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Review

# Chlorination in the pandemic times: The current state of the art for monitoring chlorine residual in water and chlorine exposure in air



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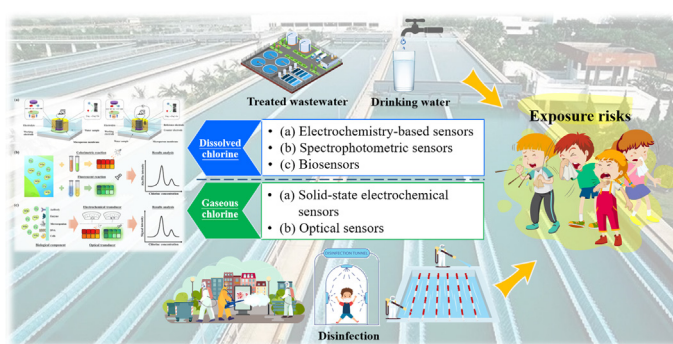
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HIGHLIGHTS

- Electrochemical-based chlorine sensors require better selectivity and stability.
- Microfluidics and 3D printing enable low-cost and sensitive sensor development.
- Membrane-based configurations can enhance the selectivity of optical sensors.
- Organic compound interferences should be considered in chlorine sensor development.

GRAPHICAL ABSTRACT



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ABSTRACT

During the COVID-19 pandemic, the use of chlorine-based disinfectants has surged due to their excellent performance and cost-effectiveness in intercepting the spread of the virus and bacteria in water and air. Many authorities have demanded strict chlorine dosage for disinfection to ensure sufficient chlorine residual for inactivating viruses and bacteria while not posing harmful effects to humans as well as the environment. Reliable chlorine sensing techniques have therefore become the keys to ensure a balance between chlorine disinfection efficiency and disinfection safety. Up to now, there is still a lack of comprehensive review that collates and appraises the recently available techniques from a practical point of view. In this work, we intend to present a detailed overview of the recent advances in monitoring chlorine in both dissolved and gaseous forms aiming to present valuable information in terms of method accuracy, sensitivity, stability, reliability, and applicability, which in turn guides future sensor development. Data on the analytical performance of different techniques and environmental impacts associated with the dominated chemical-based techniques are thus discussed. Finally, this study concludes with highlights of gaps in knowledge and trends for future chlorine sensing development. Due to the increasing use of chlorine in disinfection and chemical synthesis, we believe the information present in this review is a relevant and timely resource for the water treatment industry, healthcare sector, and environmental organizations.

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## 1. Introduction

As the COVID-19 has raged worldwide, all countries' medical and health systems are facing severe challenges. Strict disinfection has been an effective tactic to curb the spread of the virus and is predicted to become the top priority of the normalized prevention and control of the epidemic in the long term. Chlorine and its derivatives are the most commonly used disinfectants that have been widely applied on various occasions, especially in drinking water treatment and locality disinfection.

In drinking water treatment processes, disinfection is the last but crucial step, in which disinfectants are added to kill any parasites, bacteria, and viruses and prevent the water from being recontaminated during its transportation through pipelines. To date, among the various disinfection methods (e.g., chlorination, ozonation, and UV disinfection), chlorine is still the primary disinfectant utilized by the vast majority of water treatment facilities worldwide to safeguard drinking water quality (AWWA, 2018; Ren and Chen, 2021). Besides, chlorine is also commonly used in the wastewater treatment process to inactivate pathogenic bacteria/viruses before discharge. As a means to stop the COVID-19 pandemic, many authorities have changed disinfection protocols to ensure free chlorine residual concentration in wastewater disinfection greater than  $6.5 \text{ mg L}^{-1}$  (Giné-Garriga et al., 2021; Wang et al., 2020), despite the fact that a free chlorine level of  $\sim 0.5 \text{ mg L}^{-1}$  is recommended by the guideline (WHO, 2017). High chlorine dose not only enhances the generation of harmful disinfection by-products (Richardson et al., 2007), but also aggravates corrosion and causes unpleasant odours, leading to a deterioration of water quality as well as posing environmental risks by facilitating the bacterial acquisition of antimicrobial resistance (Hu et al., 2021; Lin et al., 2018; Lu and Guo, 2021; Zhang et al., 2022). In this regard, residual chlorine needs to be accurately and timely monitored to ensure the desired level is achieved. Furthermore, in recent years, rapid population growth in combination with climate change has raised concerns on water availability (Antwi et al., 2022; Rocha et al., 2020). To address this situation, water security strategies developed in many countries have considered purified recycled wastewater as a reliable water source to improve water supply capacity, especially in large cities (Gil-Meseguer et al., 2019; Radcliffe, 2010; Radcliffe, 2022; Rizzo et al., 2020). Under such a trend, demands for reliable water disinfection monitoring techniques can be expected to increase in the foreseeable future.

Chlorine and its derivatives are also dominated disinfectants in the disinfection of public spaces such as hospitals, shopping malls, office buildings, homes and outdoors, safeguarding public health, especially in the current pandemic period. While on the other hand, as toxic gaseous compounds, chlorine and its primary disinfection derivative, hypochlorous acid, can damage skin, eyes and respiratory systems with high-level, short-term contact or even low-level, long-term contact (Reis et al., 2009; Winder, 2001). The permissible exposure to gaseous chlorine ( $\text{Cl}_2$ ) for the time-weighted average (TWA) concentration and the short-term exposure limit (STEL) in the U.S. and EU are 0.5 ppm and 1.0 ppm, respectively

(HSE, 2018; Ku, 1991). There have been concerns that large-area and high-intensity water and public areas disinfection bring potential  $\text{Cl}_2/\text{HClO}$  exposure risks to people engaged in related activities (Chen, 2020; Dewey et al., 2022; Ha et al., 2021; Mattila et al., 2020; Yasseen Iii et al., 2021; Govier and Coulson, 2018; Hoyle and Svendsen, 2016). The widespread use of such disinfectants in workplaces and public places and the attendant adverse effects posed by excessive use have triggered the need to develop in situ sensing systems for exposure detection.

To address the above-mentioned issues, new monitoring technique developments are imperative and needed to meet the requirement of great accuracy, high sensitivity and stability, and broad applicability. Up to now, although extensive research has led to significant advances in chlorine detection and monitoring techniques, there is still a lack of comprehensive review that collates and appraises the recently available techniques from a practical point of view. Therefore, this study systematically reviews the advances in monitoring chlorine in both dissolved and gaseous forms. Firstly, the general aspects of the chlorine disinfection mechanism and its potential health risks are presented. Subsequently, available chlorine monitoring techniques are categorized, specified, and discussed with respect to their sensing mechanisms, analytical performance and potential environmental impacts. Finally, we include a brief discussion focused on the gaps in knowledge and trends for future perspectives of chlorine sensing development. With the increasing demand for real-time reliable chlorine control in various disinfection scenarios, we believe this review is a relevant and timely resource for the water treatment industry, healthcare sector, and environmental organizations.

## 2. Mechanisms of chlorine disinfection and exposure risks

Chlorination is the process of dosing water with chlorine or chlorine compounds for disinfection and three-step chlorination is usually used to increase disinfection efficiency and reduce by-product formation and toxicity (Li et al., 2017c; Li et al., 2017d). The two common types of chlorine applied in water treatment are gaseous chlorine and liquid sodium hypochlorite due to their relatively low-cost and high reliability. As shown in Fig. 1, chlorine disinfection is a vital step in the water treatment process, whose effectiveness highly depends on the reaction between the added chlorine and water to produce  $\text{HClO}$  (Eqs. (1) and (2)):



The disinfection mechanism of chlorination is based on the destruction of the chemical structure of enzymes, which are fundamental elements for bacteria and viruses to live and develop. Both  $\text{HClO}$  and  $\text{ClO}^-$  are capable of oxidation, with the former having much higher oxidative activity. Besides, due to the bacteria being negatively charged, it is generally thought that they are primarily disinfected by the action of  $\text{HClO}$ .  $\text{HClO}$  can spread

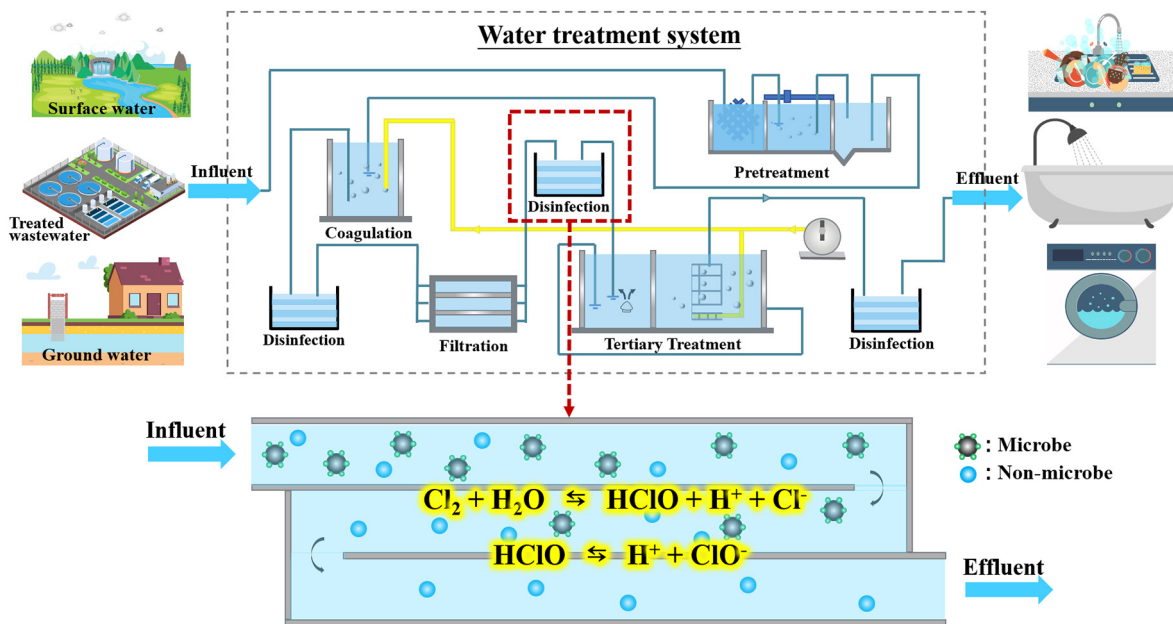


Fig. 1. Schematic diagram of chlorine disinfection process and mechanism in water.

to the surface of the bacteria and penetrate the cell wall to the inside of the bacteria, damaging the bacterial enzyme system. The fraction concentration of HClO and ClO<sup>-</sup> is related to water temperature and pH, specifically, the lower the pH (e.g., pH of 4–7), the more HClO, then the stronger the disinfection efficiency.

Usually, a residual can be produced by adding an extra dosage that is typically controlled within an operational range of 0.8 to 2.2 mg L<sup>-1</sup> (Black & Veatch Corporation, 2009), which can exert continuous disinfection effects to support secondary treatment and inhibit the growth of bio-fouling and recontamination in the distribution system. While applying high chlorine residual can enhance disinfection effectiveness, excessively high concentration of chlorine present in the treated water can lead to bad odour, high carcinogenic disinfection by-products formation, faster corrosion rates for the distribution system and potential health risks (Cantor et al., 2003; Lin et al., 2018; Price and Douglass, 2008; Wang et al., 2018a).

Amid the COVID-19 pandemic, NaClO has also been widely used for curbing the transmission of viruses through the air. When NaClO solution is sprayed into the air, it rapidly reacts with the atmospheric water vapour to form HClO, which is the primary acting compound in the disinfection process. For COVID-19 disinfection, the European Centre for Disease Prevention and Control recommended the use of 0.05% NaClO for surface cleaning (European CDC, 2020). However, an excessive amount of disinfectants was always applied as preventive measures against any potential spreads. For example, disinfection tunnels were installed in many residential places where disinfectants were continuous spraying and residents were asked to walk through. Such a protocol raised the concern of Cl<sub>2</sub>/HClO exposure within public health authorities (Chatterjee, 2020). Although NaClO is very effective, economical, and wide-used in various disinfection scenarios, the attendant risks of accidental and intentional exposures to high concentration Cl<sub>2</sub>/HClO via direct contact and inhalation can irritate skin, eyes, the upper respiratory tract, and lungs (García-Ávila

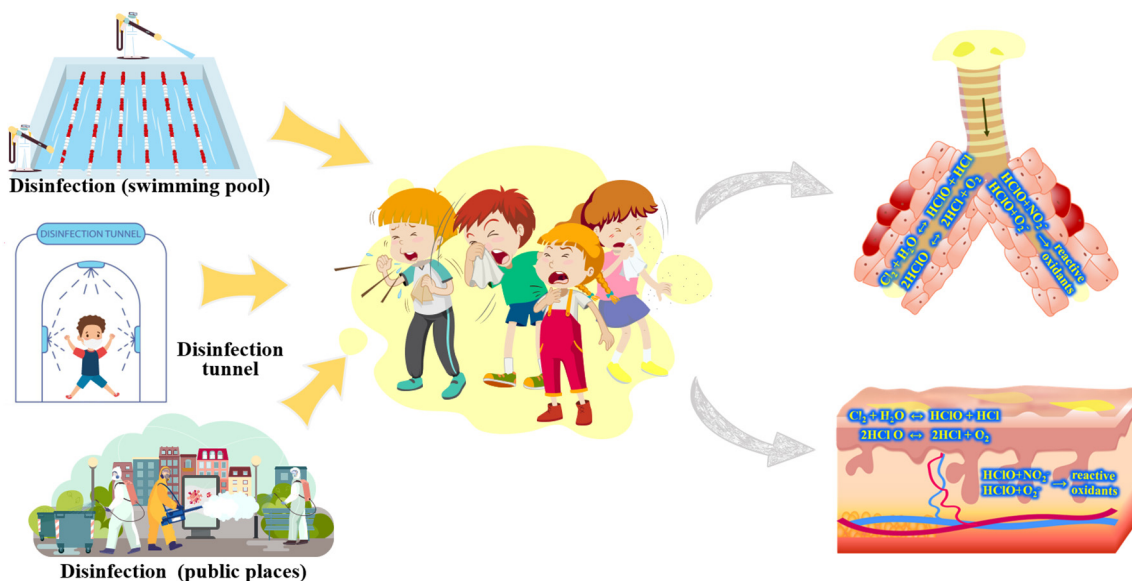


Fig. 2. Schematic diagram of the mechanism of chlorine exposure risks on human body.

et al., 2020) (Fig. 2). In addition, large scale and excessive use of highly concentrated NaClO could also induce adverse impacts on atmospheric chemistry equilibrium (Parveen et al., 2022; Wong et al., 2017). In this regard, gaseous chlorine monitoring techniques could be effective tools to acquire accurate and insightful exposure information to safeguard the health and safety of people as well as to investigate the environmental impact of using such a chemical.

### 3. Existing dissolved chlorine monitoring techniques

To date, the wide application of chlorine in water treatment has stimulated the development of various sensing techniques for its measurement. According to the difference in detection mechanisms, dissolved chlorine sensing techniques can be classified into three major categories, i.e., electrochemistry-based sensors (amperometry and ion-selective-electrodes (ISEs)), spectrophotometric sensors (colourimetry and fluorescence), and biosensors.

#### 3.1. Electrochemistry-based sensors

The sensing principle of an electrochemistry-based chlorine sensor involves detecting the change in an electrical signal (e.g., current, potential, or resistance) from chlorine adsorption by different sensing materials. The first type of most commonly used electrochemistry-based detection method for chlorine is amperometry, i.e., measuring the current changes. Detection was achieved by either using bared electrodes (Canelli, 1980; Kato et al., 2017; Marinenko et al., 1976; Matuszewski and Trojanowicz, 1988; Murata et al., 2008) or integrating electrodes with microporous membranes (Hach Cooperation, 2019; ECD Inc., 2015; Turtle Tough Inc., 2019) (Table 1).

Based on the above-mentioned principle, a typical flow-through analyzer using bared electrodes was demonstrated by Marinenko (Marinenko et al., 1976). The system employed a platinum microelectrode as the working electrode and a calomel electrode as the reference electrode. Potassium iodide solution was injected into the tested stream to consume all chlorine residual and yield iodine. A constant voltage was applied on the working electrode, where iodine was then converted back to iodide. The current produced during the reduction of the yielded iodine was proportional to the iodine concentration, and thus, to that of chlorine. The device was also able to perform self-calibration by coulometrically oxidizing a known amount of iodide to iodine in a blank sample then measuring the reduction current in the detector. The device had a linear range of 10–100  $\mu\text{g L}^{-1}$  with a detection limit of 1  $\mu\text{g L}^{-1}$ . To avoid using chemicals, more recently, Kato

(Kato et al., 2017) reported a low-cost all-solid-state residual chlorine sensor that used commercially available stainless steel in place of the commonly used noble metals. The device exhibited the same performance when compared to that of using noble metals. The discovery suggested that stainless steel could be an applicable electrode material in chlorine sensing. Compared to other chlorine sensors, bared electrode-based sensors offer the most straightforward configuration and cost-effective way to achieve field-based sensing. The major problem comes from the interference induced by the presence of other oxidants, electrode passivation, and even pH and DO fluctuations (Olivé-Monllau et al., 2009).

To overcome the interference challenges, most commercialized electrochemistry-based chlorine sensors adopt microporous hydrophobic membranes as a barrier to improve selectivity (Hach Cooperation, 2019; ECD Inc., 2015; Turtle Tough Inc., 2019). A two-electrode membrane coated sensor was first developed by Morrow Jams (Morrow, 1978), which contained a microporous hydrophobic membrane, a working electrode, a counter electrode and an electrolyte. A typical two-electrode sensor structure is illustrated in Fig. 3a, and its measurement principle is as follows. When the residual chlorine (usually HClO) in the water sample diffuses to the working electrode through the microporous hydrophobic membrane, it undergoes a reduction reaction with the working electrode, while the surface of the counter electrode is continuously oxidized to replenish electrons to create a current that can be measured. According to Faraday's law and Fick's law of diffusion, due to the difference in the concentration of residual chlorine in the water sample and that in the electrolyte, the residual chlorine in the water sample can continuously diffuse to the working electrode through the permeable membrane. Therefore, the generated current caused by constantly electrons replenishment is directly proportional to the diffusion rate of residual chlorine, which in turn is proportional to the residual chlorine concentration in the water sample. The technique possesses distinctive advantages of simple configuration, easy operation, and low cost. Unfortunately, with the increase of the residual chlorine concentration and the extension of the detection time, the continuous redox reaction reduces the concentration of HClO on the electrode surface and accumulates the reaction products. Consequently, the potential of the working electrode cannot be maintained constant, resulting in the instability of the signal output, which ultimately affects the measurement accuracy. To ensure correct measurement results, former investigators have induced periodically calibration to compensate for the signal drift, which, on the other hand, increases the operational costs. Another means to overcome this challenge was to add a reference electrode to the electrochemical system to form a three-electrode setup for the residual chlorine detection

**Table 1**

Analytical performance of electrochemistry-based sensors for free chlorine detection.

Method	Reagent	Linear range ( $\text{mg L}^{-1}$ )	LOD ( $\text{mg L}^{-1}$ )	Error	Known interferences	Ref.
Electrochemical (Amperometry)	KI	0.01–0.1	0.001	ND <sup>a</sup>	Oxidant	(Marinenko et al., 1976)
Electrochemical (Amperometry)	None	0.10–3.0	0.10	<6.0%	Bromine-, triiodide ion-, oxidants	(Canelli, 1980)
Electrochemical (Voltammetry)	None	0.10–2.0	0.0083	2.56%	Ion strength Chloride ion	(Murata et al., 2008)
Electrochemical (Amperometry)	None	0.002–0.8	0.002	ND	Oxidants Chloramines	(Matuszewski and Trojanowicz, 1988)
Electrochemical (Amperometry)	None	0.10–1.0	0.10	20%	pH DO Oxidants Chloramines	(Kato et al., 2017)
Electrochemical (Amperometry)	None	0.01–200	0.01	ND	pH DO Chloramines	(Turtle Tough Inc., 2019)
Electrochemical (Amperometry)	None	0–20	0.03	3%	Chloramines Sediment-deposits	(Hach Cooperation, 2019)
Electrochemical (Amperometry)	None	0.01–5.0	0.01	ND	pH DO Chloramines	(ECD Inc., 2015)

<sup>a</sup> ND: not determined in the reference.

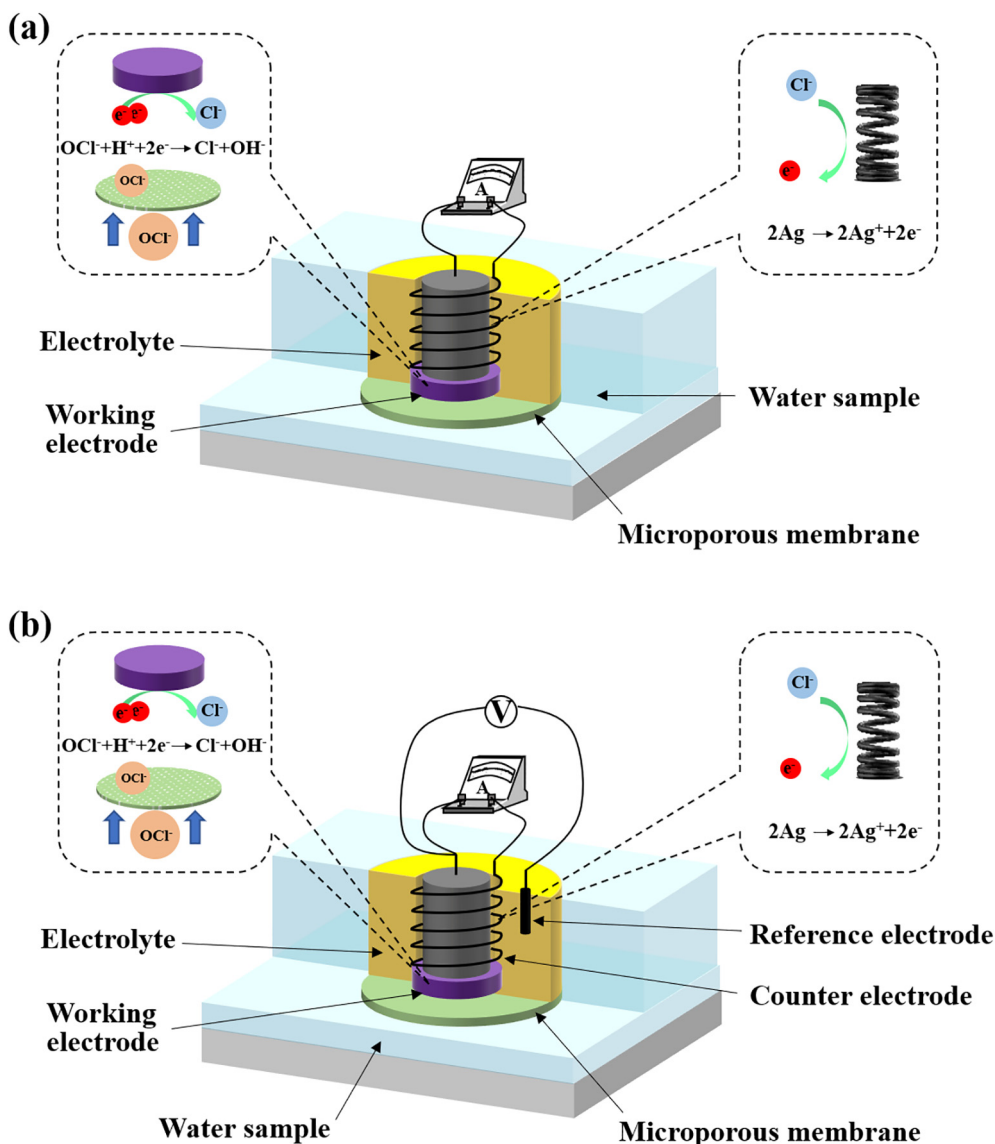


Fig. 3. Typical structure of (a) two-electrode residual chlorine sensor, and (b) three-electrode residual chlorine sensor.

(Fig. 3b). The selected reference electrode has a standard known constant potential and can be used as the reference potential of the working electrode, so it can maintain the potential difference between the working electrode and the reference electrode stabilized by continuously adjusting the applied voltage, thereby improving the measurement accuracy. The most commonly used reference electrode for chlorine monitoring is the silver/silver chloride electrode (Del Campo et al., 2005; Qin et al., 2015). Compared with the two-electrode system, the residual chlorine sensor based on the three-electrode system has the advantages of high measurement accuracy, long working life and infrequent calibration. Along with the developments in material science, some recent studies also tried to integrate microfluidic (Mehta et al., 2006), graphite (Kumar et al., 2017; Xiong et al., 2018), and different nanostructures (Qin et al., 2015; Zhou et al., 2020a) to achieve highly sensitive and selective chlorine residual sensing. More tests of robustness and stability are needed before they can be put into real field-based applications (Qin et al., 2015).

The ion-selective-electrodes (ISEs) are the second most commonly used electrochemistry-based sensors. The detection mechanism of ISEs is based on directly measuring the potential produced from the interaction of the residual chlorine and the electrode coating layers. The ISEs provide inherent advantages for field-based chlorine residual measurement, including chemical-free, equipment miniaturization, easy operation, and low cost. A

variety of ISEs has been developed for chlorine determination to date (Dai et al., 2016; Ishibashi et al., 1988; Sakai et al., 1998; Synnot and Smith, 1986). The key technique in ISE lies in developing the selective coated layer. A typical selective coated membrane was demonstrated by Sakai et al. (1998), who created a residual chlorine selective electrode based on the  $\text{PbS}/\text{Ag}_2\text{S}$  membrane. Through integration with flow-through analysis, the proposed electrode can achieve a linear range of 0.1 to  $1 \text{ mg L}^{-1}$ , with a detection limit of  $0.01 \text{ mg L}^{-1}$ . Other transition metal sulphides, which were added to the  $\text{Pb}(\text{II})$ -ISE sensing membrane, also demonstrated a similar response to residual chlorine. However,  $\text{Cu}(\text{II})$  interfered with the measurement and must be eliminated from the sample before the determination (Sakai et al., 1998). The ISE proposed by Dai et al. (2016) is the most selective ISE method to date. The electrode was fabricated by coating a glassy carbon electrode with a polyvinyl chloride coating that contains zephiran chloride. The high selectivity was achieved by introducing ferrocene as the phase transfer catalyst and ion-to-electron transducer in the membrane coating. The lack of sensitivity caused by the memory effect of the electrode and the diffusion of water to the coating interface forming a water layer was the major problem found in their investigation. Nevertheless, with a good response range from 1 to  $20 \text{ mg L}^{-1}$ , the ISE showed great potential for in situ determination of total chlorine residual with relatively high concentration.

Due to the unstable characteristics of hypochlorite ions, other approaches measured chloride ions rather than hypochlorite ions to achieve chlorine residual quantification. These approaches were realized by adding a preliminary step to convert hypochlorite ions to chloride ions. The chloride ions were subsequently measured using a chloride ion-selective electrode (Brown and Parker, 1979; Ishibashi et al., 1988; Synnot and Smith, 1986). Despite these changes, poor sensitivity and stability are two challenges that ISE-based systems still need to overcome (Dai et al., 2016; Liu et al., 2018).

### 3.2. Spectrophotometric sensors

Spectrophotometry is the most widely used sensing technique for the determination of chlorine. It offers distinct features that can meet the stringent requirements for chlorine sensing, such as high selectivity, great sensitivity, simplicity, and easy automation (summarized in Table 2). Colourimetry spectrophotometry and fluorescence spectrophotometry are the two main types of residual chlorine analysis methods, and their detection principles are present in Fig. 4.

#### 3.2.1. Colourimetry

Of all the spectrophotometric techniques, colourimetry is the most common method currently used in chlorine detection. This method quantifies the residual chlorine concentration based on Beer's Law. A chromogenic agent is used to react with the analyte and produce a colour change that is proportional to the analyte concentration (Johnson and Overby, 1969). Palin developed the first chromogenic agent with high selectivity to residual chlorine (Palin, 1957). After improvements in both the reagent stability and test procedures (Palin, 1977; Palin, 1980; Palin, 1983), this method, named N, N-diethyl-p-phenylenediamine (DPD) method, has been adopted as the standard method for chlorine residual measurement (Baird, 2017). Although another chromogenic agent, o-dianisidine, has shown good sensitivity in chlorine determination, some recent investigations revealed that the reagent was unstable (Blecher and Glassman, 1962; Washko and Rice, 1961) and only able to achieve a narrow linear range (0.05–1.3 mg L<sup>-1</sup> Cl<sub>2</sub>) (Icardo et al., 2001a; Saad et al., 2005). The DPD method is still the most reliable chlorine residual measurement method and is employed in most colourimetric-based chlorine systems (Carlsson et al., 1999; Gordon et al., 1991; Harp, 2002; Moberg and Karlberg, 2000; Wilson et al., 2019).

The field-based applications of colourimetric chlorine detection are either manually conducted using a test kit (Baird, 2017) or integrated with an automated flow analysis system (FAS) (Leggett et al., 1982). With the

increasing demand for online monitoring, colourimetric FASs have become more and more popular. A typical procedure of colourimetric FAS for chlorine detection is automated mixing of the DPD reagent and free chlorine-containing samples (Jin et al., 2004; Leggett et al., 1983; Verma et al., 1992). Such systems usually have poor accuracy due to strong interference by the presence of oxidizing ions. To improve selectivity, Motomizu and Yoden (Motomizu and Yoden, 1992) introduced a tubular porous membrane as a physical barrier for halogen measurements. Later researchers adopted this assembly and modified it with a longer channel or pre-concentration time to enhance sensitivity (Icardo et al., 2001c; Mesquita and Rangel, 2005). To reduce the cost, the most recent work by Xiong et al. (2017a) used a LED light source to replace the ordinary light source and integrated a lab-on-valve manifold to achieve a wide linear range (10–400 µg L<sup>-1</sup>) and low detection limit (3.5 µg L<sup>-1</sup>). Despite significant improvements in detection performance using the above-mentioned methods, the quantification is still based on the absolute colourimetric measurement, which can only be determined for one discrete sample at a time, thus, is unsuitable for real-time monitoring applications. Excessive chemical consumption and bulky configuration are other disadvantages of such approaches. To achieve real-time monitoring while avoiding large chemical consumption, Zhao's group proposed a uniquely configured membrane-based colourimetric FAS with a new analytical principle (Zhou et al., 2021). In this method, the real-time concentration was determined based on the DPD-chlorine colourimetric reaction-controlled membrane transport process that enables the chlorine concentration to be determined via multiple measurement data points to greatly enhance the accuracy and reliability.

To date, most of the available commercialized online colourimetric chlorine monitoring systems still employ the simple manifold to directly mix the water sample with the DPD chromogenic reagent (Harvey, 2000; Helbling and VanBriesen, 2008; Malkov et al., 2009). However, the lack of a prevention mechanism makes these systems less capable of encountering interferences from sample colour, turbidity, and other oxidants commonly found in actual samples (Helbling and VanBriesen, 2008). In this regard, the membrane-based chlorine analytical system based on colourimetric reaction-controlled membrane transport process could be a useful tool for online free chlorine monitoring applications (Zhou et al., 2021).

#### 3.2.2. Fluorescence

Fluorescent techniques generally exhibit greater sensitivity than colourimetric methods due to the common use of photomultiplier tubes to amplify the emission effects. The principle of fluorescence-based chlorine detection is the quenching effect of fluorescent compounds when

**Table 2**  
Analytical performance of spectrophotometric sensors for free chlorine detection.

Method	Reagent	Linear range (mg L <sup>-1</sup> )	LOD (mg L <sup>-1</sup> )	Error	Known interferences	Ref.
Colourimetric	4-Nitrophenylhydrazine	0.05–10	0.03	0.9%	Chlorine-dioxide Chloramines Oxidant ions Sample colour	(Verma et al., 1992)
Colourimetric	DPD	0.10–5.0	0.05	2–3%	Nitrite Oxidant ions Sample colour	(Jin et al., 2004)
Colourimetric	DPD	0.15–1.5	0.15	ND <sup>a</sup>	Ammonium Nitrate Nitrite Oxidant ions Sample colour	(Motomizu and Yoden, 1992)
Colourimetric	o-Dianisidine	0.05–1.30	0.05	1.5%	ND	(Icardo et al., 2001c)
Colourimetric	DPD	0.01–0.4	0.0035	<5%	Oxidant ions Sample colour	(Xiong et al., 2017a)
Colourimetric	DPD	0.04–6.07	0.015	3.2%	Interference-free	(Zhou et al., 2021)
Fluorescence	Nitrogen and sulfur co-doped carbon dots	0–5.2	0.0005	<3.8%	Ferric ions	(Xue et al., 2015)
Fluorescence	Protein-stabilized gold nanoclusters	0.035–56	0.035	<4.2%	Cupric ion	(Xiong et al., 2015)
Fluorescence	Amino-functionalized metal-organic frameworks	0.0035–1.0	0.0028	ND	ND	(Lu et al., 2016)

<sup>a</sup> ND: not determined in the reference.

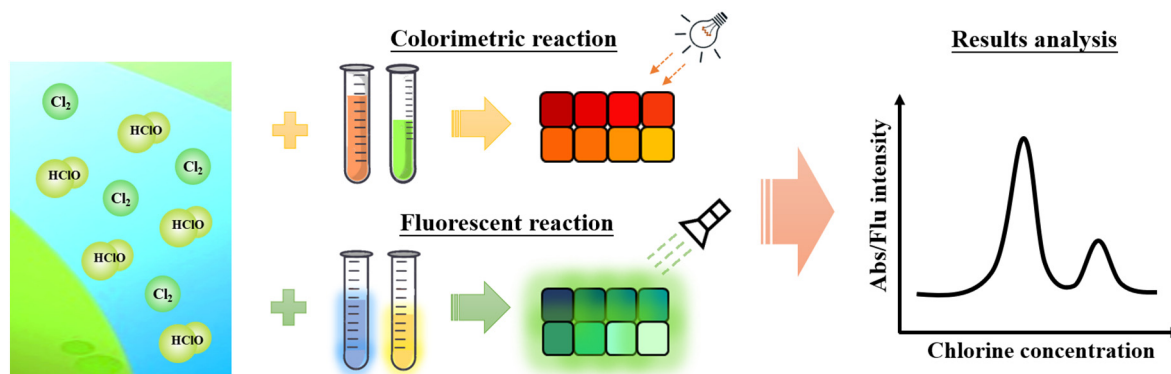


Fig. 4. Schematic diagram of colourimetry and fluorescence spectrophotometry sensors.

chlorine is present. The primary application of the fluorescence-based methods was initially in health science due to its superior sensitivity (at ppt-level). Typical fluorescent chlorine detections were achieved by modifying common fluorophores such as fluorescein (Shepherd et al., 2007), rhodamines (Kenmoku et al., 2007), and BODIPY with HClO reactive groups (Sun et al., 2008). However, these organic fluorophores have intrinsic drawbacks, including narrow excitation spectra, broad emission band, and low photobleaching resistance, which lead to insufficient stability (Xu and Bakker, 2007). These limitations were overcome by later introducing semiconductor quantum dots, which have been applied for chlorine determination in water samples (Yan et al., 2010; Zhang and Johnson, 2009). Several studies based on carbon nanodots have been reported (Ding et al., 2016; Guo et al., 2017; Lin et al., 2016; Xue et al., 2015). Of these, Zhao's group (Xue et al., 2015) demonstrated the best performance using a facile and green fluorescence probe fabricated from nitrogen and sulfur co-doped carbon dots, with a wide linear (0.01 to 100  $\mu\text{M}$ ) range and a detection limit of 5 nM. The use of other fluorophores, such as protein-stabilized gold nanoclusters (Xiong et al., 2015) and amino-functionalized metal-organic frameworks (Lu et al., 2016) also exhibited great performance. However, to the best of our knowledge, none of them was validated for environmental field-based applications. This could be due to most of these fluorophores being susceptible to various interferences and their unstable nature (Lu et al., 2016).

### 3.3. Biosensors

Biosensors measure the chlorine residual according to a specific biological event that occurs in the biological component when chlorine is present. The biological event induces physical or chemical changes that can be converted to a measurable signal, which is proportional to the chlorine concentration (Fig. 5).

To date, most biosensors are used for hypochlorous acid measurement in biological specimens (Chen et al., 2017; Xiao et al., 2017; Zhang et al., 2018), such as cells and tissues, and only a few have been applied for

chlorine detection in environmental systems (Karyakin et al., 1994; Salazar et al., 2015; Shim et al., 2010; Soldatkin et al., 1997). Among these, Soldatkin et al. (1997) fabricated a biosensor using a new enzyme developed by cross-linking acetylcholinesterase with bovine serum albumin in saturated glutaraldehyde vapour for hypochlorite species. The sensor was successfully used to detect free chlorine in water samples, with a sensitivity of 0.75  $\text{mg L}^{-1}$  as hypochlorite in the pH range 6.0–6.5. The investigation also suggested that the sensitivity could be further improved by increasing acetylcholine concentration and the inhibition time. Another study conducted by Karyakin et al. (1994) revealed that Prussian Blue (PB) exhibited catalytic performance and behaved like peroxidase, and could therefore be an artificial peroxidase in biosensors. Soon afterwards, Shim et al. (2010) incorporated PB into a carbon nanotube network and proposed a carbon nanotube/PB biosensor. The sensor exhibited a linear response behaviour in the range of 0.05–2.00  $\text{mg L}^{-1}$  for chlorine. Similar work was carried out recently by Salazar et al. (2015), who used glassy carbon as the doping electrode and applied benzethonium to assist the electro-deposition of PB. This sensor presented the best performance among all biosensors for chlorine detection in environmental samples to date, with a wide linear range from 0.009 to 10 ppm and reproducibility of 4.2%.

However, the response of biosensors relies on the enzyme triggered biological events, which are affected by the presence of dissolved oxygen, temperature, pH, and other oxidants (Zhang et al., 2018). For field-based applications in environmental systems where samples tend to be more complex, many challenges still need to be overcome, particularly in enhancing sensor stability. These might be why recent efforts made on chlorine detection by biosensors were focused on biological specimens in which testing conditions can be greatly controlled.

### 4. Existing gaseous chlorine exposure monitoring methods

The method developed by the Occupational Safety and Health Administration, United States, is the standard method for chlorine exposure evaluation in workplaces. This method determines the exposure level through

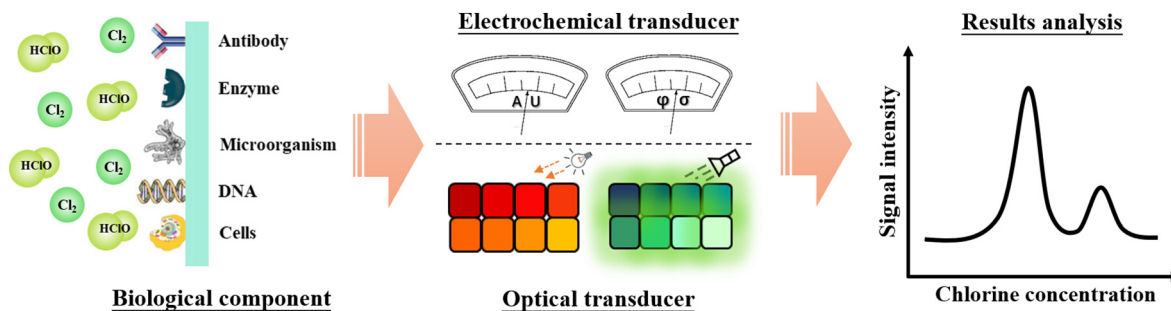


Fig. 5. Schematic diagram of biosensors.



in situ collection of the gas samples using a sulfamic acid solution. Subsequently, the samples are analyzed by a residual chlorine ion-specific electrode (Ku, 1991; White and Martin, 2010). Although widely used, this method is an indirect method that involves tedious and complicated procedures and is challenging to apply for real-time in situ chlorine monitoring. Over the past decades, extensive efforts have been dedicated to developing two major categories of gaseous chlorine sensors, i.e., solid-state electrochemical sensors and optical sensors.

#### 4.1. Solid-state electrochemical sensors

Two types of solid-state electrochemical sensors have been developed for gaseous chlorine detection, they are potentiometric sensors and conductometric sensors. Their measurement principle is similar to that of the electrochemical sensors in Section 3.1. The only difference is that the liquid electrolyte is replaced by a solid electrolyte, making the sensor more portable and flexible for chlorine exposure monitoring.

A typical potentiometric gaseous chlorine sensor consists of chloride salt as a solid electrolyte, ruthenium oxide as a sensing electrode, and Ag–AgCl coupling as the reference electrode. Under elevated temperatures, the gaseous chlorine is converted to chloride on the sensing electrode. A quantified relationship is established between the gaseous chlorine concentration present and the electromotive force changes (Aono et al., 1997; Pelloux and Gondran, 1999). To date, different solid electrolytes have been explored for gaseous chlorine sensor development, including SrCl<sub>2</sub> (Pelloux et al., 1985; Pelloux and Gondran, 1999), BaCl<sub>2</sub> (Aono et al., 1997; Yan et al., 1995a), and PbCl<sub>2</sub> (Aono et al., 1997; Niizeki and Shibata, 1998). A wide detection range (1–10<sup>6</sup> mg L<sup>-1</sup>) was achieved by Pelloux et al. (1985) using SrCl<sub>2</sub>-KCl as the solid electrolyte under an operational temperature from 120 to 400 °C. However, the technique was found impractical when applied in a moist environment due to the intensively deliquescent property of SrCl<sub>2</sub>, which significantly affects solid electrolyte stability. The use of BaCl<sub>2</sub> poses a similar problem due to its hygroscopic property. Moreover, since BaCl<sub>2</sub> is highly electrical resistant, a higher temperature (>500 °C) must be exerted to obtain a better sensitivity (Yan et al., 1995b). The later adoption of PbCl<sub>2</sub> as the solid electrolyte overcame this challenge. Niizeki and Shibata (1998) demonstrated the incorporation of fine Al<sub>2</sub>O<sub>3</sub> particles and well-sieved PbCl<sub>2</sub> - K<sub>2</sub>SO<sub>4</sub> powder to produce a gas-tight electrolyte disk to realize chlorine gas sensing under room temperature. The sensor exhibited stable performance in moist gas attributed to the non-hygroscopicity of the PbCl<sub>2</sub> electrolyte with a linear range from 10 to 10<sup>6</sup> mg L<sup>-1</sup>. Other novel solid electrolytes have also been explored, such as Ag<sup>+</sup>-β-alumina (Mari et al., 1992), MgO-stabilized zirconia (Yan et al., 1995a), Na<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub>-4SiO<sub>2</sub> (Aono and Sadaoka, 2002) and rare earth (Imanaka et al., 2003a; Imanaka et al., 2003b). The slow response was a major drawback of these approaches (Aono and Sadaoka, 2002). To tackle this, Zhang et al. (2014, 2013) proposed using chromium-based spinel-type oxides (ACr<sub>2</sub>O<sub>4</sub>, A = Zn, Co, Ni) treated with an aging process as the solid electrolyte. By incorporating the treated chromium-based spinel-type oxide and the superionic sodium conductor, the developed sensor was capable of detecting chlorine between 0.1 and 20 mg L<sup>-1</sup> in the air at 300 °C, with the minimum response time of 20 s. The analytical

performances of some typically potentiometric solid-state chlorine sensors are listed in Table 3.

Conductometric solid-state electrochemical sensors measure the conductivity changes induced by the absorption of gaseous chlorine in the oxygen vacancy formed on the surface of the metal phthalocyanine (Azim-Araghi and Krier, 1997) or the semiconducting metal oxide (SMO) (Dawson and Williams, 1996). Compared to metal phthalocyanine (Debnath et al., 2009; Saini et al., 2014; Sharma et al., 2018), SMOs are particularly attractive due to their distinct stability. A wide variety of SMOs has been investigated for chlorine detection, including, NiFe<sub>2</sub>O<sub>4</sub> (Gopal Reddy et al., 1999), WO<sub>3</sub> (Bender et al., 2001), CdIn<sub>2</sub>O<sub>4</sub> (Mahanubhav and Patil, 2007), CdSnO<sub>3</sub> (Chu and Cheng, 2004), SnO<sub>2</sub> (Chaparadza and Ranavavare, 2008; Ma et al., 2019), In<sub>2</sub>O<sub>3</sub> (Li and Fan, 2015), and ZnO (Navale et al., 2017; Patil and Patil, 2007). These SMO were produced in the form of thick films (Patil and Patil, 2007), thin films (Tamaki et al., 2002), porous structures (Zhang et al., 2019), nanorods (Van Tong et al., 2015), nanobelts (Saini et al., 2014), nanowires (Dang et al., 2016), and so on (Wang et al., 2018b).

The characteristics of some representative conductometric solid-state electrochemical gaseous chlorine sensors are listed in Table 4. Compared with potentiometric gaseous chlorine sensors, the major advance of the conductometric solid-state electrochemical chlorine sensors is sensitivity improvement. Nevertheless, some distinct drawbacks still exist. Firstly, to achieve high sensitivity, a high operational temperature must be applied for most SMO-based sensors. Secondly, almost all the currently available SMO-based gaseous chlorine sensors are subject to humidity influences (Wang et al., 2010). More seriously, according to the sensing mechanism, a refreshing time has to be applied in the absence of chlorine to allow the recovery of the sensing material before another detection. Despite these issues, sensing performances have been greatly improved in recent years by using SMO in different nanoforms. For example, the use of SnO<sub>2</sub> nanoporous film (Chaparadza and Ranavavare, 2008) and nanowire (Dang et al., 2016) have allowed the detection limit to be at ppb-level under the operational temperature of 50 °C, which could be a clue for achieving highly sensitive detection at room temperature in further sensor development.

#### 4.2. Optical sensors

In the literature, most optical-based sensors targeted dissolved chlorine measurement; only a few studies have focused on gaseous chlorine detection. These studies include the use of chemiluminescence reaction, fluorescence, and colourimetry.

The most common used chemiluminescence for gaseous chlorine quantification is the reaction between ClO<sup>-</sup> and H<sub>2</sub>O<sub>2</sub> in an alkaline solution (Takenaka et al., 1992). Red colour is produced when a chlorine sample is pumped into a solution containing H<sub>2</sub>O<sub>2</sub> and NaOH. The quantification is based on the linear relationship between the colour intensity and the gaseous chlorine concentration. Unfortunately, other chlorine species or even HCl can also participate in the reaction, leading to low selectivity (Seliger, 1964).

**Table 3**

Analytical performances of typical potentiometric solid-state chlorine sensors reported in the literature.

Cell arrangement	Linear range (ppm)	LOD (ppm)	Response time	Operational temperature	Interferences	Ref.
RuO <sub>2</sub>   SrCl <sub>2</sub> -KCl   AgCl-Ag	1–100	1.0	2–3 min	Around 420 °C	O <sub>2</sub> Moisture	(Pelloux and Gondran, 1999)
RuO <sub>2</sub>   BaCl <sub>2</sub> -KCl   AgCl-Ag	10–1000	10	>150 s	250–450 °C	O <sub>2</sub> Moisture	(Aono et al., 1997)
Pb   PbCl <sub>2</sub> + K <sub>2</sub> SO <sub>4</sub> + Al <sub>2</sub> O <sub>3</sub>   RuO <sub>2</sub>	10–10 <sup>6</sup>	10	<10 s (>400 ppm) 20 s (10 ppm)	Room temperature	O <sub>2</sub> Moisture	(Niizeki and Shibata, 1998)
RuO <sub>2</sub>   Na <sub>2</sub> O-Al <sub>2</sub> O <sub>3</sub> -4SiO <sub>2</sub>   RuO <sub>2</sub> - NaCl	1–10	1.0	100–300 s	>450 °C	O <sub>2</sub> CO <sub>2</sub>	(Aono and Sadaoka, 2000)
Au   (La <sub>0.9</sub> Ca <sub>0.1</sub> )OCl + (Al <sub>0.2</sub> Zr <sub>0.8</sub> ) <sub>4/3.8</sub> Nb(PO <sub>4</sub> ) <sub>3</sub>   Au	1000–8000	1000	<3 min	800 °C	Unknown	(Imanaka et al., 2003a)

**Table 4**

Characteristics of some representative conductometric solid-state electrochemical gaseous chlorine sensors.

Sensing materials	Linear range (ppm)	LOD (ppm)	Response time	Operational temperature	Interferences	Ref.
WO <sub>3</sub> thin film	0.5–1.0	0.05	1 min	>175 °C	Oxidizing-gases Moisture	(Bender et al., 2001)
Fe <sub>2</sub> O <sub>3</sub> –In <sub>2</sub> O <sub>3</sub> thin film	0.2–5.0	0.20	1 min (>5 ppm)	>250 °C	Oxidizing-gases Moisture	(Tamaki et al., 2002)
CuO-modified ZnO thick film	>300	300	>1 min	400 °C	Oxidizing-gases Moisture	(Patil and Patil, 2007)
CdIn <sub>2</sub> O <sub>4</sub> thick film	0.2–1200	0.20	>20 min	>250 °C	Oxidizing-gases Moisture	(Chu, 2003)
CdSnO <sub>3</sub> thick film	0.1–8.0	0.10	>20 min	>250 °C	Oxidizing-gases Moisture	(Chu and Cheng, 2004)
Sb-doped SnO <sub>2</sub> thick nanoporous film	3–20	3.0	>1 min	>45 °C	HCl, Br <sub>2</sub> , NO, NO <sub>2</sub> , H <sub>2</sub> , NH <sub>3</sub> Moisture	(Chaparadza and Rananavare, 2008)
ZnO nanoparticles (thin film)	5–200	5.0	>1 min	200 °C	H <sub>2</sub> S, Moisture	(Navale et al., 2017)
Porous SnO <sub>2</sub>	0.5–8	0.002	~30 s	160 °C	NO <sub>2</sub> Moisture	(Zhang et al., 2019)
SnO <sub>2</sub> nanowire	0.05–0.4	0.048	57 s	50 °C	Moisture	(Dang et al., 2016)

The fluorescence-based sensors detect chlorine according to the redox and optical properties of porphyrins. A fluorescence decrease can be observed when porphyrin-based films are exposed to chlorine gas (Smith et al., 1996). Smith et al. (1997) achieved the detection of chlorine gas at concentrations ranging from 0.5 to 10 ppm using a zinc porphyrin film. Although other porphyrins have also been explored for chlorine sensing (Baron et al., 1995; George et al., 1999), all these methods are interfered by other gaseous compounds, such as HCl, NO<sub>2</sub>, and SO<sub>2</sub>. Temperature also has a significant impact on the sensing signal (Baron et al., 1995; George et al., 1999).

Colourimetry is the most popular optical method applied for chlorine detection. The principle was established based on Beer's Law. In this case, the absorbance change produced from the reaction between chlorine and the chromogenic agent is proportional to the chlorine concentration in the sample. To date, several chromogenic agents have been developed for chlorine sensing (Cooper et al., 1975; Icardo et al., 2001b; Palin, 1957; Xiong et al., 2017b). However, most studies were targeted at dissolved chlorine measurement with few aimed at gaseous chlorine detection. An example was demonstrated by Liu et al. (Liu and Dasgupta, 1995), who used a droplet-based sampler to achieve automatic gaseous chlorine sensing. Tetramethylbenzidine solution was used as the chromogenic agent. By accurately controlling the droplet (~18 µL) using a syringe pump, the system was validated for measurement of chlorine ranging from 1 to 1100 ppb. Another trial reported by Momin and Narayanaswamy (1991) using a dry reagent strip as the sensing element was capable of obviating the need for sample collection involved in the droplet-based sampler. In their setup, the gas sample was delivered through a needle-valve on a gas blender and contacted the test strip placed in the flow cell. The device's sensitivity when using three different chromogenic agents (o-tolidine, o-dianisidine, and DPD) was investigated, with o-tolidine having the best performance (linearity range: 1–5 ppm, limit of detection: 0.043 ppm). Other attempts have also been carried out using dye containing porous silica films with different instrumental arrangements (Abdelghani et al., 1997; Ralfs and Heinze, 1997).

The main drawback of the currently available optical sensors is that the complicated sample delivery process involved in the measurement procedure makes them hard to use for real-world analytical purposes. Indeed, to achieve the reported high sensitivity, the sample and reagent must be precisely pumped into the sensing device, which inevitably leads to frequent system calibrations and maintenance (Ralfs and Heinze, 1997). To address these challenges, the most recent trial in using DPD based method for gaseous chlorine monitoring was demonstrated by Zhou et al. (2020b). Through using a membrane to regulate the DPD-chlorine reaction, a sensitive gaseous probe was fabricated and validated to achieve real-time chlorine monitoring within the range of 0.009–2.058 mg L<sup>-1</sup> without the need for on-going calibration. The method also incorporated a new analytical principle that enabled the probe to achieve calibration-free monitoring,

which could be a useful analytical tool for managing chlorine exposure in workplaces. However, field-based trials are still needed to be implemented to validate long-term stability.

## 5. Comprehensive comparison and applicability analysis

Fig. 6 presents the comparison of four types of dissolved chlorine-based sensors in LOD, detection range, accuracy (error) and interferences. It can be seen that the LOD of all four types of sensors could reach as low as ppb-level. Generally, the electrochemistry-based sensing technique has a wider detection range than other methods, and spectrophotometric sensors are superior to other sensors in sensing accuracy. More significant errors would be expected while using biosensors, which could be attributed to the measurement being performed based on the response of certain bio-materials to the analyte that could be easily affected by environmental condition changes. However, all these methods are subject to interference posed by some co-exist compounds and must be regularly calibrated and maintained. With regard to the gaseous chlorine exposure monitoring techniques, Fig. 7 demonstrates the comparison of the three typical methods in LOD, detection range, response time and interferences. The wide detection range can be found in both potentiometric and conductometric chlorine sensors, which indicates they could be applied in the presence of high-concentration chlorine. The optical method shows high sensitivity and fast response, suggesting its application potential for in situ detection of chlorine exposure even at low concentrations. However, environmental moisture and other gases are the main interferences of these methods, so their anti-interference ability needs to be further refined.

During the pandemic, water disinfection efforts have been enhanced and even exceeded. Accurate and reliable monitoring of dissolved chlorine is necessary for minimizing risks to the public and the environment, and the analysis of method applicability under different scenarios is essential. According to the literature, electrochemistry-based sensing techniques are more favoured by the water treatment industries, mainly because they neither need additional reagents nor produce secondary pollution, thereby allowing in-line analysis (Wilson et al., 2019). They are usually applied in drinking water surveillance systems, including water distribution networks and terminal tap waters (Seymour et al., 2020). Colourimetry-based sensing techniques are most widely recognized by both industries and households because of its classical and reliable detection principle. During the pandemic, it has always been the primary method for off-line analysis of residual chlorine in a variety of chlorine-containing water bodies and is often used for rapid qualitative in situ detection of residual chlorine in sewage and swimming pools (Zhou et al., 2021). In contrast, fluorescence-based detection technologies are not yet widely used mainly due to the weakness in robustness compared with the typically used electrochemistry-based and colourimetry-based sensing techniques. Under lab conditions, some fluorescence-based residual chlorine sensors have proven to be highly

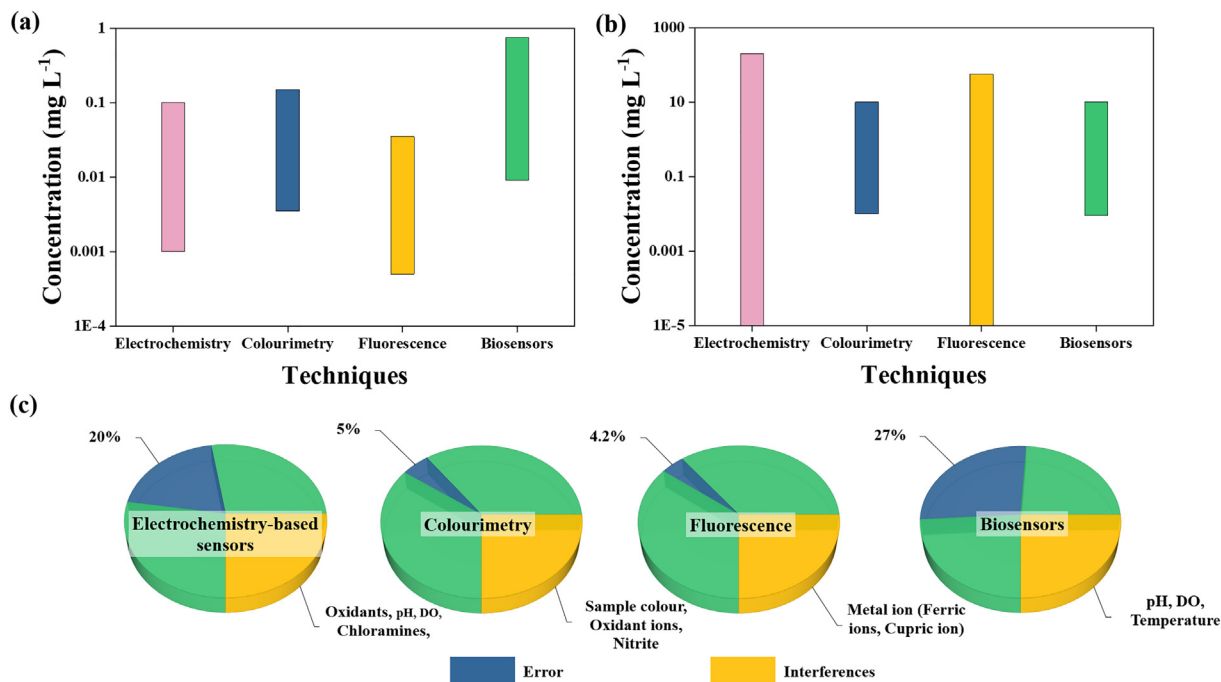


Fig. 6. Comparison of four types of dissolved chlorine monitoring methods in (a) LOD, (b) detection range, and (c) error and interferences.

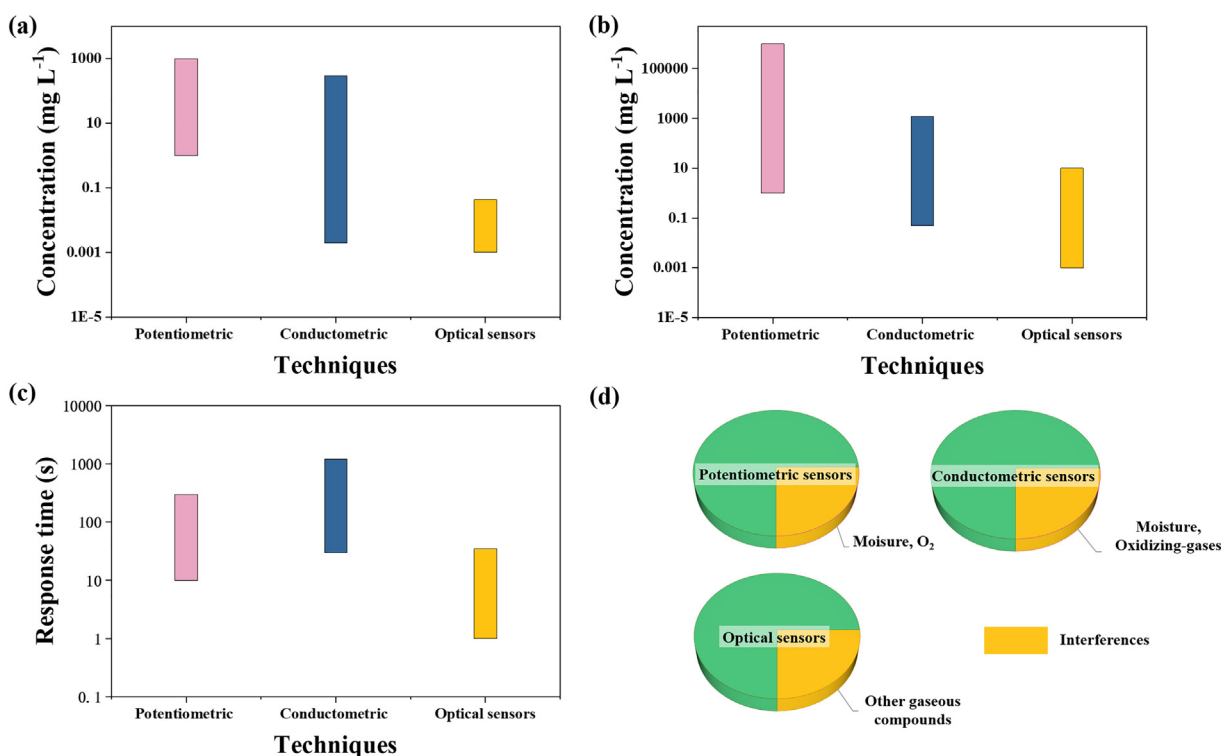


Fig. 7. Comparison of three types of gaseous chlorine monitoring methods in (a) LOD, (b) detection range, (c) response time, and (d) interferences.

sensitive and reliable, and could be an alternative for the on-site determination of free chlorine in various water samples (Uriarte et al., 2021). With regard to biosensors, due to the low tolerance of biosensing components (e.g., enzymes) to the environmental condition changes, they are often used in some specific samples, such as hypochlorous acid measurement in biological specimens (Chen et al., 2017; Xiao et al., 2017; Zhang et al., 2018). However, the latest discovery revealed the applicability of

biosensors in monitoring residual chlorine in drinking water distribution networks without routine maintenance or cleaning (Saboe et al., 2021).

Admittedly, chlorine exposure monitoring has always been a neglected issue. Until the epidemic outbreak, when constant quantities of chlorine-containing disinfectants were applied to achieve adequate disinfection, the hazard of chlorine exposure and the necessity of gaseous chlorine monitoring have aroused public concerns. Due to the strict operating conditions,

especially the high operational temperature, the solid-state electrochemical chlorine sensors can only be available for off-line sample analysis in the laboratory, limiting its application to specific situations (e.g., chlorine contamination incidents) rather than routine analysis (Dang et al., 2016). Currently, regular epidemic disinfection makes it urgent to monitor gaseous chlorine in situ. The lately developed cavity-enhanced Raman spectroscopy can detect ppb-level chlorine sensing at atmospheric pressure in ambient air with 300 s exposure time (Wang et al., 2021), and the latest development of membrane-based colorimetric gaseous chlorine sensing probe is capable of in situ real-time monitoring without tedious calibration (Zhou et al., 2020b), which presents an outstanding potential for environmental safety monitoring caused by chlorine-based disinfection.

## 6. Conclusions and future outlooks

During the COVID-19 pandemic, the widespread utilization of chlorine disinfectants and improved environmental protection awareness have triggered the demand for detecting residual chlorine in water treatment and chlorine exposure in public areas. This article reviews three broad types of commonly used sensors for detecting chlorine residual in water and chlorine exposure in air, i.e., electrochemistry-based sensors, optical sensors and biosensors.

It has been found that electrochemical-based sensors are the most prevalent technique applied for chlorine detection in both dissolved and gaseous forms. This is mainly due to their instinct features of compatibility, chemical-free, and low cost. The main challenges for electrochemical-based chlorine sensors lie in poor selectivity, signal drift along with time and the relevant low sensitivity. In this regard, the development of new sensing material with high selectivity, stability, and sufficient robustness to resist strong oxidizing environments for chlorine detection could be the focus of future developments in chlorine monitoring. With the help of interdisciplinary technologies such as microfluidics and 3D printing (Ambaye et al., 2021; Jović et al., 2015), the low-cost, portable and automated electrochemical sensors for chlorine monitoring can be expected soon be available.

Sensors based on optical detection have also attracted researchers' attention due to their well-recognized detection principle. However, most of these works were automation of the standard method, which relied on the direct mix of sample and a specific chromogenic agent and was inevitably affected by sample characteristics, such as turbidity, colour, and oxidants present in the sample. Recent attempts to use a gas diffusion mechanism with a new analytical principle showed promising results (Li et al., 2017a; Li et al., 2017b). Instead of measuring a single data point with an absolute value, the proposed method measured dynamic diffusion rate, which was proportional to the chlorine concentration in the sample. Using multiple data point measurements, the analytical principle not only massively enhanced method reliability but also allowed the calibration-free feature and minimized the use of chemicals. It thus could be a valuable technique integrated with commercialized analytical systems. Meanwhile, operators should be careful with testing results when measuring samples containing organic compounds due to the noticeable effect of chloramines on colourimetric-based chlorine detection (Engelhardt and Malkov, 2015). Such limitation will drive the development of anti-interference technology to the sensors based on optical principles. One possible way to achieve this is the incorporation of membrane technology. Hydrophobic membranes have been demonstrated to achieve superior performance in eliminating ionic species interference and massively reducing chloramine interference (Zhou et al., 2021). To date, most membrane research is targeting industrial applications for compound separation. Incorporating these membranes to enhance method selectivity could also be a promising trend in the future.

Although biological detection possesses superior selectivity, the application of these methods in the field-based analysis was rarely reported due to the strict requirements of biosensing materials for the detection environment. Therefore, the development trend of biosensors will focus on the interaction between biosensor materials and actual monitoring environments and the synthesis of biocompatible and eco-friendly biosensing material. Perhaps, the source of biosensing materials could be a breakthrough. Screening or

modifying biomaterials from the monitoring environment may be a possible approach to avoid the pollution of biomaterials to the environment and the impact of the environment on the bio-monitoring results.

Differ from dissolved chlorine detection, current gaseous chlorine detection techniques are typically solid state-based electrochemical methods. To achieve sufficient sensitivity, a higher temperature is always required, which inevitably amplifies the interference from environmental moisture. To solve this, recent attempts to use functional nanomaterials demonstrated better chlorine sensing performance by improving the density of oxygen vacancies on the material surfaces (Ma et al., 2018; Van Dang et al., 2016). Unfortunately, most of these attempts were only validated in the laboratory. In this regard, field-based long-term stability tests are highly recommended for future research to provide sufficient data to support potential applications. To date, with the development in material design and synthesis, incorporating more sensitive and more stable functional materials for gaseous chlorine sensing could be a way to further extend the method's applicability, especially in achieving room temperature monitoring. In addition, the latest study incorporated traditional passive sampling with real-time optical detection also exhibited promising chlorine sensing performance (Zhou et al., 2020b). The method can be applied for real-time monitoring of time-weight-average chlorine concentration, which is critical to exposure assessment. Nevertheless, the absorber was based on wet-chemical, which could be a less than ideal solution, implying a direction in dry-absorber-based passive sampling integrating real-time detection for future gaseous chlorine sensor research.

The spread of the COVID-19 epidemic makes chlorine disinfection closely related to people's daily life. In order to ensure the balance between disinfection efficiency and disinfection safety, chlorine monitoring is bound to be used more frequently on more occasions, which inevitably challenges the reliability, accuracy, stability, continuity, portability and environmental friendliness of chlorine monitoring technology. Given these, it is envisaged that future chlorine sensing technique development should enhance more in the aspects of selectivity, anti-interference ability, robustness, calibration-free and real-time capability. Benefiting from interdisciplinary technology development, chlorine monitoring technology will present a bright prospect in the development towards miniaturization, portability, and intellectualization.

## CRedit authorship contribution statement

**Tianling Li:** Formal analysis, data curation, writing – original draft preparation. **Zhengguo Wang:** Investigation, Data curation, Writing – editing. **Chenxu Wang:** Investigation, Data curation. **Jiayu Huang:** Investigation, Data curation. **Ming Zhou:** writing – original draft and reviewing and editing, supervision.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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