



The benefits of using refractive index for water quality monitoring in distribution networks

A comparison of Optiqua EventLab and traditional water quality parameters

Joep van den Broeke¹

Abstract

To monitor the dynamics in water quality in drinking water distribution networks, and to facilitate a quick and timely response to quality incidents and pro-active network operations, real-time water quality information is vital. Measurement devices with a sufficiently low operational footprint to allow implementation in distribution networks are only available for a small range of chemical and physical parameters, such as pH, ORP, conductivity, dissolved oxygen, UV absorption and fluorescence. The use of sensors for these traditional water quality parameters has serious limitations, both in terms of detection capabilities as well as operational aspects. Each of these sensors measures only a limited sub-set of all possible constituents of the water matrix, and therefore a multitude of sensors is required to obtain substantial coverage. Nevertheless, even using a combination of the traditional sensors, there remains a significant gap in detection capabilities, with a blind spot that includes most non-aromatic organic molecules. The response from these systems is further complicated by intrinsic characteristics of the technologies used, and include inconsistent sensitivity for different types of substances, matrix cross-interference and non-linear response. Furthermore, using a combination of sensors, which all require maintenance, is not beneficial for the robustness of the monitoring set-up, and will result in a high maintenance load. This is especially the case when electrochemical sensors are used, for example for pH, ORP and ion selective electrodes, as they demand frequent maintenance and calibration.

Optiqua has developed a generic optical sensor concept, EventLab, that can be deployed online throughout a distribution network, and that meets the four key operational requirements of such a water quality event monitoring system: (i) continuous real-time detection, (ii) generic: one sensor covering the full spectrum of possible chemical contaminants, (iii) high sensitivity, and (iv) low cost and low maintenance. EventLab measures minute refractive index (RI) changes in water. RI is a useful generic indicator of water quality as any substance, when dissolved in water, will change the refractive index of the water matrix. Intrinsic advantages include consistent sensitivity for all substances, response linear with concentration and high resistance to matrix interference.

Results from installations have confirmed the added value of EventLab. Systems installed in various distribution networks have monitored variations in baseline water quality and detected water quality events all of which were not detected by traditional sensor systems installed at the same sites. As expected on the basis of the differences in measurement principles EventLab picks up water quality variations that remain invisible to traditional sensors. These results obtained under operational conditions in distribution network applications validate the true added value of refractive index measurements. EventLab can be used as a stand-alone water quality monitoring solution, providing consistent coverage to detect any water quality variation due to dissolved substances. Alternatively, EventLab can be used as the basis for a multi-sensor monitoring strategy. A combination with other sensors can be used to further expand the range of events that can be detected, e.g. to include particles, or provide the capability for a global classification of the detected quality change.

¹: Optiqua Technologies, Hengelosestraat 705, 7521 PA, Enschede, The Netherlands

Introduction

Monitoring water quality is an important part of the operations of a water utility. Traditionally, grab sampling and laboratory analysis have been the pre-dominant approach to quality monitoring. The use of grab samples, however, is not well suited for continuous monitoring of changeable water quality, as it only provides snap shots of the water composition and no information on variation therein during the time between samples. A further drawback of this approach is the time to result, which can be hours or even days.

To monitor the dynamics in water quality, as they for example occur in drinking water distribution networks, and to facilitate a quick and timely response to quality incidents and pro-active network operations, real-time water quality information is vital.

For many parameters, the monitoring systems are simply automated laboratory set-ups. However, system requirements for use in drinking water distribution networks preclude the use of such technologies. A monitoring device used in the distribution network, especially when employed in a network with substantial numbers instruments installed in remote locations, needs to have a small operational footprint. Of prime concern is a low need for maintenance. Maintenance costs, primarily the man-hours which include travel times to and from the instruments, are the main operational cost factor and, over the lifetime of an instrument, will easily exceed the capital cost of an instrument. Minimal operational cost (Opex) is critical for the success of online water quality monitoring in the distribution network.

Traditional Water Quality Sensors for online Monitoring

Measurement devices with a sufficiently low operational footprint to allow implementation in distribution network are only available for a small range of chemical and physical parameters. Historically these include pH, electrical conductivity (EC), redox potential (ORP), dissolved oxygen (DO) and turbidity. The sensors for these parameters are available as individual instruments, but also as multiple sensors integrated into a multi-parameter probe. Over the last decade additional sensors have been coming on the market that expand the suite of parameters available for application in distribution networks. New technologies include fluorescence sensors (oil in water, chlorophyll), UV/Vis absorption (UV254, colour) and ion specific electrodes (NH₄, NO₃).

The typical objective behind the concept of using a combination of the available sensors is that it should provide a network operator with an indication of various chemical water quality variations that can occur in distribution networks. Furthermore, in some cases compromised biological quality can be detected indirectly, e.g. by detecting the change in the matrix resulting from intrusion of wastewater or grey water as a result of breached pipes or backflow events. There are however important limitations that need to be considered when configuring an array of traditional sensor for the conditions of a water distribution network. Firstly, as each traditional sensor only measures a limited sub-set of all possible constituents of the water matrix, a multitude of sensors is required to obtain substantial coverage (Figure 1). The use of such a combination will be detrimental to the robustness of the system, as each individual sensor, even when integrated into a multi-parameter probe, will require maintenance. Furthermore, there is no combination of sensors that will be able to detect all possible water quality changes. And although surrogate parameters allow detection of a range of water quality changes, they will provide insufficient information to identify the contamination, meaning grab sampling will still be required to assess the nature of a detected event. Finally, specific sensors have specific properties that can strongly impact the usefulness and reliability of such a sensor in the context of a water distribution network.

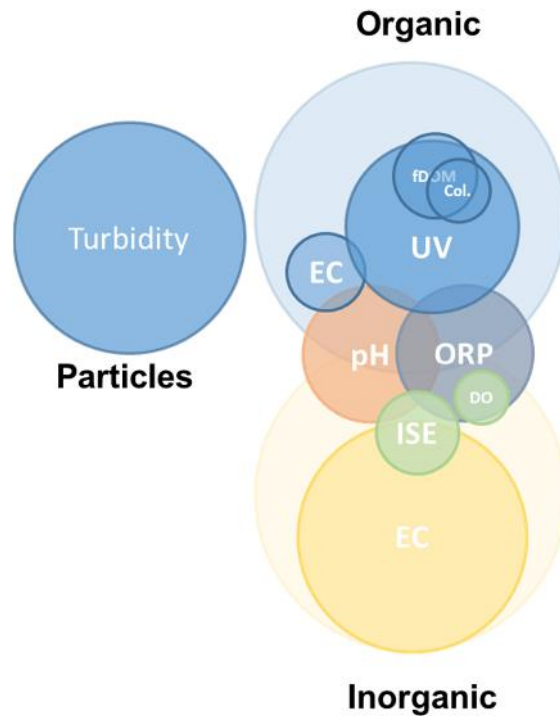


Figure 1: Different types of water quality components and sensors suited to measure them.

The available sensors can broadly be divided into two classes: electrochemical and optical. Both sensor types operate without the use of chemicals, measuring their target analytes directly. Optical sensors, especially those with solid state light sources such as LEDs, provide long term stability, with fouling of the optical interface surface being the main maintenance issue. Electrochemical sensors are intrinsically susceptible to aging; the sensing element ages over time by, amongst others, irreversible binding of ions and mechanical wear. As a result the sensor signal will drift, requiring periodical re-calibration, sensitivity will decrease over time and response time will increase over time. Eventually replacement of the sensing element, which can be the membrane, the electrode or the entire sensor, will be required.

The sensors most commonly used in distribution network applications have the following characteristics:

pH

pH Sensors are electrochemical devices with a selectivity for hydrogen ions.

pH is a measure of the acidity or basicity of an aqueous solution and determines a chemical reactivity of the total matrix, not the reactivity or concentration of single substances. The pH value is determined by the combination of all the acids and bases present, but also by the buffering capacity of the water and the temperature. Because the strength of acids and bases varies by many orders of magnitude, the sensitivity of pH to the matrix and the logarithmic nature of the parameter, it is impossible to link (changes in) pH to the changes in concentration of single acids or bases.

pH is primarily used as process control parameter at treatment plants, e.g. to ensure optimal performance for pH dependent treatment processes (coagulation, chlorination). pH is less suited for detection of general water quality changes and detection of contamination events as it responds to a limited sub-set of substances. pH also has an intrinsic cross-sensitivity for ionic strength, and is therefore matrix dependent, further reducing its usefulness in contamination detection.

Oxidation Reduction Potential (ORP)

ORP sensors are electrochemical devices equipped with an inert electrode in combination with a reference electrode. ORP is a relative measurement; the value depends on the material of the electrode in the sensor, the configuration of the electrode and the physical state of the electrode (ageing, fouling, ...).

ORP of a solution is determined by the sum of all redox active species (electron acceptors and electron donors) in a solution, but it is dominated by the strongest redox equilibrium in the solution. Redox reactions are complex and often involve more than one substance. Furthermore, ORP is influenced by the matrix of the solution, pH and temperature.

ORP is an activity measurement, not a measurement of concentration. In drinking water applications it is sometimes used as a measure of disinfection potential, showing the activity of the disinfectant instead of the applied dose. ORP is not well suited for monitoring general quality changes and for detection of contamination events, as it only responds to a limited sub-set of substances. Its suitability for this application type is further limited by the difficulty of comparing results between sensors (not consistent), due to the dependence of the measurement results on the layout of the sensor and the state of the sensor. Strong interferences from the matrix and the fact they are difficult to calibrate under field conditions further hamper successful application of ORP as a parameter for water quality monitoring in distribution networks.

Electrical Conductivity (EC)

EC sensors are solid state sensors that measure the electrical field of the water moving around the sensor electrodes. Although the sensor hardware is robust, the measurement is sensitive to flow rate and flow direction as well as micro-scratches on the electrodes (e.g. from cleaning) as these change the geometry of the measurement cell.

Electrical conductivity is a measure for the capability of a liquid to conduct an electrical current. The conducting behaviour is the result of the ions dissolved in the liquid. All ionic species are measured with EC, but the response of the sensor depends on properties of the ions (charge, ion size) and their dissociation. Therefore it is a general indicator for total ion concentration and not a concentration measurement.

Conductivity is used as a measure for the total amount of salts or solids dissolved in a solution (Total Dissolved Solids or TDS). In drinking water applications primarily used to monitor the quality (salinity) of source waters. In water quality monitoring and event detection applications in distribution networks, EC measurements can cover a major part of the spectrum of inorganic substances that contribute to water quality.

Dissolved Oxygen (DO)

Modern DO sensors are mainly of the optical luminescence type, which are robust and have a high stability. A DO sensor measures the saturation of a solution with dissolved oxygen gas. In combination with measurement of temperature, this saturation can be converted into an oxygen concentration.

Although there are target concentrations for DO in drinking water during distribution (high DO speeds up corrosion, low DO can favour undesirable biological processes), DO is not regularly measured as it is not a suitable indicator for most quality issues.

Turbidity

Turbidity is an optical measurement of the diffraction of light by a water sample. Light diffraction is primarily the result of particles in the water. Turbidity, therefore, is a measure of the particle load in the water. Turbidity measurements do not provide information on the nature of the particles (size, material).

Being an optical sensor, maintenance requirements for turbidity sensors are low. The measurement, however, is sensitive to air bubbles in the water.

Turbidity sensors have a limited measurement range. For use in drinking water highly sensitive sensors are required, but the configuration that provides the best highest sensitivity is not suited for operation in the distribution network.

Turbidity is primarily a process parameter, but will also detect water quality issues in the distribution network with an impact on the particle levels, for example re-suspension of sediments and ingress of non-treated (waste)water.

Ammonium and nitrate (NH_4/NO_3)

NH_4/NO_3 are measured with ion selective electrodes. Ion selective electrodes (ISE) are maintenance intensive to operate, requiring frequent recalibration, and have a limited linear range. ISEs have a limited measuring range, and not all ISEs are suited for low concentration measurements required in distribution networks.

NH_4/NO_3 are specific ions relevant for systems with residual disinfectant, especially when chloramines are used. These parameters are used to optimise chlorine and ammonia dosing in chloraminated systems and as early warning for nitrification. They will not respond to changes in the water composition other than changes in nitrate and ammonium level.

UV/Vis absorption

UV/Vis sensors measure the amount of light absorbed by a sample. UV/Vis absorption is measured with an optical instrument consisting in a light source and a detector. These instruments are long term stable, maintenance primarily involves keeping the optical surfaces clean. This measurement is primarily sensitive to aromatic organic molecules. Natural organic matter, such as humic and fulvic acids, are responsible for the majority of the absorption in drinking water.

UV/Vis absorption measurements can provide an indication of the colour of a drinking water as well as the total organic content (TOC) of the water. Water quality events involving substances that absorb UV light (organic molecules with aromatic or similar chemical structures) can be detected. Many organic substances, especially small organic molecules, are not detected by UV absorption measurements.

Typical applications include source water monitoring to assess treatability and adjust applied dose (e.g. coagulation, UV-disinfection, chlorination and ozonation). Also used as an early warning sensor for (aromatic) organic contaminants.

Fluorescence

Fluorescence is measured with an optical instrument consisting in a light source and a detector. These instruments are long term stable, maintenance primarily involves keeping the optical surfaces clean. Fluorescence measures the light emitted by some substances when excited by light of a specific wavelength. A fluorescence sensor uses specific excitation and emission wavelengths to achieve selectivity for specific substance groups. Fluorescence is primarily sensitive to aromatic substances.

Natural organic matter (humic and fulvic acids) as well as proteins exhibit fluorescent behaviour. Fluorescence sensors on the market focus on monitoring these natural materials (fDOM, CDOM), and on oil in water, in environmental applications. As these constituents are removed during drinking water treatment, the measurement of these parameters in the distribution network is not relevant. Other quality issues will not be detected using these fluorescence sensors, either because the substances do not show fluorescent behaviour or because the wavelengths of the sensor have been selected for another target.

Blind spot in arrays of traditional sensors

Although an array of the described sensors can provide a wide coverage, it will never be sensitive to all possible quality changes. Especially many organic substances will not be detected; if the organic substance does not react with chlorine (no effect on ORP) and does not have an aromatic group (no effect on

fluorescence or UV absorption) it will most likely not be detected. This is especially the case for many smaller organic molecules, e.g. organic solvents, which are widely used in industry, and can contaminate water sources and thus form a threat for drinking water. Also, many pesticides and some highly toxic biotoxins and chemical warfare agents fall in this category.

Refractive Index

Optiqua has developed a generic optical sensor concept, EventLab, that can be deployed online throughout a distribution network, and that meets the four key operational requirements of such a water quality event monitoring system: (i) continuous real-time detection, (ii) generic: one sensor covering the full spectrum of possible chemical contaminants, (iii) high sensitivity, and (iv) low cost and low maintenance (no consumables). EventLab measures minute refractive index changes in water, using the Mach Zehnder Interferometry (MZI) principle. Refractive Index (RI) is a useful generic indicator of water quality as any substance, when dissolved in water, will change the refractive index of the water matrix.

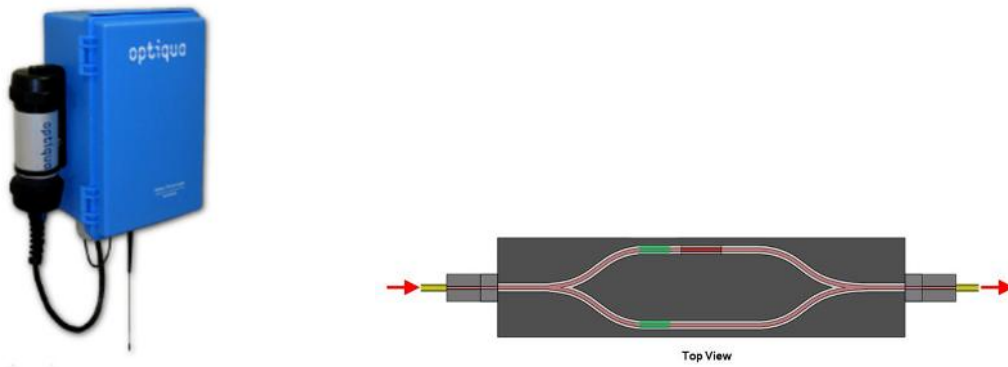


Figure 2: EventLab (left) and a schematic representation of the MZI chip used for the refractive index measurement (right).

Every substance has a specific refractive index. A mix of substances, such as a water matrix, has a combined or bulk refractive index. Any substance that is dissolved in a water matrix will contribute to the combined refractive index of that water matrix. A change in the composition of the matrix will result in a change in the refractive index. It is these changes in refractive index that are being monitored by Optiqua EventLab.

The use of refractive index has a number of advantages for water quality monitoring and the detection of water quality incidents. First of all, refractive index is the only truly generic parameter currently available. Whereas other water quality sensors are sensitive to a (small) part of the spectrum of possible contaminations, a refractive index measurement can detect all chemical changes, irrespective of their nature. Performance of EventLab in detection of various classes of substances and how it compares with traditional sensors has been evaluated by Vitens Water Company (the Netherlands) in a pipe loop system. Table 1 compares the results from the evaluated technologies. Table 2 lists a few examples of substances that, in the distribution network, only refractive index will detect.

Table 1: Response matrix comparing EventLab to other water quality sensors.

Compound Class	Compound	Event-Lab	pH	ORP	EC	DO	UV/Vis ^a	Turb. ^b
Inorganic	Sodium chloride	0	0 ^c	0 ^c	0			
	Sodium nitrate	0	0 ^c	0 ^c	0		0	
	Sodium sulfite	0	0 ^c	0	0	0		
	Cadmium nitrate ^d	0	0 ^c	0 ^c	0			
Organic	MTBE	0						
	Aldicarb ^e	0					0	
	Azinphos-methyl ^e	0					0	
	Acetylsalicylic acid ^f	0	0	0	0		0	
	Urea ^g	0						
	Formazin ^h	0					0	0

a) Absorbance at 254nm.

b) Turbidity.

c) Sensor has an intrinsic cross-sensitivity to ionic strength, and signal change recorded is due to this matrix change and not as the result of a true pH/ORP change.

d) Heavy metal.

e) Pesticide.

f) Pharmaceutical.

g) Wastewater indicator.

h) Turbidity calibration standard (polymeric emulsion).

Table 2: Examples of substances not picked up by traditional arrays of water quality parameters which will be detected by EventLab.

Solvents & Reagents		
Methanol	Ethanol	iso-Propanol
Glycerol	Pentane	Hexane
Cyclo-hexane	Octane	
Acetonitrile	Dimethylsulfoxide	Dimethylformamide
Acetone	Ethylether	MTBE
Trihalomethanes (chloroform etc).	Trichloroetane	dichloromethane
Tetrachloroethane	NDMA	Methylamine
Pesticides		
Omethoate	Malathion	Mevinphos
Tributyl tin	Lindane	Glyphosate
Other		
Arsenic	Phosphate	Glucose
Sarin	Soman	VX

Consistency in Response

Besides the generic coverage, refractive index has other advantages that make it attractive for quality event monitoring in drinking water distribution networks. Results obtained with refractive index are highly consistent across different types of chemicals. With traditional measurements (such as pH, ORP, etc.) the capability to measure, as well as the sensitivity for, various substances depends strongly on their chemical structure. As a result, detection limits can easily vary by more than a factor 10^6 even for substances within the class the sensor is expected to be sensitive for. In contrast, refractive index sensitivity differences are within a factor 50 – 100 between any substances. This consistency allows for an estimation of the order of magnitude of a contamination event, something not possible with the other parameters (except with specific ISE sensors and UV/Vis absorbance and fluorescence based applications tuned for a particular contaminant).

The benefits of using refractive index for water quality monitoring in distribution networks

Furthermore, with refractive index there is no dependence on matrix effects. Whereas especially pH, ORP and fluorescence are affected by matrix changes, refractive index of substances is not affected by the matrix.

The only external influence to RI is the temperature of the medium, but the relationship between RI and temperature is described by a simple formula and is fully accounted for in the compensation mechanism of the EventLab system.

Sensitivity

In terms of absolute sensitivity that can be achieved under operational conditions, there is little difference between the various sensor systems. Although some online sensors are theoretically capable of measuring µg/L concentrations, when sensor resolution and performance in a changeable matrix are taken into account, the lower limit of detection is typically in the low mg/L range. Amongst the current generation of sensors, only highly specialised systems, targeting a particular analyte, achieve better (10 – 100 µg/L) detection limits under favourable operational conditions. The sensitivity achieved with the Optiqua EventLab sensor is in the same order (high ppb – low ppm), but is consistent for all types of substances, whereas other sensors only achieve this type of sensitivity for their specific target substances.

Maintenance

A major issue hampering the effective implementation of many of the traditional sensors is their long term performance. Deteriorating sensor performance due to aging, e.g. slow response time and reduced sensitivity, and the unpredictability of (onset of) the aging, necessitate frequent QA/QC checks, calibration and parts replacement. Intrinsically, optical sensor systems are more stable, especially so when using LEDs or laser diodes as light source combined with photodiode detectors. For purely optical measurements, such as RI, calibration efforts are eliminated, as is the need for consumables. As with all sensor types, preventing build-up of (bio)fouling and scaling on the sensor surface is critical, as this will interfere with the contact of the water with the sensing element. Automatic cleaning systems and/or particle filters are used to prolong intervals between manual cleaning activities.

Table 3: Comparison of the performance characteristics of sensing technologies employed for distribution network monitoring.

Sensor Type	Target Analytes	Linearity ^a	Consistency ^b	Sensitivity ^c	Resistance to matrix interference ^d	Maintenance ^e
pH	Acids & Bases	--	-	low ppm	-	-
ORP	Redox active species	-	--	low ppm	--	--
EC	Salts (TDS)	+	+	low ppm	+	++
DO (LDO)	O ₂	+	++	high ppb	+	++
Turbidity	Particles	-	-	high ppb	+	-
UV254	Aromatic substances	++	-	low ppm	-	++
Fluorescence	Aromatic substances	+	-	high ppb	-	++
ISE	NO ₃ , NH ₄ , Free Chlorine	+	++	high ppb	-	-
<i>Refractive Index (EventLab)</i>	<i>All chemicals</i>	<i>++</i>	<i>++</i>	<i>low ppm</i>	<i>+</i>	<i>++</i>

a) Linearity of sensor response with respect to concentration

b) Consistency in sensitivity for different substances (disregarding substances that the system is not sensitive to)

c) Typical lower detection limit achievable under operational conditions

d) Sensitivity of the measurement to changes in matrix composition

e) Maintenance need, e.g. sensor calibration, cleaning, parts replacement, etc.

Case Studies

Vitens Water Company (the Netherlands) has installed a network of 44 EventLab sensors in the province of Friesland (the Netherlands) to monitor their drinking water from source to tap. With this sensor grid they have detected, localised and traced a number of water quality events.

Early October 2013 Vitens performed regular maintenance at one of their treatment plants which necessitated a temporary halt of water production. Although treatment was only supposed to be offline for several hours, a recurring software issue resulted in repeated stops and restarts of the plant. During these restarts, the softening process was not reactivated. This caused significant fluctuations in the quality of the water distributed, as well as substantially higher levels of calcium. EventLab systems were installed in area supplied by the affected plant. The changes in water quality were clearly visible in the EventLab signals and could be tracked throughout the affected supply zone. In March 2014 Vitens, under controlled conditions, reproduced the event. Again, EventLab responded the water quality variation and traced it through the distribution network. This confirmed that EventLab reliably detects to this nature of event.

During both events, other sensors installed at the treatment plant, including pH, conductivity and turbidity sensors, did not detect the changes in water quality (Figure 3).

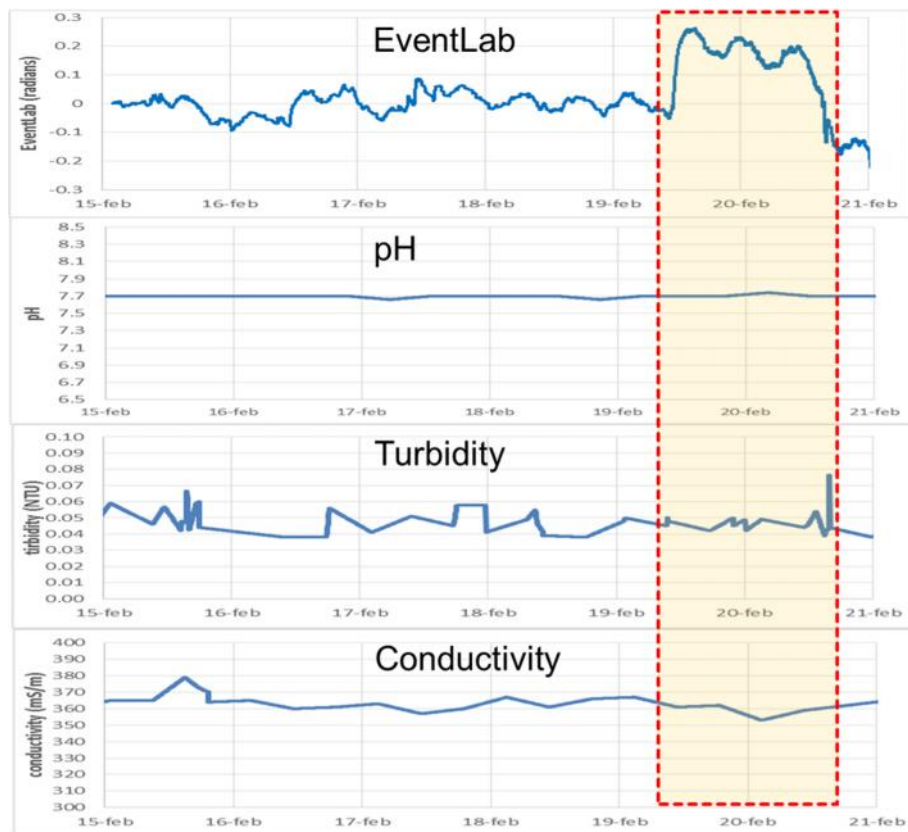


Figure 3: Only EventLab detects WQ event (duration of operational issues indicated in red).

Other installations of the Optiqua EventLab refractive index sensors alongside multi parameter arrays have also confirmed its complementary nature; using EventLab it has been possible to monitor baseline water quality variations, such as recurring diurnal patterns and short terms fluctuations that were not registered by other online water quality sensors. Furthermore, deployed EventLab systems have been able to detect water quality incidents invisible to multi-parameter probes installed in parallel. At the same time, any water quality incident detected by multi-parameter probes installed next to EventLab systems was detected by EventLab as well (for an example see figure 4).

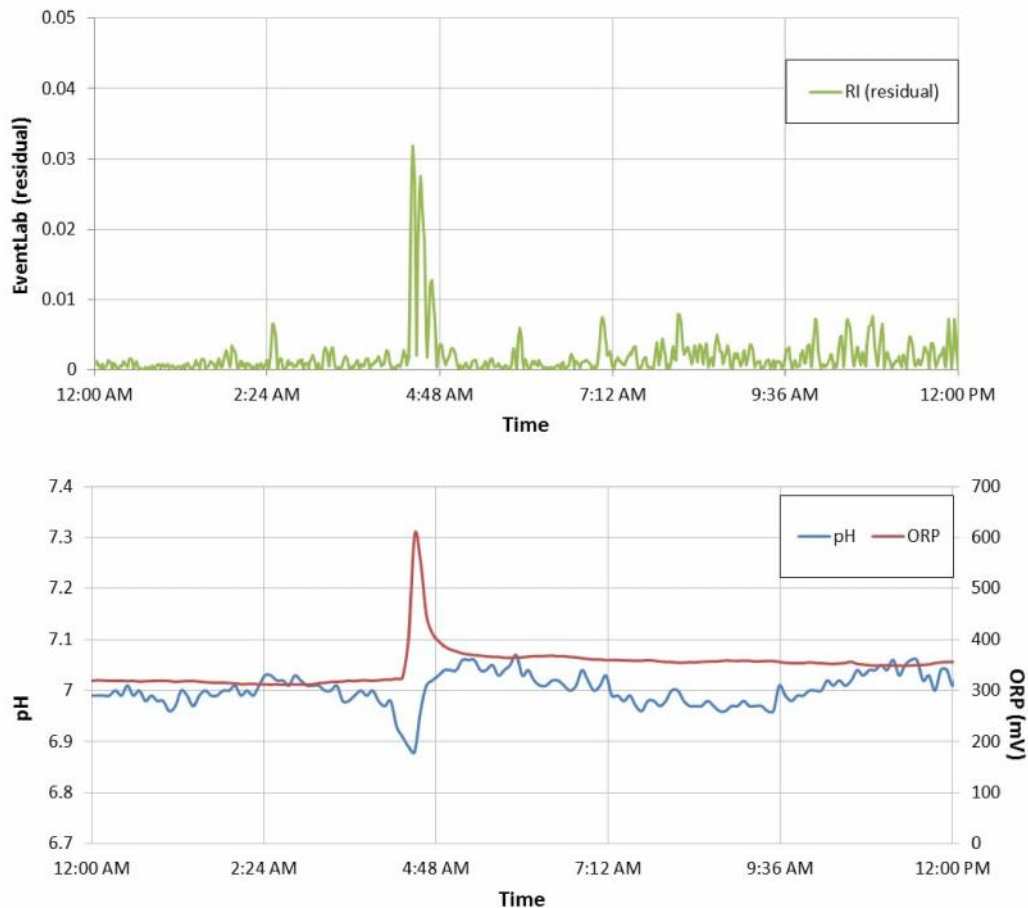


Figure 4: EventLab response matches pH and ORP in detection of water quality variation.

As expected on the basis of the differences in measurement principles EventLab picks up water quality variations that remain invisible to traditional water quality sensors. Being a generic sensing concept, measuring a physical quantity which each substance possesses, refractive index will detect all chemicals with consistent sensitivity. In doing so it is independent of the matrix in which the measurements are performed. EventLab thus closes the gaps in the coverage of traditional sensors, in particular their weakest area: small organic molecules. Water quality changes that have remained invisible in the past, because sensors were incapable of detecting the substances concerned, or because their signal was overshadowed by baseline noise or matrix effect, are now becoming visible. These results obtained under operational conditions in distribution network applications validate the true added value of refractive index measurements.

In Conclusion

Online monitoring of water quality with sensors is an increasingly important activity of water utilities. A suite of well-established sensors is available for this purpose. Despite the variety of technologies on the market, their measurement principles as well as operational aspects means that it is still impossible to monitor all

The benefits of using refractive index for water quality monitoring in distribution networks

possible variations in the chemical water quality in drinking water, especially in the distribution network. Traditional sensors are virtually blind to non-aromatic organics, including most small organic molecules. And although theoretically capable of detecting most other analytes, intrinsic properties of the technologies used mean that matrix interference, inconsistent sensitivities, as well as sensor maintenance issues, in many cases prevent effective detection. The use of highly sensitive refractive index measurements offers a solution to this monitoring challenge: it combines full coverage of chemical drinking water constituents (including all organic molecules) with a robust and easy to maintain sensor platform. Optiqua's EventLab system, which is based on refractive index measurement, is reliable and easy to operate and maintain, requires no calibration and uses no consumables.

EventLab can be used as a stand-alone water quality monitoring solution, providing consistent coverage to detect any water quality variation due to dissolved substances. For this purpose, EventLab is equipped with advanced software algorithms which analyse the baseline data and automatically pick-up and flag abnormalities. Alternatively, EventLab can be used as the basis for a multi-sensor monitoring strategy. The combination with other sensors can expand the range of events that can be detected, e.g. to include particles with a turbidity sensor, or can allow global classification of the detected quality change, e.g. into organic or inorganic by the combination with a conductivity sensor. Irrespective of its use as a stand-alone system or as part of a larger monitoring set-up, EventLab provides a unique monitoring capability in being the first system to be truly capable of monitoring all changes in chemical water quality in the distribution network online and in real-time.

Dr. Joep van den Broeke is senior project manager at Optiqua Technologies. Dr. van den Broeke is a water quality and sensing expert and has gathered extensive experience in water quality and sensor related R&D and operations working at research institutes, sensor developing companies as well as working as an independent consultant.

For more information, please contact Optiqua Technologies at info@optiqua.com, or visit www.optiqua.com.