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

O. Korostynska, A. Mason, A. Al-Shamma'a
School of Built Environment
Built Environment and Sustainable Technologies Research Institute (BEST)
Liverpool John Moores University, Liverpool, L3 3AF, United Kingdom
Emails: o.korostynska@ljmu.ac.uk, A.Mason1@ljmu.ac.uk, A.Al-Shamma'a@ljmu.ac.uk

Submitted: Feb. 9, 2012 ***Accepted: Feb. 22, 2012*** ***Published: Mar. 1, 2012***

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.

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

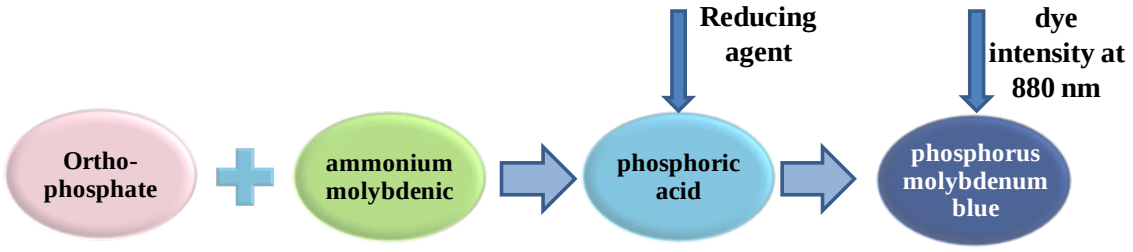
Current measurements of nutrients, such as phosphorous, ammonia and volatile fatty acids in water are mostly based on off-line monitoring and imply low frequency data sampling and delay between sampling and availability of the results. However, in past years there has been a growing interest in the use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

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

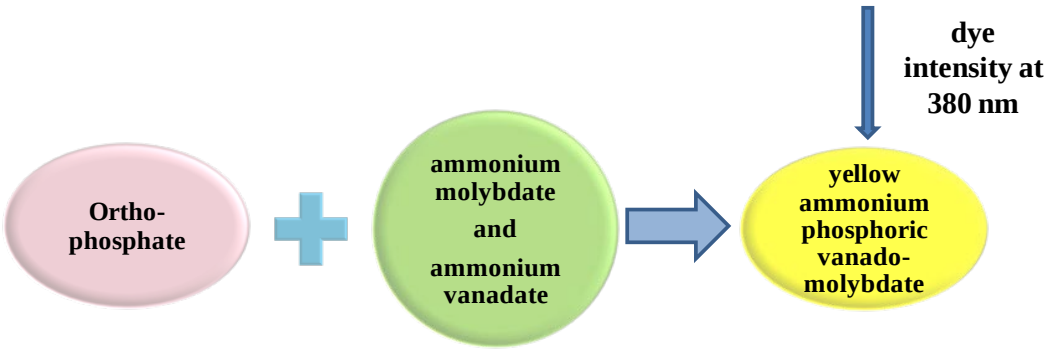
Real-time monitoring of wastewater quality remains an unresolved problem to the wastewater treatment industry [13]. Advanced autonomous platforms capable of performing complex analytical measurements at remote locations still require individual power, wireless communication, processor and electronic 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).



a)



b)

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].

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

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

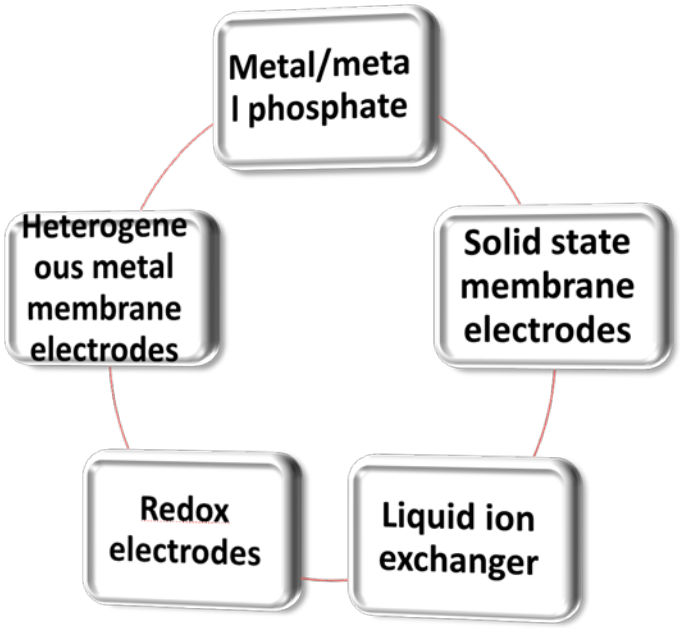


Figure 4. Potentiometric detection methods.

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.

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 1.0×10^{-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% 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

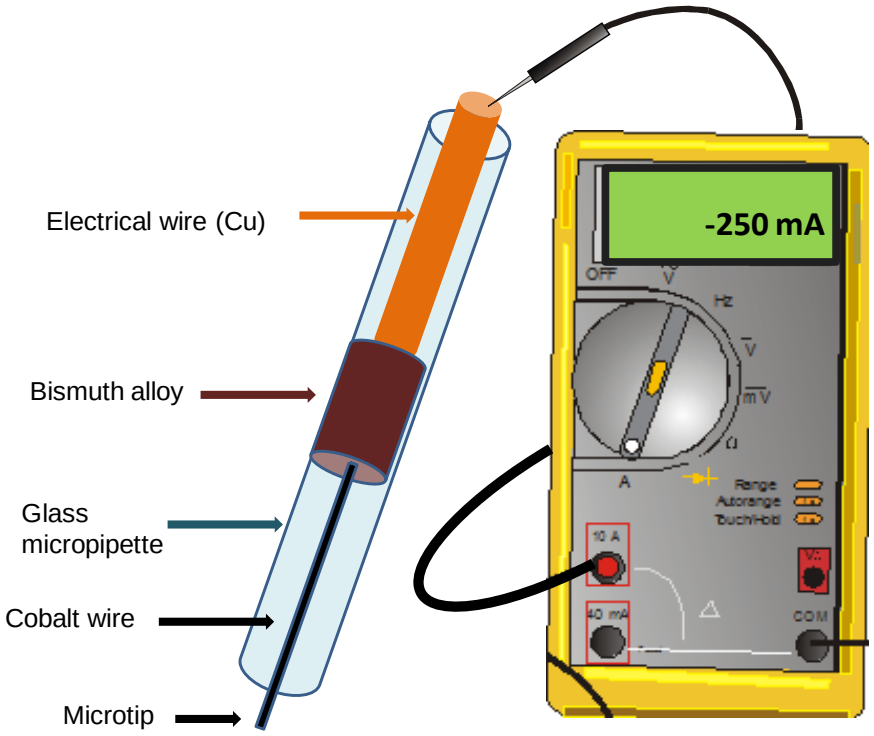


Figure 6. General schematics of phosphate microelectrode, after [28].

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.

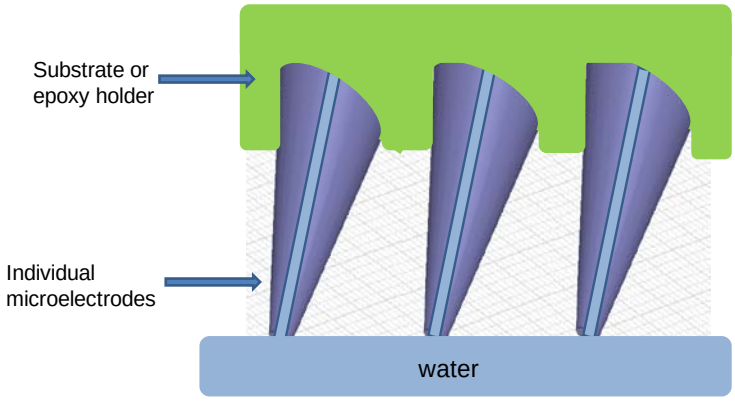


Figure 7. Microelectrode arrays.

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

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;

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.

ACKNOWLEDGEMENTS

This work is financially supported by the European Community's Seventh Framework Programme through the FP7-PEOPLE-2010-IEF Marie-Curie Action project 275201, Water-Spotcheck.

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