Topical Review

Review on Water Quality Sensors

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Abstract
Terrestrial life may be carbon-based, but most of its mass is made up of water. Access to clean water is essential to all aspects of maintaining life. Mainly due to human activity, the strain on the water resources of our planet has increased substantially, requiring action in water management and purification. Water quality sensors are needed in order to quantify the problem and verify the success of remedial actions. This review summarizes the most common chemical water quality parameters, and current developments in sensor technology available to monitor them. Particular emphasis is on technologies that lend themselves to reagent-free, low-maintenance, autonomous and continuous monitoring. Chemiresistors and other electrical sensors are discussed in particular detail, while mechanical, optical and electrochemical sensors also find mentioning. The focus here is on the physics of chemical signal transduction in sensor elements that are in direct contact with the analyte. All other sensing methods, and all other elements of sampling, sample pre-treatment as well as the collection, transmission and analysis of the data are not discussed here. Instead, the goal is to highlight the progress and remaining challenges in the development of sensor materials and designs for an audience of physicists and materials scientists.

1. Introduction

The central importance of water to life has been recognised in all civilisations, well predating our current western knowledge base [1, 2]. Even though water is plentiful on this planet, pollution of surface waters is a growing problem, and access to clean drinking water is not a given for one sixth of the world population [3]. In recognition of that, environmental regulations have been enacted in many countries in order to reduce pollution, and efforts are underway to develop robust technology for drinking water purification in remote and resource-poor locations. In this context, water quality sensors are an important emerging application of sensor technology [4]. Sensor materials research traditionally focusses on gas sensing, due to better control over the environment and more facile experimental design for sensor characterization and mechanism elucidation. At the other extreme, biosensors meet important societal and commercial needs, and have therefore undergone intense development, often based on a rather empirical

understanding of the underlying mechanisms used to translate biochemical binding events into measurable signals. Electrochemists have worked to bridge the knowledge gap and advance liquid sensing, trying to establish well-defined liquid sensing environments by incorporating fragile reference electrodes. In the end, there are many sources of ideas for designing water quality sensors, but the amount of work that remains to be done in the field is surprisingly large.

Water quality sensors are very important for guaranteeing access to potable water in urban and rural settings. Additionally, they can be used for environmental management in resource extraction industries, industrial and municipal waste water treatment, military installations as well as in agriculture. Automated, remote and real-time monitoring of run-off from mining tailing ponds, process water in industry (including oil sands), industrial and municipal waste water, agricultural irrigation and drainage could lead to immediate notification and quick remedial action that could avert large scale environmental damage. A range of international [5] and national [6] guidelines cover drinking and surface water quality parameters, including disinfectant use [7], contaminants [6] and nutrients [8]. Maintaining legislated or recommended limits is challenging [9]. Most current sensing technologies are laboratory based and not suitable for continuous sampling in a remote setting, as they are either single use, require reagents, or need technical expertise for operation or maintenance, all of which significantly increase the cost of environmental monitoring. Disinfectants and contaminants are commonly monitored colorimetrically or electrochemically or using lab-based spectroscopic methods. Colorimetric methods have a limited accuracy and are typically limited to manual, discontinuous testing. Spectroscopic methods require additional chemicals and complex instrumentation, making continued field observation or even automated sensing extremely challenging. Electrochemical methods are strongly affected by the flow rate and aging of the electrodes (especially the reference electrode), necessitating frequent calibration. Chemiresistors and ChemFETs have mostly been studied for gas sensing but are increasingly also being developed for water quality applications. They have not yet been demonstrated for the full bandwidth of analytes.

This review starts with a summary of the requirements for water quality sensing and continues by laying out the design characteristics of a chemical sensor for liquid analytes. Finally, all mayor available sensing platforms (mechanical, optical, electrochemical, electrical) are discussed in the context of their current and past successful application to water quality sensing. Strictly laboratory-based methods are not discussed, and neither are physical property sensors, biosensors, or sampling or sample pre-treatment procedures. Remote sensing technology is available that relies on satellite-, airplane- or drone-base spectrometric methods. Such methods can gather large amounts of data from large swaths of the earth's surface very quickly, but ultimately require calibration against ground-based methods and are not able to record all parameters with the required precision. Other important pieces of the puzzle are control electronics and data transmission technologies, as well as algorithms to process the large amounts of collected data to elucidate trends. This review is limited to sensing elements in contact with the analyte.

2. Water Quality Parameters

While there are a wide range of parameters to characterize water quality [10], typically only a few key parameters are monitored, depending on the application. Water quality may be monitored in surface waters (oceans, harbors, streams, lakes), including run-off from mining sites or military installations, agricultural irrigation streams or run-off, ground water, drinking water for distribution and consumption, drinking water for use in health care and food preparation, industrial or municipal waste water, industrial process water, cooling water in power plants or industry, or water in artificial environments such as swimming pools. To fully characterize water quality, one would have to take into consideration physical, chemical and biological parameters. Physical parameters include suspended particles, color, turbidity, temperature, density, conductivity and total dissolved solids. Vapour pressure, freezing point and boiling point of the water are colligative properties that depend on the total amount of dissolved species. For example, salty ocean water will have a lower vapour pressure, lower freezing point and higher boiling point than meltwater from a glacier. The density of the water also depends on the dissolved species (ocean water is denser than freshwater), but in a more complex and chemically specific way, which is why it is not considered to be a colligative property. Chemical parameters can be divided into organic and inorganic. Inorganic parameters include pH, alkalinity, acidity, hardness, dissolved oxygen, oxidation-reduction potential (ORP), disinfectants (free chlorine, chloramine, hydrogen peroxide, hypobromite, permanganate, etc.), nitrogen content (ammonia, amines, nitrate, nitrite), phosphorous content (phosphate), sulfur content (sulfides, sulfite, sulfate), micronutrients (manganese, iron, cobalt, molybdenum, zinc, copper, cadmium, boron, selenium, fluorine, iodine), and other inorganic contaminants (arsenic, lead, mercury, nickel, chromium, cyanide, silver, aluminum, beryllium, strontium, barium, tin, vanadium). Organic contaminants in water can stem from many different sources (decaying plant and animal matter or excrement, pharmaceuticals, run-off from oil sands or other fossil fuel extraction operations, explosives or chemical warfare agents from shooting ranges and military installations, pesticides, and other industrial or municipal waste, etc.). They may be summarized as total organic carbon (TOC), but due to the diversity of molecular structures and environmental impacts, this is a very broad and quickly evolving field. In most cases, speciation of organic contaminants takes place in a laboratory, not in the field, due to the lack of mobile technology. Biological parameters include various organisms from algae and phytoplankton to bacteria and human pathogens [10]. Here we focus on some of the main chemical parameters, namely pH, hardness, dissolved oxygen, ORP, disinfectants, nitrogen, phosphorous, sulfur, micronutrients, inorganic contaminants and some organic contaminants. Table 1 contains a summary of the most important chemical parameters of interest for drinking water quality, together with some national and international guidelines governing their maximum recommended or permitted concentrations in drinking water. Phosphate is not listed in this table since it is not commonly regulated for drinking water. Many phosphates have very low solubility in water, which is why the actual phosphate concentrations tend to be well below any value that would be of concern, even without efforts to limit them.

Table 1. Important Chemical Parameters for Drinking Water Quality.

Parameter	Maximum Acceptable Concentration (MAC)			
	Canada [6]	USA [11]	Europe [12]	WHO [5]

pH	range 7.0 - 10.5	range 6.5 - 8.5	range 6.5 - 9.5	--
Aluminum	200 ppb REC	200 ppb REC	200 ppb REC	--
Ammonia/Ammonium	--	--	500 ppb REC	--
Antimony	6 ppb	6 ppb	5 ppb	20 ppb
Arsenic	10 ppb ALARA	10 ppb	10 ppb	10 ppb
Barium	1 ppm	2 ppm	--	700 ppb
Beryllium	--	4 ppb	--	--
Boron	5 ppm	--	1 ppm	500 ppb
Bromate	10 ppb	10 ppb	10 ppb	10 ppb
Cadmium	5 ppb	5 ppb	5 ppb	3 ppb
Chloramines	3 ppm	4 ppm	--	3 ppm
Chlorine (Free)	--	4 ppm	--	0.5 ... 5 ppm
Chlorine Dioxide	--	800 ppb	--	--
Chlorate	1 ppm	--	--	700 ppb
Chloride	250 ppm REC	250 ppm REC	250 ppm REC	--
Chlorite	1 ppm	1 ppm	--	700 ppb
Chromium	50 ppb	100 ppb	50 ppb	50 ppb
Copper	1 ppm REC	1.3 ppm	2 ppm	2 ppm
Cyanide	200 ppb	200 ppb	50 ppb	70 ppb
Fluoride	1.5 ppm	4 ppm	1.5 ppm	1.5 ppm
Iron	300 ppb REC	300 ppb REC	200 ppb REC	--
Lead	10 ppb	15 ppb	10 ppb	10 ppb
Manganese	50 ppb REC	50 ppb REC	50 ppb REC	400 ppb
Mercury	1 ppb	2 ppb	1 ppb	1 ppb
Molybdenum	--	--	--	70 ppb
Nickel	--	--	20 ppb	20 ppb
Nitrate	45 ppm	45 ppm	50 ppm	50 ppm (short)
Nitrite	3 ppm	3 ppm	500 ppb	3 ppm (short) 200 ppb (long)
Selenium	50 ppb	50 ppb	10 ppb	10 ppb
Silver	--	100 ppb REC	--	--
Sulfate	500 ppm REC	250 ppm REC	250 ppm REC	--
Sulfide	50 ppb REC	--	--	--
Thallium	--	2 ppb	--	--
Uranium	20 ppb	--	--	15 ppb
Zinc	5 ppm REC	5 ppm REC	--	--
Small Molecule Organics				
Acrylamide	--	ALARA	0.1 ppb	0.5 ppb
Benzene	5 ppb	5 ppb	1 ppb	10 ppb
Benzo(a)pyrene	0.04 ppb	0.2 ppb	0.01 ppb	0.7 ppb
Formaldehyde	--	--	--	900 ppb
Styrene	--	100 ppb	--	20 ppb

Toluene	60 ppb	1 ppm	--	700 ppb
Xylenes	90 ppb	10 ppm	--	500 ppb
Halogenated Organics				
Carbon tetrachloride	2 ppb	5 ppb	--	4 ppb
Chlorobenzene	--	100 ppb	--	--
1,2-Dichlorobenzene	200 ppb	600 ppb	--	1 ppm
1,4-Dichlorobenzene	5 ppb	75 ppb	--	300 ppb
1,2-Dichloroethane	5 ppb	5 ppb	3 ppb	30 ppb
Haloacetic Acids	80 ppb ALARA	60 ppb	--	--
Tetrachloroethylene	10 ppb	5 ppb	10 ppb	40 ppb
2,4,6-Trichlorophenol	5 ppb	--	--	200 ppb
Trihalomethanes	100 ppb	80 ppb	100 ppb	--
Vinyl Chloride	2 ppb ALARA	2 ppb	0.5 ppb	0.3 ppb
Polycyclic Aromatic Hydrocarbons	--	--	0.1 ppb	--
Pesticides				
Pesticides (Total)	--	--	0.5 ppb	--
Atrazine	5 ppb	3 ppm	0.1 ppb **	100 ppb
Carbaryl	90 ppb	--	0.1 ppb **	--
Carbofuran	90 ppb	40 ppm	0.1 ppb **	7 ppb
Chlorpyrifos	90 ppb	--	0.1 ppb **	30 ppb
DDT	--	--	0.1 ppb **	1 ppb
Glyphosate	280 ppb	700 ppb	0.1 ppb **	--
Picloram	190 ppb	500 ppb	0.1 ppb **	--
Simazine	10 ppb	4 ppb	0.1 ppb **	2 ppb
Triafluralin	45 ppb	--	0.1 ppb **	20 ppb

ALARA - as low as reasonably achievable
REC - recommended limit for non-health reasons (e.g. aesthetic objectives)
** - included in the EU limit for individual pesticides of 0.1 ppb each
ppm - parts per million, mg/L
ppb - parts per billion, µg/L

2.1. pH

The negative decimal logarithm of the hydronium ion concentration *-log [H_3O^+]* is also known as the pH value of an aqueous solution (though the concept of pH has also been applied to non-aqueous contexts). In aqueous solutions, it is closely related to acid-base chemistry. Solubility and complex formation of aqueous species tend to be pH-dependent, and so are many redox reactions. Therefore, pH is a central concept in water quality assessment, with drinking water pH typically in the range of 6.5 to 9. The upper regulatory limit ranges from 8.5 to 10.5, depending on jurisdiction (see Table 1). The pH of the water affects the efficiency of disinfectant chemistry (most disinfectants are more efficient at lower pH), corrosion of infrastructure (lower pH is more

corrosive) and ability of aquatic organisms to survive (the acid and alkaline death points are around pH 4 and pH 11 [10]).
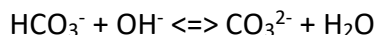
Rain water tends to be acidic due to dissolved carbon dioxide forming carbonic acid (H_2CO_3), which then dissociates into bicarbonate and hydronium ions according to

$$H_2CO_3 + H_2O <=> HCO_3^- + H_3O^+$$
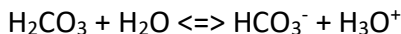
Carbonic acid is a weak acid, and so is bicarbonate. A second dissociation step is possible

$$HCO_3^- + H_2O <=> CO_3^{2-} + H_3O^+$$
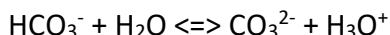
although it is most favoured in basic conditions

$$HCO_3^- + OH^- <=> CO_3^{2-} + H_2O$$

If the process starts from a bicarbonate or carbonate salt, which are commonly found in soil, hydronium ions will be consumed as a result of these equilibria, and a slightly basic pH will result. Therefore, surface and drinking water is typically bicarbonate-buffered into the correct pH range. Rain water or de-ionized process water in contact with air lacks this buffer capacity and typically is slight acidic. The carbonates of many bivalent cations (magnesium and calcium in particular, are not soluble in water (as opposed to their bicarbonates, which are very soluble) and precipitate as scale. Hence the concentration of such cations in water is known as its hardness (due to the equilibrium with carbon dioxide from air, there is never a shortage of bicarbonate to go with these cations). Water hardness is discussed in the next section. Buffer agents such carbonate and bicarbonate result in an interesting property of water, in that the hydronium ion concentration as measured by a pH sensor does not directly correlate with the amount of acid or base required in order to achieve a desired target pH, since hydronium ions may be consumed or regenerated from above equilibria, which is why the concepts of acidity and alkalinity of water exist to quantify buffer capacity, rather than actual pH. Acidity and alkalinity can be obtained from titrating an isolated sample of the water, while monitoring its pH [13].

pH is traditionally measured either colorimetrically (indicator dyes) or potentiometrically (utilizing the H^+-ion selectivity of porous glass membrane surfaces), although a very wide range of methods have been developed. Some reviews on the topic are available, covering electrochemical and optical instrumentation [14, 15, 16], but Table 2 also gives an overview over some recent sensor developments, especially based on electrical detection (chemiresistive or FET-based).

Table 2. pH sensors.

| pH Range	Sensing Principle	Ref.	Comments
2...9	optical (Raman)	[17]	
6.5...8.5	optical (fluorescence)	[18]	
3...8	optical (fluorescence)	[19]	
2.4...11.6	electrochemical (potentiometric)	[20]	
5...9	electrochemical (potentiometric)	[21]	WO_3
3...11	electrochemical (potentiometric)	[22]	graphene
4...10	electrochemical (potentiometric)	[23]	stretchable for wearable applications
6...9	electrical (chemiresistive)	[24]	conductive hydrogel

2...12	electrical (chemiresistive)	[25]	incorporated into battery-less device (RFID tag)
4...10	electrical (chemiresistive)	[26]	resistive film: graphene
2...12	electrical (chemiresistive)	[27]	resistive film: TiO_2
4...10	electrical (chemiresistive)	[28]	resistive film: Pd
5...9	electrical (chemiresistive)	[29]	resistive film: CNT
2...10	electrical (chemiresistive)	[30]	resistive film: Ni @ CNT
1...6	electrical (chemiresistive)	[31]	resistive film: polyaniline
3...11	electrical (OFET)	[32]	DDFTTF
3...10	electrical (ISFET)	[33]	HfO_2
3...8	electrical (ISFET)	[34]	Ta_2O_5
n/a	electrical (ISFET)	[13]	pH & alkalinity (2200...25000 µmol/kg) by diffusion titration
2.5...7	electrical (ExFET)	[35]	pentacene film
1...13	electrical (ExFET)	[36]	TiO_2:Ru
4.3...9.4	electrical (SGFET)	[37]	graphene
2...12	electrical (SGFET)	[38]	solution-gate field effect transistor

2.2. Water Hardness (Ca, Mg, Total)

There are several contributions to the total hardness of water: Most common are calcium and magnesium, two divalent cations that form insoluble carbonates, while their bicarbonates are soluble. Magnesium carbonate $MgCO_3$ and calcium carbonate $CaCO_3$ are common minerals in soil (limestone). They are washed out by rain containing carbonic acid under formation of their soluble bicarbonates.

$$CaCO_3 + H_2O + CO_2 => Ca^{2+} + 2\ HCO_3^-$$
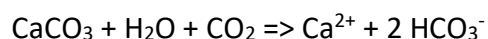
When the bicarbonate solutions are heated, carbon dioxide escapes (since its solubility in water decreases with increasing temperature) and the equilibrium is shifted back to the carbonate, which precipitates as scale in water kettles, heat exchangers and other places.

$$Ca^{2+} + 2\ HCO_3^- => CaCO_3 + CO_2 + H_2O$$
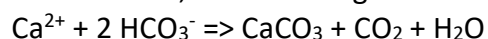
In addition to calcium and magnesium, other divalent cations can also contribute to the total hardness of water, such as iron (II), strontium, or manganese. In most cases, the concentrations of these cations are much lower than those of calcium and magnesium, however, so that in practice they are usually neglected.

Water hardness has long influenced peoples use of water for food preparation, body hygiene and laundry (impacting soap consumption), even before the industrial age, especially in regions with carbonate-rich minerals and hence "hard" water. As a result, many different units for water hardness have developed historically, such as French degrees, German degrees, Clark degree, grains per gallon, mg/L $CaCO_3$, and ppm.

Often hardness is measured indirectly as conductivity. That is fraught with error since other dissolved minerals that do not contribute to hardness (e.g. sodium or potassium salts) make a

contribution to conductivity. Often, however, Mg^{2+} and Ca^{2+} dominate, especially in hard or very hard drinking quality water, so the approximation can be quite reasonable. Other than conductivity probes, sensors have been developed that can selectively detect the ions of relevance, as summarized in Table 3.

Table 3. Water hardness sensors (other than through conductivity).

Type	Sensing Principle	Reference	Comments
Ca^{2+}, Mg^{2+}, Total	mechanical (QCM)	[39]	
Ca^{2+}, Mg^{2+}, Total	electrochemical (potentiometric)	[40]	sensing array for Ca^{2+}, Mg^{2+}, NH_4^+, K^+, Na^+, Li^+, H^+
Ca^{2+}	electrochemical (potentiometric)	[41]	
Ca^{2+}	electrical (ChemFET)	[42]	
total	optical (colorimetric test strip)	[43]	cannot distinguish Ca^{2+}, Mg^{2+}
total	optical (fluorescence)	[44]	cannot distinguish Ca^{2+}, Mg^{2+}
total	optical (colorimetric)	[45]	detects total concentration of Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}
total	optical (colorimetric)	[46]	cannot distinguish Ca^{2+}, Mg^{2+}
total	optical (colorimetric)	[47]	cannot distinguish Ca^{2+}, Mg^{2+}
total	optical (fluorescence)	[48]	cannot distinguish Ca^{2+}, Mg^{2+}

2.3. Dissolved Oxygen (DO)

Molecular oxygen is a gas with considerable solubility in water at room temperature. Much aquatic life depends on this property, which is why dissolved oxygen (DO) is one of the most important quality parameters of surface waters. In addition, DO is the most critical parameter for evaluating waste water treatment success. During the wastewater treatment process, biological waste and organic pollutant species are biochemically degraded by aerobic bacteria, consuming large amounts of oxygen. Precise monitoring and control of DO levels during this process can improve the efficiency and lower the cost of wastewater treatment.

Most commonly, the redox activity of DO is used for its quantification, although that may cause selectivity issues in the presence of disinfectants, as described in the next two sections. Molecular oxygen has also been shown to dope nanocarbon materials [49, 50], which could be used for the design of chemiresistive sensors, again with the challenge of imparting selectivity. Furthermore, many metallo-porphyrins form strong complexed with molecular oxygen, which can be used for its detection [51, 52, 53]. Fiber-optic instrumentation has been developed in the hope to automate optical DO sensing [54].

In addition to DO, chemical oxygen demand (COD) and biochemical oxygen demand (BOD) [55] are also important parameters. They correspond to kind of a 'buffer capacity' of the sample to consume available oxygen if left alone, due to reducing agents (organic carbon, Fe^{2+}, other species) dissolved in the water. These additional parameters are typically determined by leaving a sample sit in an isolated compartment, and either measuring DO as a function of time in order

to quantify its depletion, or by measuring the ability of the sample to reduce the surface of a sensing element in lieu of consuming the oxygen already dissolved. Here we mainly discuss DO sensors, as listed in Table 4.

Table 4. Dissolved oxygen sensors.

Range	Sensing Principle	Reference	Comments
2...7 ppm	electrochemical (amperometric)	[56]	
0.5...9 ppm	electrochemical (amperometric)	[57]	
0.2...6.5 ppm	electrochemical (amperometric)	[58]	
0.1...40 ppm	optical (luminescence)	[59]	very selective
4...40 ppm	optical (fluorescence)	[60]	5 ppb limit of detection claimed
0.5...43 ppm	optical (fluorescence)	[61]	lower limit not discussed
5...40 ppm	optical (fluorescence)	[62]	
2...800 Torr	optical (fluorescence)	[63]	given as gas pressure in equilibrium with liquid phase
BOD: 0...110 ppm	optical (fluorescence)	[64]	measures DO to determine BOD

2.4. Oxidation Reduction Potential (ORP)

In natural waters the dominant redox-active species is dissolved oxygen, so the oxidation-reduction potential (ORP) is dominated by that parameter. Since the dissolved oxygen concentration of water in equilibrium with air at 25°C, 1 atm pressure and pH 7 is 8.2 ppm, the ORP referenced against the standard hydrogen electrode should be 802 mV [10]. Since oxygen can be depleted by aquatic life forms or through reaction with other contaminants (especially in treated waste water), the dissolved oxygen concentration and hence ORP may be lower in actual samples, although the dissolved oxygen is replenished in surface waters that are in equilibrium with air. In water that has been treated for municipal or industrial purposes, the ORP is determined by the nature and concentration of added disinfectants, as well as the pH. The pH dependence is due to the pH dependence of many redox reactions involving common disinfectants. Since the ORP is an electrochemical parameter, the most obvious way to measure it is electrochemically (potentiometric) directly against a reference electrode. Selectivity problems do not arise since all species are equally considered. ORP measurements are similarly unspecific as conductivity measurements. Since the ORP is directly related to disinfectant efficiency, however, it has been argued that it should be used as the relevant parameter for water treatment processes in municipal drinking water plants, waste water plants, industrial water treatment and swimming pools [65, 66, 67, 68].

2.5. Disinfectants

Chemicals with high oxidation capacity such as hypochlorite (free chlorine), hydrogen peroxide, chloramine, potassium permanganate, and peracetic acid are added to water either to assist with the disinfection process or to maintain a residual concentration such that drinking water remains disinfected. It is also possible, for example, to add hydrogen peroxide to enhance the disinfection capability of UV treatment processes to remove bacterial and viral contaminants from water. In addition, the residual oxidant concentration has to be accurately controlled in a certain range around 0.5–2 mg/l to avoid both bacterial contamination (free chlorine < 0.5 mg/l) and hazard to human health (free chlorine > 2mg/l). Current standard technology for oxidant sensing requires use of reagents (e.g. N,N-diethyl-p-phenylenediamine, a.k.a. DPD) which restricts its use to manual operation or to laboratory based settings. Furthermore, reagent-based techniques may have issues with specificity when multiple redox-active species are present. Oxidant concentration can be measured by titration (iodometric or amperometric), chemiluminescence, and electrochemical methods. Titration based approaches use reagents and are not suited for continuous or autonomous monitoring. The chemiluminescence method also uses reagents, where the sample is first reacted with chemiluminescent indicators to generate optical signal intensity which is proportional to the concentration of oxidant species in the sample. In addition, the use of optical light sources and detectors increases cost. Electrochemical methods, on the other hand, are simple in design, do not need additional reactants, and directly produce electrical signals which is favorable for autonomous, continuous monitoring. Nevertheless, there are still some common drawbacks of electrochemical sensors. Frequent calibration is necessary since the sensing results are strongly affected by the flow rate and aging of the electrodes. Due to the strong interest in measuring disinfectant concentrations in water, the topic is covered by many reviews [69, 70, 71, 72, 73]. Table 5 also gives an overview of some developments in the field, both historic and recent. Note that it is still challenging to distinguish between multiple disinfectants in the field without prior knowledge of how the water has been treated. This challenge was on public display during the 2016 Olympic Summer games in Rio de Janeiro (Brazil), where an outdoor swimming pool turned green and murky after being disinfected alternatingly with hydrogen peroxide and hypochlorite, which cancelled each other out.

Table 5. Disinfectant sensors.

Disinfectant	Range	Sensing Principle	Ref.	Comments
Free Cl		colorimetric	[74]	DPD standard method
Free Cl	0.1...1.0 ppm	colorimetric	[75]	syringaldazine
Free Cl	> 0.2 ppb	chemiluminescence	[76]	luminol
Free Cl	2 µM ... 10 mM	UV absorption	[77]	reagentless (290 nm abs.)
Residual Cl	0.2...1.0 ppm	colorimetric	[78]	
Free Cl	2 µM ... 1 mM	chemiluminescence	[79]	uranine
Free+Resid Cl	0.1...8.0 ppm	colorimetric & flow-injection anal.	[80]	improved DPD method
Free Cl	0.1...1.0 ppm	amperometric	[81]	
Free+Resid Cl	0.03...10 ppm	colorimetric & flow-injection anal.	[82]	
Free Cl	> 1 ppb	amperometric	[83]	on-chip fabrication

HOCl, ClO$_2$, NH$_2$Cl, HOBr, NH$_2$Br, NHBr$_2$, NBr$_3$	> 0.1 µM	colorimetric	[84]	ABTS, limited selectivity for free chlorine (determined by difference)
Free Cl	0.7...200 µM	colorimetric	[85]	improved DPD method
Residual Cl	< 1.5 ppm	amperometric	[86]	
Free Cl	7...495 µM	voltammetric	[87]	improved DPD method
Free Cl	0.4...50 ppm	chemiluminescence	[88]	disposable test strip
Free Cl	4...400 ppm	amperometric	[89]	
Free Cl	> 0.08 ppm	amperometric	[90]	
H$_2$O$_2$	< 20 mM	chemiresistive	[91]	used for glucose sensor
Free Cl	<20 ppm	amperometric	[92]	
Free Cl	0.1...100 ppm	amperometric	[93]	
Free Cl	0.03...8 ppm	chemiresistive	[94]	
Free Cl	0.2...5 ppm	amperometric	[95]	
Free Cl	0.05...10 µM	fluorescence	[96]	
H$_2$O$_2$	100...600 µM	amperometric	[97]	
H$_2$O$_2$	2...18 µM	voltammetric	[98]	
Free Cl	0.01...10 µM	chemiluminescence	[99]	
Free Cl	0.4...521 ppm	amperometric	[100]	
Free Cl	0.06...60 ppm	chemiresistive	[101]	
Free Cl	1...6 ppm	amperometric	[102]	pencil lead, ammonium carbamide
Free Cl	0.5 µM ... 1.0 mM	chemiluminescence	[103]	
Free Cl	1...100 ppm	voltammetry	[104]	
Free Cl	>0.0006 ppm	amperometric	[105]	
Free Cl	0.009...10 ppm	amperometric	[106]	
Free Cl	0.025...3 ppm	amperometric	[107]	Prussian Blue & flow injection analysis
Free Cl	10...215 µM	amperometric	[108]	
Free Cl	0.2...14 µM	photoluminescence	[109]	
Free Cl	0.1...60 ppm	chemiresistive	[110]	substrate: pencil line
Free Cl	0.06...60 ppm	chemiresistive	[111]	substrate: pencil line
H$_2$O$_2$	50...500 µM	colorimetric; fluorometric	[112]	

2.6. Nitrogen (Ammonia, Nitrite, Nitrate)

The atmosphere consists to 78% of nitrogen (N_2) gas and is the biggest nitrogen reservoir on the planet. Atmospheric nitrogen can either be oxidized by lightning to various nitrous oxides ($\cdot$NO or $\cdot$NO$_2$ radicals, or dimers N_2O_2, N_2O_3, N_2O_4) which get washed out with the rain to form nitrites (NO$_2^-$) or nitrates (NO$_3^-$), or it can be reduced to ammonia molecules (NH$_3$) and ammonium ions

(NH_4^+) in industrial, bacterial or algae-based fixation processes. These species can be interconverted into each other or into other nitrogen-containing molecules such as urea, amino-acids, proteins, DNA, etc., and have different roles to play in aqueous environments (the "nitrogen cycle"). One complication arises from water bodies (e.g. swimming pools) rich in both reduced nitrogen (e.g. ammonia, urea) and disinfectants (e.g. free chlorine), which can react to form chloramines. While chloramines are highly undesirable side products in swimming pools, fish farms or aquariums (or outright dangerous to dialysis patients!), some municipalities have started using them as residual disinfectants in the drinking water distribution system. They are significantly more stable than free chlorine, which is desirable while the water is in the distribution system but can turn into a considerable problem at the consumer end, when they have to be removed. Disinfectants were dealt with in the previous section, so the focus here is on nitrate, nitrite and ammonium, which are regulated in water due to their nutrient nature in surface waters, toxicity of nitrate, nitrite and un-ionized ammonia, and the tendency of ammonia and ammonium to react with some common disinfectants in drinking water supplies and swimming pools. Table 6 lists common sensor types for these forms of nitrogen. Some reviews discuss nitrate and nitrite sensors as well [113, 114, 115].

Table 6. Nitrogen sensors.

Form of N	Range	Sensing Principle	Reference	Comments
NO_3^-	1.2...20 ppm	optical (colorimetric)	[116]	
NO_3^-	25 µM ... 36 mM	electrical (ChemFET)	[117]	ion-selective FET
NO_2^-; NO_3^-	1...10 mM; 1...10 mM	optical (Fluorescence)	[118]	
NO_3^-	1...1000 ppm	electrochemical	[119]	total range tested 0.1 - 10000 ppm
NO_2^-; NO_3^-	0.05...5 ppm; 0.16...5 ppm	optical (absorbance)	[120]	coupled with chromatographic separation
NO_3^-	0.025...10 mM	electrochemical (potentiometric)	[121]	
NO_2^-; NO_3^-	> 8 ppm; > 20 ppm	electrochemical (potentiometric)	[122]	coupled with chromatographic separation
NO_3^-	0.02...10 mM	electrochemical (potentiometric)	[123]	
NO_3^-	0.1...2.5 mM	electrochemical (amperometric)	[124]	
NO_3^-	6.25...3500 µM	electrochemical (voltammetric)	[125]	
NO_3^-	0.01...100 mM	optical (fluorescence)	[126]	
NH_4^+	> 2.2 µM	mechanical (QCM)	[127]	

2.7. Phosphorous (Phosphate)

Phosphorous - in the form of phosphate - is an important nutrient and as such of much concern in surface waters, as high concentrations can cause excessive growth of phytoplankton ("eutrophication") [128, 129]. Usually, phosphate is the limiting nutrient for phytoplankton growth, and its concentration in water is very low (typically below 100 ppb) due to the low solubility many inorganic phosphates such as those of calcium, aluminum, iron and copper. Inorganic phosphates are brought onto fields as fertilizers, and organic phosphates are used in surfactants and detergents, adding man-made sources of phosphate to surface waters. Sediments will act as sinks for phosphorous, resulting in a readily available reservoir to replenish dissolved phosphate that is consumed by aquatic life. It is therefore of practical importance to monitor organic and inorganic phosphate concentrations in waste water, agricultural settings and wetlands. Phosphate in aqueous solutions can occur as H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, or (rarely) diphosphates or polyphosphates, which are in chemical equilibrium with each other depending on pH and concentration. Table 7 gives several examples of field-deployable phosphate sensors. There are also some reviews giving an overview of electrochemical (potentiometric, voltammetric, amperometric) [130, 131, 132] and optical methods [131, 132].

Table 7. Phosphate sensors.

Range	Sensing Principle	Reference	Comments
0.1...100 mM	electrochemical (potentiometric)	[133]	reagent free (reusable)
0.1...10 ppb	optical	[134]	molybdenum blue reaction
1 µM ... 3.9 mM	electrochemical (potentiometric)	[135]	ion-selective membranes with ionophores
qualitative	optical (fluorescence)	[136]	
1 µM ... 20 µM	electrochemical (potentiometric)	[137]	
0.1...10 mM	electrochemical (potentiometric)	[138]	cobalt electrodes
20...100 µM	electrochemical (amperometric)	[139]	anodic oxidation of molybdenum
1 µM ... 2.5 mM	optical (fluorescence)	[140]	uranyl salophene ionophores
10 µM ... 10 mM	electrochemical (potentiometric)	[141]	cobalt microelectrodes (disposable)

2.8. Sulfur (Sulfide, Sulfite, Sulfate)

Sulfur in aqueous environments can occur in reduced form as sulfide or in oxidized form as sulfite or sulfate. Sulfate is a very common anion in water bodies, and not generally considered as toxic. Hydrogen sulfide (H_2S), on the other hand is very toxic. It is also very odorous (rotten eggs), to be out-stunk only by thioles (organic compounds containing -SH groups). Metal sulfides are common ores and are one possible source of sulfides in surface waters besides dead organic matter. Elemental sulfur is brought out in horticulture to acidify soils, but sulfur in its elemental form is not water soluble and does not play a role in water quality considerations, which are dominated by sulfides, sulfites and sulfates. Table 8 lists sensors for the different forms of sulfur.

Table 8. Sulfur sensors.

Form of S	Range	Sensing Principle	Ref.	Comments
H_2S	2...100 µM, or 68...3400 ppb	electrochemical (amperometric)	[142]	dependent on pH, response time < 100 ms
H_2S	> 10 nM	optical (fluorescence)	[143]	
H_2S	3...150 µM	electrochemical (amperometric)	[144]	
H_2S	20...200 µM	electrochemical (amperometric)	[145]	
SO_3^{2-}	> 10 nM	optical (fluorescence)	[146]	
SO_3^{2-}	1.2...69 µM	electrochemical (amperometric)	[147]	
SO_3^{2-}	40...200 µM	electrochemical (potentiometric)	[148]	enzymatic; tested on river water & sea water
SO_4^{2-}	6...120 µM	optical (fluorescence)	[149]	in 1:1 water:methanol
SO_4^{2-}	60 nM ... 70 µM	optical (colorimetric)	[150]	
SO_4^{2-}	1 µM ... 100 mM	electrochemical (potentiometric)	[151]	

2.9. Micronutrients (Manganese, Iron, Cobalt, Molybdenum, Zinc, Copper, Cadmium, Boron, Selenium, Fluorine, Iodine)

The distinction between micronutrients and other inorganic trace contaminants is a minor one when it comes to water quality control. Micronutrients are essential to various life forms in very small amounts and should therefore not be completely eliminated from the water supply. For the purpose of water quality control they are nevertheless a concern at higher doses. Except for instances of fluoridation, they are not added to the water supply on purpose, but rather expected to be consumed with food. They may be regulated due to toxicity at high concentrations, or due to cosmetic concerns (e.g. staining, odours). Table 9 lists current and emerging sensor technologies for online detection of micronutrients. A large selection of colorimetric agents is reviewed in [152].

Table 9. Micronutrient sensors.

Species	Range	Sensing Principle	Reference	Comments
F^-	qualitative	optical (colorimetric)	[153]	various anions (F^-, Cl^-, Br^-, $H_2PO_4^-$, AcO^-, BzO^-, CN^-, NO_3^-, SCN^-)
F^-	> 0.3 ppb	optical (fluorescence)	[154]	
Cu^{2+}	5...50 μM	optical (fluorescence)	[155]	
Cu^{2+}	> 0.1 nM (instrument)	optical (colorimetric)	[156]	catalytically amplified; can be read by eye (40 nM limit of det.)
Cu^{2+}	> 0.15 nM	optical (fluorescence)	[157]	commercially available probe molecules
Cu^{2+}	> 0.27 nM	anodic stripping voltammetry	[158]	
Cu^{2+}	50...300 ppb	anodic stripping voltammetry	[159]	
Zn^{2+}	> 1.4 nM	anodic stripping voltammetry	[158]	
Zn^{2+}	50...300 ppb	anodic stripping voltammetry	[159]	
Zn^{2+}	1 ppb	anodic stripping voltammetry	[160]	
Cd^{2+}	> 1.9 nM	anodic stripping voltammetry	[158]	
Cd^{2+}	50...300 ppb	anodic stripping voltammetry	[159]	
Cd^{2+}	0.1 ppb	anodic stripping voltammetry	[160]	
Co^{2+}	0.6×10^{-9} ppm	optical (SERS)	[161]	Cu, Cd, Ba Hg, Pb also tested
Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Fe^{2+}, Ca^{2+}	μM range	optical (colorimetry)	[162]	selectivity by principle component analysis
Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Fe^{3+}, Mg^{2+}, Ca^{2+}	μM range	optical (fluorescence)	[163]	selectivity by principle component analysis

2.10. Other Inorganic Contaminants

Arsenic, lead, mercury, nickel, chromium, cyanide, silver, aluminum, beryllium, strontium, barium, tin, and vanadium are inorganic contaminants in water that are not essential for life, and often toxic at low levels. Aluminum, silver, and vanadium are exceptions in that they are not toxic at the levels normally found in drinking water, although silver is utilized as an anti-microbial agent

due to its toxicity to smaller life forms, which makes it problematic in waste water streams and surface water. High levels of arsenic are naturally found in the soil (and hence ground water supply) in some regions of the world, including parts of Bangladesh and India. Lead is a common pollutant from old water pipes, while mercury and cyanide often originate from mining activity. Table 10 lists emergent sensor technologies for online inorganic contaminant sensing.

Table 10. Inorganic Contaminant sensors.

Species	Range	Sensing Principle	Reference	Comments
CN^-	1...6 ppm	Mechanical (QCM)	[164]	
CN^-	> 0.23 µM	optical (fluorescence)	[165]	demonstrated in live cells
Pb^{2+}	> 14 nM	Mechanical (QCM)	[166]	
Pb^{2+}	2.5...20 ppb	Capacitance	[167]	
Pb^{2+}	> 4.4 ppb	Anodic Stripping Voltammetry	[168]	selective against Cd, Zn
Pb^{2+}	> 15 ppb	electrochemical	[169]	emphasizes simple design
Pb^{2+}	n/a	optical (colorimetric)	[170]	after extraction to non-aqueous phase
Pb^{2+}	> 1.5 nM	anodic stripping voltammetry	[158]	
Pb^{2+}	50...300 ppb	anodic stripping voltammetry	[159]	
Pb^{2+}	2×10^{-9} ppm	optical (SERS)	[161]	Co, Cu, Cd, Ba Hg also tested
Pb^{2+}	0.1 ppb	anodic stripping voltammetry	[160]	
As^{3+}	0.8...12 ppb	anodic stripping voltammetry	[171]	contains a nice overview of electrochemical As^{3+} sensors
As^{3+}	10...100 ppb	anodic stripping voltammetry	[172]	
Hg^{2+}	n/a	optical (absorption)	[173]	after extraction to non-aqueous phase
Hg^{2+}	> 1 nM	optical (fluorescence)	[174]	
Hg^{2+}	0.1...1 µM	electrical (chemiresistive)	[175]	
Hg^{2+}	50...300 ppb	anodic stripping voltammetry	[159]	
Ni^{2+}, Hg^{2+}, Al^{3+}, Pb^{2+}, Ga^{3+}	µM range	optical (colorimetry)	[162]	selectivity by principle component analysis

Ni^{2+}, Hg^{2+}, Al^{3+}, Pb^{2+}, Ba^{2+}, Cr^{3+}	µM range	optical (fluorescence)	[163]	selectivity by principle component analysis

2.11. Carbon (TOC, organic contaminants)

Organic compounds are most difficult to detect in the field due to their diversity in structure and chemistry. Total organic carbon (TOC) is a commonly employed water quality parameter, but it is not related to actual toxicity. An incomplete list of regulated organic chemicals, halogenated organic compounds, and pesticides occasionally found in drinking water is given at the end of Table 1. This list is in fact much longer, continuously growing, inconsistent between countries, and often politicized due to commercial interests. Too often the rule is that you can't find what you don't look for, and if you don't find something, it is of no concern. Most commonly, specific organic contaminants are identified and quantified in a laboratory setting, but some online and mobile sensors that have become available are listed in Table 11.

Table 11. Organic species / Carbon sensors.

Species	Range	Sensing Principle	Ref.	Comments
phthalates	2 ppb - 2 ppm	electrochemical (impedance)	[176]	
triclosan	$10^{-12}...10^{-6}$ M	electrochemical (impedance)	[177]	antibacterial agent in cosmetics
sodium dodecyl sulfate (SDS)	$10^{-6}...10^{-3}$ M	electrochemical (potentiometric)	[178]	
anionic surfactants		electrochemical (potentiometric)	[179]	review up to year 2005
anionic surfactants	1% by weight	electrochemical (impedance)	[180]	
anionic surfactants		various	[181]	review up to year 2014
cationic surfactants	$10^{-6}...10^{-3}$ M	electrochemical (conductometric)	[182]	stable > 8 weeks
sodium dodecyl sulfate (SDS)	> 0.25 µM	optical (fluorescence)	[183]	
anionic surfactants			[184]	review
atrazine	0.1...100 µM	electrochemical (potentiometric)	[185]	response time 10 s, reversible
cyanazine, simazine, atrazine	0.1...6.6 nM	optical (SPR)	[186]	
atrazine	> 0.01 nM	electrical (chemiresistor)	[187]	good selectivity against other pesticides
atrazine	0.08...1.5 nM	mechanical (QCM)	[188]	

nitrobenzene	10...100 ppm	optical (fluorescence)	[189]	
hexachlorobenzene	> 10^{-12} M	mechanical (QCM)	[190]	
benzo(a)pyrene	> 10 ppb	optical (phosphorescence)	[191]	
trichloroethylene, tetrachloroethylene, carbon tetrachloride	> 2 ppm	optical (infrared absorption)	[192]	selective diffusion into hydrophobic polymer improves detection limit
TOC	0.5 ... 3 g/L	optical (infrared absorption)	[193]	also looked at volatile fatty acids, COD, partial and total alkalinity
TOC		photocatalytic	[194]	review
formaldehyde	> 30 ppb	electrochemical (amperometric)	[195]	
formaldehyde	0.9 ... 130 µM	optical (fluorescence)	[196]	
formaldehyde	1 µM ... 16 mM	electrochemical (amperometric)	[197]	platform technology - other species possible
formaldehyde	10...100 ppm	optical (fluorescence)	[198]	
trinitrotoluene	> 0.01 ppb	electrical (chemiresistive)	[199]	
various species		optical (fluorescence)	[200]	review

3. Chemical Sensors

In general, a chemical sensor is defined as a device that can provide information about the chemical composition of an analyte. This happens in two stages, (a) recognition/detection of a particular chemical property of the analyte, and (b) transduction into a measurable physical signal. In varying manifestations, the following steps are involved in chemical sensing:

Step 1: Analyte conditioning (pre-concentration, separation, control of environmental parameters)

Step 2: Recognition/detection of the desired chemical property

Step 3: (Proportional) transduction of the signal from chemical into a more easily quantifiable form (electrical, optical, mechanical, etc.)

Step 4: Quantification of the signal

Step 5: Interpretation of the signal(s), chemometrics, multi-parameter analysis, etc.

Here we will not concern ourselves with steps 1, 4 and 5, which in practice are often carried out external to the actual sensor device. The following text will be structured to take into account different classes of transduction mechanisms, as also summarized in Table 12. The methods are distinguished by mechanical, optical or electrical signals being generated by the chemical sensor itself. In many cases, the mechanical signals are further transduced into optical or electrical signals for processing, and if the optical sensors are not directly read by human eyes, they are usually also transduced into electrical signals. Nevertheless, those subsequent transductions are not part of the chemical sensor itself and are therefore ignored in the context of this review. Another important distinction that is made in the structure of this review, but not within the classification scheme of Table 12, is that between electrical and electrochemical sensors. The difference between the two is not always apparent at first glance, but for the purpose of this review 'electrochemical' shall be defined as the analyte solution being integral part of the electrical circuit (i.e. the current flows through the analyte, or the potential, resistance or inductance across a portion of the analyte is measured). A purely electrical sensor, on the other hand, will interact with the analyte, but it is not the analyte properties that are measured. Instead the change in electrical properties of a sensor element is measured as a result of its interaction with the analyte.

Table 12. Classification of Sensor Types.

Signal	Transduction Method	Detection Principles
mechanical	strain / deformation	swelling of thin films or surface layers
	resonance frequency	cantilever, quartz crystal microbalance
optical	emittance	fluorescence, (chemi)luminescence, phosphorescence, atomic emission
	absorbance	XAS, UV, Vis, NIR, IR, atomic absorption
	scattering	elastic (turbidity), inelastic (Raman)
	plasmons	SPR
electrical	electrode potential	potentiometry, ion-sensitive electrodes
	generated current	amperometry, voltammetry
	conductance / resistance	chemiresistor, chemitransistor, ChemFET, bulk conductance
	impedance	electrochemical impedance spectroscopy (EIS)

A number of parameters are commonly quoted to discuss the performance of a sensor:

a. selectivity (between similar analytes) & interference (of other environmental parameters)

b. accuracy & precision (repeatability, resolution)

c. limit of detection & dynamic range

d. resettability / reusability

e. response time

f. drift / calibration issues & longevity / maintenance intervals

g. operational range (w.r.t. to environmental parameters) & robustness to overdose/ abuse/ adverse condition/ operator error

h. power consumption & autonomy (manual interference, required supplies)

Many shortcomings of the physical sensing elements (such as drift or selectivity) can be compensated for by sophisticated sensing protocols, signal conditioning and data processing (incl. chemometrics [201]). Sample pre-treatment can boost the limit of detection and enhance the dynamic range of a sensor device. An important consideration in sensor design is the geometry in which it permits interaction of its receptor portion with the analyte. The most common geometries are flow sensors, dip sensors and drop sensors. Some sensors also operate by diverting a defined volume into a sample compartment and conducting the measurement similar to the geometry of the flow sensor, but with a static sample (i.e. flow = 0).

Sensor lifetime in aqueous environments is mainly affected by degradation of the sensor and by biofouling. The degradation is a challenge that is specific to each sensor design and also depends on the sensing mechanism, as will be discussed individually in the following sections. It only occurs during sensor operation, which is why sensor arrays with redundant elements are a possible solution, predicated on low cost of fabrication of miniaturized sensing elements. Biofouling is the unwanted deposition and growth of a biofilm, which contains microorganisms such as algae and/or bacteria as well as organic and inorganic debris. Usually, it is initiated by the attachment of humic acid or proteins, or other small bioactive molecules, which then encourage growth of microorganisms that form increasingly large colonies that may partially detach from the growth surface and lead to clogging of even those parts of the device that were initially immune to biofilm growth. In hard water, inorganic salts may precipitate and form scale deposits even in the absence of biological or organic matter. Such biological, organic or inorganic deposits are likely to interfere with sensor function and will form even while the sensor is not in operation. All sensor types are affected by biofouling, since optical access will be obstructed, electrodes will foul, and physical access of the receptor parts of the sensor to the analyte will be restricted. Therefore, either the sensor surface has to be physically or chemically designed to be resistant to biofilm formation and scale build-up, or a maintenance regime has to be instituted for film removal, which may include mechanical removal, irradiation, ultrasonic treatment, chemical rinses, or application of an electrical potential that either disfavours film build-up or electrochemically triggers pH (or other) changes leading to film dissolution. Some of the most common commercially available antifouling solutions are copper-based products (due to Cu^{2+} being toxic to microorganisms, but copper itself can be an undesirable pollutant in high concentrations) and plastic sleeves. Antifouling membranes or fouling resistant surface micro- and nano-structures are also under development but have not yet been commercially successful.

The importance of statistics is brought up sooner or later in any discussion of data acquisition processes, be it about scientific experiments, clinic trials for drug development, engineering data of process or instrument performance, or the signal output of chemical sensors. As impressive as feats of single molecule sensing are [202], and as much effort may be put into lowering detection limits, ultimately the reliability of a sensor design is a deciding factor in practical deployment. Distinguishing a single sensing event from noise may be possible in a very controlled laboratory environment, or for large analyte targets such as a bacterial cell or other organisms. Chemical water quality parameters, however, can be measured from a large number of events, even for sub-ppb concentrations. 1 litre of water weights around 1 kg (depending on temperature) and contains approximately 3.35×10^{25} individual water molecules. If a sensor was to sample even only 1 µL of water containing the regulatory limit of 1 ppb (or µg/L) of mercury (atomic weight 200.6 g/mol), there would still be 3×10^9 mercury atoms available for sensing. Single junction sensors with moderate sensitivity are sufficient for operation, but an even better solution would be a network of junctions that can be tolerant to moderate damage over time due to the harsh liquid environment. Hence the merits of a percolation network film geometry have been argued for sensor design [203]. Various nanomaterials have thus been fashioned into percolation network film geometries for use in electrical transduction [204, 205, 206].

4. Mechanical Transduction

Chemical reactions always have a steric aspect because molecules (or atoms or ions) take up physical space. Some catalysts and enzymes utilize this for selectivity to only certain substrates. Sensors can make use of the physical space that an analyte species takes to detect its presence. Swelling strain of a porous thin film or surface layer can be detected mechanically, for example through bending of a micro-cantilever [207]. Also, mass changes can be detected due to changes in the resonance frequency of an oscillating crystal or beam. The most common application of this effect is a quartz crystal microbalance (QCM), which can detect miniscule adsorption events and find application in water quality sensing, with some examples listed in Table 13. The mechanical signal is ultimately converted into optical (interference) or electrical (capacitance, oscillator) signals but is discussed separately here because it is not the direct conversion of chemical properties into the same.

Table 13. Mechanical Sensors

Detection Principle	Analyte	Parameters	References
cantilever	redox		[208]
QCM	CN^-	1.0 ... 6.0 ppm @ pH 3...10	[164]
QCM	Pb^{2+}	14 ... 3000 nM	[166]
QCM	NH_4^+	2.2 ... 50 µM	[127]
QCM	biofilm	can detect stages of formation	[209]
QCM	hardness (Ca^{2+}, Mg^{2+})		[39]
QCM	atrazine	0.08 ... 1.5 nM	[188]
QCM	hexachlorobenzene	$> 10^{-12}$ M	[190]

5. Optical Transduction

In optical sensors, changes in the electronic structure of the receptor molecules change the way they interact with photons. Absorbance, fluorescence, luminescence and light scattering are commonly employed optical properties. In the simplest cases, color changes of indicator paper strips can be read out by eye, or with a smartphone camera. Such sensors are cheap and easy to deploy, which is why they are very popular and heavily researched. They are of particular benefit in personal care or healthcare applications, where disposable sensors are desirable, and the ability for an unskilled person to achieve a quick and reliable read-out lowers the threshold to application. Often, only a yes/no answer (safe/unsafe or healthy/sick) is desired in order to simplify decision-making by non-experts. There is a huge field of application for such sensors, and they can drive societal change in remote and (resource)poor settings. However, they are often not able to provide sufficient quantification and cannot operate autonomously: however unskilled, an operator has to manually perform the measurement. Therefore, in addition to 'indicator papers', there is a significant body of work on how to make reliable optical precision sensors. Optoelectronic device fabrication has advanced significantly in recent years, leading to the development of economical and reliable precision light sources and detectors, in addition to fiber optic technologies. A challenge for optical transduction is that deposits, turbidity or interference from other colored species may shift the baseline of the measurement or obstruct the signal. Line of sight to the sample is required, although contact with the sample is not. Remote measurements by satellite, airplane or drone are based on optical methods. Sample interferences can be minimized if the receptor molecules are incorporated into a thin film, the front of which interacts with the sample, while the optical read-out occurs from the back. A chemiresistive read-out is of course simpler and more robust in cases where there is electrical access to the receptor thin film, but sometimes optical access is easier to maintain. Table 14 lists selected work in the area of optical sensing technologies, reflecting the diversity of optical transduction principles as well as different relevant analytes for water quality monitoring. Raman spectroscopy, surface-enhanced Raman spectroscopy (SERS), and surface plasmon resonance (SPR) are all promising techniques that are well-established in the laboratory and that are actively developed for sensing applications in the field. They are not yet considered mainstream, however.

Table 14. Optical Sensors.

Detection Principle	Analyte	Parameters	References
colorimetry / absorbance	pH		[210] [14] [16]
	total hardness		[43] [45] [46] [47]
	free chlorine	DPD	[71] [74] [80] [85]
	free chlorine	other than DPD	[75] [78] [82] [84]
	H_2O_2		[112]
	NO_3^-		[116] [120]
	phosphate	molybdenum blue	[134]
	SO_4^{2-}		[150]
	F^-		[153]

	metal cations	Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+}, Hg^{2+}, Al^{3+}, Pb^{2+}, Ga^{3+}, Ca^{2+}	[152] [156] [162] [170] [173]
chemiluminescence	dissolved oxygen		[58]
	free chlorine		[76] [79] [88] [103]
fluorescence	pH		[18] [19]
	total hardness		[44] [48]
	dissolved oxygen		[60] [61] [62] [63] [64]
	free chlorine		[96] [109]
	NO_2^-, NO_3^-		[118] [126]
	phosphate		[136] [140]
	H_2S		[143]
	SO_3^{2-}		[146]
	SO_4^{2-}		[149]
	F^-		[154]
	CN^-		[165]
	metal cations	Cu^{2+}, Zn^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, Fe^{3+}, Hg^{2+}, Al^{3+}, Pb^{2+}, Mg^{2+}, Ca^{2+}, Ba^{2+}, Cr^{3+}	[155] [157] [163] [174]
	anionic surfactants		[183] [181] [184]
	nitrobenzene		[189]
phosphorescence	benzo(a)pyrene		[191]
Raman	pH	pH 2...9	[17]
surface-enhanced Raman (SERS)	metal cations	Pb^{2+}, Co^{2+}	[161]
Surface Plasmon Resonance (SPR)	pesticides	atrazine, simazine, cyanazine	[186]

Colorimetry is the most common optical detection principle applied in sensing. It involves the evaluation of the presence and concentration of a species by the color of a surface or solution and can be qualitatively or quantitatively performed either manually (by eye, with or without additional aids such as comparator panels), semi-automatic (using instruments such as a colorimeter or spectrophotometer), or automated (specialized sensor optics). It is especially popular for disposable off-line testing (pH-paper, biological test strips such as for pregnancy, diabetes, etc.) since in most cases it requires chemical reagents (which can be immobilized on the test strips), but is very easy to read by eye, or with a regular camera, such as a cellular phone, i.e. without specialized instrumentation. There will always be a big market for these kind of sensors, but they are rather less suitable for reagent-less automated online operation, with the exception of maybe a few naturally coloured species such as permanganate, which are not usually found or desirable in water. Some more common species such as nitrate also have

absorbances in the UV region (e.g. 214 nm and 254 nm), but there is significant interference from other species (e.g. organic matter) present in surface waters. Colorimetric methods are very commonly applied in water quality testing - such as free chlorine determination - using reagent pouches and hand-held spectrophotometric readout units. Flow injection analysis (FIA) methods allow for automation of the measurement process (eliminating operator error and permitting for more frequent testing), but chemical reagents are still required, thus restricting the time frame for autonomous remote operation. In order for colorimetric sensors to gain wider acceptance in online testing, it would be necessary to design reagents that can stay in place in a matrix within the sensor and are re-usable (reversible interaction with the analyte either by reset or by equilibrium).

The second most popular optical detection principle is fluorescence, which not only requires additional reagents (like colorimetry), but also sophisticated instrumentation in order to detect the fluorescence. It has the potential of lower detection limits and better selectivity compared to colorimetry and is sometimes the only available method. Luminescence techniques, such as fluorescence, phosphorescence and chemoluminescence are techniques where the light emission from the sample as the result of a non-thermal stimulus is measured. In the case of fluorescence, light in the UV-vis-NIR range was absorbed to cause an electronic transition. Since polyatomic molecules also have a multitude of vibrational states, it is likely for the molecule to end up in an excited vibrational state within the excited electronic state as the result of that transition. It may subsequently relax into the vibrational ground state within the excited electronic state, before emitting a photon during transition back into the ground electronic state (quite likely into an excited vibrational state within the same). Due to the discrepancy in initial and final vibrational states, the energy of the emitted (fluorescence) photon will be slightly different from the energy of the originally absorbed photon. That complex procedure at the molecular level is known as fluorescence, and unsurprisingly it holds a lot of information about the molecule itself. Hence fluorescence spectroscopy is a useful analytical tool. For the purpose of sensing, however, the most commonly exploited effect is that fluorescence can be prevented by providing alternative (non-radiative) relaxation pathways for the excited molecules ("fluorescence quenching"). The presence of a particular analyte is then proportional to the disappearance of the fluorescence of a probe molecule that had been added for analysis. Chemiluminescence is the emission of a photon during the relaxation of an electronically excited molecule that arrived at the excited state not as the result of absorbing a photon, but rather as the result of a chemical reaction. For that purpose, the analyte solution is mixed with a reagent that can react with the species of interest to give such a molecule in an excited state.

While techniques such as atomic absorption spectroscopy (AAS) and atomic emission spectroscopy (AES) are common in well-equipped chemical labs, they are challenging to use in the field. Portable spectrometers are being developed, but recently a microdischarge technique has been demonstrated that is reagent-less and can even be incorporated into microfluidic devices. A very high voltage is applied to the analyte solution, vapourizing part of it and resulting in atomic emission spectra that can be utilized for chemical analysis [211, 212, 213]. The technique has not yet been fully developed or commercialized.

6. Electrochemical Transduction

Electrochemical sensors are widely used, especially for pH measurement and redox-related parameters (dissolved oxygen, ORP) [214, 215, 216, 217]. The most defining characteristic of electrochemical sensors is the need for a reference electrode. For potentiometric measurements (ORP meters, ion-selective concentration cells such as used in pH meters), it is one of only two electrodes in the circuit since no current flow is required for the measurement. The other electrode in the circuit is the working electrode that generates the potential as a function of analyte species concentration. In order to measure the working potential in a meaningful way, a stable reference potential is required. Most electrochemical measurements utilize three electrodes, however, since they involve a current flow between the working electrode and a counter electrode, while still requiring a potential reference. This requirement is a key distinction between electrochemical transduction and electrical transduction, which is discussed in the next section. Another distinct feature of electrochemical measurements is that they are electrical measurements where the analyte medium (liquid phase, i.e. aqueous solution) is included in the electrical circuit. Pure electrical transduction merely measures a change in the properties of a thin film in contact with the analyte medium, thus not requiring the potential reference. There is a wide range of distinct electrochemical techniques that sensors can be based upon (see Table 15), including potentiometry [14, 218], voltammetry [219, 220, 158, 171], amperometry [221], and electrochemical impedance spectroscopy [176]. Capacitive, or dielectric constant measurements are not strictly electrochemical, but mentioned here because they measure the bulk analyte. They are mostly used in humidity sensors [222, 223, 224].

Table 15. Electrochemical Sensors.

Method	Analyte(s)	Parameters	References
Potentiometry	pH		[14] [20] [22] [21] [225]
	hardness	Ca^{2+}, Mg^{2+}, total	[40] [41]
	ORP		[65] [66] [67] [68]
	NO_3^-	some also NO_2^-	[121] [122] [123]
	phosphate		[133] [135] [137] [138] [141]
	SO_3^{2-}		[148]
	SO_4^{2-}		[151]
	surfactants		[178] [179] [181]
	atrazine		[185]
Voltammetry	free chlorine		[87] [98] [104] [220]
	NO_3^-		[125]
Anodic Stripping Voltammetry	metal cations	Cu^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, As^{3+}, Hg^{2+}	[158] [157] [160]
Amperometry	dissolved oxygen		[56] [57] [58]
	free & residual chlorine		[81] [83] [86] [89] [90] [92] [93] [95] [97] [100] [102] [105] [106] [107] [108]
	NO_3^-		[124]

	phosphate		[139]
	H_2S		[142] [144] [145]
	SO_3^{2-}		[147]
	formaldehyde		[195] [197]
Impedance Spectroscopy	phthalates	2 ppb … 2 ppm	[176]
	triclosan	10^{-12} … 10^{-6} M	[177]
	anionic surfactants	1% by weight	[180]

The need for a reference electrode is the biggest disadvantage of electrochemical sensors [4]. An ideal reference electrode should be stable (no potential drift over time), reusable, compatible with chemical species in its environment (no undesirable side reactions), easy to construct and maintain, and have a low liquid junction potential [226, 227, 228, 229, 230, 231, 232]. The standard hydrogen electrode (SHE, H_2/H^+@Pt), that all electrochemical potentials are referenced to by default, fails most of these criteria. Fortunately, there are several reasonably robust reference electrode systems available that are in common use, in particular the saturated calomel electrode (SCE, Hg/Hg_2Cl_2) and the silver / silver chloride (Ag/AgCl) electrode. Since electrochemical potentials are dependent on the concentrations of the participating species according to the Nernst equation, all these reference electrodes rely on maintaining a constant concentration of the reactants in a particular reversible reaction by incorporating an internal reference solution. This causes complexity in design and fabrication and renders the reference electrode prone to high maintenance and frequent calibration [233].

In conductometry, the electrolytic conductivity of the analyte is measured without focussing on its origin. It can be used to online determine total conductivity of a water sample in order to approximate its hardness (see section 2.2), or offline in order to monitor progress of a titration. It is unusual among the electrochemical techniques in that it does not require a reference electrode, making it a very robust technique. It is included here under electrochemical techniques, however, since the measurement current passes through the analyte.

During voltammetric measurements, a series of potentials (often in form of a linear ramp, but other techniques exist) is applied to a working electrode relative to the reference potential, and the resulting current between the working electrode and a counter electrode is recorded as a function of applied potential [217]. The repeated sweeping of the potential from more positive to more negative (forward scan) and back from more negative to more positive (backward scan) is known as cyclic voltammetry. The forward scan results in the reduction of analyte species at particular potentials, whereas the backward scan reveals oxidation reactions of species at particular potentials. The peaks in measured current occurring at these characteristic potentials can be integrated for quantification (charge = current integrated over time). The locations of these peaks at particular potentials are characteristic of the species being oxidized or reduced. In amperometry, the potential is kept constant, and the change in current is measured over time (chronoamperometry). Often, the measurement is preceded by voltammetric determination of the optimal potential for selective detection of the desired species, which is then used for the amperometric measurement.

7. Electric Transduction

Electric transduction is simple and robust, but it requires direct contact with the analyte. In contrast to electrochemical sensors, chemiresistive sensors have the key advantage of a simpler geometry that eliminates the need for a reference electrode. Field effect geometries (gated or gateless) further serve to improve the sensitivity.

7.1. Chemiresistors

In chemiresistive sensors, the change in conductivity of an active layer is taken to be representative of the presence of an analyte. The nature of the interaction between the analyte and the active layer that affects the conductivity can vary to include physisorption, chemisorption, reactions at grain boundaries, bulk reactions or catalytic reactions. The analyte may cause oxidation or reduction of the active layer or initiate a charge transfer process leading to doping of the active layer. The most common active layers are metal oxide thin films [234, 235, 236, 237, 238], conducting polymer thin films [239, 240, 241, 242], nanocarbon thin films [243, 244, 245, 246, 247, 248, 249, 250, 251, 252], and - recently - 2D materials thin films [253, 254, 255, 256, 257, 258, 259] and colloidal metal nanoparticle films [205, 260]. The earliest chemiresistive sensors were gas phase sensors based on metal oxide films. All other active layer materials have also been studied most extensively with gas phase analytes (gases or vapours), although liquid phase applications are increasingly seen. Table 16 summarizes chemiresistor applications in water quality sensing.

The film thickness of the active layer is directly related to the response time (due to analyte diffusion) and sensitivity (due to limited interaction with the analyte) of the sensor, with a thinner film showing better performance on both counts. Thinner films tend to be mechanically less robust, however, and also have a higher resistance, which results in a lower device current. While currents in the mid-μA range can easily be detected by economical and widely available control electronics, low-μA to nA range currents require shielding and more expensive low-noise electronics. In gas sensors, this problem is commonly avoided by applying high voltages, often 10s of volts. This is not feasible in an aqueous environment. Voltages above 1 V across the sensor film can lead to water splitting, but even potentials starting at about 100 mV could cause undesirable electrochemical side-reactions to take place. DC circuitry should thus be limited to a few mV, although it might be possible to devise a pulsed or AC sensing regime that employs higher voltages while shutting out appreciable side reactions. Hence there are practical lower limits (both mechanical and electrical) to film thickness.

Table 16. Chemiresistive Sensors.

Conductive Layer	Selective Species	Analyte	Parameters	Ref.
Polyaniline	Polyaniline	pH	pH 1…6	[31]
Pd	Pd	pH	100 sec response, 5% per pH, pH 4…10	[28]
TiO$_2$	oxide	pH	pH 2…12	[27]

Graphene	defects	pH	pH 4...10	[26]
CNTs	defects	pH	pH 5...9	[29]
CNTs	Ni nanoparticles	pH	pH 2...10	[30]
hydrogel	hydrogel	pH	pH 6...9	[24]
CNTs	poly(1-aminoanthracene)	pH	pH 2...12	[25]
CNTs	CNTs	Glycerol	100 sec response, 10...50%	[261]
CNTs	CNTs	Free Chlorine	100 sec response, 0.03...8 ppm	[94]
CNTs	Oligoanilines	Free Chlorine	300 sec response, 0.06...60 ppm	[101]
Graphite (pencil line)	Oligoanilines	Free Chlorine	50 sec response, 0.1 ... 60 ppm	[110]
Graphite (pencil line)	Oligoanilines	Free Chlorine	300 sec response, 0.06...60 ppm	[111]
polypyrrole (bare or CNT-doped)	polypyrrole	H_2O_2	< 20 mM	[91]
Cu-MOF (metal-organic framework)	antibodies	atrazine	> 0.01 nM	[187]
CNTs	1-pyrenemethylamine	trinitrotoluene	> 0.01 ppb	[199]
CNTs	DNA	Hg^{2+}	0.1...1 µM	[175]

7.2. Gated Field-Effect Devices (ChemFETs)

Chemical sensors can also be derived from field effect devices. The term "field effect" refers to the perpendicular application of an electric field to a conductive channel. A positive electric field will attract negative charges (i.e. electrons) as charge carriers into the channel and repulse positively charged hole carriers. For a p-type channel (where charges are natively carried by holes), this reduces the number of charge carriers in the channel, detectable as a decreased conductivity. For a n-type channel (where charges are natively carried by electrons), application of a positive electric field would instead increase the number of charge carriers and hence lead to an increased conductivity. Hence field effect devices are resistors that are modulated by electric fields. Commonly this is employed in an electrical switch geometry in the form of a field-effect transistor (FET). It is apparent from the description that this concept easily lends itself to application as a chemical sensor. Indeed, such applications have been known for many decades, with some examples given in Table 17. In a 'normal' FET, the electric field is applied via a gate electrode, which is separated from the conductive channel by a gate dielectric. The conductivity of the channel is probed via two electrodes (fittingly named source and drain) by applying a potential between them and considering the resulting current as the output signal of the switch, the input having been the electrical potential applied to the gate electrode. Since the only current required for the input signal is the charging current of the capacitor formed by the gate electrode,

gate electric and channel, while the channel current can flow continuously for a long time, very large current amplifications are possible using FET devices. That feature is considered a big benefit in chemical sensor applications, although in the end a FET is still simply a modulated resistor, just like a chemiresistor. The distinction comes from the physical separation of the detection of the analyte and the transduction into an electrical signal. In a pure chemiresistor, both processes are collocated. In a ChemFET, the location of analyte recognition is spatially separated from the conductive channel by a dielectric, and the signal is communicated between the two via an electric field [262]. The intermediate case of recognition and conduction being separate functions, but absent a dielectric separation is known as a 'gate-less' device [110, 263], as discussed in the next section.

Table 17. Types of Field-Effect Devices.

Working Principle	Selective Species	Analyte	Parameters	Ref.
organic FET (OFET)	5,5'-bis-(7-dodecyl-9H-fluoren-2-yl)-2,2'-bithiophene (DDFTTF)	pH	pH 3...11	[32]
ion-selective FET (ISFET)	Ta_2O_5	pH	pH 2...8	[34]
	HfO_2	pH	pH 3...10	[33]
	proprietary	pH	pH & alkalinity	[13]
	Al-Si glass	Ca^{2+}		[42]
	Co-polymer	NO_3^-		[117]
extended gate FET (ExFET)	TiO_2:Ru	pH	pH 1...13	[36]
	pentacene	pH	pH 2.5...7	[35]
solution-gate FET (SGFET)	graphene	pH	pH 2...12	[38]
	graphene	pH	pH 4.3...9.4	[37]

Several different mechanisms can be employed in order to translate a chemical signal into an electric field for detection in a ChemFET. It is possible to let ions from the analyte solution take on the role of building up an electric field at the top of the dielectric layer, but for a meaningful signal to arise, some form of ion selectivity has to be implemented (ion-selective FET, or ISFET [262, 264]), typically in the form of an ion-selective membrane for liquid analytes, which can also be implemented for biological samples, and as part of electrochemical sensors. FET technology can be implemented with standard CMOS processing [262, 264] or organic electronics [265, 266]. Another configuration is popular in the case of gas sensing, known as a work function FET (WF-FET) [267]. Here the adsorption of gas molecules at the surface of the gate electrode will modulate its work function and hence the properties of the capacitor formed by it, the dielectric and the channel.

7.3. Gate-less Field-Effect or Chemical Doping

While the ChemFET configuration may be appealing due to its familiarity and ease of integration with existing CMOS technology, it increases the complexity of device fabrication over ordinary chemiresistors, where sensing layer and conducting channel are identical. Recently, devices have been reported in the literature that combine the advantages of both by incorporating the receptor moieties directly onto the conducting channel [263]. Even though the receptors are not themselves contributing to the conductivity of the channel (unlike in traditional chemiresistors), they act as dopants to the conductive channel (much like the electric field in a field effect device) and are modulated in that function by the extent of their interaction with the analyte. Effectively, these switchable dopants act as go-betweens between the analyte and the conductor, rather than the conductor being affected directly. Some uncertainty exists at present whether the effect is purely due to electrostatic gating by switching the charge on the receptor moiety, or whether the switchable doping effect causes a more complex change in the electronic structure of the conduction channel.

The word 'to dope' derives from the Dutch word 'doop' meaning 'thick dipping sauce', so 'doopen' means 'to dip'. In the context of electronic materials, it refers to introducing impurities (dopants) into or onto a material that lead to a change in its electronic properties. Such a change is easily detected, e.g. by measuring the change in resistance of a thin film or low-dimensional structure. The absence or presence of the 'dipping sauce', or dopant, can thus be determined quantitatively with great accuracy, e.g. for use in gas or liquid sensors. A challenge for such a sensor is how to remove the 'dipping sauce' afterwards in order to reuse the device. Here the concept of molecular switches as chemical dopants for thin nanocarbon (or other two-dimensional material) films becomes useful. These molecules can be switched between doping and non-doping states in the presence or absence of a particular analyte. They impart selectivity not only due to their change in doping behavior, but also by physically blocking other potential dopants in the analyte solution from interacting with the conductive film. In effect, they form a 'dipping sauce' that can stay on, because it can be made to change flavor. Based on this concept, disinfectant sensors for drinking water have been demonstrated, which are fabricated from carbon nanotube networks [101] or pencil-drawn films [110, 111] coated in redox-switchable oligoanilines. The concept can also be applied to other analytes (pH, anions, cations, etc. in drinking water), but it becomes necessary to better understand these switchable dopants, and how they work.

The concept of a free chlorine sensor using carbon nanotube (CNT) films and aniline tetramers was demonstrated first [101]. The sensor is based on the idea of using them as redox-active dopant molecules for the CNTs. Conductive random percolation network films of single-walled CNTs are deposited between two electrodes and partially exposed in a microfluidic channel. The conductivity of the CNT films is strongly dependent on whether they have been exposed to molecules that modify their electronic structure due to the formation of charge transfer complexes. This property was exploited in previous sensor designs with the analyte as a dopant (e.g. NH_3) [268], but those sensors suffer from selectivity issues (many different dopants have the same impact on conductivity) and resettability challenges (requiring the physical removal of the analyte dopant e.g. by heating). This new chlorine sensor design differs in that it utilizes permanently attached transducer molecules that are switched between at least two different

stable states in response to an environmental stimulus, such as an oxidant with a redox potential above a certain threshold. The sensor measures the conductivity of a doped CNT film that is exposed to the analyte solution flowing through a microfluidic channel. The transducer molecules stay in place on the CNTs by design, eliminating the previous challenges associated with removal of dopant molecules from the CNT surface and shielding the CNT from non-selective response to other dopants. The sensors can be reset simply by applying an electrochemical potential via an auxiliary electrode [101]. The reagent-free device can be interfaced for controlled analyte delivery and data analysis.

More recently, this design was generalized in terms of the substrate used [110, 111], in terms of exploring different redox active molecules [269], and in terms of expanding the range of analytes that can be detected. Pencil-drawn lines (several 100 nm thick) are an affordable (from IKEA pencils) and reproducible way (from 9B soft pencils) of drawing networks of graphitic flakes [111]. Very thin films of graphene-like carbon can significantly increase the sensitivity of the devices, vastly shorten the response time and eliminate the need to reset the sensors. It is also possible to utilize the transient change in pH from the reduction of HOCl to HCl as a way to quantify free chlorine concentrations and improve the selectivity to free chlorine over other oxidants [110]. Chlorination of the oligonanilines is only a concern at very low pH and extremely high free chlorine concentrations [110]. The sensitivity of the chlorinated oligoaniline sensors is even higher than that of the original devices. Hence the question arises whether other redox-active molecules can also be utilized in these sensors. It was found that not only a range of molecules is suitable for use in these redox sensors [269], but it is even possible to distinguish and quantify different disinfectants. The concept of switching dopants can be generalized.

8. Conclusion

Starting from a discussion of relevant water quality parameters, a range of chemical sensors were introduced based on a number of different detection principles. While some parameters (such as pH) are easily detected using robust online methods, other important parameters are harder to quantify. All detection methods have their strengths and their shortcomings. Optical sensors can be easy to use manually, and even in some cases be developed for remote sensing, but they usually rely on the addition of reagents, which requires off-line sampling and in many cases manual intervention. Flow-injection analysis methods have been developed to counter this problem, but they still consume reagents. Electrochemical sensors are only ever as good as the reference electrode employed, which is their weakest spot for long-term operation. Electrical sensors are very developed for gas sensing, but are often still lacking robustness for liquid environments, and are not yet well developed for many liquid-phase analytes. Several new techniques are on the horizon, and the awareness of the importance of water quality monitoring has risen in the community. Simultaneously, technology and data processing algorithms are being developed for establishment of sensor networks, and comprehensive analysis and application of the resulting data [270, 271].

Acknowledgments

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