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Smart Sensors for Monitoring pH, Dissolved Oxygen, Electrical Conductivity, and Temperature in Water

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1.1 Introduction

All life on planet Earth is supported by water and it has not been found in liquid form anywhere else in the universe. However, this precious resource suffers from issues such as pollution. To solve these problems and to avoid them in the future, it is critical to continuously monitor the quality of water. Water quality monitoring is defined as the collection of data at regular intervals from set locations across and along the water body to establish accurate values of various parameters such that trends, variations, and conditions can be observed. Water can be contaminated by pollutants due to human activities, especially industrial and agricultural practices [1]. Polluted water is unfit for use and poses a threat to the health of humans and other organisms including plants and animals that depend on water for the sustenance of life. Use of harmful chemical and the disposal of untreated waste into the environment pollute the groundwater as well as the surface water. A few examples of such activities are mining of materials, manufacturing of products, addition of chemical fertilizers to the soil, production of energy, improper treatment and disposal of sewage, and transportation via waterways.

The traditional laboratory-based methods of water quality testing are time-consuming and expensive with low value for money because they require specific infrastructure and equipment, skilled personnel, sample collection, transportation, and storage. When water samples are collected from the site and transported to the laboratory, the final result of the quality test may be biased because different

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errors are introduced during collection and transportation, such as contamination and changes in data [2]. Additionally, some oxidation–reduction processes and parameters such as temperature must be measured on-site. Laboratory-based testing also does not provide real-time data. This is dangerous because the faster we know about a problem in the water, the faster we can act on it. Real-time water quality data is the paramount requirement for early warning systems (EWS) and contamination warning systems (CWS) which help to immediately notify the responsible authorities of undesirable changes in the water. Sensors are crucial in this process because for engineers and operators handling such systems, accurate sensors aid in tracking changes in water quality, predicting the generation of regulated compounds, and ensuring their elimination after a treatment or remediation process. Online water quality monitoring is designed for faster data collection and communication using smart sensor systems that eliminate the need for sample collection and transportation using wireless communication and Internet of Things (IoT). Consequently, this reduces the overall time, expense, space, workforce, and energy required for water quality monitoring.

1.2 Water Quality Parameters and Their Importance

Water quality testing indicates the health of water and informs us whether it is fit or unfit for a particular application such as drinking, agriculture, recreation, or disposal to open waters and thereby acts as the guiding factor in decisions related to national and international environmental regulations for water quality. Additionally, the variation in a particular parameter may indicate the presence or absence of a threat such as a microbial community or ecosystem warming. Therefore, real-time water quality monitoring simultaneously acts as an early warning system and thus the importance of low cost, miniaturized, and effective wireless sensors is well acknowledged by researchers, industries, and environmental authorities worldwide.

Compared to microbial parameters, physicochemical parameters such as electrical conductivity, temperature, pH, and chlorine are cheaper, simpler to detect, and have the ability to be measured using online instrumentation [3]. Moreover, variation in a parameter can also act as an indicator of changes in another parameter.

1.2.1 Impact of pH on Water Quality

There have been many studies showing evidence of the impact of pH on water quality and consequently aquatic life [4–6]. Marine ecological systems are so fragile yet complex that changes in one water quality parameter can lead to a domino

effect causing changes in the hydrologic system and put an entire species at risk, eventually affecting other species including humans, their health, and livelihood. For example, Bradley and Sprague [6] found that zinc toxicity to rainbow trout (*Salmo gairdneri*) was directly related to pH and water hardness levels. Zinc toxicity rose by factors of two to five when pH changed from 5.5 to 7.0 and at pH 9.0 it was 10 times more toxic. However, at higher pH, zinc precipitated and has much lesser lethality to fish. Another study by Schubaur-Berigan et al. [4] observed that total ammonia was more toxic at higher pH to a species of nonbiting midge larvae (*Chironomus tentans*) and blackwork (*Lumbriculus variegatus*). At high pH, more unionized ammonia prevails which is important for determination of toxicity of ammonia to the two species.

1.2.2 Impact of Dissolved Oxygen on Water Quality

Dissolved oxygen (DO) is a very crucial parameter while monitoring water quality, especially to ensure the well-being of aquatic creatures [7]. In wastewater treatment, if DO level is too low, the important bacteria that decompose the solids will die whereas if DO content is too high, aeration consumes much more energy. In aquaculture, DO acts as the lifeline of fish and if it is too low, the fish will suffocate and perish.

1.2.3 Impact of Electrical Conductivity on Water Quality

In water quality monitoring, electrical conductivity is nonselective and does not consider the individual concentrations of various ions but instead their collective concentration. Regardless of that, changes in conductivity act as a warning signal of contamination and environmental changes. High levels of electrical conductivity can be due to industrial or urban runoff, low-flow conditions, or long periods of dry weather whereas low levels might occur due to organic compounds such as oils [8]. The measurement of electrical conductivity of water is therefore a good method to investigate the dissolved substances, chemicals, and minerals in it.

1.2.4 Impact of Temperature on Water Quality

Temperature has garnered more attention from researchers than any other environmental variable for aquatic organisms, possibly because of the simplicity in measuring it for both field and laboratory experiments [9]. Temperature alone may be lethal. Most aquatic organisms are ectothermic which means that they have a body temperature that is similar to their environment. The worrisome phenomenon of coral bleaching has very often been attributed to elevated temperatures [10]. A study by Gock et al. in 2003 highlighted that temperature with respect

to water activity strongly impacted the germination of xerophilic fungi, which is responsible for spoilage of bakery and very important in food quality testing [11].

Therefore, in order to safeguard delicate natural ecosystems, it is vital for environmental authorities to have continuous real-time data of water quality parameters on a high spatial resolution at various depths. For example, rapid detection of hydrologic variability is crucial for EWS and subsequent swift response [12].

1.3 Water Quality Sensors

A sensor is a machine or a device that detects a change or an event in its environment and sends a signal to another electronic device to display the message. It is usually used in combination with another electronic device that translates its signal into a readable output. A sensor may be quantitative or qualitative. Quantitative sensors give numerical output in respective units whereas qualitative sensors suggest the descriptive value or a specific feature of a sample. A sensor may furthermore measure chemical, physical, or biological properties of water and examples of their quantitative counterparts are pH, temperature, and bacterial density, respectively. On the other hand, odor and taste are qualitative physical properties of water.

The progress in online environmental monitoring goes hand in hand with the technological development of solid-state sensors. With the possibility of miniaturization and controlled by a signal processing unit, they have no moving parts and require a single parameter measurement such as impedance, current, or voltage alongside a linear calculation of the signal. Such features additionally allow for increased portability of sensors, on-site testing, remote sensing, applicability on flexible substrates, and integration of multiple sensors within a single platform. The interest in thin and thick film solid-state sensors over traditionally used water quality sensors also arises from the development of new materials such as metal oxides (RuO_2, IrO_2, TiO_2, etc.) and the variety of technologies that can be used to manufacture them, such as printing (screen, ink-jet, 3D, etc.) and sputter deposition (magnetron, radio frequency, reactive, etc.). Additionally, they have a longer shelf life as they are less prone to breakability and can tolerate extreme environmental conditions.

In a water quality monitoring setup, it is advisable not to interfere with the environment in which the parameter needs to be tested. Therefore, it significantly depends on the sensor to work well with its environment and deliver an accurate reading. This is why the most important component of the solid-state sensor which decides the fate of its performance is the material used to fabricate it and the design that is most well aligned with the principle in operation. The relationship between the material and the electrolyte is defined by the electrochemistry

that takes place upon their contact. When there is a change in the morphological and structural properties of the sensing electrode of the sensor, there is a significant impact on key sensor characteristics such as response time, sensitivity, and selectivity [13]. Therefore, manipulation of sensor material and design is a popular strategy among researchers to improve the quality of solid-state sensors.

Described here are the principles, designs, and materials used for making sensors that detect four different types of water quality parameters: pH, DO, temperature, and conductivity.

1.3.1 pH

Introduced as the hydrogen ion exponent with notation pH [8], the Danish chemist S. P. L. Sørensen was the first to present the concept of pH as a measure of acidity and alkalinity in 1909 at Carlsberg Laboratories in Copenhagen [14]. In 1922, W.S. Hughes invented the famous pH glass electrode, recorded as the first chemical sensor [12]. According to the International Union of Pure and Applied Chemistry (IUPAC), the base-10 logarithm of the inverse, of the hydrogen ion activity in a solution is defined as the pH of that solution [15]. The equation to represent this relation is:

$$\mathrm{pH} = -\log[\mathrm{H}^+]$$

Instead of hydrogen ion concentration, it is more advantageous to define pH with respect to hydrogen ion activity because ionic activity can be measured directly using potentiometry [10].

1.3.1.1 pH Sensors: Principles, Materials, and Designs

pH measurement can be classified in various groups such as optical sensing, acoustic, electrochemical, and nuclear magnetic resonance (NMR) method. Most common among these groups are electrochemical methods and they are the most developed class of sensors fabricated to detect pH due to their faster response, simplicity, and low cost. pH sensors may depend on one of the principles of potentiometric, chemiresistive, chemi-transistor, conductimetric, ion-sensitive field effect transistor (ISFET), extended gate field effect transistor (EGFET), etc., and the primary materials to fabricate them are glass, metal oxides, mixed metal oxides, polymers, and carbon [16].

1.3.1.2 Glass Electrode

The typical glass electrode has established itself as a comfortable favorite over the past few decades not just as a laboratory pH measurement device but also a household tool for measuring pH in aquarium ponds, culinary arts, soil for gardening, etc. The glass electrode relies on the principle of an electrochemical cell.

The materials comprising a glass electrode are usually an external body and sensing bulb made from specific glass, an internal electrode (calomel or silver chloride electrode), and an internal solution which is usually a buffer solution of pH 7. However, the glass electrode is very dependent on position when used or stored [17]. They are challenging to minimize, mechanically delicate, instable in aggressive electrolytes [18], and require wet storage with the bulb immersed in electrolyte [19]. A critical quality of solid-state sensors that sets them apart from the glass electrode is the absence of an internal electrolyte solution. This is the motivation for development of all-solid-state electrodes with large pH range and low sensitivity to redox agents.

1.3.1.3 Solid-State Ion-Selective Electrodes

Solid-state ion-selective electrodes (ISE) are associated with smaller size, easier fabrication, and simpler operation in comparison to conventional ISE such as the glass pH electrode which has an internal filling solution. The first solid-state ISE design to be invented was a coated-wire electrode but the blocked interface between the ionically conducting ion-selective membrane and the electronic conductor resulted in an unstable potential. Hydrogel-based electrolytes, instead of the liquid internal electrolyte, help to overcome the issue of blocked interface by providing a distinct and clear pathway for the ion-to-electron transduction. Another modification in solid-state ISEs is the application of an intermediate layer of redox active compounds between the ion-selective membrane and the electronic conductor. Due to this requirement of high redox capacitance in the intermediate layer, conducting polymers are applicable as ion-to-electron transducers. Conducting polymers are suitable for use in solid-state ISEs because they are electroactive, soluble, electronically conducting, and can be easily deposited on the conductor by the electro-polymerization of big and diverse monomers [20].

1.3.1.4 Metal Oxide pH Sensors

pH measurement techniques that have gained popularity in recent times using oxides as pH-sensitive layers are conductimetric/capacitive, potentiometric, and ISFETs, based on standard metal oxide field effect transistor (MOSFET). Among these methods, the potentiometric was the most commonly found technique in commercial devices due to its simplicity in fabrication and advancement in technology over the years [21].

Several possible mechanisms of pH sensitivity in metal oxides were suggested by Fog and Buck [22]. They include oxygen or hydrogen intercalation, ion exchange in the surface layer, corrosion of the material, and a possible equilibrium between the two oxidizing forms of the metal. They strongly supported the possibility of oxygen intercalation because there is nonstoichiometric oxygen

content in the oxides. This implies that the activity of oxygen in the solid phase should also be considered while calculating the electrode potential.

Among the many metal oxides that have been researched, ruthenium dioxide (RuO_2) and iridium dioxide have been most promising [18] with fast response due to their resistance to space charge accumulation which is credited to high conductivity and chemical stability. RuO_2 is especially a favorite among researchers as it shows close to Nernstian response even in the presence of strong oxidizing agents [22], organic sediments [23], and contaminants [24].

Different methods of fabricating RuO_2 electrodes are screen printing [16], radio frequency magnetron sputtering (RFMS) [25], molecular beam epitaxy [26], physical or chemical vapor deposition [27], thermal decomposition [28], sol–gel [29, 30], and ultrasonic spray pyrolysis [31]. The most preferred method to fabricate RuO_2 electrodes is screen printing because it has been reported to deliver the best sensitivity and response time [16]. Additionally, it gives the flexibility to use various sizes and compositions along with being fast and cost effective [32].

Binary metal oxides have been used for pH sensing most commonly as dimensionally stable anodes (DSA) in various applications [33]. In these systems, chemically inert oxides are mixed with an active transition oxide which helps to enhance electrochemical properties, stability, and longevity [16]. For example, doping has been found to improve antifouling properties in RuO_2 electrodes. Both un-doped nanostructured RuO_2 [34] and doped RuO_2 or mixed with other metal oxide have been recommended for pH sensing [16, 33, 34]. Some mixtures have been described below.

Utilization of tin oxide (IV) for electrode fabrication allows increase of the lifetime of the electrodes and shortens response time to five to nine seconds. RuO_2–SnO_2 mixed oxide-based electrodes show the Nernstian response with the sensitivity of −56.5 mV/pH for the RuO_2:SnO_2 ratio of 70 : 30 wt.% [35]. Since RuO_2 is expensive, combination with TiO_2 is used to reduce the cost. Furthermore, substituting part of RuO_2 with TiO_2 allows higher electric conductivity [36]. The sensitivity of RuO_2:TiO_2 70 : 30 mol% ratio was found to be −56.11 mV/pH when fabricated by the Pechini method [18] and −56.03 mV/pH when fabricated by screen-printing [35]. The RuO_2-TiO_2 electrode fabricated by Pocrifka et al. [18] experienced very low interference from anions such as Li^+, Na^+, and K^+ which is a desirable quality in pH sensors. Combination of RuO_2 with Ta_2O_5, which is known for its use as ISFET [37], allows to lower the cost, minimize potential drift, and time response [38–40]. Doping of RuO_2 with up to 20 mol% of Cu_2O allowed to produce electrodes with the nonporous surface that is favorable from the point of antifouling and stable performance even after three months of implementation [41, 42]. Sensitivity of 10 mol% Cu_2O-doped RuO_2 electrode was −47.4 mV/pH and did not change with the increase of Cu_2O concentration [42].

1.3.2 Dissolved Oxygen

The amount of oxygen dissolved in a unit volume of water or other liquids is termed as DO and is expressed in the unit milligram/litre. For pure water at 25 °C and 1 atm, the saturation level of DO is known to be 8.11 mg/l. DO means the free, non-compounded oxygen (O_2) molecules in the water which are not bound to any other element. Therefore, when measuring DO levels, the bound oxygen molecule in water (H_2O) which is in a compound is not considered. By natural processes, DO may enter water through slow diffusion from air across the water surface or aeration of water by various forms of running water such as waterfalls, waves, groundwater discharge, etc., and by aquatic plants, seaweed, algae, and phytoplankton as a byproduct of photosynthesis.

1.3.2.1 DO Sensors: Principles, Materials, and Designs

There are three ways to measure DO based on three different principles: chemical, electrochemical, and photochemical. These principles and the types of methods based on them are shown in Figure 1.1.

1.3.2.2 Chemical Sensors

The classical titration also known as volumetric analysis or the indicator method is the oldest known method of measuring DO with a chemical test and it is considered the benchmark of DO measurement [43]. The most popular indicator method for DO detection and measurement is Winkler's method or the iodometric method. Its principle is to produce manganese hydroxide (II) by adding manganese sulfate and alkaline potassium iodide to water. Due to unstable nature, manganese hydroxide produces manganic acid by combining with DO. Potassium

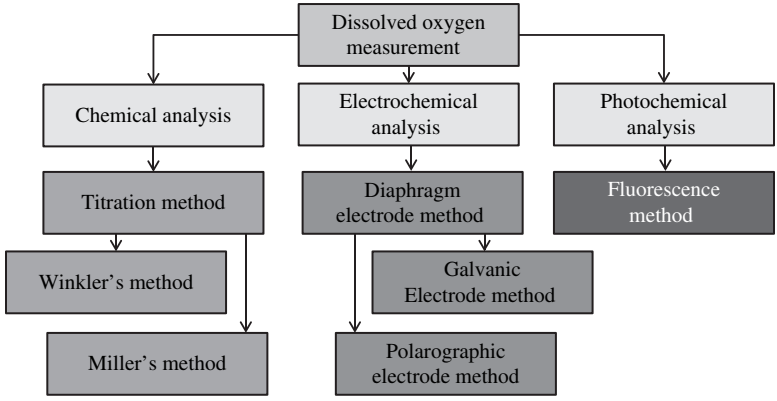

Figure 1.1 Principles and methods of measuring dissolved oxygen.

iodide and concentrated sulfuric acid are added to separate the iodine and react with DO, respectively. Using starch as an indicator, the amount of DO can be calculated with the titration of released iodine with sodium thiosulfate. Another method of DO measurement by titration is called Miller's method in which the oxidation of ferrous ions is measured in an alkaline medium [44]. Titration methods are only prevalent in laboratories and are not used for online measurement of DO because the design is simply too complicated to serve the demands of a continuous water quality monitoring system [43].

1.3.2.3 Electrochemical Sensors

Even though all methods are good and sensitive, in wireless sensor networks, electrochemical methods are most preferred due to miniaturization, robustness, and high resistance to fouling. The most commonly used type of electrochemical sensor is Clarke cell [13], shown in Figure 1.2. This sensor is controlled by a flux of oxygen that diffuses through the gas-permeable membrane (usually a polytetrafluoroethane film) separating the cell and the solution. By Fick's law, this flux which is indicated by the current produced is proportional to the DO concentration. The oxidation occurs at the anode (negative electrode) and the reduction occurs at the cathode (positive electrode) immediately when the oxygen diffuses through the film. Commonly used electrode material for Galvanic DO sensors are lead, iron, or zinc for anode and silver or platinum for cathode.

The two primary electrochemical techniques in practice for DO measurement are galvanic and polarographic. They both are electrode systems but with a slight difference between them. In a polarographic DO sensing system, an external voltage is applied. However, in the galvanic DO sensing system, an external potential is not required because the electrode materials are selected such that there is a

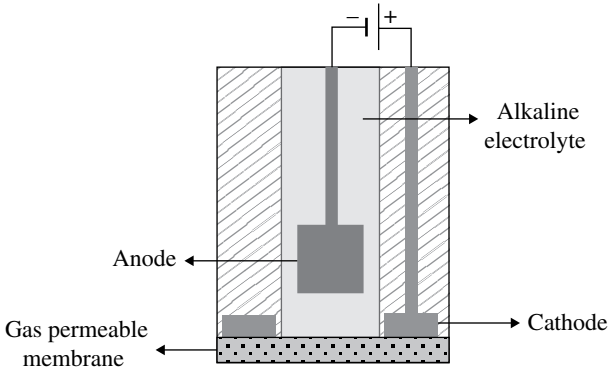

Figure 1.2 Schematic representation of as Clarke cell-type electrochemical DO sensor.

−0.5 V or greater potential between the cathode and the anode. Electrodes in the diaphragm method, on the other hand, measure the amount of oxygen passing through the gas-permeable diaphragm.

Semiconductor-Based Potentiometric DO Sensors Solid-state sensors based on semiconductors have helped to overcome the limitations of size and maintenance while providing researchers with the flexibility to explore various designs and materials. For example, a DO sensor was developed using platinum thin film electrodes which were coated with a solid-state proton conductive matrix (PCM) and the surface of the planar membrane electrode was covered with solid proton conductive material using spin coating process [44]. Therefore, instead of the traditional Clarke sensor which has a built-in electrolyte, this sensor had a solid polymer electrolyte. DO sensing systems made with RuO_2 as sensitive electrode and Ag/AgCl, Cl^- as reference electrode exhibited linear response with detection limits of 0.5–8.0 ppm [45].

Doped semiconductors are a popular choice of electrode material for electrochemical DO sensors. For example, nanostructured RuO_2 has been found to exhibit one of the best performances for DO sensing [13]. When doped with ZnO and Cu_2O oxides, it shows an increase in DO sensitivity by −48.6 mV/decade for 10 mol% ZnO [46] and −47.4 mV/decade for 10 mol% Cu_2O [42], respectively. When a semiconductor is doped, there is a formation of donor levels located on the upper band of the semiconductor due to the deviation in electronic structure of the doped mixed oxide. These donor levels contribute to the enhancement of sensor properties. As a charge donor, the dopant increases the conductivity of the electrode by transforming the structure of the nano-oxide and supplying excess carriers to the conductivity band [47].

1.3.2.4 Optical or Photochemical Sensors

There are different optical principles which can be used to measure DO such as the phosphorus quenching principle, near-infrared principle, the absorption principle, and the fluorescence principle. Among these principles, currently the most commonly used one is the fluorescence quenching principle and a DO sensor based on it consists of three constituents: excitation light sources, an optoelectronic detection element, and a substrate film attached to fluorescence-sensitive substances. In fluorescence quenching, the sensitive material absorbs the ultraviolet light of specific wavelength and the electrons gain energy which they release in order to return to ground state by emitting fluorescence. The amount of DO in the water can be estimated by the intensity of fluorescence or the fluorescence lifetime generated at the sensitive interface because the collisions between oxygen molecules and excited fluorescent substances interfere with the excitation process of fluorescent substance.

Sensitive materials that are fluorescent substances and used for the film are pyrene butyric acid, fluoroanthene, and polycyclic aromatic compounds [43]. Fluorescence indicators used in optical DO sensors to improve DO detection sensitivity include platinum phosphor porphyrins such as platinum octaethyl porphyrins (PtOEP), platinum tetrafluorophenyl porphyrins (PtTFPP), and ruthenium–chromium complexes. The choice of substrate material while fabricating optical DO sensors is critical because the DO sensors are principally based on the oxygen quenching effect of fluorescence of the luminescent body fixed in the matrix [43].

1.3.3 Electrical Conductivity

A measure of the ability of a solution to conduct electrical current indicated by the amount of free-flowing electrons and/or ions is termed as conductivity or specific conductance since conductivity is directly proportional to conductance ($1/R$, where R is resistance of the circuit). Expressed in Siemens per meter (S/m) or micro-Siemens per centimeter (μS/cm), conductivity is the inverse of the electrical parameter of resistance (ohm).

Measurement of conductivity is used for the determination of the following [13]:

- Number of free ions in the water influences some physiological processes in living organism.
- Sudden changes in waste and natural water systems.
- Amount of reagent required or sample sizes in chemical analysis of water.
- Concentration of total dissolved solids.

The conductivity of deionized and pure distilled water is about 0.05 μS/cm, drinking water is 200–800 μS/cm, and sea water is 50 mS/cm.

1.3.3.1 Conductivity Sensors: Principles, Materials, and Designs

Conductivity sensors are usually based on Ohm's law wherein the resistance of the water sample can be calculated from known values of resistor, voltage, current, and cell constants, i.e. area and length of the sample [3]. Such sensors are called conductive, contacting, or electrode sensors. In a conductive or electrode sensor which may have two, three, or four electrodes [48], the geometrical design of the sensor is based on the target conductivity range and determines the proportionality coefficient (KC) [8]. In three- or four-electrode system, if there is any damage, fouling, or polarization on the electrodes, the reference voltage allows compensation for it. Therefore, the reference electrode helps in achieving better accuracy over wide ranges unaffected by minor changes in electrode condition. In this system, an electric field is generated within the electrolyte when an electric

current is applied on one of the electrodes causing the negatively charged ions to the cathode and the positively charged ions to the anode. Therefore, the current in the electrolyte is carried by the ions, meaning that an increase in their mobility and concentration is expected to increase conductivity [13].

In traditional dip or flow-through style two-electrode conductivity sensors, electrodes are usually made of platinum, graphite, titanium, or gold-plated nickel. A comparative study [23] of four-electrode systems found electrodes which have high resistance to be more sensitive than electrodes made from Ru nanostructures. Metallic Pt/Ag/Pd alloys exhibited ion sensitivity within the range of 5–200 μS/cm with a response time of approximately one to three seconds whereas Ru-based electrodes system had a lower limit of 500 μS/cm and response time of two minutes [13]. Figure 1.3 presents the schematic representation of two-electrode and four-electrode types of conductivity sensors.

Another way to measure electrical conductivity of water is by using the inductive method based on the principle of mutual inductance [49]. Conductivity sensors based on this method are called toroidal or inductive sensors. This type of sensor has two conducting coils enclosed in a casing made of nonconducting material. By Faraday's law of induction, when an electrical current is induced by the first coil in the water, the second coil measures the magnitude of the induced current [8]. This measured value is directly proportional to the conductivity of the water sample.

Between conductive and inductive sensor, there is a vast divide between their prevalence in practice. Even though electrode conductivity sensors run the risk of delivering inaccurate measurements due to corrosion or deposition of fine

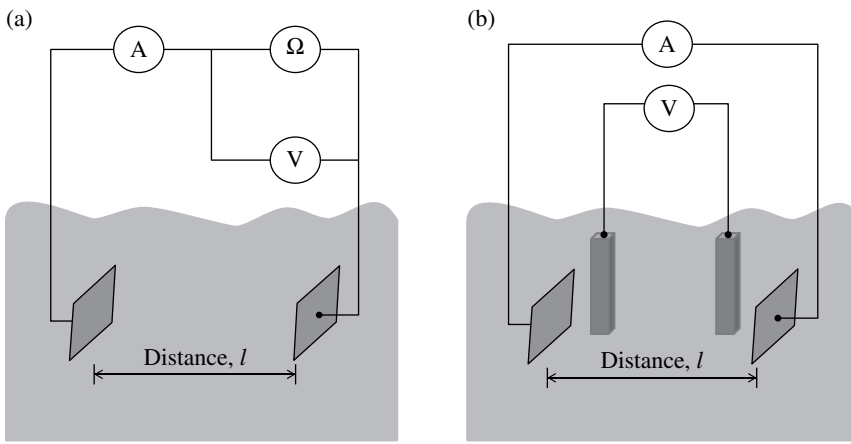

Figure 1.3 Schematic representations of (a) two-electrode and (b) four-electrode types of conductivity sensors where *I* is the current source, *R* is the resistance, and *V* is the voltage.

particles or bacteria on the electrode [49], their popularity far outweighs that of the inductive conductivity sensor due to simpler maintenance, lower cost [3], reduced fringe effect, sensitivity to contact resistance, and extendable linearity which can be achieved by varying the excitation voltage of the cell [48].

However, some researchers are of the opinion that from the perspective of long-term monitoring, the requirement of the electrodes to be repeatedly cleaned and replaced is somewhat contradictory to the objectives of wireless sensor networks [49]. The reason for their skepticism toward the precision of conductive sensors is that several factors such as volume of water, salinity of water, and size of coils [50] that influence the magnitude of induced current are overlooked in the conductive methodology but not in inductive methodology. Nevertheless, the lack of exploration in the potential of inductive sensors has left them with a commercially failed fate in industry. Researchers have not been as vocal in their criticism of inductive sensors as they have been in their appreciation of conductive sensors. Hence, it is most probable that the coil was simply too complicated in comparison to the two-dimensional electrode as suggested by a group of researchers [48] who prefer conductive sensors over inductive sensors due to simple and practical advantages such as ease in fabrication, directness in operational principle, and miniature size. However, the same researchers admit that the inductive sensor has a circuitry such that the input and output points do not come in contact with the water, thereby reducing the probability of fouling but there can still be signal loss and electrical interference.

Commercially, such a bias does not exist as both inductive and electrode conductivity sensors are easily available on the market. An example of commercial inductive conductivity sensor is AANDERAA Conductivity Sensor 4319 (range: 0–75 mS/cm, material of coil: titanium) and an example of commercial electrode sensor is YOKOGAWA Model SC4A (two-electrode system, range: 0.1–50 mS/cm, material of electrode: Stainless steel AISI 316L). In solid-state sensors, conductivity can be measured using either two electrodes or four electrodes.

1.3.4 Temperature

One of the most common data logging applications, temperature measurement is required across a multitude of industries and in almost every practical application. When two objects are at the same temperature and do not exchange any thermal energy, they are said to be in thermal equilibrium with each other. A scalar unit, temperature can be expressed using various units according to the thermometric scale used. Most popular temperature measurement scales are Kelvin (K), Fahrenheit (°F), and Celsius (°C). Based on the three physical states of matter, fundamental fixed points defining the temperature scales are listed in Table 1.1.

Table 1.1 Fixed points defined by temperature scales.

Material physical state	*K*	°F	°C
Absolute zero[a]	0	−459.67	−273
Ice point of water (1 atm)	273	32	0
Boiling point of water (1 atm)	373	212	100

[a] Temperature at which adiabatic and isothermic processes occur at the same time.

The environmental temperature is proportional to the current or voltage output generated using voltage reference or a diode with a well-established voltage versus temperature characteristic. For example, Analog Device AD 592 transducer has an output current of 1 μA/K with output of 248 μA at −25 °C. Many such IC temperature sensors are available commercially. They have an operation range of −55 °C to +150 °C and an accuracy of 0.3–0.5 °C.

1.3.4.1 Temperature Sensors: Principles, Materials, and Designs

Temperature sensors can be broadly divided into two design types: contact and non-contact. Figure 1.4 presents a classification of different types of temperature sensors. Contact temperature transducers implement transduction using heat transmission to create energy balance in the system when it comes in contact with the medium. Different types of contact temperature transducers

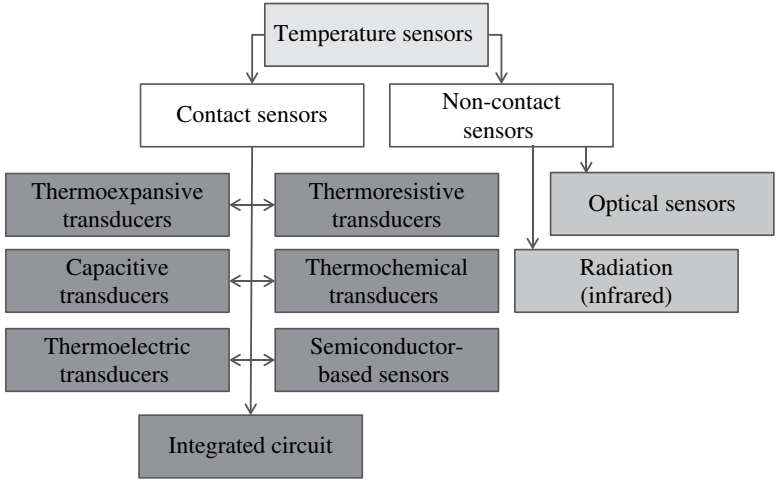

Figure 1.4 Different types of temperature sensors.

work using different types of principles such as capacitive transduction, thermochemical and thermoelectric transduction, thermoexpansive and thermoresistive transduction, semiconductor elements, and transduction with diodes. Contactless or non-contact temperature sensors use electromagnetic radiation of an object with temperature above 0 K. This radiation has an intensity which depends on the temperature of the object. Hence, these temperature sensors, also known as pyrometers, do not need any physical contact with the object. Although contactless temperature sensors can be used to measure temperature of water surface, they are mostly used for solid surfaces. In water quality monitoring, contact sensors are more common and the most popular ones have been discussed later in this chapter.

The following four types of temperature sensors are currently available in the market [43]:

1.3.4.2 Thermocouples

These sensors operate on the principle of Seedbeck effect. In this mechanism, two distinct electrodes produce a voltage difference that is proportional to the temperature difference between them [51].

1.3.4.3 Resistance Temperature Detector

Resistance Temperature Detectors or RTDs measure the change in electrical resistance of the material. Most commonly used materials for fabricating RTDs are pure metals because their temperature coefficients are small, positive, and accurate. RTDs made using platinum wire are known to be linear from temperatures ranging from −259 to 600 °C, well characterized and most precise.

1.3.4.4 Thermistor

The sensor design is similar to RTD and the only exception is that instead of a metal inside the device, there is a ceramic or a polymer [52]. The temperature-sensitive resistor has a negative temperature coefficient that is large and nonlinear which means that as the temperature increases, the resistance nonlinearly decreases. Their maximum usable temperatures range between 150 and 300 °C.

Since a thermistor is a nonlinear and very sensitive detector, it must be regularly calibrated based on desired temperature ranges. However, it responds linearly over small temperature ranges. Thermistor suffers from poor repeatability and is susceptible to self-heating errors caused by the power ($P = I^2R$) produced in it.

Therefore, magnitude of passing current is suggested to be kept at minimum in a thermistor. Most commonly used composition for making thermistors is mixture of semiconducting materials.

1.3.4.5 Integrated Circuit

Also known as monolithic or semiconductor temperature transducers, integrated circuits (IC) with two terminals produce a voltage signal that could be digital or analog or a current. This voltage signal is directly proportional to the absolute temperature. Typically, an IC operates over a temperature range of 0–100 °C in which it delivers an output of 10 mV/K.

1.4 Smart Sensors

Smart or intelligent sensors are the electronic systems which include in addition to detection and measurement, a complete and wireless system for the conditioning and collection of analog signals. They are more popular than traditional sensors because they have the advantage of combining multiple features and processes in one device, including the connection to a wider network of sensors over the internet. A smart sensor system consists of a detection/transduction system which converts the analog signal into a digital signal, a measurement and signal processing interface, a calibration system to properly process the data, and an autonomous power source to ensure uninterrupted operation of the sensor device [53]. In a smart sensor, a microcontroller is embedded in the device for the purpose of internal calculations and processing with a bidirectional communication channel which receives instructions and transmits the results. Overall, a smart sensor is simply a device containing a sensor with an attached facility for data computing and wireless transmission in one common enclosure.

1.5 Conclusion

The demand for real-time data in water quality monitoring grows simultaneously with the demand for advanced materials and sensor technologies, especially for application in CWS. Temperature, pH, DO, and conductivity are some of the most critical indicators of the health of a water body. Sensors are devices which aid in the measurement of these parameters. Recent research has paved the way for alternative methods for water quality testing based on thick film solid-state sensors which provide an array of advantages over traditional methods such as lower cost, ease of manufacturing, applicability in online monitoring system, deposition on flexible materials, robustness, and longer operational time. Knowledge of

different principles, designs, and materials of these water quality sensors enables manufacturers, researchers, and operators to apply them effectively for the purpose of remote and real-time water quality testing.

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