

Continuous Chlorine Detection in Drinking Water and a Review of New Detection Methods

Residual disinfectant in drinking water should be monitored from the plant to the tap. Sensor fouling remains an obstacle to the development of reliable, low-maintenance, continuously-operating sensors

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Chlorination is necessary to prevent epidemics of waterborne disease however excess chlorination is wasteful, produces harmful disinfection byproducts, exacerbates corrosion and causes deterioration in aesthetic qualities, leading to consumer complaints. Residual chlorine must be continuously monitored to prevent both under- and over-chlorination and factors including pH, temperature and fouling must be considered as these also affect the disinfectant strength of residual chlorine. Standard methods used by water utility companies to determine residual chlorine concentration in drinking water distribution systems are appraised and found to be unsuitable for continuous monitoring. A selection of newly developed methods for residual chlorine analysis are evaluated against performance criteria, to direct research towards the development of chlorine sensors that are suitable for use in

water systems. It is found that fouling tolerance in particular is generally not well understood for these selected sensor technologies and that long-term trials in real systems is recommended.

1. Introduction

The disinfection of drinking water has virtually wiped out diseases caused by waterborne pathogens such as cholera and dysentery (1). Globally, the principal methods of disinfection which are used in public water systems are chlorination/chloramination, ultraviolet (UV) radiation and ozonation, which can be used alone or in combination (2). Chlorine is a popular disinfectant due to its low cost and relatively slow rate of decay in distribution systems or storage which enables proper water hygiene to be maintained for longer (3). This is possible, barring the presence of especially chlorine-resistant microorganisms (such as *Cryptosporidium* and *Giardia*), as long as a minimum level of chlorine residual (as free and combined chlorine) is present as water travels from treatment sites and through water distribution systems. In the United States, it is a requirement that populations of at least 3300 are served by water treatment works which chlorinate and have continuous chlorine monitoring (4). Chlorine disinfects water by disabling or killing bacteria through oxidation reactions with cellular components including cell membranes and proteins, leading to disruption of essential cellular processes. This damage causes a reduction in the

rate of respiration, deformation then breaking of cell membranes, introduction of genetic defects and disruption of protein synthesis, leading to cell death and disinfection (5, 6).

Free chlorine (defined as the sum of the concentrations of solvated chlorine gas (Cl_2), hypochlorous acid (HOCl) and hypochlorite (OCl^-)) oxidises organic compounds which can result in the formation of disinfection byproducts (DBPs) including trihalomethanes and haloacetic acids (HAA) (7). All of these compounds are undesirable in drinking water due to possible carcinogenic and mutagenic properties, foul odour and taste (8–10) and accelerated evolution of antibiotic resistant bacteria (11). It is essential that water is sufficiently chlorinated to inactivate microorganisms to prevent disease but not over-chlorinated as this promotes the formation of DBPs. The World Health Organization (WHO) recommends not exceeding 5 ppm of free chlorine in drinking water to prevent toxic effects from chlorination (12, 13) and the production of excess disinfection byproducts (14, 15). Corrosion is also more likely to occur at elevated levels of chlorine as well as higher temperatures and lower pH (16), resulting in an increase in chlorine demand (17).

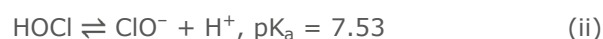
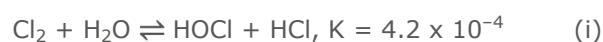
Ad hoc mathematical models are available for predicting the disinfectant ability of chlorine in drinking water (18), however real data would clearly be preferable. In the following section, a review of practical methods of chlorine residual analysis is provided. These methods include standardised, official methods of chlorine detection and selected emerging techniques which are evaluated for their use in continuous residual chlorine monitoring in drinking water distribution systems.

There is a lack of new residual monitoring technologies with adequate antifouling measures for use in water distribution systems. Methods of improving fouling resistance are based on established antibiofouling technologies such as antimicrobial copper tape and antifouling paint (19) which are not designed to be permanent solutions. Other suggested methods use non-specific coatings or filters (20) which by their nature will require replacement which interrupts measurements and limits the use of sensors in non-accessible locations, underground in water distribution systems for example. This review aims to appraise newly developed sensors for use in real world situations, which includes an analysis of how these sensors would cope with fouling.

2. Factors Affecting the Disinfectant Ability of Chlorinated Drinking Water and the Implications for Chlorine Sensing

2.1. Chlorine Demand

Chlorine is added to drinking water either in its gaseous form (Cl_2) or as a hypochlorite-containing salt, typically sodium hypochlorite (NaOCl), in the form of a solution or a powder. Chlorine gas disproportionates in water into hydrochloric acid and HOCl , the latter disassociates to form ClO^- (Equations (i) and (ii)):



If a hypochlorite salt is added, the hypochlorite ion speciates in a pH-dependent fashion to form the oxidising agents HOCl and ClO^- ; the sum of these two concentrations, typically expressed in parts per million (ppm), is known as free chlorine. It is desirable to maintain a residual concentration of free chlorine in drinking water to prevent the proliferation of pathogenic microorganisms. The WHO recommended level for drinkable water is 0.2–0.5 ppm minimum (14, 15) and 2–5 ppm maximum (12, 13) free chlorine. With respect to time, the minimum free chlorine level should be 0.5 ppm after 30 minutes contact time at a pH of less than 8 with a turbidity less than 1 nephelometric turbidity unit (NTU) (1). This can also be expressed as 15 mg of free chlorine per minute per litre of water. As chlorine is added to untreated water, free chlorine is not produced until a breakpoint is reached (21) (**Figure 1**), after this point the residual free chlorine rises with added chlorine. Initially, chlorine oxidises compounds including hydrogen sulfide (H_2S), iron(II) (Fe^{2+}) and manganese cation (Mn^{2+}). When these are exhausted, chlorine more readily oxidises ammonia and organic compounds (22). On reaction with ammonia, monochloramines are formed (Equation (iii)). However as excess chlorine continues to be added and a weight ratio of 5:1 $\text{Cl}_2:\text{NH}_3\text{-N}$ is reached, monochloramine disproportionates to dichloramine and ammonium. Dichloramine in the presence of excess chlorine reacts with nitrogen gas and other nitrogen compounds in a series of complex reactions to form trichloramine. Chloramines can be used as disinfectants which produce less DBPs than free chlorine, although the disinfectant strength of hypochlorous acid is 2000–10,000 times greater

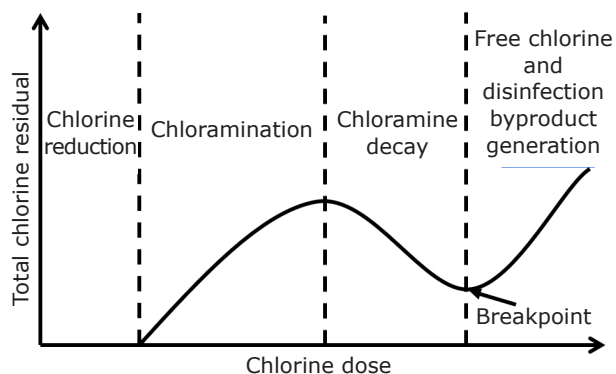
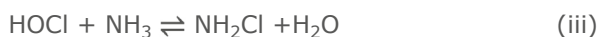


Fig. 1. The generation of residual chlorine in drinking water. Chlorine reduction: oxidising compounds in drinking water reduce chlorine until the oxidising compounds have been depleted. Chloramination: This process takes place in drinking water containing ammonia and produces monochloramines. Chloramine decay: monochloramines are converted into dichloramines and trichloramines, releasing increasing quantities of nitrogen gas until a breakpoint weight ratio is reached. Free chlorine and disinfection byproduct (DBP) production: at this point, there is little available ammonia to produce more monochloramines and so subsequently added chlorine will produce a free chlorine residual. Adapted from (21) by permission. Copyright © (2013) the American Water Works Association

(12, 13). The contribution to the total chlorine residual from chloramines and chlororganics is termed the 'combined chlorine' residual; an important distinction due to a lesser disinfectant ability than free chlorine. Free chlorine and combined chlorine are added together to calculate total chlorine. When the weight ratio reaches 7.6:1 Cl₂:NH₃-N under standard conditions, the ammonia content has been exhausted, the chlorine demand has been met and converted to nitrogen gas as chloramines decay (Equation (iv)). This is the breakpoint and subsequent additions of chlorine will contribute to the free chlorine residual. The weight ratios used above are dependent on both pH and temperature (23).



The reduced disinfectant strength of combined chlorine necessitates monitoring of the free chlorine residual of drinking water during dosing and as organics or microorganisms leach or infiltrate the supply during storage or distribution.

2.2 Formation of Hypochlorous Acid

HOCl compounds are greater oxidisers and this can be seen from their half-cell potential values at 25°C (Equations (v) and (vi), also shown in Table I) (24), where HOCl compounds have greater oxidation potential than ClO⁻ compounds and ions. Determination of the minimum effective residual to achieve 3-log inactivation of *Escherichia coli*, a waterborne pathogen, of both chlorine products shows that HOCl (the dominant form of free chlorine under experimental conditions of 5°C at pH 7) is 100 times more effective than hypochlorite (dominant at 5°C at pH 10.7) (27–29).

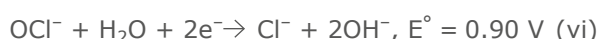


Figure 2 shows the effect of temperature and pH on the percentage formation of hypochlorous acid. When measuring free chlorine residual, these parameters must be determined as an increased

Table I Chlorine Half-Reactions for Amperometric Sensors (25, 26)

Reaction	E°, V (SHE)	E°, V (Ag/AgCl, saturated KCl)
$\text{HClO}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{HOCl} + \text{H}_2\text{O}$	1.645	1.448
$\text{HClO}_2 + 3\text{H}^+ + 3\text{e}^- \rightleftharpoons \frac{1}{2}\text{Cl}_2 + 2\text{H}_2\text{O}$	1.628	1.431
$\text{HOCl} + \text{H}^+ + \text{e}^- \rightleftharpoons \frac{1}{2}\text{Cl}_2 + \text{H}_2\text{O}$	1.611	1.414
$\text{HClO}_2 + 3\text{H}^+ + 4\text{e}^- \rightleftharpoons \text{Cl}^- + 2\text{H}_2\text{O}$	1.570	1.373
$\text{HOCl} + \text{H}^+ + 2\text{e}^- \rightleftharpoons \text{Cl}_2 + \text{H}_2\text{O}$	1.482	1.285
$\text{ClO}_3^- + 6\text{H}^+ + 5\text{e}^- \rightleftharpoons \frac{1}{2}\text{Cl}_2 + 3\text{H}_2\text{O}$	1.470	1.273
$\text{ClO}_3^- + 6\text{H}^+ + 6\text{e}^- \rightleftharpoons \text{Cl}^- + 3\text{H}_2\text{O}$	1.451	1.254
$\text{ClO}_4^- + 8\text{H}^+ + 7\text{e}^- \rightleftharpoons \frac{1}{2}\text{Cl}_2 + 4\text{H}_2\text{O}$	1.390	1.193
$\text{ClO}_4^- + 8\text{H}^+ + 8\text{e}^- \rightleftharpoons \text{Cl}^- + 4\text{H}_2\text{O}$	1.389	1.192
$\text{Cl}_{2(\text{g})} + 2\text{e}^- \rightleftharpoons 2\text{Cl}^-$	1.358	1.161
$\text{ClO}_2 + \text{H}^+ + \text{e}^- \rightleftharpoons \text{HClO}_2$	1.277	1.080
$\text{ClO}_3^- + 3\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{HClO}_2 + \text{H}_2\text{O}$	1.214	1.017
$\text{ClO}_4^- + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{ClO}_3^- + \text{H}_2\text{O}$	1.189	0.992
$\text{ClO}_3^- + 2\text{H}^+ \rightleftharpoons \text{ClO}_2 + \text{H}_2\text{O}$	1.152	0.955
$\text{ClO}_{2(\text{aq})} + \text{e}^- \rightleftharpoons \text{ClO}_2^-$	0.954	0.757
$\text{ClO}^- + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{Cl}^- + 2\text{H}_2\text{O}$	0.810	0.613
$\text{ClO}_2^- + \text{H}_2\text{O} + 4\text{e}^- \rightleftharpoons \text{Cl}^- + 4\text{OH}^-$	0.760	0.563
$\text{ClO}_2^- + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{ClO}^- + 2\text{OH}^-$	0.660	0.463
$\text{ClO}_3^- + 3\text{H}_2\text{O} + 6\text{e}^- \rightleftharpoons \text{Cl}^- + 6\text{OH}^-$	0.620	0.423
$\text{ClO}_4^- + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{ClO}_3^- + 2\text{OH}^-$	0.600	0.403
$\text{ClO}_3^- + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{ClO}_2^- + 2\text{OH}^-$	0.330	0.133

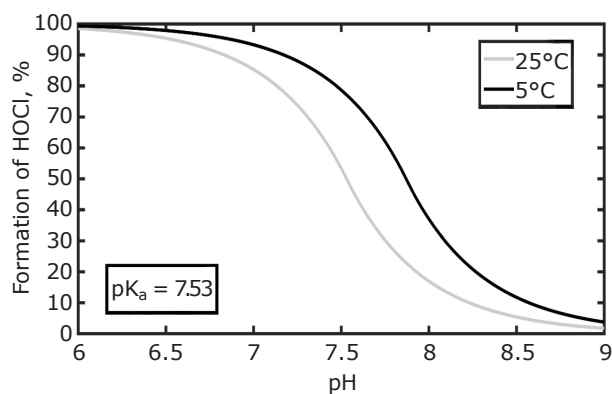


Fig. 2. The effect of temperature and pH on the speciation of hypochlorous acid. The pK_a values for HOCl at 25°C and the enthalpy of dissociation (1488 kJ mol^{-1}) were taken from the NIST WebBook (30). The change in pK_a at 5°C and subsequently the percentage formation of HOCl was calculated from the Van't Hoff isotherm. The formation of HOCl is defined as: % formation of HOCl = $([\text{HOCl}])/([\text{OCl}^-] + [\text{HOCl}])$

dose may be required to ensure adequate disinfection in situations where the temperature or pH of the bulk water increases as it enters further treatment steps or into distribution. Standard physicochemical data for chlorine compounds and ions is presented in **Table II** (adapted from (24)).

2.3 Fouling

The two categories of sensor fouling in drinking water systems are: (i) fouling by bacteria and biofilm deposition (biofouling); and (ii) fouling caused by the accumulation of minerals (mineral fouling or mineralisation). Trace amounts of bacteria present in bulk water colonise surfaces within water distribution systems and concentrate to form biofilms which disrupt analytical instruments. The consequences of biofilm formation on analytical performance are manifold but include: (i) interference with mass transport to the surface of electrochemical sensors; (ii) partitioning of the analyte which can lead to non-representative concentrations in the vicinity of the sensor; and (iii) in the case of electrochemical sensors, electrode reaction kinetics can be impaired if the electrode material (typically electrocatalytic in nature) contacts the biofilm. Bacterial metabolism can affect local pH and oxygen levels, promote mineralisation and secondary metabolites such as pyocyanin may directly interfere with sensors. Other damaging consequences include clogging of mechanisms (1), microbial-induced corrosion (31) and covering the surface of optical sensors (32). Biofilms also increase chlorine demand as water is pumped through distribution systems and as such are an important consideration in calculating chlorine decay (33).

Table II Standard Physicochemical Data Series of Chlorine Compounds and Ions (25)

Name	Formula	Mol. wt.	CAS Reg. No.	ΔH_f (g), kJ mol^{-1}	ΔG_f (g), kJ mol^{-1}	S° (g), $\text{J mol}^{-1} \text{K}^{-1}$	C_p (g), $\text{J mol}^{-1} \text{K}^{-1}$
Chlorine (diatomic)	Cl_2	70.90	7782-50-5	0		223.1	33.9
Chlorine (atomic)	Cl	35.453	22537-15-1	121.3	105.3	165.2	21.8
Chlorine dioxide	ClO_2	67.452	10049-04-4	102.5	120.5	256.8	42.0
Chlorine monoxide (oxygen dichloride)	Cl_2O	86.905	7790-89-8	-50.3	-51.8	217.9	32.1
Chlorine oxide	ClO	51.452	14989-30-1	101.8	98.1	226.6	31.5
Chlorine superoxide	ClO_2 (ClOO)	67.452	17376-09-9	89.1	105.0	263.7	46.0
Hydrogen chloride (hydrochloric acid)	HCl	36.461	7647-01-0	-92.3	-95.3	186.9	29.1
Hypochlorous acid	HOCl	52.460	7790-92-3	-78.7	-66.1	236.7	37.2
Chloride ion	Cl^-	35.453	16887-00-6	-167.2 (aq)	-131.2 (aq)	56.5 (aq)	-136.4 (aq)
Hypochlorite ion	ClO^-	51.452		-107.1 (aq)	-36.8 (aq)	42.0 (aq)	
Chlorite ion	ClO_2^-	67.452		-66.5 (aq)	17.2 (aq)	101.3 (aq)	
Chlorate ion	ClO_3^-	83.451		-104.0 (aq)	-8.0 (aq)	162.3 (aq)	
Perchlorate ion	ClO_4^-	99.451	14797-73-0	-129.3 (aq)	-8.5 (aq)	182.0 (aq)	

Mineral fouling is commonly seen in the form of limescale: the deposition of layers of calcium carbonate (CaCO_3) on household appliances. This occurs in drinking water systems on the inside of pipes, taps and on sensors (34). A relatively high pH environment is conducive to mineral fouling; sensors which use cathodic reduction to detect free chlorine and other compounds are more likely to foul than non-electrochemical sensors at least partly attributed to local rises in pH as hydroxyl ions are generated (or protons consumed) in the electrode reaction. This leads to the precipitation of minerals, including CaCO_3 and related materials on the surface which hinder mass transport, can impair electrocatalysis and the fixed charge density can lead to solute partitioning for charged species.

Both mineral fouling and biofouling can occur simultaneously as biomineralisation. The presence of particular bacteria can result in increased CaCO_3 precipitation (35) and bacteria can exist on the surface of minerals in order to uptake nutrients (36) or to avoid destruction by free chlorine (37).

2.4 Summary of Challenges for Chlorine Sensors in Drinking Water

It is not safe to assume that because free chlorine concentration is monitored at the water treatment works that no additional monitoring throughout the rest of the distribution network is required. As shown in this section, the breakpoint chemistry of chlorine in water containing organic compounds influences the disinfectant strength of water due to speciation. Drinking water travels through pipes in varying states of repair and corrosion which creates different quantities of organic compound infiltration and can reduce the effective dose of disinfectant and affect the production of DBPs. Mathematical modelling may be able to account for these changes to an extent, however a scientific approach to the problem would be to use a network of sensors to ensure consistent water quality from treatment to the consumer. A network of sensors, together with existing sensors in water treatment works would allow for better regulation of chlorine residual to prevent under- and over-chlorination.

Chlorine sensors must be reliable, suitable for use in inaccessible parts of water networks and operating continuously but not only at the point of disinfection. Distributed, free chlorine sensing is challenging due to fouling. Water quality sensors which can reduce the impact of fouling to ensure longer periods of reliable monitoring without maintenance would be welcomed by the water

industry and enable optimisation of distribution networks for water quality.

3. Chlorine Detection Methods

A critical review of standard tests for residual chlorine and selected new techniques is presented here. The new techniques were chosen for this review based on the novelty of the underlying technology and to show the range of technologies being developed for use as water sensors. Performance data for these methods, including possible interferences, are summarised in **Table III**. This is by no means a comprehensive account of the performance of these sensors and methods in drinking water as many are in development. Important factors such as response time, stability, reliability, lifetime and cost are not included. This review divides the chlorine detection methods presented here into reagent-based and reagentless electrochemical methods which reflect the two branches of research into new methods. Limits of detection and linear ranges of the methods listed here, units of ppm of chlorine are used (with conversions from original data where necessary).

3.1 Reagent-Based Methods

Reagent-based methods of assessing water quality are, in addition to well-established titrimetric methods, broadly either colorimetric or luminescent/fluorescent. Colorimetric methods are those which produce a change in the colour of a solution, the intensity of which corresponds to the quantity of chlorine present or indicates the endpoint in a titration. Luminescent methods produce light where the intensity is used as an indicator of residual chlorine, whereas fluorescent methods measure the re-emission of incident electromagnetic radiation.

3.1.1 Titration with Sodium Thiosulfate

Titration with sodium thiosulfate is used for measuring the total chlorine in tap water samples (38, 39). In the presence of hypochlorite or combined chlorine, iodine is liberated from an acidified solution of potassium iodide (Equations (vii) and (viii)), thus depleting tri-iodide and the resultant yellow colour (Equation (ix)).

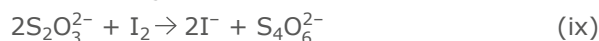


Table III Summary of Methods of Chlorine Detection

Method	Signal	Linear range, ppm	LOD, ppb	Error, %	Known interferences
Spectrophotometric DPD method (38)	Colorimetric	0.01–5	4	4–7	Metal ions, chloramines, organic compounds, oxidants
FACTS or syringaldazine (39)	Colorimetric	0.1–10	100	10	UV light, pH range 6.5–6.8, ≥ 35 ppm monochloramine, ≥ 26 ppm oxidised manganese
Titration with FAS and DPD indicator (39)	Colorimetric	0.02–5	11	5	Metal ions, chloramines, organic compounds, oxidants
Amperometric DPD (39)	Amperometric	0.01–5	4	4–7	Metal ions, chloramines, organic compounds, oxidants
Iodometric titration with sodium thiosulfate (38)	Colorimetric	1–20	150	2–4	Nitrite, oxidants, transition metal ions
Example of commercially-available platinum electrode (40)	Amperometric	0–20	5	2	Metal ions, oxidants, biofilm, scale
ABTS (41)	Colorimetric	0.012–0.7	2	4	Bromine and brominated organic compounds
BSA-coated gold nanoclusters (42)	Fluorometric	0.012–0.60	3.5	4.35	Must be refrigerated to prevent denaturation
Polyluminol-based sensor arrays (43)	Luminometric	0–1.4, 1.8–28	18	6–10	Not known
Gold film nano-transducers (44)	Amperometric	0.2–5	20	5	Biofilm, must be stored in inert environment when not in use
CdSe – ZnS quantum dots (45)	Fluorometric	0.018–0.18	9	8–11	Not known
Nitrogen and sulfur co-doped carbon dots (46)	Fluorometric	0.00035–3.5	0.18	2.5–3.8	Not known
MnO₂ nanosheets (47)	Colorimetric	0.007–0.35	2.8	1.1–1.2	pH and temperature sensitive
Detection with DPD by evanescent-wave analysis on optical fibre	Colorimetric	0.005–0.4	1.5	1.59	Microfluidic system, possibly prone to clogging in drinking water
Pencil-drawn chemiresistive sensor	Chemiresistive	1.5–9	0.06	4.5–6.5	Not known
Multiwalled carbon nanotube/epoxy amperometric nanocomposite sensors with CuO nanoparticles (48)	Amperometric	0.056–446.2	0.6	2.69–2.77	Not known
Surfactant-modified Prussian blue sensor (49)	Amperometric	0.009–10	9	4.2	Not known
Azobenzene sensor (50)	Colorimetric	0–2.47	100	Not known	Not known
Oxidative cleavage-based probe (51)	Fluorometric	0.123–1.26	4	1.6	Not known
Boron-doped diamond electrode (52)	Amperometric	0.1–2	8.3	2.56	Not known

The disappearance of the yellow colour is difficult to detect and so a starch indicator solution, which forms a deep blue colour in the presence of tri-iodide, is added. The disappearance of the blue colour clearly marks the endpoint in the reaction. Two moles of sodium thiosulfate are consumed by one mole of iodine which is formed by one mole of hypochlorite and so from the volume of thiosulfate consumed (and the concentration of the thiosulfate solution), the total chlorine residual can be calculated. The range of application is between 1 ppm and 20 ppm although dilution of samples can effectively extend the upper limit. There is a bias to titrate to slightly before the endpoint, leading to an estimated 10% error in chlorine concentrations in values from 0.025–1 ppm (38).

3.1.2 *N,N*-diethyl-*p*-phenylenediamine Methods

N,N-diethyl-*p*-phenylenediamine (DPD) (**Scheme I(b)**) is used by water utility companies as a standard method of chlorine determination (53). At-line, automatic DPD analysis instruments, designed to require very little manual input and for minimal maintenance, can be connected to bypasses and programmed to periodically sample water from the chlorination process or at various locations at treatment works. The self-contained units add DPD, either as a solution, tablet or powdered form, to water samples which results in the formation of a red colour in the presence of chlorine (40). The reaction produces a doublet peak with maxima at wavelengths of 512 nm and 553 nm which can also be judged by eye with the aid of a colour chart. The chemical basis for this change is the conversion of DPD into Würster dye by chlorination (54). Würster dye can be further oxidised to form a colourless imine and therefore this method is unsuitable for use in water containing non-chlorous oxidisers – such as potassium permanganate – and analysis of the colour change must be carried out immediately after the initial colour change.

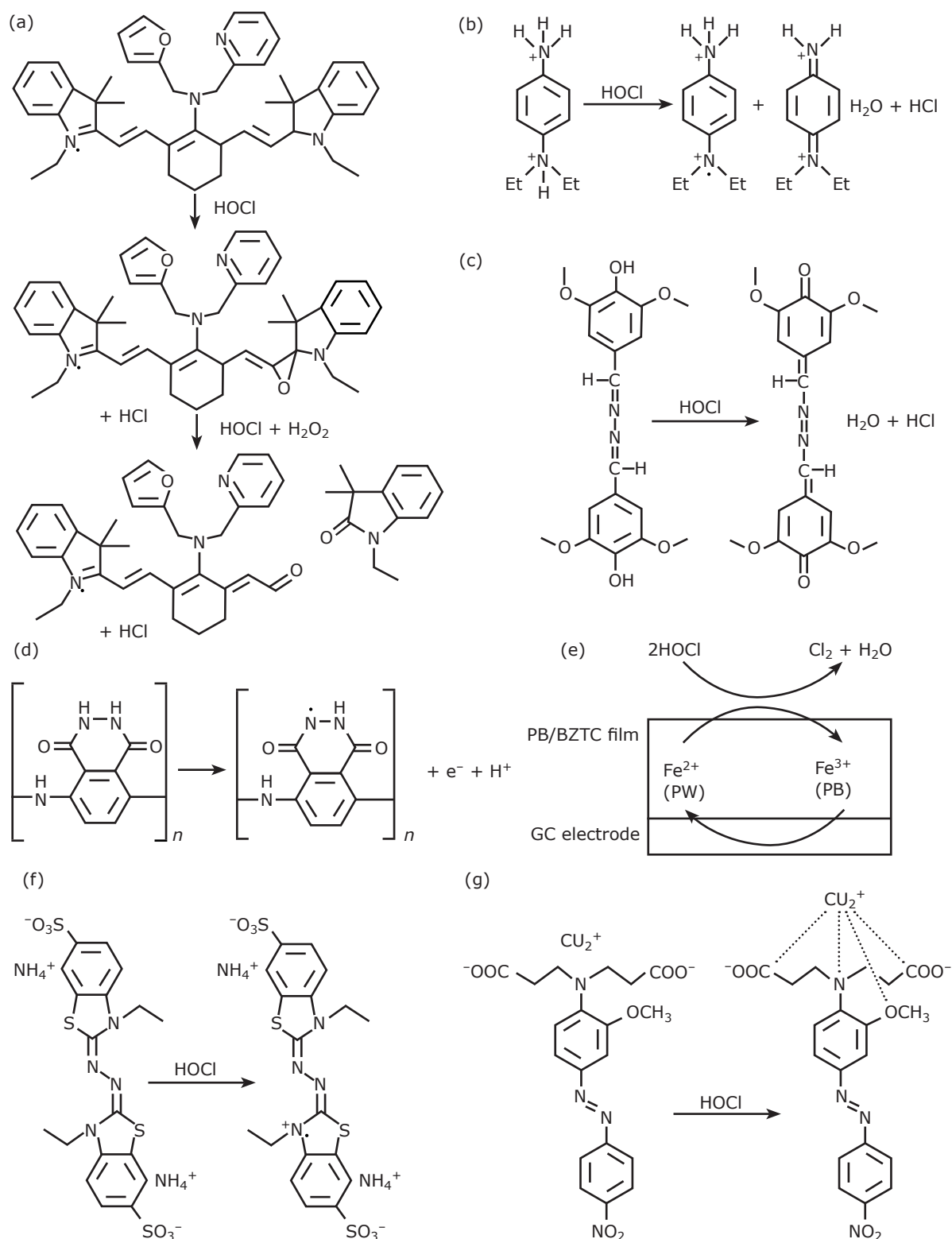
If total chlorine measurements are desired, an excess of potassium iodide can be added to the reaction, releasing chloramine to react with sodium thiosulfate. The combined fraction is then calculated by subtracting the free chlorine concentration from the total chlorine concentration. The range of this method is between 0.02 ppm and 5 ppm for free or total chlorine and has a maximum allowable margin of error of 15% (38). Metals can interfere with results as can non-chlorous oxidising agents, monochloramine and organic contaminants. Prior

to testing, ethylenediaminetetraacetic acid (EDTA) can be added to chelate copper ions (38) or barium chloride to precipitate chromate compounds. DPD reagents are also sensitive to light, moisture and temperature. The doublet peak requires wavelength measurements to be made between the peaks – manufacturers of different DPD kits do not all agree on where exactly the measurement should be taken. Alternatively, a titrimetric method using DPD as an indicator and titrating with ferrous ammonium sulfate (FAS) can be used (39) for drinking water of chlorine concentration 0.5–5 ppm with 6–8% error (55). It is relatively toxic compared with sodium thiosulfate and is consequently, not as widely used.

Another DPD-based method uses evanescent waves (EW) sensing in optical fibres in a microfluidic system containing DPD and water samples (56). The relationship between the formation of Würster dye in the DPD reaction with free chlorine and the resultant intensity of the EW allows for determination of free chlorine. The limit of detection (LOD) is reported as 1.5 parts per billion (ppb), the range is 5–400 ppb with a relative standard deviation (RSD) of 1.59%. The volume of sample is very small – 1.2 μl – and the channel diameter is 50 μm . As is the case with many microfluidic-based devices, this sensor would be prone to fouling and the principal benefit would appear to be a smaller overall size than existing DPD systems.

3.1.3 Titration with FACTS (Syringaldazine)

3,5-dimethoxy-4-hydroxybenzaldazine (syringaldazine) (**Scheme I(c)**) in solution with 2-propanol is known as free available chlorine test with syringaldazine (FACTS) (39, 57). A purple-red colour is seen on reaction with chlorine with an absorbance maximum at 530 nm (**Scheme I(c)**). Problems with this method include the instability of the reagent, which is largely insoluble in water and only partially so in 2-propanol with regular sonication for periods of several hours. FACTS is also unstable in UV light and must be prepared at room temperature so as to not diminish its sensitivity. It is also sensitive to weak acid solutions and attempts to control this with buffers are not recommended as this increases the sensitivity of the test to CaCO_3 (200 ppm). FACTS is applicable in the range 0.1–10 ppm with a maximum error of 10%. The reagent is sensitive to other oxidising agents such as manganese ions but is overall less susceptible to interferences than DPD or sodium thiosulfate methods.



Scheme I. Structures and reactions of organic chemistry-based methods of free chlorine detection: (a) Oxidative cleavage-based probe reacts with free chlorine to produce a colorimetric product which is detectable at 490 nm. The probe is unstable as subsequent reactions with chlorine produce a colourless byproduct; (b) DPD produces a red colouration on reaction with free chlorine which produces a doublet peak with maxima at 512 nm and 533 nm; (c) FACTS or syringaldazine reacts with free chlorine to produce a product detectable at 530 nm; (d) poly(luminol) produces light on reaction with free chlorine; (e) reaction scheme for the conversion of Prussian white to Prussian blue on a glassy carbon electrode with a PB/BZTC film, in the presence of free chlorine; (f) ABTS produces a reaction product which absorbs at 405 nm on reaction with free chlorine; (g) azobenzene 'Chemosensor 1' chelates with copper ions in solution in the presence of free chlorine, generating a colour change from red (490 nm) to white

The essentially quantitative and kinetically rapid reaction between oxidant disinfectants (including ozone, bromine and free chlorine) and phenolic compounds has recently been exploited as an analytical technique (58). The method uses high-performance liquid chromatography (HPLC) to quantify the 2-chlorophenol and 4-chlorophenol formed. Other phenolic quenching agents are proposed for ozone and bromine (cinnamic acid and 2-bromo-dichlorophenol respectively) enabling simultaneous quantification during the HPLC step. These methods have been employed in analysis of oxidants and disinfection byproducts in saline ballast water (59, 60).

3.1.4 Amperometric Titrations

The end point of the sodium thiosulfate titration can also be detected amperometrically. Samples are titrated with thiosulfate as a constant negative potential is applied through a platinum electrode which promotes the reduction of hypochlorite to chloride as shown in Equation (vi). This produces an increase in current as the volume of the titrant increases. When the endpoint is reached, the rate of change in current will be zero. This method is used for chlorine analysis in wastewater samples as the formation of iodine is vulnerable to interferences (39). A back titration can be carried out to prevent chlorine decay from interfering with samples; this is done by adding a known volume of sodium thiosulfate in excess and titrating the unreacted thiosulfate with an iodine solution. This method is sensitive to 0.01 ppm. A high degree of skill is required to perform this manually although amperometric analysers with motorised, stepped titrant pumps are available for fine control of the titrant volume (61). Testing with standard DPD methods has several advantages over amperometric titrations including portability, ease of use and comparable accuracy (62).

3.1.5 Azobenzene Chemosensor

Copper-based chemosensors exploit the colour change of red to colourless seen in the oxidation of Cu^+ to Cu^{2+} in solution. The authors developed a chemosensor, 'Chemosensor 1' (**Scheme I(g)**), which is a nitrobenzene moiety with attached phenyl iminodiacetate receptor (50). The compound promotes a colour change at 490 nm when the receptor binds to Cu^{2+} which is added to chlorinated water. The reaction has one clear peak ($\lambda_{\text{max}} = 490 \text{ nm}$), unlike DPD, is linear within

the range 0.1–2.4 ppm for ClO^- and not subject to interference from a wide selection of compounds. Several of these ions including NO_2^- , Br^- , OBr^- and IO_3^- are causes of interference for DPD-based methods. Selectivity for total or combined chlorine was not presented. The authors note that the addition of sodium ascorbate to samples may be required to prevent Chemosensor 1 degrading in the presence of oxygen. Further details on reagent stability are not provided.

3.1.6 ABTS

2,2'-Azino-bis(3-ethylbenzothiazoline)-6-sulfonic acid-diammonium salt (ABTS) (41) (**Scheme I(f)**) has been developed to detect hypochlorous acid, chlorine dioxide and monochloramine in drinking water. It features improved stability of its reaction product ($\lambda_{\text{max}} = 405 \text{ nm}$), lower range of detection (2 ppb) and faster colour development than the DPD method. The reported RSD was found to be 4% with a range of 0.07–0.7 ppm.

3.1.7 BSA-Coated Gold Nanoclusters

Albumin-stabilised gold nanoclusters were prepared from chloroauric acid (HAuCl_4) and bovine serum albumin (BSA) before use for free chlorine analysis or storage at 4°C (42). Nanoclusters have previously been used to selectively detect heavy metals in water, glucose and amino acids and have now been adapted for use with chlorine. Free chlorine selectively oxidises amino acid residues on the surface of the nanoclusters which quenches a red fluorescence which is visible at excitation at 480 nm, 619 nm and 837 nm. The detection limit is 5.2 ppb. Interference testing was carried out by addition of various ions at 50 times the concentration of added HOCl and none was found for monochloramine or for any of the ions which were tested. Interference from biofouling or destabilising reactions between BSA and microorganisms were not examined, although suitability for use in distribution systems would be limited by the need for low temperature storage.

3.1.8 Poly(luminol)-Based Sensor Arrays

Poly(luminol) (**Scheme I(d)**) is a conductive polymer which was previously used in several electrochemical applications (63, 64). Electropolymerisation of luminol on transparent indium-tin oxide (ITO) electrodes is accomplished

using cyclic voltammetry. Arrays of electrodes with microwells for water samples were prepared to provide a series of one-shot reaction vessels. Luminol reacts with hypochlorite to form diazoquinone which then reacts with hydrogen peroxide to produce aminophthalates that can be detected by chemiluminescence (65) (**Scheme I(d)**). The sensors, once polymerised with poly(luminol), have a shelf life of at least one year, far more than some of the reagents used in the previously discussed colorimetric methods.

The linear range is between 0.03 ppm and 21 ppm with an error of 6%, which is typical of standard methods described here. Reagent stability and pH sensitivity may limit the possible applications outside of the laboratory.

3.1.9 Cadmium Selenide-Zinc Sulfide Quantum Dots

Quantum dots (QDs) are semiconducting nanocrystals that exhibit quantum properties. Their electronic behaviour is dependent on the size of the nanocrystals and nanoclusters produced and is considered to be between that of individual molecules and bulk semiconductors (66). Yan *et al.* (45) developed water-dispersible cadmium selenide (CdSe)-zinc sulfide (ZnS) dots with conductive layers for free chlorine. As with gold nanoclusters, the dots produce a fluorescence ($\lambda_{\text{max}} = 590 \text{ nm}$) on excitation with a 405 nm laser which is quenched on reaction with free chlorine and so the degree of quenching allows calculation of free chlorine concentration. The LOD is 0.002 ppm. The sensitivity and selectivity of QDs is at the top end of the range approached by the other techniques listed here. The standard error of 8–11% is also typical of existing chlorine detection methods. The toxicity of CdSe is a significant barrier to adoption, given that relatively low toxicity methods (such as DPD-based methods) are readily available.

3.1.10 Nitrogen and Sulfur Co-Doped Carbon Dots

Carbon dots are composed of sp^2 hybridised carbon, rather than the heavy metals used in QDs, to reduce toxicity. Carbon dots produce a blue fluorescence at 420 nm when excited at 345 nm in solution. Added chlorine quenches this reaction thus free chlorine can be determined fluorometrically. Interference from 0.1 mM Fe^{3+} was substantial (40% of the fluorescence intensity of hypochlorite at 10%

of the hypochlorite concentration). However, since 3.6 μM of iron is the maximum permitted in England's drinking water (67) this does not seem critical in this application. The limit of detection of this method is the lowest of the methods reviewed (46). The impressively wide linear range is 0.35 ppb to 3.5 ppm, with an error of 2.5–3.8% though between 10 minutes and 1 hour is required for the quenching reaction to stabilise.

3.1.11 Oxidative Cleavage-Based Probe

Whilst intended for monitoring the activity of myeloperoxidase in neutrophils, the CY-FPA near-infrared (NIR) fluorescent probe is nonetheless an interesting method of detecting hypochlorous acid by fluorescence quenching (51). CY-FPA is based on an existing cyanine dye-based probe (CY-Cl) which has been modified by addition 1-(furan-2-yl)-*N*-(pyridin-2-ylmethyl)-methanamine (FPA) to enhance stability and for selective detection of hypochlorous acid (**Scheme I(a)**). Free chlorine added to the probe at pH 7.4 quenches fluorescence ($\lambda_{\text{ex}} = 700 \text{ nm}$) of CY-FPA at 774 nm.

This probe is intended for studies of the enzymatic activity of myeloperoxidase in cells, however the authors have shown that it may be used for free chlorine analysis in water. The linear range for this method is 0.123–1.26 ppm with a 1.6% error. Interference from several common ions was not detected.

3.1.12 Manganese Dioxide Nanosheets

Two-dimensional (2D) nanostructures of manganese dioxide (MnO_2) nanoparticles (nanosheets) have been investigated for analytical applications, various colorimetric assays and high-capacity capacitors (68–70, 47). MnO_2 nanosheets fluoresce at 370 nm. When dissolved in ascorbic acid, dehydroascorbic acid and Mn^{2+} are produced leading to fluorescence quenching. In solutions with free chlorine and nanosheets, ascorbic acid is oxidised by free chlorine thus inhibiting the dissolution of the nanosheets and reducing the extent of quenching. The LOD of this method is 5.7 ppb and the linear range is 0.041 ppm to 0.7 ppm. The authors also tested for selected possible drinking water contaminants at concentrations of 0.7 ppm, in several cases higher than emitted levels, and found no significant interference (67) and an estimated error of 1.2%.

3.1.13 Summary of Reagent-Based Methods

With the exception of the special case of online automatic DPD analysers, the reagent based-methods discussed here are not automated. Trained staff are typically required to carry out the procedures, the reagents are often unstable or toxic and the samples cannot be retested after analysis: these are 'single shot' methods. Interferences from temperature and pH changes, transition metal ions and oxidisers are also common to some methods. These methods have errors of at most 10% and most have ranges of application that cover the crucial 0.2–2 ppm range. The detection limits of these methods generally outperform what is required for drinking water analysis however the barriers in using reagents for remote monitoring and continuous analysis remain problematic.

3.2 Electrochemical Methods

Electrochemical methods for continuous chlorine analysis in water are well established (71, 72). Several factors can influence the performance of electrochemical sensors including salinity, specificity, pH, temperature and electrode material. Membranes were developed to improve specificity and prevent fouling (73). Electrochemical detection by oxidation or reduction are both possible (74–76): the standard reduction potentials for free and elemental chlorine (HOCl , OCl^- or Cl_2) are given in **Table I**. Clear (though pH-dependent) diffusion-limited plateaux can be observed for the reduction of free chlorine species on platinum (77) and gold electrodes (78) where Pletcher reports diffusion limited reduction currents at neutral pH at potentials more negative than 0.5 V and 0.4 V respectively (*versus* saturated calomel electrode (SCE)) (78). Interference from concomitant O_2 (aq.) reduction is a potential problem, although van den Berg reported (for a thin film microfabricated Pt device) a potential window between +0.3 V and +0.4 V (*vs.* SCE) where the free chlorine reduction wave is essentially independent of potential and O_2 reduction does not significantly contribute to the current (79). The strong pH dependency of the wave positions for both electrodes does not rule out interference in all samples, however. This is addressed by del Campo by exploiting the larger overpotential of Au, compared with Pt, for O_2 reduction (80). Jović *et al.* report free chlorine reduction on inkjet printed silver AgCl/AgO_2 electrodes, allowing customisation of the electrode

shape to potentially fit into any part of water distribution systems (76).

The relative merits of Au, Pt and glassy carbon electrodes for sensing in the anodic mode have been compared (74), where the authors favoured Pt electrodes for drinking water analysis. New materials are also being investigated to address the flaws with conventional electrodes (81).

3.2.1 Platinum Electrodes

Platinum sensors are well established as the most reliable electrochemical technology available for continuous monitoring. An example commercially available instrument can be used for chlorine concentrations of 0.05–1 ppm with a 10% RSD (61). Electrode fouling, or mineralisation and biofouling, is a common problem, even in treated drinking water (31, 82). To mitigate this, online amperometric free chlorine analysers use filters, mechanical wipers, copper tape and other antifouling measures which require regular replacement as a precaution (19). The electrode may have to be serviced or recalibrated if the fouling is particularly damaging. After five days of continuous free chlorine measurements in tap water, oxide layers form on Pt sensors in a process that is not well understood and potentially aggravated by the presence of trace organics (83). The most reliable of continuous online chlorine sensors are susceptible to fouling, which necessitates regular replacement of filters or electrodes and limits their use in areas of drinking water systems that are less accessible than treatment works.

3.2.2 Gold Thin-Film Transducers

Recent advances in microfabrication have allowed for the development of gold thin-film microelectrodes which are integrated within a flow cell to extend their lifetime for practical use in the field. Such devices have been used to detect chlorine in drinking water (44). The authors use an analytical potential of 0.350 V for the anodic detection of free chlorine which was chosen after a period of optimisation (44). The range of the device is between 0.2 ppm and 10 ppm with a 5% error.

The researchers note that biofouling of the electrode decreased the accuracy of the measurements and that cleaning with sulfuric acid is recommended. While these devices report absolute values for chlorine within an acceptable range, the problems of biofouling and storage remain which makes the deployment of such

devices for continuous chlorine detection difficult. The authors expressed concern that gold electrodes degrade in solutions of chlorine however no long-term testing in drinking water was carried out. The authors propose adding a protective film or filter to prevent biofilm from covering the electrode, an approach which is currently used on existing amperometric sensors, or by storing the device in an inert atmosphere when not in use.

3.2.3 Multiwalled Carbon Nanotube/Epoxy Nanocomposite Sensors with CuO Nanoparticles

This is an amperometric sensor technology that incorporates conductive copper oxide (CuO) nanoparticles in a three-dimensional (3D) epoxy matrix to maximise sensitivity by maximising the available electrode surface area (48). The particles are incorporated from a powdered form which is subsequently added to epoxy that is allowed to harden on the surface of the sensor. The catalysts did not show degradation in response to repeated use and the authors emphasise that whilst CuO nanoparticles were used in this sensor, other nanoparticles could be used to catalyse specific reactions and produce specific responses. The sensitivity to fouling is not known. The linear range was reported as 0.056–450 ppm with 2.7% error and a LOD of 0.6 ppb. This sensor uses an analytical potential of -0.35 V.

3.2.4 Surfactant-Modified Prussian Blue Sensor

This sensor was prepared by electrodeposition of successive layers of Prussian blue (PB) and benzethonium chloride (BZTC) onto a glassy carbon electrode. BZTC is a cationic surfactant which is used to increase the electrochemical and electrocatalytic response of PB immobilised on the surface of glassy carbon electrodes (49). PB is commercially available, easily prepared and in this instance was electrodeposited onto the electrode surface along with BZTC to form a film. The reduced form of PB is Prussian white (PW) which catalyses the reduction of hypochlorous acid to chlorine gas (**Scheme I(e)**). Therefore, the intensity of blue colouration decreases and turns to white with increasing chlorine concentration. Although PB acts as a colorimetric agent, the free chlorine concentration is determined by the resultant current when a constant reducing potential of -0.2 V is applied. It is reported that the sensor is

intended to be used continuously in drinking water systems however the authors have not ascertained the effects of biofouling or interferences on the electrode (49). The linear range is 0.09–1 ppm with an error of 4.2%.

3.2.5 Boron-Doped Diamond Sensor

Boron-doped diamond (BDD) is a synthetic diamond, doped with boron to produce a material which is corrosion-resistant, fouling-tolerant and sufficiently conductive to be used as an electrode in place of less stable precious metal electrodes (84, 85). BDD sensors are being developed for use in drinking water for disinfection by production of oxygen radicals from water (86) and for chlorine detection (74, 52), separate methods which when combined could result in a reagentless chlorine sensor that can remove microfilm and mineral deposits from the sensor surface. *In situ* surface regeneration would allow BDD electrodes to operate continuously without maintenance, cleaning or the use of disposable membranes. BDD sensors that are capable of surface cleaning have been developed for biomedical applications (87). Murata *et al.* report that they have developed a BDD sensor with a linear range of 0.1–2 ppm, a LOD of 0.083 ppm and an error of 2.56%. The authors carried out their analysis, using anodic oxidation, with a fixed potential of 1.1 V (52). An *in situ* regenerating BDD-based free chlorine sensor has been developed and tested in drinking water samples (88), although further testing is required to meet water industry standards of reliability and accuracy.

3.2.6 Gold-Graphite Chemiresistive Sensor

Chemiresistive sensors use a conducting material bridge, situated between two electrodes, which chemically interacts with analytes resulting in a change in resistance between the electrodes. Graphite is a commonly-used electrochemical sensor material, however graphite originating from a pencil is less conventional (89). The study's authors claim that the advantage of such a device is the low cost of the pencil when compared with other electrochemical sensors. Their sensor was constructed from two gold electrodes connected by a conductive phenyl-capped aniline tetramer (PCAT)-graphite film bridge, where the graphite used originated from a pencil. The PCAT oligoanilines are oxidised in the presence of chlorine

and other oxidising compounds, which changes the resistance between the gold electrodes and allows for quantification of the chlorine residual.

The authors showed that the addition of PCAT to the graphite bridge increases the recorded error for free chlorine detection without interferences originating from wastewater from about 3.5% to 6%. The paper shows a concentration range of 0.06 ppm to 60 ppm with an error ranging from about 2.5–25%. In a separate figure, a range of 1.5–9 ppm with an error of about 4.5–8.5% is also presented. The authors tested for the effects of biofouling, however this trial was limited to 30 minutes duration. Further testing of this sensor should be carried out in drinking water infrastructure over longer periods.

3.2.7 Summary of Electrochemical Methods

Reagentless, amperometric methods promise to be automatic, remote, accurate and low-maintenance. With no reagents to replace and without any requirements for trained personnel to maintain and operate them, electrochemical sensors would appear to be the ideal free chlorine sensor. However, degradation of precious metal electrodes, microfouling by organisms attached to the sensor surface and mineralisation limit widespread use for long-term applications. Of the new novel electrode materials, BDD looks like the most promising candidate due to fouling resistance, chemical inertness and mechanical stability. The problems of reproducibility, identification and optimisation of electrochemical parameters and high cost remain, but these are likely to be addressed by improved processes. Biofouling, mineralisation and instability in long-term use are the principle obstacles that will have to be overcome if electrochemical sensors are to replace existing reagent-based systems.

4. Conclusion

This paper has discussed the factors which affect measurements of free chlorine and a review of standard and newly-developed methods of chlorine detection. The development of new online chlorine analysis has been shown to be challenging due to fouling, maintenance and problems associated with the use of reagents. An analysis by Hach in 2002 (61) concludes that the colorimetric and titration DPD methods, developed in the 1950s, remain the two preferred methods for chlorine analysis. The stability, cost effectiveness and relative ease

of automation set these techniques apart from all others.

Technologies that have been developed over the past decade centre on the upgrading of existing methods and equipment. Replacing DPD with ABTS or other reagents, coating ABTS or poly(luminol) on existing electrodes, embedding electrode materials in polymer matrices or developing new films or add-on polymers that are specific to chlorine are approaches used in the methods presented here. As tried-and-tested techniques for chlorine detection remain in constant use and continue to be held as standard methods, it remains to be seen if the approaches taken by the majority of researchers in this area will be effective in addressing the problems discussed above. Other methods, such as the use of QDs, are entirely novel but are more suitable for medical imaging and other niche applications.

Few of the newly-developed methods discussed consider the need for continuous online analysis in drinking water distribution systems. The problem of biofouling or how sensors will be physically integrated are rarely discussed. Existing methods use probes which emerge from the walls of pipes or are connected to bypass systems for the delivery of reagents to drive reactions or to control flow conditions. These methods have inherent complications which are not taken into account, however the use of flow injection analysis (FIA) and flow cells has been discussed for some of the amperometric methods. A true evaluation of the performance of chlorine sensors must involve real samples and field trials, however the proposed new technologies are carried out in laboratory conditions, with few exceptions using real water samples instead of prepared hypochlorite solutions. None were tested in distribution systems where conditions such as pressure, dissolved oxygen and mineral composition fluctuate in the long and short term. More radical methods could include the development of new electrode materials, seen in the development of BDD-based amperometric sensors, as precious metals degrade in hypochlorite solution and coatings have limited lifespans or potentially toxic components. BDD is a promising sensor material as it can be configured to carry out chlorine analysis and localised disinfection however it remains to be seen if this is effective when used in water distribution systems.

This review attempts to stress that unless fouling tolerance is seriously considered from the onset, other innovations such as miniaturisation, reliability over short periods in laboratory conditions, cost and detection limits in non-representative solutions are

less useful. The ideal chlorine sensor is one which combines the simplicity and reagentless operation of electrochemical sensors with the robustness of offline methods. Such a sensor would be deployable anywhere in a drinking water distribution network with minimal manual operation and maintenance. This would ensure that drinking water supplies are continuously monitored, which removes the guesswork of modelling, to better protect consumers from potentially harmful fluctuations in disinfectant concentration.

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