Spectroscopic Methods for Online Water Quality Monitoring

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Abstract Sensors deployed in smart water systems need to meet a number of criteria, first and foremost robustness of performance, autonomous operation and low maintenance. Solid-state, optical sensors are at the forefront in the development of the next generation of sensors for smart water systems. A range of optical sensor technologies is currently in use for (near) real-time water quality analysis and between them can cover most of the relevant quality parameters. Technologies used in the water industry include UV/Vis absorbance, fluorescence and NIR absorbance spectroscopy. Spectroscopic methods with potential for broader application include Raman spectroscopy and laser-induced breakdown spectroscopy. All approaches share the following properties: fully solid-state hardware, no reagents or other consumables required for their operation, and automatic interpretation of the sensor data performed

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by increasingly advanced chemometric solutions. This chapter provides a brief overview of the fundamentals behind these technologies and reviews their use in water quality monitoring applications.

1   Introduction

Understanding and monitoring the quantity and quality of one of the world's most precious resources, water, are essential. Currently, the most common method of analysis of water quality consists of (grab or composite) sampling followed by laboratory investigation. This approach fails to fully indicate the dynamics of water quality, since it only provides snapshots of specific points in time. Furthermore, due to delays in transportation, sample preparation and analysis, laboratory analysis only reveals a history of water quality, and not its current state.

Management of water and wastewater networks, meeting operational demands and regulatory compliance while simultaneously minimising costs, is becoming increasingly challenging. The water industry is beginning to recognise that further progress will be limited as long as assets are operated independently of each other and retrospectively with regard to changes in load and failures. An integrated approach to water management potentially offers major advantages to the water industry, hence the quickly expanding interest in smart water solutions.

The holistic approach that is at the cornerstone of smart water systems requires greater system knowledge and improved control. The use of real-time control will enable more flexible and efficient use of existing assets and will provide the ability to respond proactively to both short-term changes and longer-term challenges. Examples of areas where smart water solutions can achieve gains include in treatment processes, e.g. to enable more efficient operation, achieve compliance and reduce the carbon footprint; in water distribution systems, e.g. allowing reaction to operational problems and threats to public health and safety and reducing operational costs; in the sewerage network, e.g. to deal with (rain) events in real-time and moving from hydraulic to quality control; and in asset monitoring, e.g. to allow better forecasting and targeting of asset maintenance. For a brief introduction, see Peleg [1]; for a more detailed review, see Owen [2]. Additionally, there is a trend in the industry towards small-scale, distributed water systems [3]; although these systems remove the need for capital-intensive distribution and collection systems, they pose a special challenge to monitoring as there is no skilled workforce to supervise them and smaller volumes mean lower equipment costs are required. Without reliable automation and control solutions, small-scale systems will not be viable.

Real-time information about the water quality and quantity is the basis for smart water solutions. This information is collected by sensors distributed throughout the water network. Not all sensors are suited for use in smart water systems. The deployment of sensors in large numbers, possibly in locations that are difficult to

access, such as in underground pipe systems, brings a number of requirements. Amongst the most important technical preconditions are robustness of performance, autonomous operation and low maintenance requirements. The latter means the instruments themselves are stable, e.g. free from drift and other effects that necessitate recalibrations, do not need (replacement of) consumables and are self-maintaining, e.g. that keep themselves clean and compensate for deviations. For a full discussion on the considerations concerning sensor selection and operations, please refer to van den Broeke et al. [4].

2 Spectroscopy

One type of instrument that is particularly suited for such demanding applications is the spectrometer. This chapter will describe the principles and applications of a number of optical methodologies that are in use as water quality sensors. This chapter is not intended as an exhaustive review, but provides a brief introduction in the application of various spectroscopic methods in water monitoring and includes references to more exhaustive texts.

The technologies described in this chapter have been selected because they are purely optical; they analyse the primary interaction of light with a sample matrix and its constituents. No additional aids are used to achieve selectivity or to enhance the signal, apart from sensitive photo detectors to collect the light after its interaction with the sample and subsequent data processing. Although other optical techniques are widely used, e.g. reagent-based photometric methods, the discussion herein focuses on techniques that meet, or have the potential to meet, the requirements set out above for sensors suitable for integration in smart water solutions. Most importantly, these technologies make use of solid-state, long-term stable components, do not require chemicals and are compatible with effective auto-cleaning techniques. Furthermore, with the development of ever smaller electric and optical components, they lend themselves to further miniaturisation and reduced power consumption that will be required for large-scale, autonomous deployment in distributed (water) networks.

The analysis of the interaction of light with matter, incidentally, is the oldest methodology for studying the chemical composition of samples. The history of spectroscopy begins with the publication of the studies on refraction of light by a prism by Isaac Newton in 1672. In this work, Newton proved that white light is composed of light of various colours. Subsequently it became clear that different chemicals absorb light of various colours and that this was a property that could be used to study their concentrations in a matrix. The step towards analysis of water samples was made in 1856 with the development of Nessler's method, in which ammonia in water reacts with mercuric iodide and potassium, forming a reddish-brown colloid. The colour intensity of the reaction product depends on the initial concentration of ammonia in the sample.

With the development of photomultiplier tubes in the middle of the twentieth century, spectroscopy, especially absorption spectroscopy in the UV, visible and (near) infrared wavelength ranges, became firmly established in analytical laboratories, both for the analysis of whole samples as well as single components after separation by chromatography. By the mid-1990s, the online at-site spectrometer instrument had reached a mature development stage and is since seeing increasing use in real-time quality monitoring and process control. Applications include monitoring feed and product composition and quality in such diverse industries as pharmaceuticals, petrochemistry, food, as well as water quality monitoring. The most commonly used types of spectroscopy in such at-site, sometimes even in situ, devices are UV/Vis absorbance, near-infrared (NIR) absorbance and fluorescence spectroscopy. Further methodologies include refractive index measurement, Raman spectroscopy, laser-induced breakdown spectroscopy (LIBS) and image analysis.

3 Interaction of Light and Matter

All spectroscopic methods rely on the interaction of light with atoms and molecules. The interaction of light and matter can be described by two different models, one assuming light as a wave phenomenon and the other assuming light to consist of particles. The wave approach is most appropriate to describe such interactions as reflection, refraction and interference. For spectroscopic methods, the interaction of light with atoms and molecules can best be described using the particle approach, with the light particles being called photons. The important parameters of a photon are its energy E, wavelength λ and frequency f, which are related according to Eq. (1):

$$E = \frac{hc}{\lambda} = hf \tag{1}$$

where h is the Planck constant (6.63×10^{-34} Js). From Eq. (1), it follows that the energy of a photon is proportional to its frequency and reciprocal to its wavelength. For the discussion herein, the most important parameter is the wavelength, often expressed in units of [nm] or [μm]. Another parameter regularly used in spectroscopy is the reciprocal of the wavelength, the wavenumber $\bar{\nu}$, often expressed in [cm^{-1}].

Although the electromagnetic spectrum is broadly divided into eight regions, ranging from highly energetic γ-radiation to radio waves (Fig. 1), spectroscopy of aqueous samples is focused on the ultraviolet (UV) (200–400 nm), visible (Vis) (400–700 nm) and near-infrared (NIR) (750–1,400 nm) domain, with lower wavelengths corresponding to higher photon energies. The primary reasons for the prevalence of these domains in water analysis are the transparency of water to radiation at these wavelengths and the fact that spectrometers using these wavelengths do not require exotic materials or extreme operating conditions.
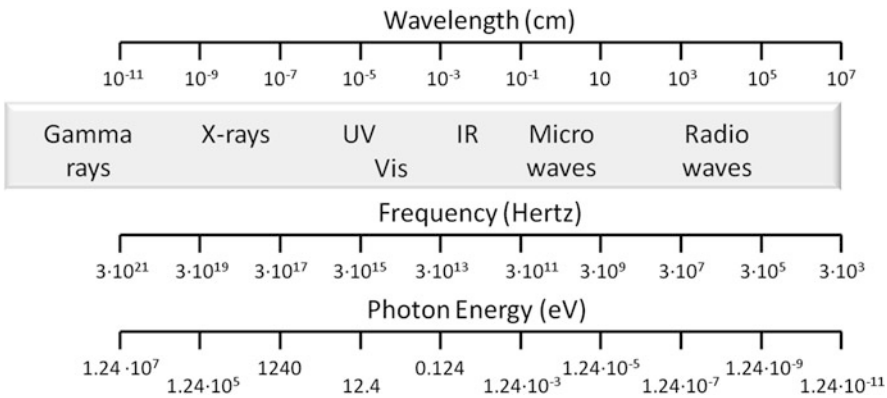
Fig. 1 The electromagnetic spectrum

Table 1 The fundamental light-matter interactions, which form the basis for most spectroscopic methods

Absorption	Matter absorbs light and undergoes a change in energy
Emission	Matter releases radiative energy, e.g. after excitation by light
Elastic scattering and reflection	Interaction between matter and light that changes the direction but not the energy of the photons
Inelastic scattering	Interaction between matter and light that changes the direction as well as the energy of the photons

UV/Vis, (N)IR and fluorescence spectroscopy are all based on absorption, in the case of fluorescence followed by emission (Table 1). Photons can be absorbed if the atom/molecule has energy states that differ by the same amount of energy corresponding to the photon energy. For ultraviolet and visible radiation, absorption of a photon results in one of the molecule's valence electrons being excited to a higher energy state, while infrared absorption changes the vibrational energy of a molecular bond. The possible energy transitions that a molecule can undergo are discrete and determined by its molecular structure and by its environment in solution. As a result, absorption measurements as a function of the wavelength (reciprocal of the photon energy) result in spectra that are fingerprints for atoms/ molecules. Figure 2 shows a simplified view of a photon's absorption and subsequent emission.

Although the possible energy transitions for one molecule are very precisely defined, in practice the signals observed in absorption spectroscopy and fluorescence are not as well defined. Whereas spectral lines for individual transitions may be visible in a vacuum, in a solution effects of temperature, inhomogeneities, solute-solvent interactions and in particular hydrogen bonding mean that each molecule may have slightly different vibrational levels. Especially in complex molecules, the possible energy transitions can be so close together that they cannot be distinguished and are observed as one overlapping signal (Fig. 3). The result is a number of closely
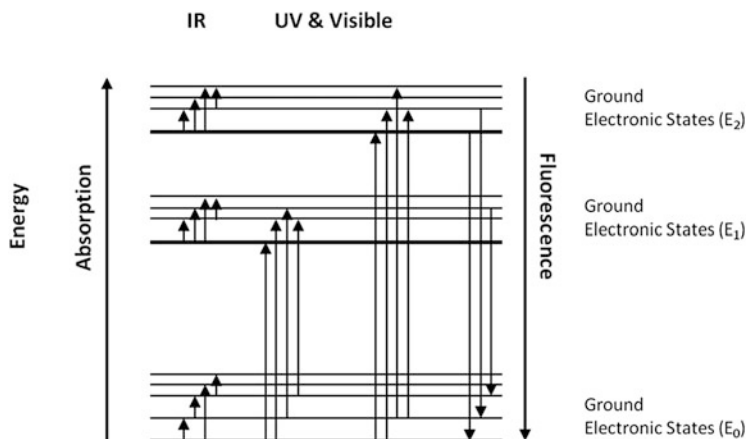
IR   UV & Visible

Fig. 2 Transitions between various electronic levels (E0, E1 and E2) and vibrational levels. Absorption of infrared radiation will cause a change in vibrational level, whereas absorption of UV or visible light will cause a change in the electronic energy level. Fluorescence is the falling back to a lower electronic energy level by emission of a photon, which will have higher wavelength (lower energy) than the photon that excited the molecule. The difference in energy is not lost, but converted to heat through vibrational relaxation. In case a molecule does not fluoresce, the excited electron falls back to its original level radiationless. Note that only some possible states are represented, with a typical molecule having many more electronic and vibrational energy levels
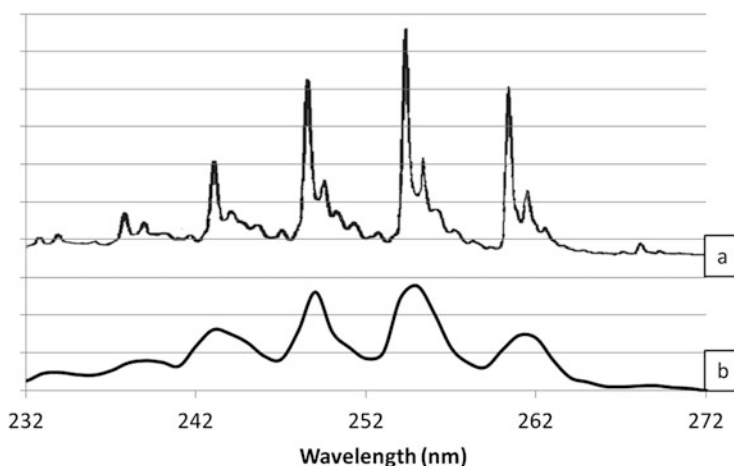

Fig. 3 Example of peak broadening in UV/Vis spectroscopy: (**a**) benzene in vapour phase, (**b**) benzene in hexane

spaced absorption bands that merge together to form a single broad absorption band as the spectrometer has insufficient resolution to resolve the individual peaks.

4   Signal Treatment

A water sample, whether natural water, drinking water or wastewater, will contain a wide range of substances in varying concentrations. The signals from all these chemicals are recorded simultaneously and in many cases overlap. In spectroscopy employed for smart water systems, the in situ and real-time nature of the monitoring requires that a sensor automatically extracts relevant information on the composition of the water from the superposed spectra. Effects that interfere with the signal, and therefore must be taken into account when analysing spectral data, include the absorption and scattering of light by particles and/or air bubbles, wear and tear of optical surfaces of the sensor (scratches, fouling, scaling), variations between measurements due to slight changes in the spectrum and intensity of the light source and variations in sensitivity as well as noise in the detector.

4.1   Data Validation

To turn raw data into useful information, modern spectrometers make use of mathematical algorithms. These clean up the signal and use correlations between the light intensity at various wavelengths and analytical parameters to calculate concentrations of specific (groups) of chemicals. Whether spectrometric data is used for the development of an automatic detection algorithm or for real-time autonomous data interpretation by the sensor system, the first step in analysis is always data validation. Because of the amount of data generated, and because of the fact that real-time process control requires making (near) real-time decisions, it is not possible to manually verify whether data are reliable and valid. For smart water systems, automatic validation is critical, ensuring only high-quality measurement results are used in the automated decision-making processes.

Data validation checks whether the sensor system was working properly during the measurement and whether the sample analysed was representative of the medium being monitored. If results are valid and representative, the data is considered reliable. Typical components in the data validation process include sensor status checks, noise analysis and detection of outliers, drift, gaps and steps in data. Tests to validate correct sensor operation include checks against realistic range, detection of constant values and signal-gradient monitoring [5] as well as hardware and software error messages. Once identified, anomalous or missing sensor data might be corrected for, e.g. by interpolation, data smoothing and averaging. More advanced validation methods include data forecasting [6] and the use of distributed algorithms in sensor networks where the results for one particular sensor can be inferred from those of its neighbours [7].

For spectral data averaging is a widely applied method: a set of subsequently recorded spectra is combined to average out fluctuations in the instrument and
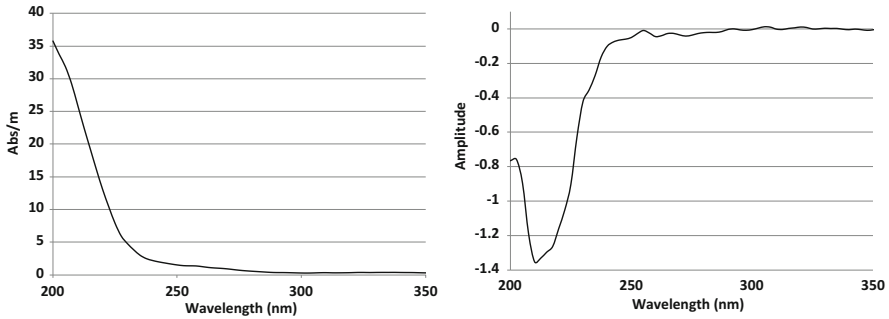
Fig. 4 Raw spectrum (left) and first-order (right) derivative of a UV/Vis absorption spectrum which shows the changes in the slope of the original spectrum

rapidly changing properties of the medium, such as fluctuations in light reflections and scattering by air bubbles and particles.

4.2 Transformations

When dealing with raw data that have a low signal to noise ratio, mathematical transformations can be used to extract useful information. The most widely used operation for removal of measurement noise is the Fourier transform (FT) [8]. This utilises the fact that a signal can be represented as a combination of periodic functions. If the noise and drift on time series data have a significantly different frequency compared to the signal, they can be filtered out. Typically, low-pass filtering is used to suppress noise and high-pass filtering to remove drift. Next to cleaning up the measurement signal, FT is also used in so-called Fourier transform infrared spectroscopy (FT-IR), a specific method of infrared spectroscopy with a very good signal to noise ratio and a high wavelength accuracy.

Another operation frequently used to optimise signal to noise ratios and help with (visual) identification of spectral features is derivatisation [9], as shown in Fig. 4. This removes spectral interferences such as the gentle absorption increase vs. wavelength caused by turbidity in UV/Vis spectra, the fouling of the optical surfaces and light scattering due to air bubbles in the medium, which predominantly result in offsets in the spectra. Most used is the first derivative, which in particular helps with visual identification of features such as shoulders on peaks. Practically, third of higher-order derivatives are not useful as the result of too high noise levels.

4.3 Chemometrics

Chemometrics is the chemical discipline that uses mathematics and statistics to design or select optimal experimental procedures and to obtain knowledge about a chemical system, such as a water matrix. In spectroscopy the primary uses for data analysis algorithms are grouping and classification and modelling relationships between different analytical data. Examples include the classification of samples, such as chemical compounds or materials, based on spectra, and the building of calibration models for calculation of concentrations of chemical constituents in a mixture, e.g. a water sample. The superposition of numerous single substance signals in real-world samples causes cross-sensitivities; when the concentration of an analyte is directly deduced from the signal at one individual wavelength, it will often respond to other, non-related, variations in the matrix. Chemometric models are required to extract information on the specific parameters from the spectra.

The most frequently used method to develop calibration models is indirect modelling using multivariate analysis [10]. In indirect modelling, a calibration model is built from a dataset containing spectral data and the concentrations of the parameters of interest. These concentration values are acquired through separate analytical methods, such as the standard methods for water quality analysis [11]. The multivariate approach has the advantage that interactions between analytes, or between analytes and the matrix, can be accounted for in the calibration model. Also, indirect modelling can deal with any correlations between target analytes. In water applications such correlations are often quite prevalent, such as, for example, the strong correlation between chemical oxygen demand (COD) and total suspended solids (TSS) in wastewater. The first step in the indirect modelling approach is the grouping of analytical data into clusters. An example of a projection method often used in spectroscopy is principal component analysis (PCA) [9]. PCA reduces the dimensionality of a set of variables while conserving the variability within the data as much as possible. In other words, PCA tries to explain the variance-covariance structure of the data using a new coordinate system that is lesser in dimension than the number of original variables; spectra typically consist of 200+ wavelength measurements (variables). The deduced principal components (PC) are new, uncorrelated, orthogonal variables that describe a maximum of variance in the dataset. Another method widely used in spectroscopy is partial least squares (PLS) regression [8]. Working in a similar way as PCA, PLS reduces a complex multidimensional dataset into a smaller number of components accounting for as much variation as possible while also modelling the Y-variables (the reference values). Because PLS is suited for cases with insufficient data to construct a model to predict all variability, it is especially popular in industrial applications where sufficiently complete datasets are often impossible to obtain. Both PCA and PLS are combined with cross-validation procedures and outlier tests to reach both high correlation quality and robustness of the model [8]. The result of the calibration procedure is a function describing how to combine a selection of wavelengths to calculate the target variables. The goodness of fit is described in the recovery
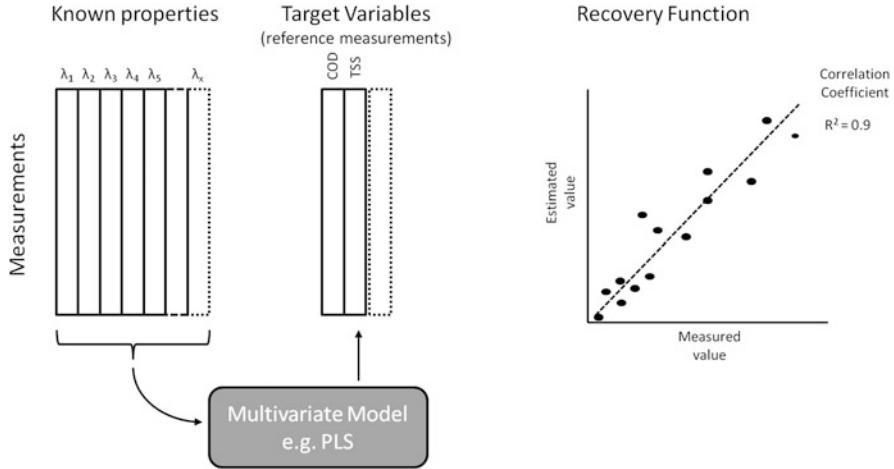
Fig. 5 Scheme of the multivariate calibration procedure

function (Fig. 5), which is obtained by plotting the reference measurements (actual targets) vs. the predicted values (estimated targets).

With increasing sensor complexity, connected sensors and the possible integration of metadata (e.g. weather data, water quantity information or even social media data), more advanced data treatment methodologies are required to find meaningful patterns. Machine learning can be used to find correlations in such big datasets [12]. Supervised machine learning algorithms, in which the computer is presented with example inputs and the desired outputs to these inputs, can be used to develop calibration models in cases where the datasets are too complex to handle by PCA or PLS. Non-supervised learning is used when looking for hidden patterns in the data. Not only can this be used to analyse big datasets but also for feature extraction (e.g. from 3D spectral datasets) and image analysis.

5 In Situ Spectroscopy for Water and Wastewater Analysis

5.1 UV/Vis Absorption Spectroscopy

In the water and wastewater industry, UV/Vis absorption spectroscopy is the most widely applied spectroscopic method for in situ and/or at-site, real-time monitoring. For an in-depth study of the principles of UV/Vis absorption spectroscopy and its application in water and wastewater analysis, Thomas and Burgess [9] provide a detailed treatise and Mesquita et al. [13] a comprehensive review of parameters analysed in wastewater systems.
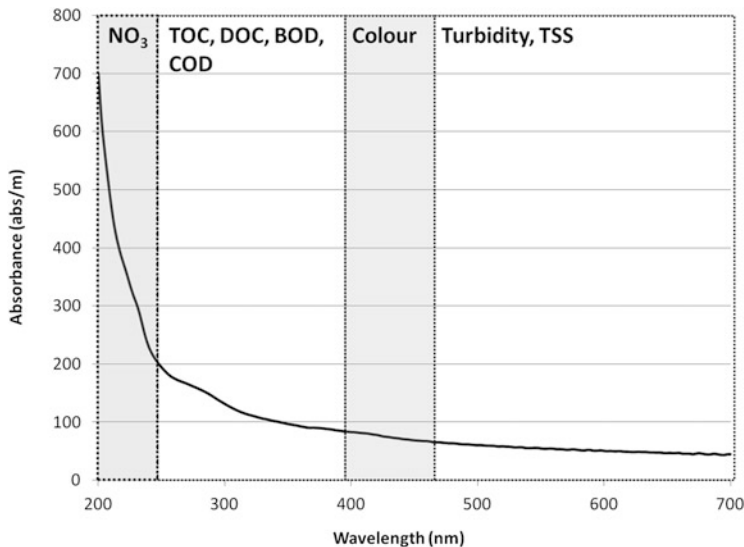
Fig. 6 Typical UV/Vis absorption spectrum of municipal wastewater. Areas used for determination of common UV/Vis parameters are indicated

UV/Vis absorption spectroscopy uses the linear dependence between the absorption measured and the concentration of the analytes, called the Lambert-Beer relationship, to determine parameter concentration values:

$$A = \varepsilon \times c \times L \qquad (2)$$

$$A_{\text{total}}(\lambda) = \sum_i \varepsilon_i(\lambda) c_i L \qquad (3)$$

where A is the absorption value, $\varepsilon(\lambda)$ is the molar extinction coefficient of the molecule or ion at wavelength λ, c is its concentration and L is the distance the light travels through the sample. The absorption at a particular wavelength A_i of multiple species i in a complex matrix can be linearly added to give a total absorption value $A_{\text{total}}(\lambda)$. For the purpose of water quality monitoring, spectrometer devices use a reference spectrum recorded in high-purity water which is subtracted from every measurement. Figure 6 shows an example of a typical UV/Vis absorption spectrum of wastewater after subtraction of the reference spectrum, illustrating the absorption of dissolved and suspended matter in the water.

Online UV/Vis spectroscopy started out as a method to estimate the level of organic matter in water by monitoring the light absorption at 254 nm. The use of 254 nm was the result of initial instruments using a low-pressure mercury light source, which has a strong emission line at 254 nm. The absorption at this wavelength correlates with the concentration of natural organic matter (NOM); as many organic compounds commonly found in water and wastewater (e.g. lignin, tannin,

humic acids, fulvic acids, proteins, various aromatic substances) absorb UV light, this signal can be used as a surrogate measure of NOM.

These early devices had serious limitations; apart from the limited lifetime of the mercury lamp, the use of a single wavelength makes the measurement sensitive to cross-interference; a change in the composition of the matrix, such as caused by heavy rainfall, the influx of industrial wastewater or the daily and seasonal changes in composition can cause strong changes in the relationship between UV254 and the true parameter of interest. For improved correlation, devices using multiple wavelengths were developed. The following types of instruments are now widely available:

- Dual wavelength, with a second wavelength used to compensate for turbidity and suspended matter.
- Multiple discrete wavelengths using LEDs with emission spectra at various wavelengths. Specificity is achieved through basic algorithms.
- Full spectral instruments, measuring the entire UV (200–400 nm) or UV/Vis (200–700 nm) range with nanometre resolution allowing for advanced algorithms.

UV/Vis spectrometers are offered both as submersible in situ probes and flow-through devices that can be used to monitor a sidestream. The sensitivity of the instrument depends on the length of its measurement compartment; a longer path length gives higher sensitivity but also a reduced maximum concentration level at which the instrument can operate. Therefore, a device with an optical path that fits the application needs to be used. Typical path lengths available are in the order of 0.5–100 mm.

5.1.1 Sum Organic Parameters

Natural water as well as domestic and industrial wastewater consists of a mixture of various organic substances. Using UV/Vis spectroscopy, the sum of all the absorption signals in the mixture is measured (Eq. 3). The recorded spectra are typically broad and lack characteristic features, because they consist of overlapping spectra of the individual components in the sample. Determination of individual substances is possible only in few applications, with substances with highly characteristic signals in areas of the spectrum where absorption by other components is low. It is, however, possible to accurately calculate sum organic parameters from absorption spectra, even when individual components cannot be identified. Parameters that can reliably be derived from the spectrum include total organic carbon (TOC), chemical oxygen demand (COD) and biological oxygen demand (BOD). As the traditional analytical methods for these parameters are time-consuming, e.g. the 5-day BOD test, or require toxic chemicals such as perchromate, a purely optical method to obtain an accurate indication of their concentration levels in real-time is a powerful tool. Using mathematical turbidity compensation, e.g. based on the description of the optical properties of turbidity and suspended matter [14], it is possible to filter out the
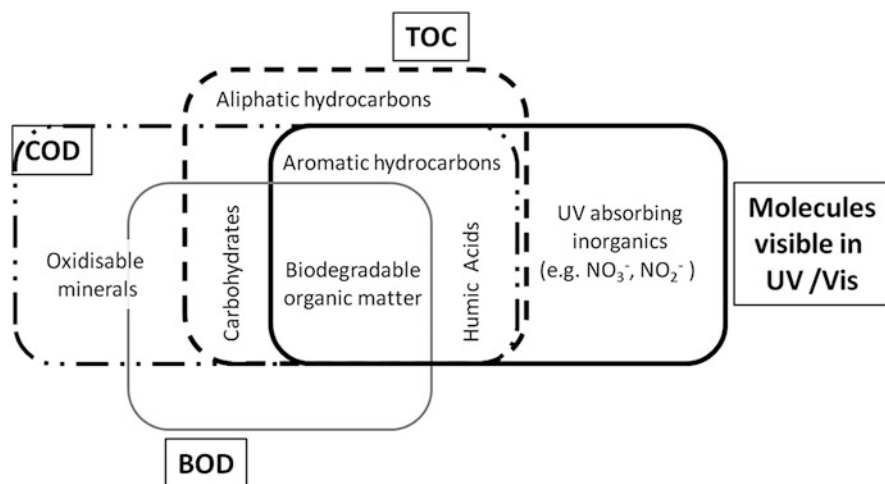
Fig. 7 The relationship between UV response and sum organic parameters

signal of the particulate matter and determine the dissolved organic carbon (DOC) and COD filtered (COD_f) concentrations. Although each of these sum parameters describes a different sub-group of the organic matter, using calibration models each can be estimated on the basis of the spectral information (Fig. 7).

Online monitoring of sum organic parameters is used in water and wastewater treatment, as well as environmental studies. In drinking water, TOC is a relevant quality parameter of water resources, allowing treatment process control such as coagulation [15] as well as optimisation of disinfection and prediction of disinfection by-products formation [16]. In finished drinking water, it is a quality indicator primarily related to aesthetics (taste and odour). In wastewater, COD and BOD are monitored in the wastewater treatment plant (WWTP) influent to determine pollution load, to optimise treatment and to protect the plant from overloading. In the plant effluent, COD can be monitored to determine treatment performance and for consent monitoring. In environmental studies, TOC is of particular interest in studies related to impact of human activities and climate change on lakes and rivers and the release of natural organic matter, e.g. from peat lands and boreal forests [17].

5.1.2 Nitrate and Nitrite

Although real-time UV/Vis spectroscopy is primarily suitable for the monitoring of sum organics, it is also particularly capable of measuring nitrate and nitrite concentrations. Both these ions have a strong absorption signal; in natural waters and drinking water, their signal dominates the 200–230 nm wavelength range, whereas in wastewater it is strong enough to allow reliable derivation from the spectral data using PLS calibration models [10]. Because the spectra of nitrate and nitrite are very similar, in most cases their combined concentration is determined. Using instruments

with 1 nm or better spectral resolution, however, it has been possible to obtain concentrations of both ions individually [18]. Nitrate and nitrite monitoring is primarily used to monitor and control nutrient removal processes in WWTPs and to monitor the nutrient load in surface waters.

5.1.3 Colour

Online monitoring of colour is mainly of interest in drinking water treatment. Colour in water is caused by the absorption of visible light by dissolved and colloidal substances and by the scattering of light by suspended particles. Both organic compounds, such as humic acids, and inorganic compounds, such as iron, copper and manganese, can be responsible for colour in water. The colour of natural water is typically yellow to brown. Although colour in itself does not constitute a health risk, high colour is considered aesthetically displeasing, and therefore, limits are defined for colour in drinking water regulations. The most commonly used standard method expresses the colour intensity compared to a solution of a platinum-cobalt complex using Pt-Co units, also referred to as Hazen [11]. A distinction is made between "apparent colour" for samples which include suspended matter and "true colour" for samples that do not include suspended matter (after filtration through a 0.45 μm filter). Both can be determined using online spectrometer instruments, where the apparent colour value is obtained after applying a turbidity correction on the raw spectral data.

5.1.4 Turbidity and Suspended Solids

Non-dissolved matter and colloidal matter cause scattering of the light passing through a water sample. This scattering is referred to as turbidity and is observed as a cloudiness or haziness of the liquid. A number of standard methods have been defined to measure turbidity in water. The most common methods are US EPA method 180.1 and ISO 7027, which measure scattering of light at a 90° angle with a white (tungsten) and infrared (860 nm) light source, respectively. Instead of 90° scattering, UV/Vis spectrometer devices measure the attenuation of light at 180°. The extinction of the signal observed in this instrument layout is caused by the combination of scattering, blocking and shading by particles as well as absorption by dissolved and particulate matter. Because the effect of turbidity on the spectrum is predictable [14] and as in natural water and domestic wastewater the particulates are the prime absorbers at wavelengths longer than 450 nm, turbidity and total suspended solids can be derived from the absorption in the visible range of the spectrum. Turbidity is used to assess the treatability of water and as quality control in drinking water. For example, an increase in turbidity in the distribution network can be an indication of ingress of foreign water, e.g. wastewater, resuspension of sediments or the release of biofilm from pipe walls. In water treatment it can be used to monitor particle carry-over from (sand) filters, helping in the optimisation of

the backwashing and cleaning regimes. In wastewater treatment, TSS or the closely related mixed liquor suspended solids (MLSS) are used to monitor sludge concentrations in aeration tanks and to control sludge recirculation and removal.

5.1.5 Other Direct Parameters

Various other substances have a strong and/or characteristic absorption signal that allows direct measurement. Those relevant for water and wastewater treatment include the treatment chemicals ozone (O_3) and permanganate (MnO_4^-) and pollutants such as BTEX (benzene, toluene, xylene), phenol, iron and chromium, which are indicators for contamination of water with hydrocarbons or industrial waste. In sewer systems, hydrogen sulphide (H_2S) can be measured. H_2S is formed under anoxic conditions and is both dangerous (it is highly toxic) and corrosive, leading to biogenic sulphuric acid corrosion of pipe materials.

5.1.6 Indirect Parameters

Not all parameters can be measured directly using UV/Vis spectroscopy. In many cases either the concentrations of the target analytes are too low to detect, or they do not absorb enough light at the wavelengths monitored. In some cases, however, the covariance of the invisible analytes with other, detectable components in the medium allows the building of a calibration model that exploits this relationship. Such calibration models for the indirect measurement of parameters have been reported for a wide range of parameters, including ammonium, total nitrogen and orthophosphate in wastewater, assimilable organic carbon (AOC) in drinking water and bacteria (*E. coli*) in surface waters and drinking water. As these models rely on a consistent relationship between the visible components and the invisible target analyte, they are often specific for a particular monitoring location, and their validity needs to be checked regularly.

Another type of indirect parameter is the process parameter. In this case, a calibration model is built between (variations) in the spectrum and the (desired) states in a treatment process. These parameters are used as real-time control inputs and facilitate optimisation of water treatment through reduction of chemical and energy consumption while safeguarding or improving treatment effectiveness. Examples of such process parameters include prediction of coagulation dose [15], prediction of chlorine demand and prediction of disinfection by-product formation [19].

One method which has been applied especially for the building of models for process parameters is differential spectroscopy, i.e. the subtraction of spectra measured before and after a process. The resulting "delta-spectrum" reflects the change in the composition of the water as a result of the process [9].
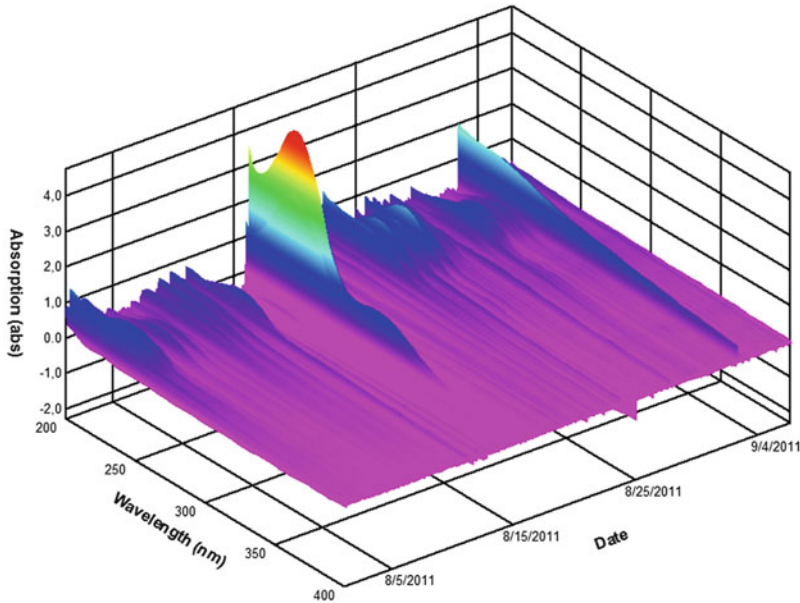
Fig. 8 3D absorption plot of a contamination event as it develops over time

5.1.7 Spectral Fingerprint and Contamination Alarm

Whereas differential spectroscopy for process control evaluates the changes in the water due to a particular (intentional) effect on the water, contamination alarm systems focus on detecting unexpected and often unpredictable changes (Fig. 8). The method used relies on automatic monitoring of the shape of the spectrum ("fingerprint") and comparing this shape to known conditions. When the fingerprint corresponds to a known undesirable state, or in case it does not correspond with a previously seen shape, the spectrometer reports an alarm. Alarm systems are available in many forms; the simplest versions monitor the absorption values at specific wavelengths. More advanced systems treat each spectrum as a vector (the number of dimensions being equal to the number of wavelengths) and perform a nearest neighbour analysis in the vector space [20]. With increasing computing power and storage capacity, more powerful statistical methods capable of handling bigger historical datasets are becoming available embedded in the sensors themselves, increasing real-time event detection capabilities.

The most typical applications for event detection are the monitoring of source waters for drinking water production (detection of harmful contaminations before the intake) and monitoring finished drinking water to safeguard its quality during storage and distribution (provide early warning in case of accidental or intentional contamination). The primary driver in these drinking water applications is protection of the public health. In wastewater early warning systems are used to monitor the influent of the WWTP. Here they can detect peak loads and warn for the presence of

harmful (industrial) contaminations, which can cause failure of the biological treatment resulting in costs for plant recovery and economic damages due to noncompliance of the discharged effluent.

5.1.8 Remote Sensing

A recent addition to the field of UV/Vis spectroscopy for water monitoring is remote sensing. Remote sensing is primarily used to determine levels of chlorophyll, suspended solids and chromatic dissolved organic matter (CDOM) in lakes and seas. It uses either long-range satellite-based optical sensors; close-range sensors that can be hand-held, fixed or mounted on drones; or a combination of both. The sensors are radiometers, i.e. they measure reflected natural light. Satellites are used to map the water quality over large areas, whereas smaller land-based systems provide higher-resolution measurements and have the advantage that they can also be operated under cloud cover. These are used independently as well as for validation of optical satellite data. The big advantages of remote sensors are the fact that they work from a distance, removing the need to physically access a location, and their ability to cover a large area where in situ sensors only provide spot sampling.

5.2 Fluorescence Spectroscopy

Another method widely used for water quality monitoring is fluorescence spectroscopy. Light absorbed by a molecule excites it to a higher energy state. Generally, molecules fall back from this higher energy state to their equilibrium energy state through various non-radiative mechanisms (Fig. 2). With fluorescent materials, however, part of the energy is emitted through the emission of a photon. This photon has a longer wavelength (i.e. lower energy) than the excitation energy. The intensity of the light at the emitted wavelength (known as fluorescence) is a measure for the concentration of the fluorescent molecules.

A fluorescence spectrometer is an instrument consisting of the following main components: a light source, a measurement compartment and a detector. The light source sends a beam of light at a wavelength tuned to the molecules of interest through the sample in the measurement compartment. The detector measures the intensity of the fluorescence generated. Generally, a wavelength filter is placed in front of the detector, allowing only the fluorescence to fall on the detector. This filter makes the measurement specific and reduces interference from natural light. Different types of online fluorescence spectrometer instruments are available:

- Single excitation – emission pair (excitation at a specific wavelength, emission measured at a specific wavelength). Often the excitation and/or emission wavelengths can be changed, by the user or the manufacturer, via the selection of different filters and/or different LEDs.
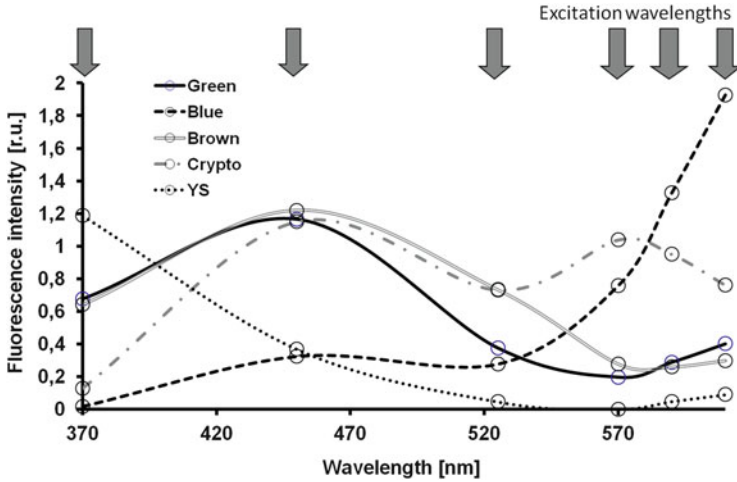
Fig. 9 Intensity of fluorescence emission of various types of algae plotted against the excitation wavelength (source: BBE Moldaenke, www.bbe-moldaenke.de)

- Suitable for the measurement of one target substance (group).
- Multiple discrete excitation wavelengths (using multiple LEDs as light source in combination with a broadband detector).
  - Suitable for the measurement of multiple target substances or groups; requires more advanced calibration and signal processing for deconvolution of the measurement signal into individual parameters (Fig. 9). An example is fitting of known spectra of individual analytes to the measurement results; the best fit will produce coefficients which can be used to determine the concentration of each component used in the fit.
- Laser-induced fluorescence, in which a laser source excites the target molecules with higher quantum efficiency than achievable with broadband light sources. The stronger emission signal allows for remote sensing or spectral analysis using diode array detectors.
- Fluorescence excitation-emission matrices (EEMs) in which emission spectra are recorded across a range of excitation wavelengths. Typically used for fingerprinting complex mixtures such as natural organic matter in surface waters and wastewaters.

5.2.1 Algal Pigments

In algae, fluorescence is a natural by-product of the photosynthesis process. Although most light captured by the algal pigments is used for the photosynthesis, a small portion leaks out in the form of fluorescence. The intensity of the

fluorescence can be used to estimate the concentration of algae and to track developments in the algal population, e.g. as early warning system for algal blooms. The central pigment responsible for photosynthesis is chlorophyll. However, as this is widely present in most photosynthetic organisms, the measurement of chlorophyll alone does only allow for monitoring total algal concentrations, but not classification. As some algae use auxiliary pigments next to chlorophyll A for the collection of photons, using multiple light sources to selectively excite the specific pigments, differentiation between classes becomes possible [21]. An example is the use of red light for the detection of the pigment phycocyanin that is present in cyanobacteria, which are a major cause for toxic algal blooms. Alternatively, the red fluorescence of the accessory pigment phycoerythrin is used to monitor some salt water cyanobacteria. The more advanced instruments attempt to distinguish between cyanobacteria, green algae and diatoms using spectral curve fitting methods [21], although adaptation of the calibration to the algae that are predominant in the waters analysed is often necessary.

It should be noted that in situ measurement of algal pigments does not provide quantitative information about cell concentrations or biovolumes, as signals strongly depend on the algae present, their physiological state and environmental factors such as brightness of the sunlight.

5.2.2 Dissolved Organic Matter

All natural waters as well as drinking waters contain natural organic matter (NOM). Common NOM compounds include proteins, polysaccharides and humic substances, which originate primarily from the breakdown products of plant material. Although NOM does not pose a risk to human health on its own, some NOM compounds are known to react with chlorine and chloramines to produce disinfection by-products (DBPs), some of which are carcinogenic and genotoxic. Monitoring the NOM levels in source waters is used to optimise water treatment and minimise DBP formation. In particular in surface waters with highly fluctuating compositions, e.g. strong seasonal influences, or high sensitivity to runoff during heavy rainfall, monitoring NOM is critical for water treatment performance.

NOM is also receiving attention in research related to climate change, with a particular focus on the release of NOM from boreal forests [22]. In this work, NOM levels and composition are used as indicators for changes in the biochemical cycles and mobilisation of organic matter (e.g. from permafrost) as a result global warming. Furthermore, changes in NOM may require adaptation of the water treatment systems to ensure continued supply of safe drinking water.

Monitoring of NOM is focusing on detection of humic and fulvic acids, both groups of substances with an aromatic character. Due to this aromatic character they are easily detected using fluorescence. This parameter is referred to as fluorescent dissolved organic matter (FDOM) and typically measured using fixed excitation-emission pair filter spectrometer devices. More detailed characterisation can be
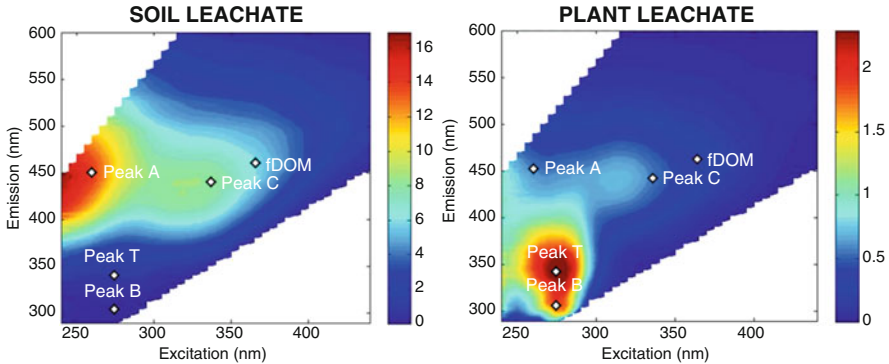
Fig. 10 An example excitation-emission matrix (EEM) showing the general locations of selected fluorescence peaks, with letter indication characteristic peaks (Reproduced from US Geological Survey, https://ca.water.usgs.gov/OMRL/OpticalProperties.html)

performed using EEM spectroscopy, but its use has been limited to measurement of discrete samples in static laboratory spectrometers.

5.2.3 Wastewater

Similarly to natural waters, municipal wastewater contains organic matter. A main role of wastewater treatment plants (WWTPs) is the removal of the majority of this organic matter. Still, the effluent of a WWTP is a complex mixture of dissolved effluent organic matter (dE_fOM), containing dissolved natural organic matter, soluble microbial products, endocrine disrupting compounds, pharmaceuticals and personal care product residues, disinfection by-products and more. Although current online sensors are not capable of monitoring the individual components in the wastewater effluent, it is possible to measure sum parameters. In Sect. 5.1.1 monitoring of BOD and COD using UV/Vis absorption spectroscopy was described. Fluorescence spectroscopy can also be used to monitor sum parameters, and using the ratio between characteristic peaks for natural organic matter (humic acids) and nonnatural organic matter (protein like), sewage contamination of surface waters can be detected. This is done by comparing *peak C* (humic like), with excitation at 350 nm and emission at 420–480 nm, and *peak T* (protein like), with excitation at 250 nm and emission at 340 nm (Fig. 10) [23]. Peak T has been found to correlate strongly with BOD in rivers and sewer systems. Furthermore, as it correlates strongly with the concentration of tryptophan, an amino acid derived from microbial matter, it is also used to estimate the levels of bacterial contamination in sewage-affected surface waters. For more advanced analysis, EEM can be combined with advanced statistical methods or automated characterisation and quantification of substance/contaminant classes [24].

5.2.4 Oil in Water

Contamination with mineral oils is a recurring issue in surface- and groundwater. Fluorescence sensors can be used to detect such contaminations. Monitoring the removal of mineral oils in industrial wastewater treatment, before discharge to sewer systems or surface waters, is another application. Mineral oils can be monitored with fluorescence as they typically consist of a mixture of aromatic and aliphatic hydrocarbons. It is the aromatic fraction which is detectable. Using fluorescence sensors employing fixed excitation-emission wavelength pairs in the UV range, either monocyclic aromatics (BTX) or polycyclic aromatic hydrocarbons (PAH) are measured. The presence of substances from these groups is used as an indicator for contamination for different types of mineral oil products, e.g. BTX as indicator for refined oil products (such as gasoline, diesel and kerosene), which are rich in these components.

More detailed analysis of the oil type can be done using fluorescence spectroscopy, where a high-resolution spectrometer is used as detector instead of the typical filter-covered photomultiplier or photodiode. Such instruments, often using laser-induced fluorescence to get sufficient signal to noise levels, can distinguish between different oil types. These laser-induced fluorescence (LIF) systems are primarily used in the offshore industry, refineries and applications where contamination with lubricating or cooling oils is common, e.g. industrial or bilge water in ships. The oils in these applications are low in aromatic contents and therefore difficult to detect using LED-induced fluorescence. A further issue with oil and hydrocarbon products is their poor miscibility with water, meaning a submersed sensor may not detect a contamination as is poorly mixed or floats on the surface of the water. To detect floating layers, remote sensing can be used; using a laser mounted above the water, the oil layer is illuminated, and the induced fluorescence is recorded. This allows detection of oil films down to 1 μm.

5.3 NIR

Infrared (IR) spectroscopy is similar to the previously described UV/Vis spectroscopy but uses a lightsource with a higher wavelength, i.e. lower-energy photons. The infrared spectrum is divided into near infrared (NIR) (750–2,500 nm), mid infrared (MIR) (2.5–16 μm) and far infrared (16–1,000 μm). For water quality analysis, the NIR spectrum is most widely used.

Because photon energies in IR are lower than in UV/Vis, it probes a different property of the molecule: instead of exciting electrons to a higher electronic energy level, it changes the vibrational state. IR radiation changes the vibrations of atomic bonds, with the behaviour of specific bonds depending on the atoms in the bond and their environment (both within the larger molecular environment as well as the physical environment, e.g. temperature, solution state). Similar to the electronic

levels, these vibrational states are discrete, and an IR spectrum reflects these discrete energy transitions.

In the MIR the absorption bands are well defined, and it is possible to identify specific atomic bonds. However, radiation in the MIR region does not penetrate water well enough for direct measurement of water samples. The lower absorption of NIR radiation by water allows for enough sample thickness to achieve sensitive direct measurements. Absorption bands in the NIR represent the overtones of the fundamental bands in MIR, and these overtones are relatively weak and not clearly delineated; whereas the much sharper signals in the MIR range often allow identification of individual substances, NIR spectra often do not provide such detailed information.

The applications of NIR are therefore found in situations where simple mixtures are analysed. Examples include quality control in food and pharmaceutical industry, where the expected NIR spectrum is known. A NIR sensor, monitoring deviations between the measured spectrum and that of a pure product, is a tool in quality control. Multivariate techniques such as principal component analysis (PCA) and partial least squares (PLS) regression are used for development of calibration models.

In the water industry, NIR has been used for various experimental studies, e.g. for oil in water monitoring or studies on microalgae [25] and extracellular polymeric substances in wastewater processes [13]. Commercial NIR systems for in situ analysis of water samples primarily use reflection instead of transmission spectroscopy; in the transmission mode (e.g. as in UV/Vis spectroscopy), a beam of light passes through a sample, and attenuation of the light by the sample is measured. Reflection spectroscopy, however, analyses the light reflected by the top layer of the matrix, where the makeup of the incident light is modified by the processes of absorption and scattering. It is used for the analysis of contaminations that float on the surface of water, e.g. oil slicks, and on media not transparent enough for transmission spectroscopy. An example is the dewatered sludge from WWTPs [13, 26]. Parameters measured in sludge include dry matter, ammonia and organic matter. The application in sludge monitoring offers the possibility for smart process control, allowing dosing control of polymers used in dewatering and safeguarding optimal composition of sludge for subsequent digestion.

5.4 Further Optical Technologies with Potential for Online Use in Smart Water Systems

UV/Vis absorbance and fluorescence are the most widely used spectroscopic methods in the water industry. NIR also has a well-established place, especially in industrial applications. Next to these technologies, there are optical methods with potential for wider use in the near future. A selection is discussed in this section.

5.4.1 Raman Spectroscopy

As opposed to absorption of fluorescence, Raman spectroscopy studies the scattering of photons by molecules. When a sample is irradiated with monochromatic light, a small proportion of photons (0.0001%) are scattered undergoing a shift in frequency; this inelastic scattering of photons is known as the Raman effect. The difference in the frequencies of the input and scattered light corresponds to the quantised energy levels of the molecule studied. For a more complete treatise on the principles of Raman and instrumentation used, see Li et al. [27].

Raman spectra are more distinct and less overlapped than UV/Vis/NIR absorption spectra. Therefore, Raman is complementary to absorption and fluorescence spectroscopy, as it offers a more selective signal. This allows for classification and in some cases even identification of target substances. It has successfully been applied to determine organic and inorganic analytes, including various metals, in a water matrix with examples including polycyclic aromatic hydrocarbons, pesticides, mercury and arsenic [28, 29]. In the case mixtures are analysed, if the components are known, the relative peak intensities can be used to generate quantitative information about the mixture's composition. In the case of water applications, however, the number of components may be so high that also Raman spectra overlap, and identification of individual species becomes impossible. Furthermore, the low percentage of photons undergoing inelastic scattering means Raman detection limits are significantly higher than those achieved with UV/Vis/NIR and are insufficient for application in online water quality monitoring as discussed here.

Surface-enhanced Raman (SERS) is a technique where Raman scattering is measured after adsorption of the target molecules on a substrate. This substrate enhances the sensitivity, in some cases allowing analysis of single molecules or single cells. As such it has been used to identify bacterial cells. SERS offers potential for general bacteria classification and pathogen detection [30] and label-free detection of biotoxins [31].

One promising application for Raman spectroscopy is the characterisation of microplastics. Although sample pretreatment remains a challenge, the characterisation of single particles with Raman, e.g. in combination with a flow cytometer, is a promising development [32].

5.4.2 Laser-Induced Breakdown Spectroscopy

Whereas all technologies discussed thus far analyse sample composition on a molecular level, laser-induced breakdown spectroscopy (LIBS) is an elemental analysis technique. In LIBS, a pulsed laser is used to heat a very small spot of the sample to extremely high temperatures (in excess of 30,000 K). As a result, a small amount of the material is transformed into a plasma consisting of free electrons, ions and excited atoms. As the plasma cools and electrons fall down from high-energy to lower-energy atomic orbitals, light is emitted at wavelengths characteristic for the

Fig. 11 Schematic representation of a LIBS measurement setup. The sample can be either solid or liquid
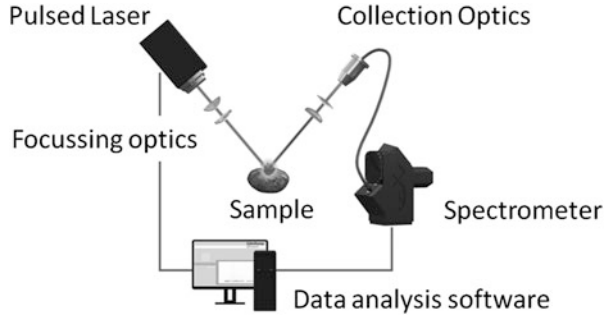
elements present in the plasma. The emission spectrum thus allows a rapid determination of the chemical composition of the sampled material (Fig. 11).

LIBS has been used since the 1970s but has only recently become available for rapid analysis outside of laboratory conditions. Although primarily used for the elemental analysis of raw materials (e.g. for production of pharmaceuticals and in mining), recently various applications in environmental and water analysis have also been described [33]. A potentially interesting application is the determination of ionic species, in particular heavy metals, which remain out or reach for other online sensor technologies. Sensitivity of LIBS is typically in the low ppm range, although the use of ultrashort laser pulses (femto seconds) and double pulsed lasers has been reported to offer the potential of sensitivity improvements. The sensitivity of LIBS, however, differs widely between various elements. Furthermore, for certain elements such as arsenic a controlled environment is required as emission lines are located at such short UV wavelengths that water vapour in the atmosphere will absorb all the emitted light.

5.4.3 Refractive Index

Refractive index is an optical property of a material that describes the propagation of light through it. Every substance has a specific refractive index. A mix of substances, such as a water matrix, can be described by a weighted sum of their individual refractive indices; all substances dissolved in a water matrix will contribute to the refractive index of that water matrix. A change in the composition of the matrix will result in a change in its refractive index. As such, monitoring the refractive index of a liquid provides information about the stability of the composition of the liquid; a change in composition will trigger a change in the refractive index. This is particularly useful for the monitoring of matrices with high stability, e.g. drinking water, or high-purity water in semiconductor industry; a rapid change in their composition indicates there is an issue with the water treatment or an intrusion of a contamination.

Although the refractive index itself does not provide information about the nature of the contamination, it can provide an early warning of a quality incident. Moreover, preliminary classification becomes possible when it is combined with one or more other measurements such as electrical conductivity or UV absorption spectroscopy. With refractive index being sensitive to all types of substances, both organic and inorganic, and other technologies being primarily sensitive to either of these groups of substances, a combination of sensors with intelligent data analysis software will be able to classify the nature of the agent [34].

A number of technical solutions exist for the accurate tracking of refractive index changes required to reach ppm and sub-ppm level sensitivity. These include the Mach-Zehnder interferometer and the optical ring resonator. A crucial factor for accurate refractive index measurement by these devices is the temperature compensation of the signal. Both have also been used in combination with surface coatings, such as antibodies, to increase their sensitivity and make them selective to specific molecules and even microorganisms [35].

5.4.4   Image Analysis

With the growing processing power and image analysis algorithms, various systems have now been introduced that perform fully automated scanning the particles of water samples. In such systems a set of optical properties of each particle is measured. This then allows the classification of the individual particles. Applications include counting and analysis of algae in surface water as well as monitoring the total number of bacteria in drinking and wastewater. An approach used in commercially available products for water analysis is 3D scanning with a microscope, collecting images at different depths in a sample and analysing the in-focus objects. Another approach uses flow cytometry to analyse individual particles, collecting scattering and fluorescence spectra of each particle that passes through a laser beam. Both methodologies assess a range of optical parameters for each particle, such as shape, size and optical density, in order to classify them. Although not capable of monitoring hygienic parameters in drinking water, which require single cell detection and identification in large volumes, these systems provide automatic culture- and reagent-free analysis of sum microbiological parameters, e.g. total cell count (TCC) and intact cell count (ICC), based on the characteristics of individual cells. Products of this type have been arriving on the market over the last 5 years and are used to monitor drinking water treatment processes and reservoirs, where an increase in cell counts can be indicative for failure of the treatment or contamination of a reservoir. They are also used to detect harmful algal blooms [36], for quality control in aquaculture and to monitor ballast water to prevent dispersion of nonindigenous organisms [37].

6   Discussion

In the previous sections, a variety of spectroscopic and related optical methods has been described, each with current applications in online water quality monitoring or the potential to be used in such applications. These technologies all share the sole use of interaction between light and matter as their principal measurement. The fully solid-state sensor hardware and the lack of reagents mean these sensors are potentially highly robust and potentially provide long-term performance stability. The current generation of sensors, however, is used in limited numbers and only very rarely in larger numbers as would be expected in smart sensor networks. The main reasons for their limited use are maintenance requirements, power requirements, instrument price and approach to data interpretation.

All optical instruments have an interface where the light used for the analysis crosses from the interior of the instrument into the sample and subsequently the same interface or a secondary, for collection of the light and guiding it to the detector. As only the interaction of the light with the sample is of interest, the optical interface should be fully transparent. However, when it is in contact with the sample, there is a risk of buildup of foreign material. Typical issues include scaling and (bio)fouling. It is therefore critical that optical systems deal with these issues if they are to be deployed in larger numbers, as otherwise the maintenance will be prohibitive. This issue is currently not solved in a satisfactory manner. Although manual cleaning intervals in drinking water applications are often satisfactory, in natural waters and especially in wastewaters, these sensors require frequent (weekly–monthly) maintenance. New methods to prevent contamination of optical surfaces (e.g. antifouling coatings) and/or methods to recognise and correct for fouling in the data processing are required to deal with this issue.

Virtually all spectrometers use an artificial light source. The majority of the advanced systems described in this chapter make use of incandescent lamps and arc lamps. Examples are the xenon, deuterium, deuterium/halogen, tungsten/halogen and mercury/argon lamps. Except for the xenon lamp, which is often used as a flash lamp, these lamps are used in continuous mode. As the lifetime of these lamps is measured in hundreds or thousands of hours, they need replacement. Furthermore, the power requirements for these lamps are such that a main power supply is required to operate the instruments. LED technology provides an alternative to these lamps. Although not all relevant wavelengths are currently available using LEDs, UV spectroscopy and fluorescence devices are making use of this technology. Although LEDs offer an advantage regarding cost and power consumption, allowing for long-term battery-powered operation, they suffer from decreasing brightness over time, which needs to be monitored and corrected for. As a result such instruments require occasional recalibration or replacements of LEDs, e.g. every 1–2 years.

Instrument prices for the devices described vary widely but are all in the 1,000+ euro range. The simplest LED-powered single or dual wavelength devices can be acquired for a few thousand euro, whereas the more advanced spectrometers may cost upwards of 30,000 euro. Even the costs for the simpler instruments prohibit

their large-scale deployment. It has to be noted, however, that the production volumes of these devices are low, typically in the hundreds or at most a few thousand per year. Therefore, these are all specialty products, which are intrinsically less cost-effective to produce than mass products. With ongoing miniaturisation of components and increasing demand (e.g. in situ UV/Vis spectrometer sales volumes have been increasing steadily for the last 15 years), prices can be expected to decrease in the future.

Perhaps the biggest challenge to wider use of these instruments is the data interpretation. This is less of technological challenge than a conceptual one. Most spectroscopic methods, as described previously, do not provide information on specific compounds but on the general state of the sample and/or on substance groups. In the water industry, however, a substance specific look at water quality is deeply ingrained. Spectrometer devices are traditionally compared against laboratory methods and are in many cases found to be less sensitive and less specific and therefore disregarded. However, they provide a different type of information: continuous insight into water composition and a much broader coverage and descriptive power on the state and state changes of a medium than can be achieved with the traditional grab-sampling and laboratory approach. The complementary nature of the online approach is of prime importance; the online methods are not likely to replace the laboratory altogether, but they provide another level of information. It is especially this real-time information that allows the direct monitoring of water systems and allows for operational and control applications. Furthermore, the continuous monitoring of the state of the water and changes therein provides useful inputs for smart water systems, especially when combined with other data sources.

Although all the methods described have the potential to produce results (near) real-time, each methodology provides a different type of information. The established methodologies primarily provide information on classes of chemicals and a small number of selected substances. The techniques that so far remain in limited use or have only been demonstrated to have potential in academic research are either more generic offering a generic chemical status indicator (refractive index) and generic microbiological status indicator (image analysis) or are highly specific for molecules (Raman) or elements (LIBS). Table 2 provides a short overview of the different methods and their strengths and weaknesses.

The primary application of the technologies described is found in process control and early detection of incidents or process failures. These are applications where a rapid response is essential. This is where the current generation of online systems comes into its own. The possibility to monitor processes and, through better understanding, optimise operation and control means a positive return on investment can be achieved. The case for quality monitoring, e.g. for drinking water, is often more difficult to make as it primarily provides more insight but not necessarily any gains in operational efficiency or reduction in costs. Online monitoring of wastewater effluent for compliance purposes is, however, in some cases being applied as it can be used to determine the total contaminant load discharged as well as failure of the treatment. Monitoring for legislative purposes on individual substances remains

Table 2 Overview of spectroscopic methods and their general characteristics

Method	Generic properties	Advantages	Disadvantages
UV/Vis (absorption)	• Measures broad spectrum and uses calibration algorithm to extract desired information • Broad spectral signals • Primarily sensitive for organic substances with unsaturated bonds (e.g. aromatics) • Sensitivity down to high ppb level for substances with high absorption coefficients	• Good for sum parameters (BOD, COD, TOC, TSS) • Good at fingerprinting (distinguish between normal/abnormal conditions)	• Limited capability to identify individual compounds • Sensitivity varies widely per compound, with poor sensitivity for aliphatic hydrocarbons and most inorganics • Cross-sensitivity to substances with overlapping spectra can be an issue when not compensated through calibration algorithms
Fluorescence	• Uses combinations of excitation an and emission wavelength to measure specific groups of substances • Primarily sensitive for organic substances with unsaturated bonds (e.g. aromatics) • ppb level sensitivity	• Good for sum parameters (BOD, FDOM, oil in water) • Good at detecting algal pigments • High sensitivity for polycyclic aromatics (low ppb to high ppt levels) • Suitable for noncontact/remote applications and monitoring of floating layers	• Difficulty with identification of individual compounds • Sensitivity varies widely per compounds, with poor sensitivity for aliphatic hydrocarbons and most inorganics • Equipment not flexible: excitation and emission wavelengths fixed, not flexible in substances that can be detected
Near infrared (absorption)	• Measures broad spectrum and uses calibration algorithm to extract desired information • Measures molecular bonds (e.g. O-H) • Broad spectral signals • ppm level sensitivity	• Good at fingerprinting (distinguish between normal/abnormal conditions) • Reflection spectroscopy useful in inhomogeneous and nontransparent media	• Difficulty with identification of individual compounds • Cross-sensitivity to substances with overlapping spectra can be an issue when not compensated through calibration algorithms
Raman (scattering)	• Spectra with distinct signals	• Suited for both organic and inorganic analytes, including metals • Allows identification of individual substances • SERS offers possibility for pathogen detection	• Detection limits higher than with UV/Vis/NIR • Sensitivity varies widely per compound
LIBS (emission)	• Provides elemental information • Mid-ppm level sensitivity	• Capable of measuring all elements, from hydrogen to uranium • Capability to detect	• Sensitivity insufficient for low level detection of most contaminants

(continued)

Table 2 (continued)

Method	Generic properties	Advantages	Disadvantages
		independent of the nature of the analyte-plasma releases all atoms from their chemical environment. Use, e.g. to detect total concentration of an element, such as P, As or Cr	• Sensitivity varies with element and with sample matrix • Provides elemental composition of the sample, no information on chemical composition
Refractive index	• Measures physical property of sample, which is responsive to the chemical makeup of the sample • ppm level sensitivity	• Generic, sensitive to all types of chemicals, both organic and inorganic • Good for monitoring stability/variability of the sample composition • Consistent sensitivity, with only minor variations between different types of substances	• Generic, not possible to identify the cause for a change in signal
Image analysis	• Analysis of combinations of optical properties of particles • Targeting samples with cell concentrations in the 1,000/mL or higher	• Culture- and reagent-free analysis of microbiological properties, such as total cell counts • Combinations of optical properties sometimes allow for classification of cells	• Only suited for analysis of particles • Time-consuming when analysing properties of individual cells (e.g. flow cytometry)

limited to nitrate; spectroscopic measurement of nitrate is listed as a standard method [11]. Especially for trace contaminations, where individual substances concentrations are requested at the low ppb or even ppt levels, the current generation of spectrophotometric devices is lacking in sensitivity when applied in a water matrix. Typical sensitivities for each technology type are given in Table 2.

7 Outlook

Smart water systems are expected to revolutionise the water industry. Through the combination of information from various sources at all levels in the water system, more effective management will become possible. This will help reduce costs, increase safety and ensure that infrastructure will be able to cope with changing demands, such as urbanisation, climate change and decentralisation. In this data-driven approach, sensors are an essential link in the chain, as they provide the raw

data upon which the whole system is built. As smart systems are expected to acquire information not only from traditional monitoring locations such as water treatment plants, but actually from the entire water system, there is a requirement for durable, autonomous, networked and affordable sensor technology. Optical sensor systems provide a good basis for this sensor generation: they are robust and low maintenance. In this chapter a selection of technologies has been described, which have proven they can provide valuable information on the composition and quality of water. Although the current application of these methodologies in real-time online sensing remains limited, such sensors, UV/Vis absorbance and fluorescence devices in particular, have become widely accepted and established in the water industry. Their use is on the rise, especially in process monitoring and control and as early warning systems. This is expected to gain further momentum as the performance and cost-effectiveness of these systems increase further.

References

1. Peleg A (2014) Investment in smart water networks on the rise. Water Technology
2. Owen DAL (2018) Smart water technologies and techniques – data capture and analysis for sustainable water management. Wiley, Oxford
3. Makropoulos CK, Butler D (2010) Distributed water infrastructure for sustainable communities. Water Resour Manag 24:2795–2816
4. van den Broeke J, Carpentier C, Moore C, Carswell L, Jonsson J, Sivil D, Rosen JS, Cade L, Mofidi A, Swartz C, Coomans N (2015) Compendium of sensors and monitors and their use in the global water industry. IWA Publishing, London
5. Sun S, Bertrand-Krajewski J-L, Lynggaard Jensen A, van den Broeke J, Edthofer F, do Céu Almeida M, Silva Ribeiro À, Menaia J (2011) Literature review for data validation methods. Deliverable 3.1.1, PREPARED (EC FP7 Programme project number 244232)
6. Hyndman RJ, Athanasopoulos G (2018) Online open access textbooks. www.otexts.org/fpp2/
7. Bettencourt LMA, Hagberg AA, Larkey LB (2007) Separating the wheat from the chaff: practical anomaly detection schemes in ecological applications of distributed sensor networks. In: Aspnes J, Scheideler C, Arora A, Madden S (eds) Lecture notes in computer science, vol 4549. Springer, Berlin
8. Otto M (1999) Chemometrics: statistics and computer application in analytical chemistry. Wiley, Weinheim
9. Thomas O, Burgess C (2017) UV-visible spectrophotometry of water and wastewater, 2nd edn. Elsevier, Amsterdam
10. Langergraber G, Fleischmann N, Hofstaedter F (2003) A multivariate calibration procedure for UV/Vis spectrometric quantification of organic matter and nitrate in wastewater. Water Sci Technol 47(2):63–71
11. Rice EW, Baird RB, Eaton AD (2017) Standard methods for the examination of water and wastewater. AWWA Catalog no. 10086, American Public Health Association, American Water Works Association and Water Environment Federation
12. Bishop CM (2006) Pattern recognition and machine learning. Springer, New York
13. Mesquita DP, Quintelas C, Amaral AL, Ferreira EC (2017) Monitoring biological wastewater treatment processes: recent advances in spectroscopy applications. Rev Environ Sci Biotechnol. https://doi.org/10.1007/s1115701794399
14. Huber E, Frost M (1998) Light scattering by small particles. J Water Supply Res Technol 47(2):87–94

15. Fabris R, Chow C, Dexter R, Colton J, Knoblauch J, Drikas M (2013) Feed-forward coagulant control using online UV/Vis monitoring. Water Sci Technol Water Supply 13(2):420–426
16. Korshin GV, Li C-W, Benjamin MM (1997) The decrease of UV-absorbance as an indicator of TOX formation. Water Res 31(4):946–949
17. Erlandsson M, Futter MN, Kothawala DN, Köhler SJ (2012) Variability in spectral absorbance metrics across boreal lake waters. J Environ Chem 14(10):2643–2652
18. Rieger L, Vanrolleghem PA, Langergraber G, Kaelin D, Siegrist H (2008) Long-term evaluation of a spectral sensor for nitrite and nitrate. Water Sci Technol 57(10):1563–1569
19. Chow C, Fabris R, Dixon M (2008) Case studies using S::CAN on-line monitoring system. Research report 75, Water Quality Research Australia
20. van den Broeke J, Edthofer F, Weingartner A (2011) Clean data and reliable event detection – turning results from online sensors into information. In: Borchers U, Thompson KC (eds) Water contamination emergencies: monitoring, understanding and acting. RSC Publishing, Cambridge
21. Beutler M, Wiltshire KH, Meyer B, Moldaenke C, Lüring C, Meyerhöfer M, Hansen U-P, Dau H (2002) A fluorometric method for the differentiation of algal populations in vivo and in situ. Photosynth Res 72:39–53
22. Eikebrokk B, Vogt RD, Liltved H (2004) NOM increase in northern European source waters: discussion of possible causes and impacts on coagulation/contact filtration processes. Water Sci Technol Water Supply 4(4):47–54
23. Hansen AM, Fleck JA, Kraus TEC, Downing BD, von Dessonneck T, Bergamaschi BA (2018) Procedures for using the Horiba Scientific Aqualog® fluorometer to measure absorbance and fluorescence from dissolved organic matter. U.S. Department of the Interior, U.S. Geological Survey, Open file report 2018-1096
24. Markechova D, Tomkova M, Sadecka J (2013) Fluorescence excitation-emission matrix spectroscopy and parallel factor analysis in drinking water treatment: a review. Pol J Environ Stud 22(5):1289–1295
25. Gowen AA, Tsenkova R, Bruen M, O'donnell C (2012) Vibrational spectroscopy for analysis of water for human use and in aquatic ecosystems. Crit Rev Environ Sci Technol 42 (23):2546–2573
26. Garcia-Sanchez F, Galvez-Sola L, Nicolas JJM, Muelas-Domingo R, Nieves M (2017) Using near-infrared spectroscopy in agricultural systems. In: Kyprianidis K, Skvaril J (eds) Developments in near-infrared spectroscopy. IntechOpen, London
27. Li Z, Deen MJ, Kumar S, Selvaganapathy PR (2014) Raman spectroscopy for in-line water quality monitoring – instrumentation and potential. Sensors 14(9):17275–17303
28. Li Z, Wang J, Li D (2016) Applications of Raman spectroscopy in detection of water quality. Appl Spectrosc Rev 51(4):333–357
29. Collette TW, Williams TL (2002) The role of Raman spectroscopy in the analytical chemistry of potable water. J Environ Monit 4(1):27–34
30. Tanchou V (2014) Review of methods for the rapid identification of pathogens in water samples. Scientific and Technical Research series, Joint Research Centre, European Commission
31. Grow AE, Wood LL, Claycomb JL, Thompson PA (2003) New biochip technology for label-free detection of pathogens and their toxins. J Microbiol Methods 53(2):221–233
32. Araujo CF, Nolasco MM, Ribeiro AMP, Ribeiro-Claro PJA (2018) Identification of microplastics using Raman spectroscopy: latest developments and future prospects. Water Res 142:426–440
33. Gaudiuso R, Dell'Aglio M, DePascale O, Senesi GS, DeGiacomo A (2010) Laser induced breakdown spectroscopy for elemental analysis in environmental, cultural heritage and space applications. Sensors 10:7434–7468
34. Williamson F, van den Broeke J, Koster T, Klein Koerkamp M, Verhoef JW, Hoogterp E, de Graaf BR (2014) Online water quality monitoring in the distribution network. Water Pract Technol 9(4):575–585. https://doi.org/10.2166/wpt.2014.064

35. Ramachandran A, Wang S, Clarke J, Ja SJ, Goad D, Wald L, Flood EM, Knobbe E, Hryniewicz JV, Chu ST, Gill D, Chen W, King O, Little BE (2008) A universal biosensing platform based on optical micro-ring resonators. Biosens Bioelectron 23(7):939–944
36. Zhou Q, Chen W, Zhang H, Peng L, Liu L, Han Z, Wan N, Li L, Song L (2012) A flow cytometer based protocol for quantitative analysis of bloom-forming cyanobacteria (Microcystis) in lake sediments. J Environ Sci 24(9):1709–1716
37. Peperzak L, Zetsche E-M, Gollasch S, Artigas LF, Bonato S, Creach V, Dubelaar GBJ, Henneghien J, Hess-Erga O-K, Langelaar R, Larsen A, Maurer BN, Mosselaar A, Reavie ED, Rijkeboer M, Tobiesen A (2018) Comparing flow cytometry and microscopy in the quantification of vital aquatic organisms in ballast water. J Mar Eng Technol. https://doi.org/10.1080/20464177.2018.1525806