

Water Sensor Technology Applications

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Introduction and Background

The quality of our surface waters is paramount to the health of aquatic ecosystems, the health of the human population, and the cost-effective operation of industries. A supply of fresh water is also essential for the majority of power generation facilities, which relies on a supply of water primarily for cooling operations. In order to insure the sustainability of our freshwater resources we need to 1) identify the quality and quantity of our existing resources, and 2) monitor the state of these resources in order to detect change and implement timely mitigation strategies in the event that the quantity and/or quality of the existing water supply begins to change.

This brief is intended to provide a description of the state-of-the-art technologies that are currently employed to monitor the quantity and quality of our fresh water resources. Since measurement of water quality is only limited by the vast number of chemical constituents that are commonly dissolved or suspended in fresh water, this brief is limited to a review of the technologies used to monitor the most common water quality parameters. These parameters include temperature, conductivity, pH, turbidity, nutrients (nitrate, ammonia, phosphate) and dissolved oxygen. This parameter set was selected because, when measured concurrently, their relative magnitudes provide a good general assessment of the quality of water. A brief description of each parameter and its importance is provided in the following section.

Water Chemistry Parameters

Discharge

The measurement of stream discharge is a critical component of aquatic system monitoring. When discharge is measured concurrently with water quality information, the mass flux of each chemical constituent can be calculated. This may be especially important if there is a lake or estuary downstream of the sampling location, as it enables estimates of loading to the downstream waterbody to be calculated.

Temperature

Temperature exerts a major influence on virtually every aspect of aquatic ecosystems. Temperature affects biological activity and the rate of growth of biological organisms. The natural temperature regime of a waterbody dictates what biological species will live there. Temperature also influences the chemistry of water. Chemical reaction rates, the leaching of organic compounds from soil (1), and the mineralization of nitrogen (2) in soils are all positively correlated with temperature, while

cooler water can contain higher concentrations of gas such as dissolved oxygen. Temperature can also influence the toxicity of chemical compounds; unionized ammonia (NH_3) is toxic to aquatic fauna and more of the ammonium ion (NH_4^+) is converted to toxic ammonia as the temperature of water increases.

Conductivity

Conductivity is a measurement of the electrical conductance of a water sample, and is directly related to the concentration of ions that are dissolved in a water sample. Collecting data on conductivity can be used to determine total dissolved concentration of solutions, detect the presence of contaminants, and determine the purity of water.

pH

pH is a measure of the concentration of free hydrogen and hydroxyl ions in water. Water that has more free hydrogen is more acidic, whereas water with more hydroxyl ions is more basic. pH is an important water quality parameter to measure because it affects the solubility (the amount that can be dissolved in water) of chemical constituents in water. pH also influences the bioavailability (the ability of an organism to utilize a chemical compound for growth) and toxicity of nutrients and some heavy metals. For certain parameters (e.g., unionized ammonia, aluminum), solubility determines the toxicity to biological organisms, with higher toxicity occurring at lower pH.

Turbidity

Turbidity is the measure of relative clarity of a liquid. It is an optical characteristic of water and is an expression of the amount of light that is scattered by material in the water when a light is shined through the water sample. Turbidity is often measured as part of a water quality sampling plan because turbidity influences light penetration, which in turn affects biological productivity. Turbidity also affects biological habitat quality, and recreational value of the waterbody. The turbidity of a water body is influenced by upstream watershed alteration (increased runoff and erosion) and natural factors including the erodibility of the soil. Therefore, high turbidity is often, but not always related to upstream disturbance.

Nutrients

The measurement of nutrient concentrations is typically a core component of aquatic ecosystem monitoring. Nitrogen and phosphorus are nutrients that are natural and essential parts of fresh and saltwater systems. The forms of nitrogen and phosphorus that are of primary concern in aquatic environments include ammonia-nitrogen, nitrate-nitrogen, and orthophosphate. These forms are bioavailable, meaning that they can be readily used by aquatic organisms for growth. They support the growth of all photosynthetic organisms, which serve as the base of the aquatic food chain, and provide habitat for many of the organisms that live in water.

When too much nitrogen and phosphorus enter surface waters, the nutrients cause photosynthetic organisms to grow faster than the ecosystem can handle. This imbalance is referred to as eutrophication, one of America's most widespread, costly, and challenging environmental problems (3). Eutrophication, even at relatively low levels, can lead to degraded water quality, aquatic habitat, and fluctuations in dissolved oxygen. In extreme cases, eutrophication can lead to algae blooms which can deplete dissolved oxygen concentrations below the level required for fish and other organisms to live, leading to large-scale mortality of these species. Algae blooms can also harm humans because they can produce elevated levels of toxins and bacteria that can make people sick if they come in contact with the water or ingest fish or shellfish harvested from the impacted water body.

While eutrophication can occur naturally (4), it is most commonly caused by anthropogenic addition of limiting nutrients in the upstream watershed (5). Anthropogenic sources of nutrients in aquatic ecosystems include municipal and industrial point source discharges, and non-point source runoff from agricultural operations and residential fertilizer application. In certain locations, deposition from the atmosphere can be a significant source.

Dissolved Oxygen

Dissolved oxygen is the mass of oxygen (O_2) that is dissolved in a volume of water. Dissolved oxygen is breathed by fish and zooplankton and is needed by them to survive. While the interrelationships between waterbody morphology, temperature, dissolved oxygen, the other constituents dissolved in the water, and biological components of the aquatic ecosystem are complicated, dissolved oxygen concentration tends to decrease with increasing pollution and upstream watershed alteration (6). As dissolved oxygen concentrations decrease the aquatic biological community will become increasingly stressed and eventually die off.

Water Sensor Types

The type of sensors that are currently being used to measure each of the water quality parameters outlined in the previous section are described herein. This list is not intended to be comprehensive. It is a list of the state-of-the-art technologies that are currently being used to analyze the concentration of the selected water quality constituents. These sensors were identified as representative of the state-of-the-art by reviewing both the current scientific literature and the literature that is available from the companies that manufacture and sell water quality analysis instrumentation.

It is important to recognize that the total cost associated with the implementation of a water quality sampling plan is likely to significantly exceed to cost of sampling equipment alone. The cost of the instruments can be a minor expense when compared with the cost of site preparation, sensor maintenance, data QA/QC, and other factors. These costs can be estimated by considering that the U.S. Geological Survey (USGS), which maintains the most extensive water quality monitoring network in the United States, charges \$20,000–\$40,000/year to operate a continuous water quality monitor for their core parameter suite (temperature, pH, DO, conductivity), and the expense increases substantially with each additional parameter (personal communication, Dr. Caleb Tzilkowski, Aquatic Biologist, National Park Service, August 7, 2017).

Discharge Measurement

There are several different approaches that can be considered for discharge measurement. These approaches include acoustic doppler velocity measurement, and cup or propeller-style mechanical devices. The bucket and propeller style devices operate by using the force of flowing water to turn either a wheel of four to six metal cups that revolve around a vertical axis or a propeller mounted on a horizontal axis. The number of times that the wheel or propeller rotates in a given amount of time is related to the current velocity. Acoustic doppler current profilers (ADCPs) operate by sending a sound pulse into the water and measuring the change in frequency of that sound pulse as it is reflected back to the instrument by sediment, detritus and other suspended particles in the flowing water. The change in frequency, or doppler shift, is used to calculate the velocity of the flow. The time it takes for the sound pulse to reach the bottom of the water column and return to the sensor is also recorded and used to calculate water depth. The depth and velocity information are used to calculate the stream discharge.

While cup, propeller, and ADCP approaches are all considered to be acceptable methods of discharge measurement, the ADCP represents the state-of-the-art and has several advantages over the traditional methods. The ADCP has significantly reduced the amount of time it takes to make discharge measurements because the instrument automatically measures depth and velocity at a great number of points throughout the water column and integrates this information into a discharge measurement. This instrument can also measure discharge in certain flood conditions that were previously to dangerous or difficult to make using traditional measurement techniques. Lastly, the ADCP provides far greater resolution of measurements than can be made with a mechanical meter, leading to a more accurate calculation of discharge.

Continuous monitoring of stream discharge requires the development of a relationship between stream discharge and water surface elevation. The relationship between stream stage and stream discharge is called a rating curve. Once sufficient data have been collected (using either mechanical devices or an ADCP), stream stage is measured on a regular interval (e.g., every 15 minutes) and converted to stream discharge using the rating curve. Continuous stream stage data are typically collected using a stilling well or via pressure measurement (7).

Thermistors

A thermistor is the most common type of sensor employed for temperature measurement. Thermistors have an electrical resistance that is proportional to temperature. This property is common to all conductors, but in the case of thermistors, the property has been exploited so that they are more sensitive to temperature than other types of conductors. When the thermistor is placed in a water sample and an electrical current is applied, the resistance can be measured and used to calculate the temperature of the sample. The measured resistance is dependent upon the construction of the thermistor and therefore the formula that is used to calculate temperature varies by construction. The basic mathematical model for thermistors is the Steinhart-Hart equation:

$$1/T = A + B \ln R + C[\ln R]^3$$

Where, T = temperature in degrees Kelvin; A, B, and C are coefficients related to the thermistor; and R is the electrical resistance at temperature T in Ohms.

Paired Electrodes

Paired electrodes are used to measure the electrical conductivity of a water sample. To measure conductivity, a pair of electrodes is placed in a sample and an electrical potential is applied between them. The resulting electric current is measured and converted to conductivity according to Ohms law:

$$I = V/R$$

Where, I = conductivity in amperes (measured as current in the receiving electrode), V = voltage across the sample in volts, and R = resistance in Ohms. Since the charge on ions in solution facilitates the conductance of electrical current (i.e., reduces resistance), the conductivity of a solution is proportional to its ion concentration.

Ion Sensitive Electrodes (ISE)

Ion sensitive electrodes (ISEs) are electrochemical sensors that measure the concentration of chemical constituents over the range that typically occurs in aquatic environments (mg/L for most, ug/L for some). The sensors can be used to make individual measurements or can be deployed for continuous measurement. ISE analysis is a potentiometric procedure, meaning that the measured signal

occurs as a difference in electric potential between the ISE and a reference electrode. The difference in electrical potentials that develops is the result of the difference in the ion concentration between the measurement and reference electrode, and is converted to a concentration according to the Nernst Equation:

$$U_{ion} = U_{ion}^0 \pm S \cdot \log(\beta_{ion})$$

Where, U_{ion} is the electrical potential measured by the sensor, U_{ion}^0 a fixed, ion-dependent value dependent upon the measuring system, S = slope defining how much the electrical signal changes with a change in ion concentration, and β_{ion} = concentration of the ion of interest in mg/L.

Figure 1 illustrates the general ISE design. The materials used to build an ISE are dependent upon the ion to be measured, and the intended use of the instrument (laboratory, industrial application, field use, etc.). The function of each component of the ISE is briefly described below, with the numbers corresponding to the labels in Figure 1.

1. The **electrode body** is designed to house the instrumentation, and can be constructed out of plastic, metal or glass. Glass is required for high heat applications, while metal and plastic bodies are used for field applications because of their greater durability.
2. The **internal electrode** is the ion sensitive electrode. The electrical potential at the membrane-sample interface is measured by the internal electrode. The difference in electrical potential between the internal electrode and the reference electrode is measured as a voltage and is used to calculate the concentration of the ion in the sample.
3. The **inner buffer solution** provides the connection between the membrane and the internal electrode.
4. The **membrane** is the location where the electric potential is formed, and its construction dictates the electrode's sensitivity for a particular ionic species. Membranes can be constructed of glass, salts, or synthetic materials.
5. The **reference electrode** is designed to maintain a constant electrical potential that is independent of the sample composition and temperature. The reference is compared to the electric potential of the internal electrode, which is dependent upon the ion concentration in the sample. The ion concentration is calculated based on the difference in electrical potential between the internal and reference electrodes (voltage).
6. The **reference electrolyte solution** is connected to the sample via the reference junction, and serves to close the electrical circuit in the ISE. The reference electrolyte must be chemically neutral, have good electrical conductivity, and must not react with the ions in the sample that are to be measured. Ions in the electrolyte solution must diffuse at equivalent rates so that a diffusion potential does not form.
7. The **reference junction**, also known as a diaphragm, creates electrical contact between the reference system and the solution. Junction materials are selected to allow a slight but consistent flow of the reference electrolyte solution out of the electrode to minimize diffusion voltages across the membrane. The membrane should also be as electrically conductive as possible, and must be chemically inert so that it doesn't react with either the reference electrolyte solution or the sample. Plastic fibers, platinum, and ceramics can be used for the reference junction.

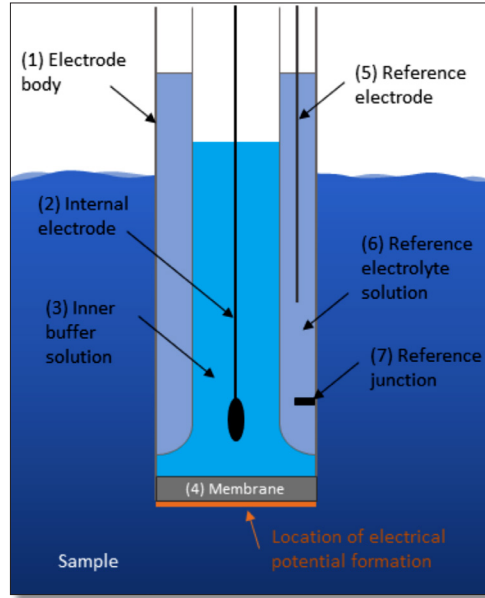


Figure 1. Ion Sensitive Electrode (ISE) diagram

ISEs have been developed for a number of different chemical parameters relevant to freshwater systems. These parameters include pH, ammonium/ammonia, and nitrate.

Optical Sensors

The development of optical sensors for measurement of chemical concentrations in fresh water is one of the most promising recent advances in water quality monitoring. Optical sensors rely on the light scattering, absorbance, or reflectance properties of chemical compounds that are either dissolved or suspended in a water sample. Each of these properties are defined in Table 1. The three configurations of optical sensors that are most commonly used for water quality analysis are illustrated in Figure 2.

Table 1. Properties of light

Property	Definition
Scatter	A change in direction of light due to a collision with a particle or wave in which an interaction occurs (the wavelength of the light changes).
Reflectance	A change in direction of light due to a non-interacting collision (the wavelength of the light remains constant).
Absorbance	Light hits a particle and does not scatter or reflect. The energy associated with the light is absorbed by the particle.

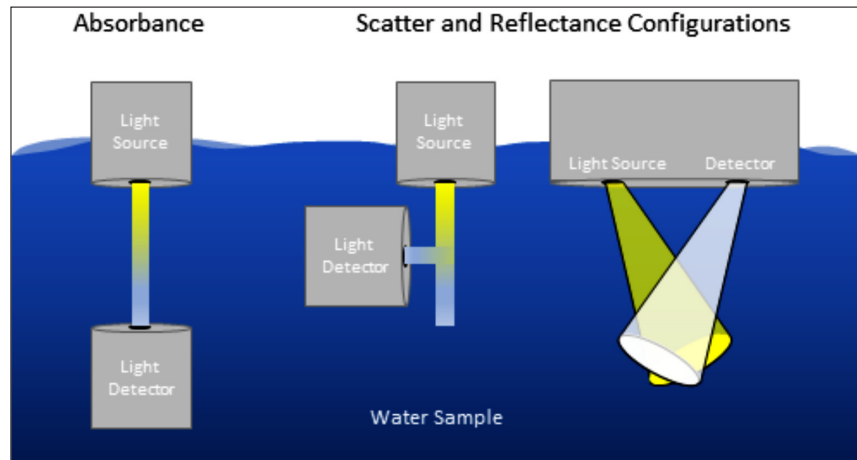


Figure 2. Optical sensor diagrams

The specific configuration of an optical sensor is dependent upon whether scattering, absorbance, or reflectance is being measured. If absorbance is the desired property, the photometer will be constructed in a fashion similar to the absorbance diagram in Figure 2. If scattering or reflectance is the property to be measured, the light detector mechanism will be positioned at an angle to the light source.

Optical sensors are used to measure a number of water quality parameters including ammonia, nitrate, phosphate, dissolved oxygen and turbidity. For the nutrient suite, optical sensors can be employed to measure the products that result from reactions that are facilitated by Wet Chemical Sensors. The current wet chemical sensors utilize colorimetric and fluorimetric sensors to measure the concentration of reaction products, then convert these readings back to nutrient concentrations. The general design of photometers designed to analyze dissolved oxygen and turbidity data are discussed below.

There are two different types of photometers that can be used to measure dissolved oxygen concentration in aqueous solution. Both measure luminescence (the emission of light by a substance not resulting from heat) as it is affected by the presence of oxygen; however, one type of sensor measures the lifetime of the luminescence while the other type measures the intensity of the luminescence. While products that utilize each of these methods are currently available, the lifetime measurement approach is generally preferred because the lifetime sensor is more stable over the long term, requiring less maintenance and calibration. Optical DO sensors operate on the principle that dissolved oxygen quenches both the lifetime and intensity of the luminescence of specific chemical dyes. An optical dissolved oxygen probe measures dissolved oxygen by emitting a blue light of the proper wavelength. The blue light hits a layer with a special dye coating which luminesces (glows red). The lifetime of the luminescence, measured by the probe, is inversely proportional to the dissolved oxygen concentration. The relationship is represented using the Stern-Volmer relationship:

$$I_0/I = 1 + k_q t_0 * O_2$$

Where, I_0 = luminescence in the absence of D.O.; I = luminescence in the presence of D.O.; k_q = quenching rate coefficient; t_0 = luminescence lifetime of the chemical dye; and O_2 is the concentration of dissolved oxygen in the sample.

Turbidity is measured using a type of photometer called a nephelometer, that is constructed to measure the degree of light scatter caused by particles suspended in a water sample. Turbidity is measured by placing a UV light detector at a 90-degree angle to the light source. Suspended particles in the water sample will cause the emitted light to reflect. The intensity of reflected light that is received by the detector is directly proportional to the concentration of suspended particles in the water sample.

Wet Chemical Sensors

The term “wet chemical sensor” is somewhat of a misnomer. Wet chemical sensors are essentially mobile wet chemistry laboratories that can conduct all steps of laboratory water quality analysis automatically. These “sensors” are automated mechanical devices that can calibrate the on-board measurement equipment, take water samples, analyze the sample for concentrations of a selected suite of chemical components, record the results, rinse the equipment, and repeat the process on a recurring time interval. This process is facilitated using a very small sample (1.5 mL) volume and even smaller quantities of reagents so that the device can be deployed in the field for up to several months at a time without the need to refill the calibration, reagent, or washing supplies. They can be deployed to sample at the water surface or at depth (generally less than 10 meters depth).

Wet chemical sensors operate by collecting a water sample, sequentially injecting and mixing the required reagents to perform the specific analytical reaction, then measuring the concentration of reaction product using an array of on-board optical sensors. The type of optical sensor used is dependent upon the reaction product to be measured. A combination of different optical sensor types (Absorbance, fluorimetry, UV reflectance, UV scatter, nephelometry) is commonly included in multi-parameter wet chemistry sensors. Each of these sensor types is discussed in the Optical Sensors section of this report.

Conclusion

Table 2 summarizes the best option(s) available for the analysis of each hydraulic and water quality parameter discussed in this brief. Wet chemical sensors are capable of analyzing all of the selected water quality parameters, since they are essentially floating water chemistry labs and can be outfitted with any combination of sensor types. For the majority of the water quality parameters, one technology in addition to the wet chemical sensor is recommended as the state-of-the-art. Nutrients are the exception to this rule – nitrate and ammonia can be measured using wet chemistry techniques, optical photometry, or an ion selective electrode. Therefore, the decision as to which sensor type to use to measure nutrient concentrations is often dependent upon other considerations including cost, maintenance, accuracy of measurement, the intended length of sensor deployment, etc. Table 3 summarizes the published measurement ranges for each of the water quality parameters. The ranges provided are a summary of information obtained from equipment manufacturer websites and are provided to illustrate general sensor capabilities. The specifications vary between manufacturers, so these numbers should not be considered absolute. The accuracy of each type of electrode varies by the chemical constituent and manufacturer. This information is not provided in the table, but manufacturers are reporting that the accuracy of the measurement is typically within +/- 1% under ideal conditions. Therefore, the accuracy of field measurements is likely to be affected more by the correct application and maintenance of the equipment than by limitations of the equipment itself.

The general advantages and disadvantages of each sensor type are well summarized by Pellerin et al. (8), who synthesized information on the different sensors available for extended deployment, nutrient concentration measurement. The results of their analysis are provided in Table 4.

Table 2. Options for measurement of the selected hydraulic and water quality parameters

Parameter	Options for Analysis				
Hydraulics	Acoustic Doppler	Mechanical			
Velocity	✓	✓			
Depth	✓	✓			
Water Quality	Optical Photometry	Wet Chemical Sensors	Ion-Sensitive Electrodes	Thermistor	Paired electrodes
Temperature		✓		✓	
Conductivity		✓			✓
pH		✓	✓		
Turbidity	✓	✓			
Nutrients					
Nitrate	✓	✓	✓		
Ammonia	✓	✓	✓		
Phosphate		✓			
Dissolved Oxygen	✓	✓			

Table 3. Measurement range of the different sensor types

Parameter			
Hydraulics	Acoustic Doppler	Mechanical	
Velocity	0 – 10 m/sec	Limited by practical application	
Depth	0 – 200 m		
Water Quality	Optical Photometry	Wet Chemical Sensors	Ion-Sensitive Electrodes
pH			0 - 14
Turbidity	10 – 500 NTU	0 – 500 NTU	
Nutrients			
Nitrate	0 – 20 mg/L ¹	0 – 10 mg/L	0.4 – 62,000 mg/L
Ammonia	0 – 1 mg/L ¹	0 – 500 ppb	0.02 – 17,000 mg/L
Phosphate		0 – 1000 ppb	
Dissolved Oxygen	0.05 – 20 mg/L		

¹ Available as handheld, stand-alone instruments from certain manufacturers. The sensors are different from, and have different specifications from wet chemical sensors which also measure using the optical properties of reaction products.

Table 4. Advantages and disadvantages of optical sensors, wet-chemical sensors, and ion-selective electrodes

Type	Operating Principle	Advantages	Disadvantages
Optical Sensors	Spectral absorption by a photometer	• High resolution, accuracy, and precision • Chemical-free • Fast response time • Additional optical information in spectra	• Expensive (>\$15,000) • High power requirement and maintenance costs • Not available for all nutrients (only nitrate and ammonia currently)
Wet-chemical sensors	Wet chemical colorimetric reaction with detection by photometry	• High resolution, accuracy, and precision • Potential for in situ calibrations • Relatively fast response time • Available for ammonium, nitrate, and phosphate	• Expensive (>\$10,000) • High power requirement and maintenance costs • High potential for fouling • Requires reagents (generates waste)
Ion-selective electrodes (ISE)	Direct potentiometry between a sensing electrode and a reference electrode	• Inexpensive (<\$1,000) and easy to use • Fast response time • Not influenced by color or turbidity • Available for ammonium and nitrate	• Low resolution, accuracy, and precision • Subject to ionic interferences • High instrument drift • Limited shelf life

Lastly, it is important to remember that other options do exist for most parameters (e.g., secchi disk for turbidity measurement, pH test strips for pH measurement, etc.). While these options are not considered to be state-of-the-art, they are proven methods that have been used to measure the concentration of these constituents in surface waters. These alternative methods are generally less expensive, but have a number of potential drawbacks including decreased accuracy, decreased precision, and increased maintenance.

Value Statement

For utilities, sensors are important for a variety of reasons. These include ecological protection, since water quality changes can affect the riparian and freshwater habitats. Similarly, sensors can detect elements which affect human health. In terms of utility service area stakeholders, sensors can detect changes which may affect agricultural operations. For example, sensors can detect salinity in the San Joaquin River Watershed which could affect crops. Regulatory compliance is an important area where sensors play a role, as well as intake for industrial applications.

This issue brief focuses on state of the art sensors. There has been a recent proliferation of low-cost sensors which are often connected to or compatible with mobile/cell applications. An upcoming issue brief on low-cost water sensors is planned for the near future, which along with this current brief, may give utilities an introduction to the range of sensors available for monitoring water resources.

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