Bleaches and Sterilants☆

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Glossary

Amperometry An analytical method that uses electrical current at an appropriate applied voltage to measure analytes in solution.

Bleach (chemical) A chemical agent used to remove color from various substances, such as paper, food, and textiles. Some bleaching agents may also act as disinfectants or serilants.

Breakpoint chlorination The addition of chlorine until all chlorine demand has been satisfied.

Chlorine demand Free (available) chlorine (FAC) that is required to react with all oxidizable species present in the water. In practice, chlorine demand is the difference between the chlorine added and the amount remaining after a given contact time.

Chlorine dose The amount of chlorine required to satisfy the chlorine demand plus the amount of chlorine residual required for disinfection.

Combined (available) chlorine Available chlorine in the form of undissociated *N*-chloro compounds that can hydrolyze to produce hypochlorous acid.

Disinfectant (chemical) An antimicrobial chemical agent that destroys microorganisms such as bacteria and fungi living on inanimate objects. Disinfectants may not destroy all bacterial spores and so are not considered as effective as sterilants in eliminating microorganisms.

Free (available) chlorine, FAC Chlorine in the form of dissolved Cl_2 gas, hypochlorous acid (HOCl), and hypochlorite ion (ClO^-) that is available to react with oxidizable species present in the water.

On-line monitor A device that permits the automated or semi-automated measurement of changes in selected process parameters, without the need for sample removal.

Reference method An analytical procedure considered sufficiently reliable that it can be used to validate a new analytical procedure for the same analyte.

Standard method (procedure) A testing method chosen by a recognized standards organization that is considered acceptable (approved) for measuring a particular property of a system, such as standard methods approved by the EPA for testing water quality.

Standard reduction potential, $E°$ A measure of the tendency of a chemical agent to acquire electrons and become reduced, that is, to act as an oxidizing agent. The more positive the potential, the greater the oxidizing strength of the agent. The standard reduction potential is measured under standard state conditions and defined relative to the standard hydrogen electrode, which is arbitrarily assigned a potential of 0.00 V.

Standard state (conditions) A set of reference conditions (purity, pressure, concentration, etc.) for a material, as defined by the International Union of Pure and Applied Chemistry. Standard state conditions are used as the reference state of a material when discussing thermodynamic properties, such as electrode potentials, which are directly related to Gibbs free energy.

Sterilant (chemical) A chemical agent that eliminates all biological forms of life, including potentially infectious organisms such as highly resistant bacterial spores and viruses. Sterilant efficacy is achieved when less than a specified number of microbes remain viable following treatment.

Total (residual) chlorine Sum of free chlorine (FAC) and any combined chlorine remaining after the chlorine demand of the treated water has been satisfied.

Introduction

Bleaching agents remove or prevent unwanted discoloration of a substrate. Chemical disinfectants and sterilants destroy unwanted microorganisms on contact. This article surveys the more important chemicals employed for these purposes. Because the residual levels of disinfectants following municipal water treatment are subject to governmental regulation, this article gives particular attention to the standard analytical methods for determining chlorine residuals in drinking water, such as volumetric methods based on

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iodine, colorimetry using *N*,*N*-diethyl-*p*-phenylenediamine, amperometry, and colorimetry using syringaldazine. Some additional, promising non-standard methods, such as colorimetric analysis using leucocrystal violet, chromatography and flame infrared emission are discussed, as well as on-line monitoring techniques useful in industrial process control.

Major Areas of Use and Applications

The terms bleaches, disinfectants and sterilants refer to a number of chemical agents found in common use throughout modern society. While the three terms are sometimes used interchangeably, their definitions are not the same because their actions are different.

Bleaching Agents

Bleaching agents are formulations that whiten or lighten a substrate by solubilizing color-producing substances or by altering their light-absorbing properties. Bleaching agents are used extensively in the pulp and paper industry, the textile industry, and commercial and household laundering.

The chemistry of bleaching agents is predominantly that of oxidizing agents: chlorine (Cl_2) and some of its compounds or peroxygen species such as hydrogen peroxide (H_2O_2), ozone (O_3), and sodium perborate ($NaBO_3 \cdot nH_2O$; $n = 1$–4). The decolorizing reaction generally involves the removal of chromophoric sites in which electron delocalization over conjugated double bonds has made the substrate capable of absorbing visible light. The bleaching agent will typically react by irreversibly cleaving or adding across these double bonds.

A few bleaching compounds act by chemical reduction; these include sulfur dioxide (SO_2), sulfurous acid (H_2SO_3), hydrogensulfite (HSO_3^-), sulfite (SO_3^{2-}), and dithionite ($S_2O_4^{2-}$), as well as sodium tetrahydroborate (borohydride) ($NaBH_4$). Their application is primarily in pulp and textile manufacturing, where the bleaching action is thought to occur by reduction of a chromophoric carbonyl group. Other applications include the bleaching of glues, gelatin, soap, and food products.

Chemical bleaching of textiles (as opposed to bleaching by sunlight, a process known as crofting) had its advent soon after the discovery of the element chlorine by Scheele in 1774. Finding that aqueous solutions of chlorine gas weakened the fiber of textiles, Bertholet experimented with solutions of potassium hypochlorite (KOCl), made by dissolving chlorine gas in a solution of caustic potash (KOH). Labarraque made hypochlorite solutions industrially economic by replacing the more expensive caustic potash with caustic soda (NaOH). The liquid household bleach normally available today is a 5% solution of sodium hypochlorite (NaOCl).

Disinfecting Agents

Disinfectanting agents kill microorganisms, but endospores may be resistant. Chemical disinfection with chlorine gas was recommended as early as 1801 and was widely installed in British and European hospitals by 1823. Following the discovery of the microbial basis for contagious diseases, Robert Koch (1881) demonstrated that hypochlorites were effective in killing bacteria. In 1905, following an outbreak of typhoid fever in London, continuous chlorination of the public water supply was inaugurated. Chemical disinfection of a public water supply was first practiced in the United States in 1908, and since that time has been a routine part of municipal water treatment. Chemical disinfectants are also used extensively in the production of bottled water and the manufacture of containerized beverages of all types, in the treatment of waste water, and in the treatment of water in swimming pools and spas.

Sterilants

Sterilants are strictly defined by the US Environmental Protection Agency as substances that totally destroy or irreversibly inactivate all forms of microbial life, including viruses, bacteria, fungi, and their spores on inanimate surfaces, in water, or in the air. Many substances that render objects microbiologically safe for specific applications (i.e., reduce the level of living microorganisms below some predetermined level) are also commonly referred to as sterilants.

Sterilization can be accomplished by treatment with powerful chemicals, such as pure chlorine and chlorine dioxide, as well as by physical processes such as heat, cold, and intense radiation. Chemical sterilants are typically oxidizing agents, and their effectiveness is related to their ability to oxidize the cell wall of the microorganism and to diffuse through the cell wall and disrupt cellular activity.

Chemicals Used as Bleaches, Disinfectants and Sterilants

A comprehensive discussion of the analytical chemistry of bleaches and disinfectants is complicated by the diversity of chemicals that are employed.[1] Table 1 shows some of the more commonly used agents and their oxidizing strengths.

Many of the same substances that act as bleaching and disinfecting agents are also used extensively as sterilants. The following sections provide a brief survey of some of the more important chemical agents used for these purposes.

Table 1 Oxidizing strengths of some typical bleaching agents and disinfectants as represented by their standard reduction potentials in aqueous solution

Chemical agent	*Standard reduction potential (V)*	*Half-cell reaction*
Cl_2 Elemental chlorine	+1.3595	$Cl_2 + 2e^- \rightarrow 2Cl^-$
Br_2 Elemental bromine	+1.0652	$Br_2 + 2e^- \rightarrow 2Br^-$
I_2 Elemental iodine	+0.5355	$I_2 + 2e^- \rightarrow 2I^-$
O_3 Ozone	+2.075	$O_3 + 2H_3O^+ + 2e^- \rightarrow O_2 + 3H_2O$
ClO_2 Chlorine dioxide	+0.954	$ClO_{2(aq)} + e^- \rightarrow ClO_2^-$
Further reaction	+0.76 (pH = 7)	$ClO_2^- + 2H_2O + 4e^- \rightarrow Cl^- + 4OH^-$
Further reaction	+1.570 (pH = 0)	$HClO_2 + 3H_3O^+ + 4e^- \rightarrow Cl^- + 5H_2O$
H_2O_2 Hydrogen peroxide	+0.763	$H_2O_2 + 2H_3O^+ + 2e^- \rightarrow 4H_2O$

Rumble, J. (ed.). CRC Handbook of Chemistry and Physics. NY: CRC Press, (2017).

Chlorine-Based Agents

Modern chlorine-based bleaching agents include elemental chlorine (Cl_2 gas), a variety of hypochlorites (OCl^-), certain *N*-chlorinated organic compounds (RR′NCl), and chlorine dioxide (ClO_2).[2–4]

Elemental chlorine and hypochlorites

Elemental chlorine (Cl_2 gas) and hypochlorites (OCl^-) that function as bleaching agents hydrolyze to produce hypochlorous acid (HOCl) in aqueous solution according to the equilibria in reactions (1) and (2).

$$\begin{gathered} Cl_2 + 2H_2O \rightleftharpoons HOCl + H_3O^+ + Cl^- \\ K_{\text{hydrolysis}} = 3.9 \times 10^{-4}\left(25^\circ C\right) \end{gathered} \tag{1}$$

$$\begin{gathered} OCl^- + H_2O \rightleftharpoons HOCl + OH^- \\ K_{\text{base}} = 3.8 \times 10^{-7}\left(25^\circ C\right) \end{gathered} \tag{2}$$

Fig. 1 shows the effect of pH on the chemical form of dissolved chlorine in aqueous solution for a fixed chloride ion concentration of 1×10^{-3} mol L^{-1}.

The neutral hypochlorous acid molecule, which is thought to be more effective in penetrating cell walls than the charged hypochlorite ion, has a disinfecting ability that is greater than that of OCl^- by two orders of magnitude. As a result, an aqueous solution of chlorine will have its maximum disinfecting ability over a pH range from ~2 to 7.

Solutions of hypochlorites and hypochlorous acid are subject to gradual deterioration, forming chlorite (ClO_2^-) and sometimes chloride (Cl^-) and oxygen (O_2) over a period of time. In general, the lower the pH, the less stable the solution. (Solid preparations of hypochlorite salts are quite stable if kept dry and cool.) HOCl and ClO^- react strongly with organic matter and, for maximum effectiveness, organic contamination must be removed prior to use.

Chloramines and N-chlorinated organic agents

Chloramines ($NH_{3-n}Cl_n$) and certain *N*-chlorinated organic compounds also have disinfecting properties because at the proper pH, they gradually hydrolyze to HOCl (reaction (3), where R and R′ represent H-, Cl- or suitable organic groups).

$$RR'NCl + H_2O \rightarrow RR'NH + HOCl \tag{3}$$

As a result, these compounds are considered secondary disinfectants and, if present in water, are called combined chlorine.

Monochloramine (NH_2Cl) has been used as a drinking water disinfectant in a number of US cities since the 1930s. Concentrations up to 4 mg L^{-1} are considered safe by health agencies, such as the US EPA and the World Health Organization.[3]

While monochloramine is a weaker oxidizing agent than chlorine, it persists for a longer time, providing a longer acting residual in municipal distribution systems. Its use also helps to reduce the formation of trihalomethanes, which are known carcinogens and a by-product of chlorine oxidation. Monochloroamine can be introduced into drinking water by adding ammonia and allowing the resulting mixture to react with dissolved chlorine.

Several *N*-chlorinated organic compounds that are used as disinfectants, especially in recreational waters such as swimming pools, include chloramine-T (*N*-chloro-*p*-toluenesulphonamide) (**1**), *N*-chlorohydantoins, (**2**), and various chlorinated isocyanurates (**3**).

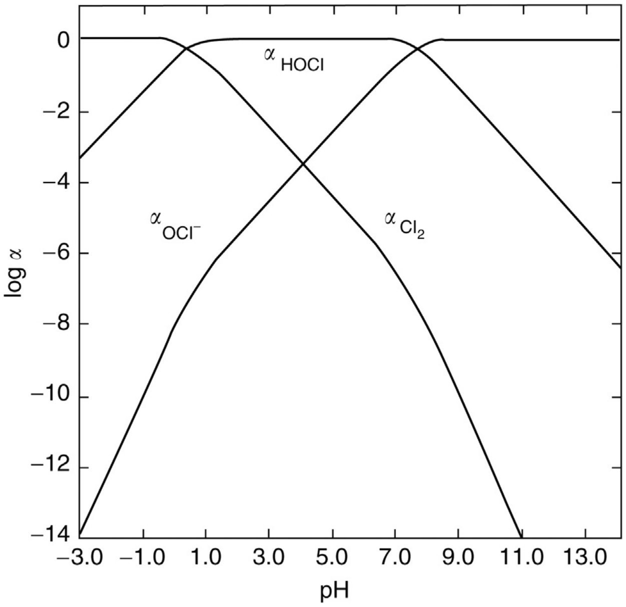
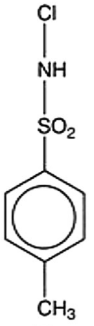
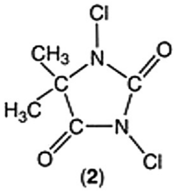


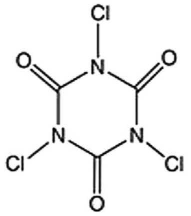
Fig. 1 Distribution diagram for aqueous chlorine in a closed system at 25°C with $[Cl^-] = 1 \times 10^{-3}$ mol L^{-1}. The fraction present in a given form (α) is equal to the concentration of the given species divided by C_T where $C_T = [Cl_2] + [HOCl] + [OCl^-]$.



(1)
Chloramine-T



(2)
1,3-Dichloro-5, 5-dimethylhydantoin



(3)
Trichloroisocyanurate [1,3,5-trichloro-*s*-triazine-2,4,6 (1*H*, 3*H*, 5*H*)-trione]

Their low solubility and/or hydrolysis in water affords poor bleaching ability. Sodium dichloroisocyanurate dihydrate, which is the most water soluble, the fastest to dissolve, and the least hazardous, is an exception and is widely used as a cleansing agent and disinfectant.

Chlorine dioxide

In acidic solution, chlorine dioxide (ClO_2) is a good oxidizing agent (Table 1), becoming completely reduced to chloride ion in a series of steps involving chlorite (ClO_2^-), hypochlorite (ClO^-) and chlorine (Cl_2), which all act as oxidizing agents. The overall reaction that ultimately yields chloride ion represents a 5-electron change, giving ClO_2 a high capacity for disinfection. While chlorine dioxide is less corrosive than chlorine, it does not react with ammonia.

Chlorine dioxide is fast replacing aqueous Cl_2, particularly in pulp and paper manufacture, because the reaction of ClO_2 with organic materials does not appear to form carcinogenic trihalomethanes (THMs) as side-products and because ClO_2 is 10 times more effective as a disinfectant under high chlorine demand.

Chlorine dioxide is an explosive gas and is usually prepared onsite by the hydrolysis of an alkali-stabilized solution of sodium chlorite ($NaClO_2$) as shown in reactions (4) and (5).

$$NaClO_2 + H_2O \rightarrow HClO_2 + NaOH \qquad (4)$$

$$5HClO_2 \rightarrow 4ClO_2 + HCl + 2H_2O \qquad (5)$$

Somewhat higher yields are afforded by reacting sodium chlorite with chlorine gas (reaction 6):

$$2NaClO_2 + Cl_2 \rightarrow 2ClO_2 + 2NaCl \qquad (6)$$

Excess chlorine must be removed from the mixture prior to use to prevent THM formation. Somewhat larger amounts of chlorine dioxide, such as needed in pulp processing and textile bleaching, are generally prepared by reduction of chlorate with hydrochloric acid (reactions 7 and 8):

$$HClO_3 + HCl \rightarrow HClO_2 + HOCl \tag{7}$$

$$HClO_3 + HClO_2 \rightarrow 2ClO_2 + H_2O \tag{8}$$

Oxygenated Agents

Peroxides

Hydrogen peroxide and other peroxy compounds derived from hydrogen peroxide are also used as bleaching agents.[1] These compounds contain the peroxide linkage (—O—O—). Liquid solutions of hydrogen peroxide are commercially available (30%–35%, 50%, or 65%–70% by weight); however, stable, solid peroxy compounds that hydrolyze in solution to give hydrogen peroxide offer improved stability and convenience in handling.

Typical among this class of solid bleaching agents (so-called safety bleaches) is sodium perborate, which is formed by reacting borax with hydrogen peroxide in the presence of base (reaction 9). For simplicity, waters of hydration on the borax are not shown.

$$Na_2B_4O_7 + 4H_2O_2 + 2NaOH \rightarrow 2Na_2B_2O_4(OH)_4 + H_2O \tag{9}$$

Hydrogen peroxide is a very weak acid and is relatively stable in acidic solution. Bleaching is performed in alkaline solution, where part of the hydrogen peroxide is converted to the perhydroxyl anion (HO_2^-), believed to be the active bleaching agent (reaction 10):

$$H_2O_2 + H_2O \rightleftarrows H_3O^+ + HO_2^- \tag{10}$$

Disproportionation to water and oxygen is markedly accelerated by the presence of heavy metals, and metal chelating agents are often added to solutions of H_2O_2 as stabilizers.

Ozone

Concern over the adverse health effects of trace amounts of THMs produced during the chlorination of drinking water has led to the use of nonchlorinated disinfection agents, such as ozone (O_3), in the treatment of domestic water, particularly in Europe. Ozone has not been extensively employed in the United States because it is difficult to maintain an active residual once the water leaves the treatment plant. Ozone gas is also used in hospitals to sterilize instruments and surgical dressings.

Ozone decomposes rapidly to oxygen (O_2) and must be generated on demand, in close proximity to the utilization site. Ozone is generated by passing air or oxygen through a high-voltage corona discharge. Aqueous solutions are prepared by bubbling the gas through a column of water.

Sulfur-Based Reducing Agents

Sulfur dioxide (SO_2) is a gas, formed by burning sulfur in air. When dissolved in water, SO_2 forms sulfurous acid, a complex mixture of various hydrates of SO_2 and the ions H_3O^+, $S_2O_5^{2-}$, and HSO_3^-. The predominant species present in solution depend on pH, but since all of the sulfur-containing species are good reducing agents, the bleaching effect is essentially independent of pH over the range 3–10.

Sodium dithionite, also known as sodium hydrosulfite ($NaHS_2O_4$), is one of the most industrially important reducing bleaches. When used in conjunction with a complexing agent, it is effective in removing rust stains and is employed in certain industrial dyeing processes and in the bleaching of wood pulp.

Determination of Chlorine Residuals in Drinking Water

The terminology associated with the use of chlorine in drinking water is highly specific.[5] The Glossary provides concise definitions of several of the more important terms. For the purpose of discussion, the relationships between some of these terms are summarized below.

$$\text{Chlorine dose} = \text{Chlorine demand} + \text{Chlorine residual}$$

$$\text{Chlorine residual (Total chlorine)} = \text{Combined chlorine} + \text{Free (available) chlorine (FAC)}$$

Effect of Addition of Chlorine to Surface- or Groundwater: Analytical Considerations

When chlorine is added to a surface water or groundwater, a number of species present in the water can consume chlorine. Reactions with inorganic species such as iron(II), manganese (II), and sulfides produce chloride ion (Cl^-), which has no residual oxidizing power. Nitrogenous bases, such as ammonia (NH_3), urea, and amino acids, form chloramines and other organically bound chlorine.

As the reaction with chlorine continues, much of the N-bound chlorine also reacts, eventually producing species such as nitrate ion (NO_3^-) or nitrogen (N_2), which also have no residual oxidizing power. The chlorinated nitrogenous bases remaining after a prescribed period of contact time with FAC are called combined chlorine. These compounds retain some residual disinfectant properties because they can hydrolyze to form hypochlorous acid (reaction 3). The combined as well as free forms of available chlorine remaining after the chlorine demand of the water has been satisfied are called the chlorine residual (or sometimes total chlorine).

Combined chlorine is a less aggressive oxidizer than FAC, and its disinfectant properties are correspondingly weaker. As a result, governmental regulations generally specify that the FAC residual in treated water, rather than total chlorine residual, be monitored and adjusted to maintain disinfectant levels sufficient to (1) inactivate water-borne, disease-causing organisms and (2) to protect the water from recontamination during storage and circulation through the municipal water system. Thus, the chlorine dose at the treatment plant must be sufficient to meet the chlorine demand of the water and leave enough FAC residual to keep the water safe for consumption.

Much effort has been invested in the development of standard analytical methods for FAC determination in municipal water samples over the concentration range from 0.001 to 10 mg L^{-1} (expressed as Cl_2), in the possible presence of combined chlorine. The overriding challenge has been the need to distinguish between the free and combined forms of residual chlorine. If combined chlorine is measured along with free chlorine, the true residual FAC will be overestimated, and the FAC disinfectant level may be inadequate to guarantee potable water.[6–9]

In the case of drinking water, periodic monitoring of the presence of chlorine-based disinfectants is required by the Surface Water Treatment Rule (US EPA). Depending on the size of the facility, monitoring might be carried out by removing samples from the treated water, followed by laboratory analysis using standard procedures. However, water utilities are increasingly following the practice of continuous monitoring with automatic control of chlorine feed to meet a preset value for chlorine dose. Continuous monitoring is also important in industrial settings where continuous analysis is frequently carried out by automated or semi-automated procedures that are related to standard laboratory methods.

Breakpoint Chlorination

The problem in distinguishing between residual FAC and combined chlorine can be illustrated by breakpoint chlorination. In breakpoint chlorination, dissolved chlorine is added to the water in a stepwise manner to determine the total chlorine demand and to allow for the formation of chloramines.

Fig. 2 is an idealized plot of total residual chlorine as a function of the chlorine dose added to a water sample that contains only ammonia.

Initially, addition of chlorine causes rapid formation of monochloramine (NH_2Cl), and the chlorine residual rises. A maximum in the curve occurs at a Cl_2/NH_3 molar ratio near 1, where residual chlorine is present only as monochloramine and some unstable dichloramine ($NHCl_2$). At a higher chlorine dose, nitrogen gas (N_2), nitrate (NO_3^-), and chloride ion are formed (reactions 11 and 12),

$$3Cl_2 + 2NH_3 + 6H_2O \rightarrow N_2 + 6Cl^- + 6H_3O^+ \tag{11}$$

$$4Cl_2 + NH_3 + 12H_2O \rightarrow 8Cl^- + NO_3^- + 9H_3O^+ \tag{12}$$

causing the residual chlorine to decline. Finally, when all of the ammonia has been consumed, a minimum (breakpoint) is reached. At the breakpoint, the chlorine demand of the water has been satisfied, and further addition of chlorine causes the chlorine residual (now present as FAC) to increase linearly.

Survey of Standard Methods for the Determination of Chlorine Residuals in Drinking Water

In industrial operations like pulp and paper manufacturing and textile bleaching, the selection of analytical methodology is largely dictated by process analytical and quality control requirements. By contrast, the methods used for the determination of residual levels of disinfectants in drinking water are highly regulated by national and local governments. Since government-mandated methodology can generally be adapted for the analysis of bleaching agents in industrial processes, this article will focus on the standard analytical procedures developed for water analysis.[10]

At present, four general methods are recognized as standard methods for determining chlorine residuals. They are:

- Methods involving iodine
- Methods involving *N*,*N*-diethyl-*p*-phenylenediamine (DPD)

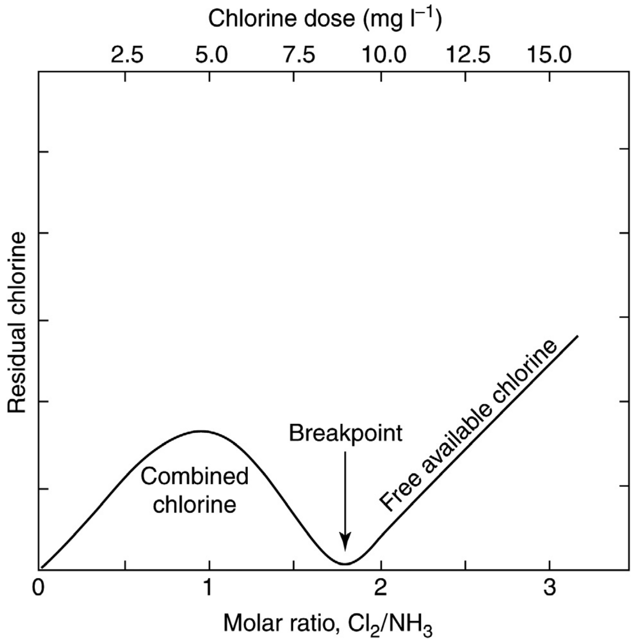


Fig. 2 Idealized breakpoint chlorination curve showing chlorine residual as a function of chlorine dose for a water sample at pH 7 that contains only ammonia at a concentration of 1 mg nitrogen (as NH_3) per liter.

- Amperometric methods
- Methods involving syringaldazine (FACTS)

Although no ideal method exists, at present, that can distinguish between free and combined chlorine without interference, analytical methods based on amperometry and the use of *N*,*N*-diethyl-*p*-phenylenediamine (DPD) are the most frequently employed in water analysis. With both of these methods, FAC is first determined in the absence of iodide (I^-). Iodide can then be added to the solution, and the iodine (present as triiodide ion, I_3^-) formed from the oxidation of iodide by combined chlorine is determined.

Methods using iodine

Iodide ion (I^-) is readily oxidized by dissolved chlorine (Cl_2), forming triiodide (I_3^-) if excess iodide is present. However, standard solutions of iodide are subject to decomposition due to reaction with contaminants frequently found in drinking water and volatility of the resulting iodine. As a result, methods using iodine directly (iodimetric) are usually performed indirectly (iodometric).

Iodometric (indirect) method

Starch-iodide titration is one of the oldest methods for determining chlorine. The iodometric procedure serves as a reference method for the determination of total residual chlorine at concentrations greater than 1 mg L^{-1} (as Cl_2). The procedure involves addition of a known, but excess amount of KI, to a known volume of aqueous sample. The method is not highly specific. All oxidizing agents having a reduction potential ($E°$ value) much greater than +0.54 V will react to form iodine (present as I_3^-), which is titrated with a standard solution of sodium thiosulfate ($Na_2S_2O_3$) according to reaction (13).

$$2S_2O_3^{2-} + I_3^- \rightarrow S_4O_6^{2-} + 3I^- \qquad (13)$$

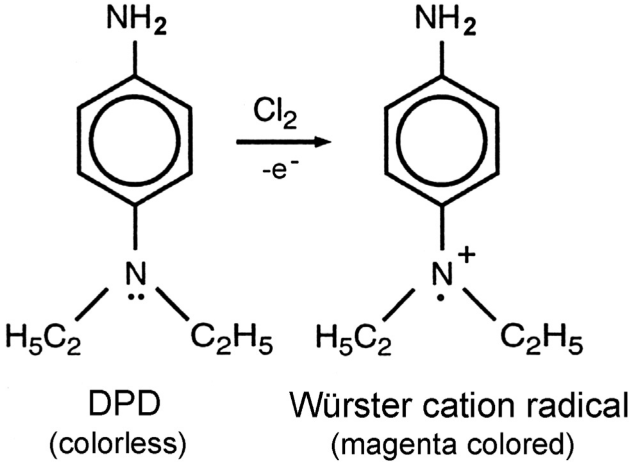
The equivalence point is taken as the volume of titrant required to react with all of the I_3^- formed. The endpoint can be determined using a starch indicator (i.e., at the disappearance of the blue starch–iodine complex) or by amperometry.

Iodimetric (direct) method

For polluted waters or chlorinated waste waters where residual chlorine is present mainly in the combined form, analytical methods do not need to distinguish between FAC and combined available chlorine. Iodometric titration is not recommended because these water samples typically contain small amounts of reducing agents that can react with, and thereby reduce the liberated iodine (I_3^-) over the course of the titration. In this case, an iodimetric procedure is recommended. Arsenic(III) (as arsenic trioxide, As_2O_3) is added to the sample in a known amount that is in excess of the combined chlorine. Once the combined chlorine has reacted, excess As(III) is titrated with a standard solution of I_3^- to a starch endpoint (formation of a blue color).

Methods using N,N-diethyl-p-phenylenediamine (DPD)

DPD (*N*,*N*-diethyl-*p*-phenylenediamine) is reversibly oxidized to a magenta-colored cation radical known as a Würster cation (reaction 14).[11]



(14)

This reagent has replaced neutral *ortho*-toluidine as the indicator in the standard titrimetric determination of FAC by ammonium iron(II) sulfate ($(NH_4)_2Fe(SO_4)_2$) (reaction 15):

$$HOCl + 2Fe^{2+} + H_3O^+ \rightarrow Cl^- + 2Fe^{3+} + 2H_2O \tag{15}$$

In the standard procedure, the FAC reacts instantly with DPD to produce a red color, and the titration is continued until the red color of the indicator disappears. Because mono- and dichloramines hydrolyze slowly in solution to release hypochlorous acid (reaction 3), titrations must be carried out rapidly to reduce the interference of combined chlorine.

The concentration of the Würster cation produced by reaction with FAC can also be determined spectrophotometrically at 515 nm. The absorbance should be measured within 1 min following the addition of DPD reagent to avoid interference of combined chlorine. Calibration standards for the spectrophotometer can be prepared from previously standardized chlorine solutions (by titration with ammonium iron(II) sulfate) or by using standardized potassium permanganate ($KMnO_4$) solutions to develop the DPD color.

Both turbidity and colored water samples can produce an interference in the spectrophotometric procedure. Oxidizing agents such as bromine, iodine, chlorine dioxide, ozone, and oxidized forms of manganese will also interfere with either the titrimetric or the spectrophotometric DPD procedure.

In aqueous solution, the DPD indicator is catalytically oxidized by oxygen when trace metals are present. In the standard method, the DPD solution is mixed with a strong phosphate solution, buffered at pH 6.2, and ethylenediaminetetraacetate (EDTA) is added to complex trace metals. Thioacetamide (CH_3CSNH_2) can be added immediately following the addition of DPD to decrease the interference from monochloramine. Addition of mercury(II) chloride ($HgCl_2$) to the phosphate buffer has also been found to reduce the interference from monochloramine, presumably by complexation of trace iodide by Hg^{2+}.

When both free and combined chlorine are to be measured, the FAC is determined first using an excess of DPD. Potassium iodide is then added to the solution and reacts readily with chloramines to produce I_2, which, in turn, reacts with part of the excess DPD. If only a small amount of KI is added, monochloramine will be the primary reactant. If an excess of KI is added, both mono- and dichloramine can be made to produce I_2. Thus, sequential addition of KI to the sample can, in principle, allow the various chlorine fractions to be determined.[3]

Amperometric methods

Amperometric methods are based on the measurement of current produced in an electrochemical cell at an appropriate applied voltage.[12] **Fig. 3** shows a typical cell employed for the amperometric determination of dissolved chlorine, which consists of a reference electrode, whose potential is fixed, and a working electrode, whose potential can be adjusted. If a reducible substance is present in the cell and the cell potential is sufficiently high, the diffusion current will be proportional to the concentration of the reducible species.

In amperometric titrations, the diffusion current is plotted versus the volume of titrant added to give a titration curve consisting of two straight-line segments. **Fig. 4** corresponds to the titration of a reducible analyte with a titrant that is not reducible. The titrant volume corresponding to the intersection of the two straight-line segments is taken as the endpoint.

In the amperometric determination of dissolved chlorine (**Fig. 3**), a Ag/AgCl reference electrode is employed, and a spontaneous cell is formed between the platinum working electrode (reaction 16) and the reference electrode (reaction 17), yielding the net reaction (18),

$$\begin{gathered} Cl_2(g) + 2e^- \rightarrow 2Cl^-(aq) \\ E^{\circ}_{red} = +1.360\ V \end{gathered} \tag{16}$$

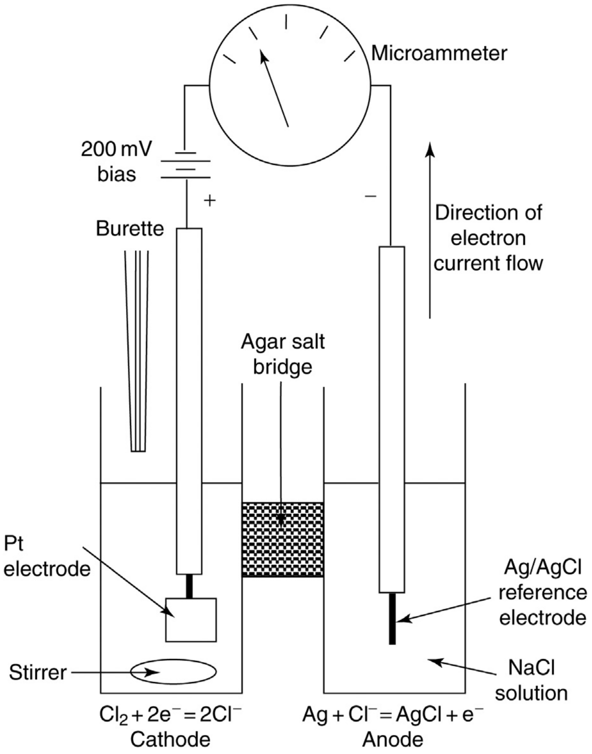


Fig. 3 Amperometric titration apparatus for the determination of dissolved chlorine.

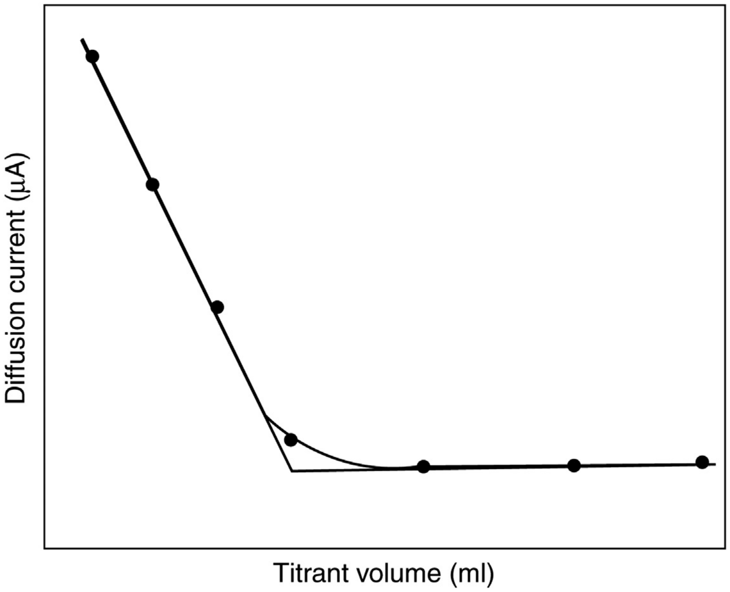


Fig. 4 Amperometric titration curve showing diffusion current versus titrant volume for a reducible analyte and a titrant that is not reducible.

$$2Ag(s) + 2Cl^-(aq) \rightarrow 2AgCl(s) + 2e^- \quad E^\circ_{ox} = -0.222\,V \tag{17}$$

$$\text{Net reaction} : 2Ag(s) + Cl_2(g) \rightarrow 2AgCl(s) \quad E^\circ_{cell} = +1.138\,V \tag{18}$$

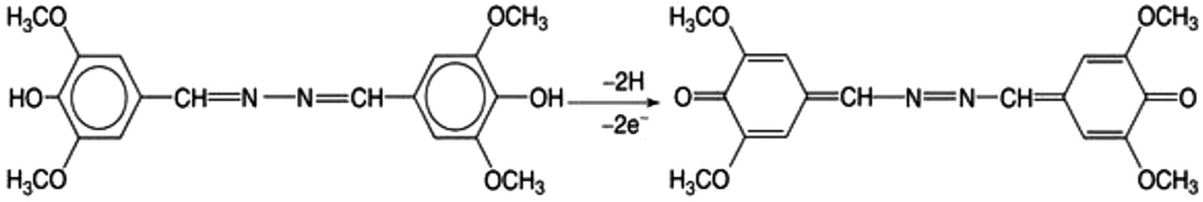
In equations (16–18), the reactions have been represented in terms of standard state conditions. The true voltage will be somewhat less than that shown in reaction (18) because the Cl_2 is present in solution and its vapor pressure will be much less than 1 atm, as implied for standard-state conditions. Nevertheless, it is apparent that the voltage produced by this spontaneous cell is more than sufficient to provide limiting current conditions at the platinum electrode. However, most standard methods suggest that +200 mV be applied to the platinum electrode to improve sensitivity (Fig. 3).

Amperometric titration is the standard method for comparison of accuracy in determining residual chlorine in drinking water. FAC is determined by titration with a standard solution of As(III) (in the form of phenylarsine oxide, C_6H_5AsO) at a pH between 6.5 and 7.5. In this pH range, combined chlorine reacts slowly. Total chlorine may be determined by addition of KI to the sample, followed by amperometric titration of the iodine (liberated by the free and combined forms of chlorine) using a standard solution of phenylarsine oxide.

By comparison with spectrophotometric procedures, amperometric methods require somewhat greater skill. The solution must be well mixed and contain sufficient inert supporting electrolyte to reduce the ohmic potential gradients that interfere with the development of a uniform diffusion layer through which the electroactive species must diffuse in order to reach the working electrode. For accurate work, however, care must also be taken to avoid volatilization losses of chlorine from solution by mechanical stirring.

Methods involving syringaldazine

In the colorimetric method for FAC using syringaldazine (FACTS), syringaldazine (formed by reacting syringaldehyde with hydrazine dihydrochloride in basic solution) is dissolved in 2-propanol. At a pH between 6 and 7, an aqueous solution of this reagent has an intense yellow color, but upon oxidation by FAC forms a violet, quinone-type product that has an absorption maximum at 530 nm (reaction 19). The pH range between 6 and 7 represents a compromise condition that produces rapid color development, but slow color fading.



Syringaldazine (4-hydroxy-3,5-dimethoxybenzaldazine)

(19)

Monochloramine (up to 18 mg L^{-1}), dichloramine (up to 10 mg L^{-1}), and oxidized forms of manganese (up to 1 mg L^{-1}) do not interfere with the determination of FAC with syringaldazine. The primary difficulty with the FACTS method is the relative insolubility of the syringaldazine in 2-propanol or water, which causes problems in reagent preparation and color stability.

On-Line Chemical Sensors for Monitoring Disinfectant Levels

On-line chemical sensors permit the automated measurement of changes in disinfectant levels on a continuous or semi-continuous basis and are often employed in industrial process control. These sensors typically fall into two broad categories: sensors based on colorimetry and sensors based on amperometry.[13–15]

Colorimetric Monitors

Fig. 5 shows a conceptual, schematic diagram of a hypothetical on-line, microprocessor-controlled colorimetric monitor. The monitor, which is based on the laboratory DPD-colorimetric method discussed earlier, can be configured to measure both free- or total-residual chlorine by changing reagents.

The colorimeter module uses a glass cell with an optical path length *b*. Radiation from a light source at 515 nm passes through the colorimeter cell to a photodetector, which produces a signal that is proportional to the light intensity striking the detector. The signals from the photodetector are digitized and stored in the microprocessor for use in calculating the residual chlorine concentration.

In operation, the microprocessor activates a sequence of valve openings and closings that repeats every 2.5 min. At the beginning of the sequence, Valve 2 is opened to drain the colorimeter sample cell. Valve 1 is then opened to flush the cell with fresh incoming sample. When the sample cell has been flushed, Valves 2 and 1 are closed. At this point in the cycle, a blank sample intensity measurement (I^o) is taken. When the I^o value has been measured and stored in the microprocessor, Valves 3 and 4 open to introduce precisely metered amounts of *N*,*N*-diethyl-*p*-phenylenediamine (DPD) reagent and a buffer solution into the cell, which are mixed with the sample by means of a stirring bar. After a suitable delay for color development, the transmitted intensity (I) of the sample is measured.

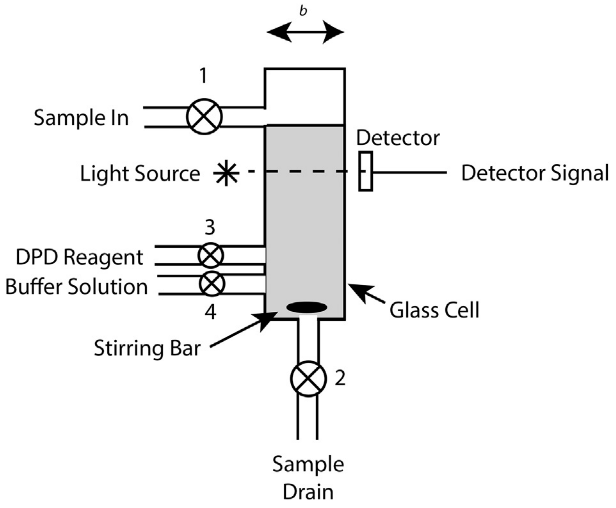


Fig. 5 Schematic diagram of a hypothetical on-line, microprocessor-controlled colorimetric monitor.

The free-residual chlorine is calculated by the microprocessor by taking the ratio of the signals from the two intensity measurements and using Beer's law (20),

$$C = \frac{\log \frac{I^o}{I}}{a_{515} b} \tag{20}$$

where C is the concentration of free-(or total-)residual chlorine in mg L^{-1}, a_{515} is the known absorptivity of the DPD solution at 515 nm in L mg^{-1} mm^{-1}, b is the path length of the sample cell in mm, and log (I^o/I) is the absorbance of the sample. Since both the absorptivity a_{515} and the path length b are known for the given experimental conditions, the chorine concentration can be determined directly from (20). As a result, the monitor does not need to be calibrated in the field.

The same basic monitor can also be configured to determine total-residual chlorine levels by adding KI to the buffer solution. An advantage of the DPD-colorimetric on-line monitor is that measurement mimics the DPD laboratory test, making laboratory measurements easy to compare with the on-line monitor results. The useful range of the monitor is 0–5 mg L^{-1} of chlorine residual.

Amperometric Monitors

On-line monitors for chlorine based on amperometry are also available. In contrast to the amperometric titrations discussed previously, where a plot of the diffusion current is used to signal the endpoint in a titration (**Fig. 4**), amperometric monitors use the magnitude of the diffusion current itself to indicate the chlorine level.

The goal in designing a functioning on-line chlorine monitor is to ensure that the measured diffusion current produced by a galvanic (spontaneous) cell is proportional to the residual free chlorine content of the sample. A chief disadvantage is that the measured amperometric current is a function of many parameters, including the surface area and condition of the working electrode. As a result, careful design and frequent maintenance and calibration are required for any chlorine monitoring using an amperometric on-line system.

On-line amperometric monitors can be classified into two groups: one using bare electrodes directly in contact with the flowing sample solution, and the other using a membrane, which is permeable to HOCl, to isolate the electrodes from the flowing sample solution.

General design and operation

For purposes of illustration, consider a solution containing dissolved chlorine in the form of hypochlorous acid (HOCl). Suppose that this solution is introduced into a hypothetical electrochemical cell consisting of two dissimilar metals—a platinum working electrode and a Ag/AgCl reference electrode. Since the two electrodes are dissimilar metals, a spontaneous galvanic cell will be produced (i.e., a small battery). In this cell, the overall spontaneous reaction is given by (21).

$$\mathrm{HOCl} + 2\mathrm{Ag}_{(s)} + \mathrm{Cl}^- + \mathrm{H_3O}^+ \rightarrow 2\mathrm{AgCl}_{(s)} + 2\mathrm{H_2O} \quad \text{(overall reaction)} \tag{21}$$

Under proper experimental conditions, the observed current produced by the cell will be limited by the hypochlorous acid concentration in the solution and can be measured with an ammeter. In this cell, the cathodic reaction involves the reduction of hypochlorous acid in solution at the platinum electrode (22).

$$\mathrm{HOCl} + \mathrm{H_3O}^+ + 2e^- \rightarrow \mathrm{Cl}^- + 2\mathrm{H_2O} \qquad \text{(platinum working electrode)} \tag{22}$$

In a cell using a silver electrode, the anodic reaction will result in the oxidation of the silver electrode and consumption of chloride ion (23).

$$\mathrm{Cl^- + Ag_{(s)} \rightarrow AgCl_{(s)} + e^-} \qquad \text{(reference electrode)} \tag{23}$$

For extra stability, the anode can be composed of a Ag/AgCl reference electrode and a sacrificial Ag auxiliary (or counter electrode), resulting in a so-called three-electrode configuration. To make the spontaneous cell potential even more positive (i.e., to increase the driving force for the cell and to ensure the current through the cell is actually diffusion limited by the hypochlorous acid concentration), a small positive potential is sometimes imposed on the platinum-working cathode.

It is clear from reaction (21) that both the silver electrode and electrolyte ($\mathrm{Cl^-}$ ion) are consumed in the overall spontaneous reaction. Since the measured cell current is a function of electrode surface condition, electrode surface area, and electrolyte concentration (all of which are changing over time), it is also clear that amperometric, on-line chlorine monitors will require frequent maintenance and calibration to ensure consistent, reliable results. While offering considerable convenience, they are primarily designed for process control and have a fairly limited accuracy range, typically ±20% of the calibrated value (±1–2 mg $\mathrm{L^{-1}}$).

Bare electrode approach

In the bare electron approach, the electrodes are in direct contact with the flowing sample solution and can easily be damaged if the sample solution is corrosive or has a high content of foulants, as in paper pulp processing. In such cases, it may be beneficial to isolate the electrodes from the sample solution using a semi-permeable membrane.

Membrane approach

Fig. 6 shows a schematic diagram of a flow-through amperometric monitor that employs the membrane approach.

For membrane-based monitors, sample flow rate and pressure must be controlled to ensure consistent mass transport of HOCl across the membrane. Other factors, in addition to sample flow rate and pressure that can impact the proper functioning of membrane-based monitors include membrane fouling and pH.

For free-residual chlorine measurement using membrane-based monitors, the ideal pH range for operation is 5.0–7.0, a range where hypochlorous acid dominates (see Fig. 1). Since most water treatment plants produce an output with a pH of 7–8, external pH adjustment may be required to produce reliable results. This is usually accomplished by adding an appropriate buffer from a reservoir to the in-coming sample prior to entering the amperometric cell. Since pH is an important factor in maintaining reliable results with a membrane-based chlorine monitor, on-line monitoring of the pH of the in-coming sample is often recommended to alert the operator of any unexpected fluctuations that might compromise the chlorine readings.

Other Analytical Methods for Determining Chlorine Disinfectants in Water

In addition to the four standard methods discussed previously for drinking water, some other non-standard methods for determining chlorine residuals are available.

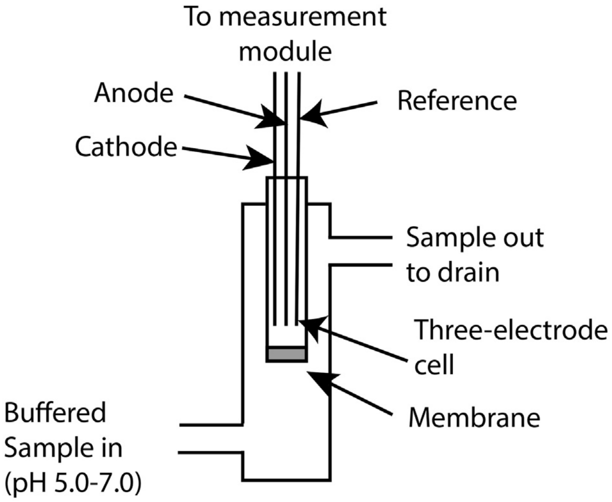
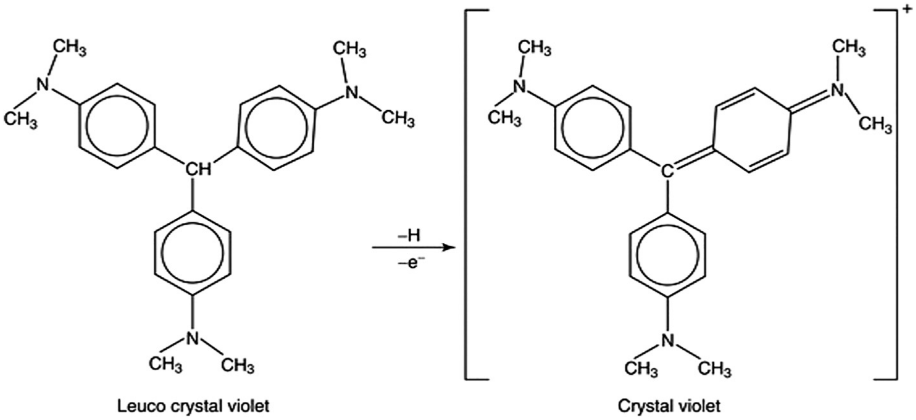


Fig. 6 Schematic diagram of a flow-through amperometric monitor that employs the membrane approach.

Colorimetric Methods

Another colorimetric method for the determination of FAC uses leuco-crystal violet (LCV) as a color-developing reagent. In the LCV method, excess LCV is added to the sample and rapidly reacts with FAC to form crystal violet (LC^+, reaction 24), which has a bluish color and an absorption maximum at 588 nm. Interference from combined available chlorine can be avoided if the test is carried out within 5 min of reagent addition.



(24)

Total chlorine determination can be accomplished by the reaction of FAC and combined chlorine with iodide ion to form dissolved iodine species. The dissolved iodine species react instantly with the LCV, producing LC^+. Once FAC and total chlorine are determined separately, combined available chlorine is calculated by difference.

Chromatographic Methods

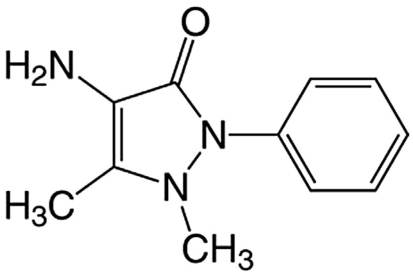
Chlorine dioxide is being used with increasing frequency in kraft mills that convert wood into wood pulp, and for water treatment because it does not form potentially carcinogenic THMs the way chlorine does. Since iodometric methods for the determination of chlorine dioxide are questionable, they should be avoided. While chlorine dioxide can be determined by amperometric titration and by colorimetry, chromatographic methods are becoming increasingly popular.

Both high-performance liquid chromatography and ion chromatography (IC) have been used to determine inorganic chlorine species in aqueous samples. Since chlorine dioxide itself is not ionized in solution, it must be converted to chlorite (ClO_2^-) for IC analysis. To accomplish this conversion, samples are prepared in a basic solution containing hydrogen peroxide,

$$2ClO_2 + H_2O_2 + 2OH^- \rightarrow 2H_2O + O_2 + 2ClO_2^- \tag{25}$$

The ClO_2 present is determined by difference between the chlorite found in a treated sample and that found in a separate aliquot that has not been dissolved in basic hydrogen peroxide.

Chlorine dioxide and hypochlorite have also been determined simultaneously in aqueous samples by high-performance liquid chromatography. The analytes are first separated on an anion-exchange column, followed by a postcolumn reaction with 4-aminoantipyrine (5) and phenol to produce a chromogenic substance that absorbs at 503 nm and subsequent determination using a colorimetric detector.



(5)

4-Aminoantipyrine

Flame-Infrared Emission

Flame infrared emission (FIRE) has been shown to be useful in determining FAC in liquid bleach.[16] In the FIRE method, solutions of sodium hypochlorite are acidified to produce aqueous Cl_2 (reactions (1) and (2) and **Fig. 1**). Dissolved Cl_2 is liberated from solution in a purge tube and converted to vibrationally excited HCl molecules in a hydrogen–air flame. The intensity of the P-branch ($\Delta J = -1$, where ΔJ is a change in rotational quantum number) of the HCl stretching vibration at 3.8 μm is monitored using a simple filter infrared photometer that employs a lead selenide detector.

By contrast with other methods for the determination of available chlorine, which are all based on oxidation–reduction chemistry and subject to potential interference from other oxidants present in the sample, FIRE actually measures a signal that is solely related to the amount of dissolved Cl_2. The sample is purged within seconds following addition of acid and is not affected by the presence of chlorinated compounds that hydrolyze slowly in acid solution. A flow injection procedure has been developed that makes use of a continuous purge cell.

Analytical Methods for the Determination of Other Bleaching Agents and Disinfectants

A variety of methods exist for the determination of bleaching agents and disinfectants that do not depend on chlorine or chlorine-containing compounds for their action.

Oxygen-Based Agents

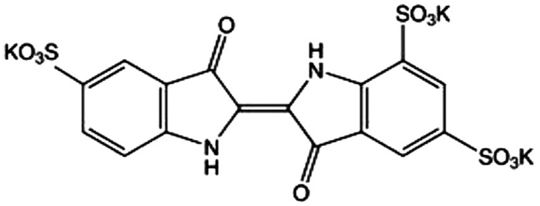
Oxidizing agents like peroxides and ozone are typically determined using variations of the methods used to determine FAC in solution.

Peroxides can be determined by iodometric titration, by means of a colorimetric method based on syringaldazine, or by chemiluminescence. For example, red chemiluminescence is observed at 635 nm when hydrogen peroxide reacts with hypochlorite ion in alkaline solution. Unfortunately, the reaction is not sensitive enough for application to potable waters; however, substances such as luminol or lophine, which give chemiluminescence upon being oxidized, may provide increased sensitivity.

Determination of ozone in aqueous solution is perhaps the most problematic for a variety of reasons: (1) ozone is unstable; (2) ozone is volatile and easily lost from solution; and (3) ozone reacts with many organic compounds to form products such as ozonides and hydrogen peroxide that are also good oxidants.[17] Careful study of the use of iodometric methods for the determination of ozone in aqueous solution has revealed that the stoichiometric ratio of ozone reacted to iodine (I_3^-) produced in the reaction varies from 0.65 to 1.5, depending on pH, buffer composition and concentration, iodide ion concentration, and other reaction conditions. As a result, iodometric methods are not recommended.

Ozone can be determined iodimetrically by addition of an excess of a standard solution of As(III), followed by titration of the excess As(III) with a standard solution of iodine to a starch endpoint. Methods using DPD, syringaldazine, and amperometric titrations have also been developed.

In comparison to standard procedures involving iodide/iodine, colorimetric determination of ozone with indigo trisulfonate (**6**) has fewer interferences. In this procedure, indigo trisulfonate is oxidized by ozone to a leuco (colorless) form, and the decrease in absorbance is monitored at 591 nm. Ozone decomposition products and ozonolysis products formed from organic compounds do not interfere. Moreover, chlorite (ClO_2^-), chlorate (ClO_3^-), perchlorate (ClO_4^-), and hydrogen peroxide do not decolorize the indigo reagent.



(**6**)

Potassium indigo trisulfonate

Sulfur-Based Reducing Agents

Methods for the determination of dissolved sulfite and dithionite generally involve reaction with oxidants. For example, aqueous solutions of sulfite can be determined by iodometric titration to the disappearance of the blue starch color at the endpoint (reaction 26):

$$SO_3^{2-} + I_3^- + 2OH^- \rightarrow SO_4^{2-} + 3I^- + H_2O \tag{26}$$

Hydrogen sulfite can be determined in the presence of sulfite by oxidation with hydrogen peroxide to form hydrogen sulfate and sulfate (reactions 27 and 28),

$$HSO_3^- + H_2O_2 \rightarrow HSO_4^- + H_2O \tag{27}$$

$$SO_3^{2-} + H_2O_2 \rightarrow SO_4^{2-} + H_2O \tag{28}$$

followed by titration of the acidic hydrogen sulfate ion with sodium hydroxide.

Aqueous solutions of dithionite ion can be determined by iodometric titration to the disappearance of the blue starch color at the endpoint (reaction 29).

$$S_2O_4^{2-} + 3I_3^- + 8OH^- \rightarrow 2SO_4^{2-} + 9I^- + 4H_2O \tag{29}$$

Dithionite solutions can be determined without interference from sulfite by the addition of formaldehyde. Formaldehyde reacts with sulfite ion to form an adduct that is not oxidized by iodine. Spectrophotometric methods for dithionite solutions are based on the reductive bleaching of dyes.

Sampling

Aqueous solutions of chlorine are not stable and decrease in strength with time. Exposure to strong light accelerates the decomposition. Strong agitation should be avoided to prevent loss of chlorine gas by volatilization. Samples should be analyzed as soon as possible after collection and not stored. Most analytical methods require 100–200 mL of sample.

Because of the relative instability of chlorinated water samples, determination in the field is often required. Colorimetric test kits are available commercially for this purpose.

Precautions in Handling

Bleaching agents and disinfectants are all strong oxidants that in concentrated form can react explosively with reductants, including organic matter. Disinfectants are effective because they are toxic to microorganisms, and in sufficient concentration will produce adverse health effects in humans. Chlorine gas, which is commercially available in steel cylinders as a gas over liquid, is a powerful irritant that can cause fatal pulmonary edema. Inadvertent addition of acid to liquid bleach (NaOCl) causes the release of poisonous Cl_2. While chlorine dioxide dissolved in water is stable (if kept cool and away from light), the gas will detonate at pressures above 300 torr. To avoid formation of explosive concentrations of ClO_2 above the solution, the concentration of chlorine dioxide must be kept below 5 g ClO_2 per liter of H_2O. Concentrated solutions of hydrogen peroxide also react explosively with organic matter.

Preparation of standard solutions of iodine and the amperometric determination of chlorine in water samples make use of arsenic trioxide (As_2O_3) or phenylarsine oxide (C_6H_5AsO), respectively, as reagents. These titrations generate toxic waste that must be disposed of in an environmentally safe manner. The cost of collecting and disposing of these reagents must be included in the cost of performing such determinations. Crystal violet is also a suspected carcinogen, and solutions formed from the leuco crystal violet method should also be treated as toxic waste.

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Further Reading

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