successfully used as a sensing method for various industrial applications including water solution concentrations [50] and water level measurements [51], material moisture content [52, 53], for continuous process monitoring for biogas plants [54] and of course in the healthcare industry, for example for non-invasive real-time monitoring of glucose in diabetic patients [55, 56].

Microwave analysis (or microwave spectroscopy) can be applied to suit a broad range of requirements [57, 58] and has a number of advantages over competing technologies for wastewater sensing applications, including: 1) true real-time sensing, since an analyte material flows past or through the sensor and an instantaneous measurement is acquired without the need for significant pre-processing; and 2) direct sample measurement – a feature currently unavailable in many competing technologies.

The principle of sensing properties of materials, i.e. composition of water, using electromagnetic waves in the GHz frequency range is based on the fact that an object under test interacts with the electromagnetic waves in a unique manner, which can be specifically correlated with the properties of this material. 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 tested water sample.

A microwave resonator is made of a section of transmission line with open or shorted ends. Depending on the type of transmission line, the resonators can be for example coaxial, microstrip, stripline, slotline, or cavity resonators. When the resonator is used as a sensor, the object to be measured is brought into contact with at least some part of the electromagnetic field in the resonator. As a consequence, the resonant frequency and the quality factor will change in relation to the permittivity of the object. Due to the large variety of possible structures, sensors can be designed for measurement of almost any kind of object. The major advantage of the technique using microwave cavities is the capability to measure materials non-destructively, without contact from a short distance, using penetrating waves, without health hazards to personnel. Disadvantages are the usually high degree of specialization and the simultaneous existence of several variables affecting the microwave measurement (temperature, density, structure, etc.) in material measurements [59]. Initial results for in-situ monitoring of phosphorus levels in the treated wastewater [10, 49] validate the potential of microwave sensors for a real-time water quality monitoring, and this topic is discussed in greater depth elsewhere in this book.

9 Further Challenges and Possible Solutions in Developing Real-Time Water Monitoring Platform

This chapter reviewed the most common laboratory based methods of water pollutant detection, namely standard UV-Vis measurement methods, mass spectrometry, ion-sensitive electrodes and amperometric sensors. In addition, modern real-time monitoring approaches were examined, in particular fiber optic sensors, lab-on-chip sensors, biosensors and electromagnetic wave sensors, including microwave sensors. These are illustrated in Fig. 6.

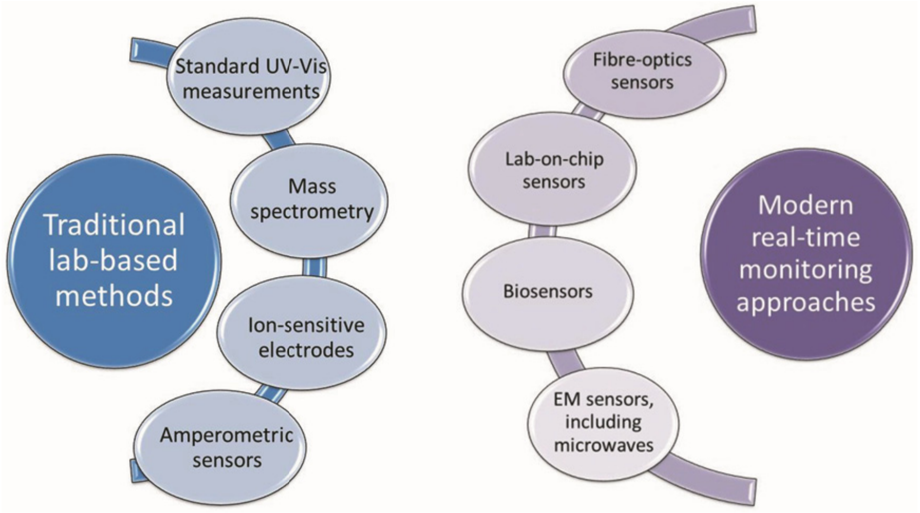

Fig. 6. Traditional lab-based and modern real-time approached to monitor wastewater

Even a brief overview of the traditional and state-of-the-art real time water monitoring methods given above reveals that it is not possible to achieve adequate simultaneous detection of different water parameters by using only one type of sensor. New instruments need to be introduced that are more robust, more sensitive and more accurate than before, to allow the detection of minute quantities of pollutants with high confidence and minimum sample preparation. Alternative solutions 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 [60].

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 [61]. 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 [62]; 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 [61], 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 [63, 64].

One such attempt, a multi-sensor system to monitor water quality parameters, namely pH, temperature, conductivity, turbidity and dissolved oxygen, is reported

[62]. 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. However, this system suffered from bio-fouling within days of deployment and the sensors required regular maintenance.

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.

Real-time monitoring of wastewater quality remains an unresolved problem to the wastewater treatment industry [65]. 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. The above analysis of the available technologies shows that due to the complex pollutant matrix and generally hostile environment [66], the lack of accurate, cost-effective and robust sensors, the automation of wastewater treatment and monitoring systems remains a challenge. There exists a need for better on-line monitoring of water systems given that existing laboratory-based methods are too slow to develop operational response and do not provide a level of public health protection in real time [67].

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.

To further preserve valuable water resources, a paradigm shift in water purification can be proposed by rethinking the distribution strategy at point-of-use and developing decentralized purification methodology based on region specific contaminants. This unique approach would assist in addressing the challenges in water purification so that clean water is available to everyone.

10 Conclusions

It is demonstrated that monitoring of water quality is currently 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 control demands are not being met due to the infrastructure and maintenance costs of conventional sensing models. The interest in the use of field-based real-time 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.

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.

This chapter reviewed the most promising approaches for real-time water monitoring. It is suggested that since none of the methods alone can satisfy all the regulatory requirements, sensor fusion is required. Namely, multi-sensor platforms that utilize the best available methods combined into a single monitoring process are seen as the only way to achieve overall superior sensitivity, selectivity and long-term stability, while at the same time enabling real-time wireless data collection for enhanced cost-effectiveness. Also proposed is a paradigm shift in water purification by rethinking the distribution strategy at point-of-use and developing decentralized purification methodology based on region specific contaminants.

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