Chlorination, Chloramination and Chlorine Measurement

Terry L. Engelhardt
Application Development Manager, Drinking Water

Vadim B. Malkov, PhD
Product Applications Manager, Process Instrumentation

Hach®
Loveland, Colorado

The purpose of this document is to summarize basic information about use of chlorine as a disinfectant and to convey information about the chlorination and chloramination processes. This document will also explore measurement of chlorine and chloramine residuals. There is no attempt to provide an exhaustive description of chemical reactions, various chlorination or chloramination schemes, or a comparison of relative merits of the various approaches. Consult citations in the list of references if information that is more detailed is desired.

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Historical Perspective

Karl Scheele, a Swedish chemist, identified Chlorine as a chemical element in 1774. Chlorine has an atomic number of 17 and atomic mass of 35.45. It is a member of the halogen family on the Periodic Chart. Other members of the family include Fluorine, Bromine and Iodine. Each of these compounds plays an important role in water treatment.

One of the first uses of chlorine in water and wastewater treatment was addition to sewers in London, England in the 1830's, not as a disinfectant but rather as a deodorant. This practice followed cholera outbreaks. It was believed controlling the odor from the sewers might help control the spread of the disease. The germ theory of disease and thus the practice of purposely adding chlorine for disinfecting water did not occur until nearly 70 years later.

Disinfection of water is not the sole domain of a chemical such as chlorine. Whether for municipal drinking water, treatment of wastewater, or use of water for manufacture of another beverage, disinfection is the result of the proper application and operation of physical, biological and chemical treatment processes. This principle is illustrated by the chart below demonstrating implementation of various treatment techniques vs. the incidence of typhoid in Denver, Colorado from approximately 1887 to 1940.

In the practice of water treatment one should keep in mind proper operation and control of all the steps within the treatment process are important to achieving a properly disinfected effluent. The balance of this document will focus solely on use of chlorine for disinfection.

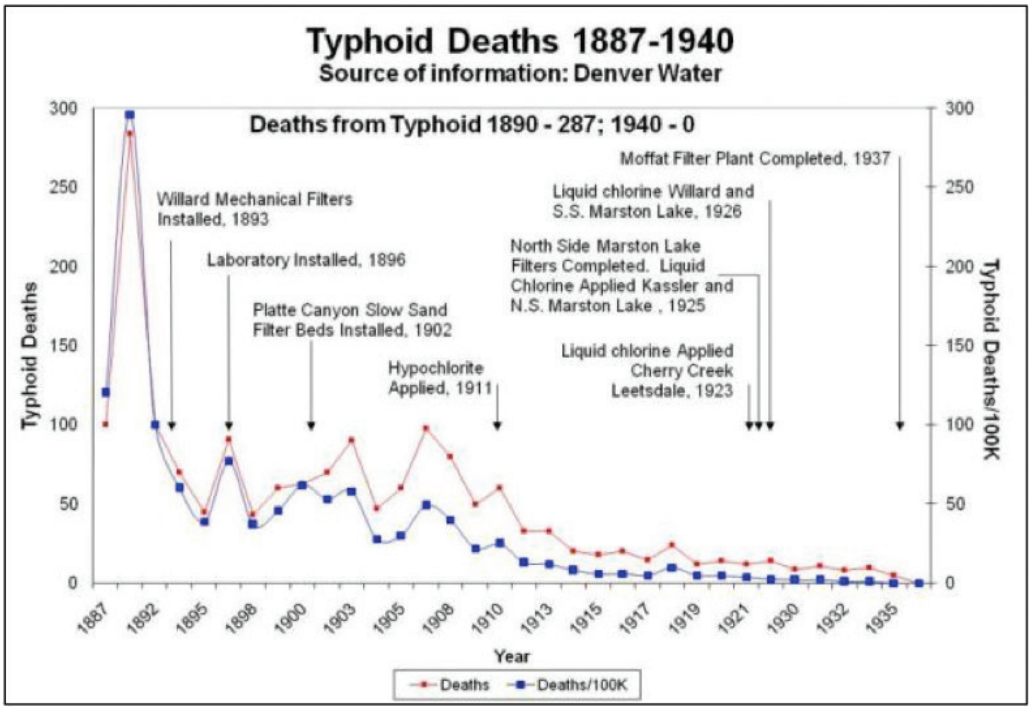

Figure 1: Typhoid deaths vs. treatment techniques for Denver, Colorado. Used with permission of Denver Water.

Overview of Chlorine Chemistry in Water Treatment

When chlorine is added to water at a pH greater than 4, hypochlorous acid (HOCl) is formed as illustrated by the empirical equation below[1]:

$$Cl_2 + H_2O \leftrightarrow HOCl + H^+ + Cl^-$$

As the pH increases above 4, the hypochlorous acid will dissociate to form the hypochlorite ion (OCl^-):

$$HOCl \leftrightarrow H^+ + OCl^-$$

The processes of chlorination and chloramination are more complex than they appear to be from the empirical reactions. The reactions depicted contain a double-headed arrow to denote reversible reactions. In the first equation, if the pH is greater than 4, the reaction is to the right, favoring formation of hypochlorous acid. If the pH should drop below 4, chlorine gas can come out of solution.

Under the proper conditions, most if not all the reactions one encounters in chlorination and chloramination are reversible. At a given set of conditions, many different chlorine species may be present in water simultaneously. For example, see White, 5th ed., page 95, figure 2.4.

Chlorine existing in water as hypochlorous acid or as the hypochlorite ion is termed free available chlorine. The following figure illustrates the relationship of these two species to pH and temperature.

Hypochlorous acid and hypochlorite ion species are disinfectants. Hypochlorous acid (1.4 eV) is a stronger disinfectant than the hypochlorite ion (0.9 eV), however, this is only a qualitative characteristic.

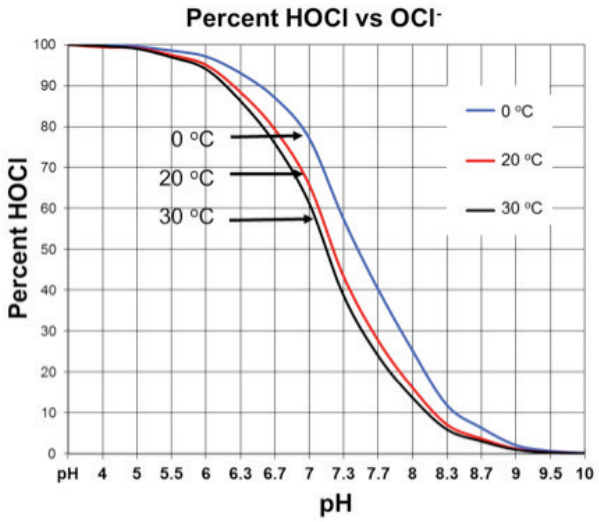

Figure 2: pH vs. chlorine species

Reactions of chlorine with nitrogen containing compounds (ammonia, nitrites and organic amines) are of particular interest when disinfecting water. The reactions normally of greatest interest are those with chlorine and ammonia typically represented by the simplified empirical reactions that follow. Note that as above, the reactions are reversible:

1. $HOCl + NH_3 \leftrightarrow NH_2Cl + H_2O$
2. $HOCl + NH_2Cl \leftrightarrow NHCl_2 + H_2O$
3. $HOCl + NHCl_2 \leftrightarrow NCl_3 + H_2O$
4. $HOCl + NCl_3 \leftrightarrow HOCl + *$

1. Chlorine reacts with ammonia to form monochloramine , NH_2Cl.
2. With continued addition of chlorine, chlorine reacts with monochloramine[2] to form dichloramine, $NHCl_2$.
3. Continued addition of chlorine results in formation of nitrogen trichloride (NCl_3), also called trichloramine, which is very unstable.
4. If chlorine addition is continued, the nitrogen trichloride is destroyed leaving primarily hypochlorous acid and other products (* = N_2, Cl^-, H_2O, H^+, NO_3^- and other species).

[1]One may see the molecular formula for hypochlorous acid, HOCl, also written as HClO. Similarly one may see the formula for the hypochlorite ion, OCl^-, written as ClO^-. However most recent references use the forms HOCl and OCl^- because they most accurately describe the structure of these species; but HClO and ClO^- are also acceptable.

[2]Reaction 1 illustrates one mole (mol) of hypochlorous acid combines with one mole of ammonia and since each mole of ammonia contains one nitrogen atom. Correspondingly, each mole of hypochlorous acid represents one molecule of Cl_2 that combines with one mole of nitrogen. Thus, one can represent the molar ratio of hypochlorous acid to ammonia as 1:1 Cl_2:N. This should not be confused with weight ratio as it is normally used in the industry and which becomes 71.5:14 or 5:1.

The breakpoint curve is used to represent the reactions represented above. The breakpoint reaction (and resulting breakpoint curve) typically is credited to the work of two individuals, A.E. Griffin and C.K. Calvert in the late 1930's although, many individuals had been studying the reactions. As with the reactions above, one should not interpret the breakpoint curve as absolute. The curve depicted assumes the molar ratios of the Cl_2 and NH_3-N from the empirical equations shown above. In actual practice, the shape of the breakpoint curve varies based on pH, temperature, the form of nitrogen present and time.

One should take care in interpreting these simplified reactions. They do not tell the whole story.

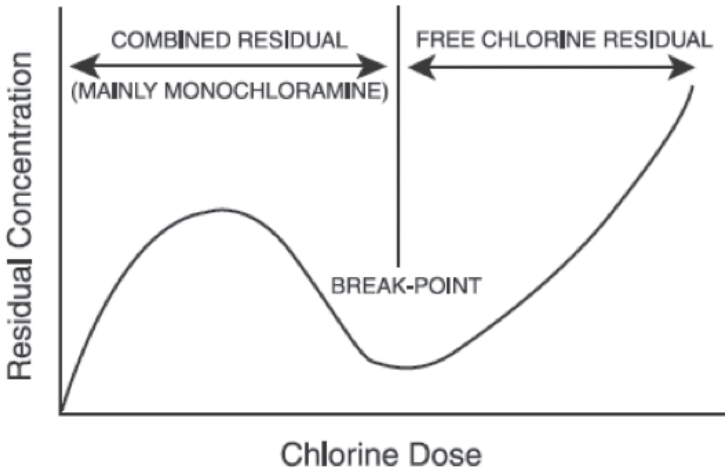

Figure 3: Typical stylized breakpoint curve

The goal of disinfection with chlorine in water treatment is to maintain predominately either free residual chlorine or to maintain predominately monochloramine. If one purposely controls the ratio of chlorine to ammonia (nitrogen) to maintain monochloramine, the practice is referred to as chloramination. If the only nitrogen compound present is ammonia, monochloramine will predominate if a Cl2:N molecular weight (mass) ratio of less than 5:1 is maintained. Free residual chlorination (or breakpoint chlorination) results by maintaining a Cl2:N weight ratio of greater than 9:1. The line labeled 'break-point' in figure 3 corresponds to a point where total ammonia should reach zero. In actual practice there may be measureable total ammonia beyond the breakpoint but it should be a very little.

Free Residual Chlorination

If one considers only the empirical chemical equations, only free residual chlorine (the sum of hypochlorous acid, HOCl, and the hypochlorite ion, OCl^-) exists beyond the breakpoint. Due to the complexity of the chemical reactions, this may not be true. Some references will provide a rule of thumb stating when free residual chlorine is a certain percentage of total residual chlorine (typically stated as at least 93-95%) then one is beyond the breakpoint. One should not rely on such rules of thumb or guidelines. They can be very misleading. To assure the process is beyond breakpoint one needs to measure! Total ammonia must be zero or very near zero. Hach suggests measurement of total ammonia with the Salicylate Method.

At the breakpoint, there are competing reactions producing free chlorine, monochloramine, dichloramine, trichloramine, and organic chloramines. Identification of these species individually in the mixture is difficult, especially in a solution that is not particularly stable. It is reasonable to assume that nuisance residuals formed just beyond the breakpoint, and in the absence of organic nitrogen, consist primarily of trichloramine and monochloramine. When organic nitrogen is present, the nuisance residual titrates as if it were composed of dichloramine, but it is probably made up mostly (about 90%) of organic chloramines, with much lesser amounts of monochloramine and trichloramine (White's 5th ed., pg 121).

The only way to be certain one is beyond the breakpoint is to measure!

- Measure the free and total residual chlorine. Free residual chlorine should approach the same value as total residual, Free Residual Chlorine ≤ Total Residual Chlorine
- Measure the total ammonia. Total ammonia should be zero or very near to zero.

Chloramination

Chloramination refers to the purposeful mixing of chlorine and ammonia to control the chlorine to nitrogen ratio. Chloramination in drinking water has been practiced since about 1917. Chloramination increased in use until the beginning of World War II. During World War II, ammonia was needed for the war effort and thus its use in water treatment was discouraged. Chloramination has reemerged since the mid 1970's and the use continues to spread. According to Li (Water Conditioning and Purification, 2011), from 2007 to 2010 the number of water utilities in the United States practicing chloramination increased 37% from 944 to 1,298; and the total population served by chloraminated water increased from approximately 54 million to over 68 million. By 2010, one or more water systems in 43 States practiced chloramination.

Concern about formation of undesirable disinfection byproducts (DBPs) from chlorination generated renewed interest in chloramination in the 1970's. DBPs are produced by the reaction of chlorine with organic matter occurring in the water. Using monochloramine formed by pre-reaction of the chlorine with ammonia lessens the formation potential for DBPs. However, chloramination is not the panacea for DBPs it was once believed. Research indicates other DBPs (i.e. Nitrosodimethylamine, NDMA) are generated by the chloramination process. The DBPs resulting from chloramination are being studied to determine the negative health impact, if any.

Due to the lower oxidation potential (~0.6-0.8 eV) chloramines are not as effective disinfectants as either hypochlorous acid (~1.4 eV) or the hypochlorite ion (0.9 eV).

Log Removal	*Giardia*						Viruses					
	<1˚C		10˚C		20˚C		<1˚C		10˚C		20˚C	
	Cl_2	NH_2Cl	Cl_2	NH_2Cl	Cl_2	NH_2Cl	Cl_2	NH_2Cl	Cl_2	NH_2Cl	Cl_2	NH_2Cl
0.5	40	635	21	310	10	185	--	--	--	--	--	--
1	79	1270	42	615	21	370	--	--	--	--	--	--
2	158	2535	83	1230	41	735	6	1243	3	643	1	321
3	237	3800	125	1850	62	1100	9	2063	4	1067	2	534

Source: USEPA LT2ESWTR T&C Document, Exhibit 2.1, Dec. 2005 "Exhibit 2.1 demonstrates that chloramine is relatively ineffective compared to free chlorine for Giardia *and virus inactivation. In addition, chloramine is ineffective for inactivation of* Cryptosporidium *(Peeters et al. 1989, Korich et al. 1990)." USEPA LT2ESWTR and T&C Document*

Figure 4: CT values for chlorine vs. chloramines

Monochloramine is considered a good disinfectant. It does not contribute significant taste or odor and is more stable in solution than free residual chlorine. Chloramination often is useful in systems with long distribution lines or with large amounts of storage where the water age might be too long to maintain free chlorine residual.

Dichloramine is a better disinfectant than monochloramine but contributes undesirable taste and odor. Nitrogen trichloride or trichloramine is undesirable because it has a disagreeable taste and odor and is very unstable in solution.

The key to chloramination is to control the ratio of chlorine to nitrogen to favor formation of monochloramine and prevent formation of dichloramine and trichloramine. The breakpoint curve best illustrates this point. Addition of a secondary vertical axis to represent ammonia helps to illustrate the important considerations.

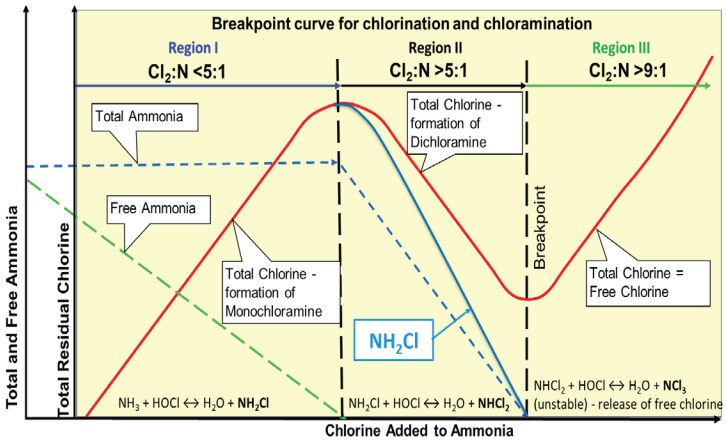

Figure 5: Breakpoint curve with ammonia

As chlorine is added, it reacts with ammonia to form monochloramine. Notice total ammonia remains unchanged as chlorine is added as long as the ratio of chlorine to nitrogen (Cl2: N) is less than 5:1. Total ammonia is the ammonia naturally occurring in the water plus ammonia added purposely, including the formed chloramines[3]. Monochloramine is an ammonia compound. Using a portion of the ammonia to form monochloramine does not change the total ammonia! Monochloramine is included in the total ammonia measurement. Addition of chlorine corresponds to a decrease in unreacted ammonia free ammonia.

The closer free ammonia is to zero, the better the chloramination system will operate. Free ammonia left in the water is a nutrient for microorganisms. Under favorable conditions of temperature, pH, and time, organisms can flourish causing significant operational and aesthetic problems in the water distribution system. Excess ammonia can lead negative health effect due to nitrification and formation of nitrites and nitrates in water.

The problem most commonly associated with chloramination is nitrification. As previously cited, the reaction forming monochloramine is reversible. With time and under favorable conditions, a series of reactions can cause monochloramine to

[3]*Anhydrous ammonia, granular ammonium sulfate ((NH4)2SO4) liquid ammonium sulfate (LAS, 38-40%) and aqua ammonia (ammonium hydroxide, 19%), are commonly used for addition of ammonia. See Appendix D.*

deteriorate and result in release of free ammonia adding even more nutrient to the system.

The start of undesirable formation of dichloramine corresponds to the point where the free ammonia (unreacted ammonia) reaches zero. Looking at the simplified empirical equations it appears only monochloramine can exist as long as Cl2: N is less than 5:1. Hence, one might expect free chlorine residual to be zero and monochloramine residual to equal total chlorine residual. Alternately, one might expect, if at least some amount of free chlorine is present, the monochloramine should equal total residual chlorine minus free residual chlorine. In reality, this chemistry is more complex. Total residual chlorine minus free residual chlorine does not necessarily equal monochloramine! The only way to know monochloramine concentration is to measure monochloramine!

A method developed by Hach measures monochloramine specifically without interference from organic amines, dichloramines, free chlorine, organic chloramines, nitrites or manganese. See Indophenol Method for Monochloramine, below.

Due to the complex nature of the reactions, one cannot rely on rules of thumb. Measure!

- Measure total residual chlorine (TRC), monochloramine (Mono) and free residual chlorine (FRC) **TRC ≥ Mono > FRC**
- Measure total ammonia throughout the process, total ammonia should not change if a ratio of Cl_2: N remains less than 5:1
- Measure free (unreacted) ammonia (FA). FA > 0 during monochloramine formation

It is common to operate to achieve less than 0.1 mg/L free ammonia. Many water systems will attempt to operate at 0.05 mg/L or less. Attempting to operate at very low concentrations of free ammonia makes attention to detail in the indophenol method critical.

1. The reaction rate of the free ammonia test is temperature sensitive. The reaction time at 25°C (77°F) is 2 minutes. The reaction time at about 16°C (61°F) is 6 minutes. The free ammonia analytical procedures for Hach spectrophotometers and colorimeters contain a chart of reaction times vs. sample temperature. It is important to follow the chart for the proper reaction time.
2. At low free ammonia concentrations, the color contributed by the reagents can be significant. Determine reagent blank by using chlorine and ammonia free DI water. Subtract the reagent blank from the free ammonia result for the sample. Hach's analytical procedures for free ammonia contain instructions that are more detailed.

Natural Organic Matter

Natural organic matter, NOM, and other nitrogen compounds present in water other than ammonia can have a significant impact on chlorination, chloramination and thus the shape of the breakpoint curve.

The curves represented in Figures 3 and 5 do not necessarily represent what one may encounter at a specific water source. The Golden State Water Company was attempting to solve a problem with formation of THMs in their distribution system due to high amounts of NOM in a well source. Notice the effect of the NOM on the shape of the curve as well as the impact of time. Point labeled "A" typically corresponds to a Cl2:N ratio of 5:1. In this instance, the point is greater than 6:1! Where the breakpoint normally occurs at a ratio of about 9:1, these data indicate the breakpoint occurred at greater than 14:1, point "B".

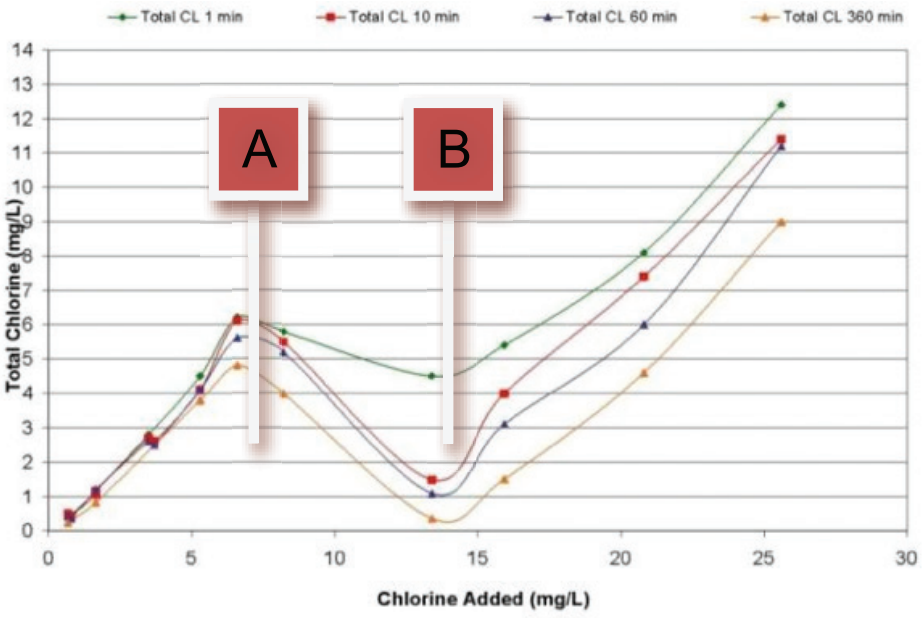

Figure 6: Breakpoint curve due to a significant amount of NOM. Used with permission of the Golden State Water Company.

The water company decided the best solution was to destroy all nitrogen compounds by passing the breakpoint; that is, driving ammonia to zero. As one can see from the chart at right, it was determined they would have to establish a Cl2:N ratio of approximately

16.4:1, point "C", well in excess of what theoretical data would suggest.

Process control, especially in chlorination and chloramination, requires measurement of multiple analytes!

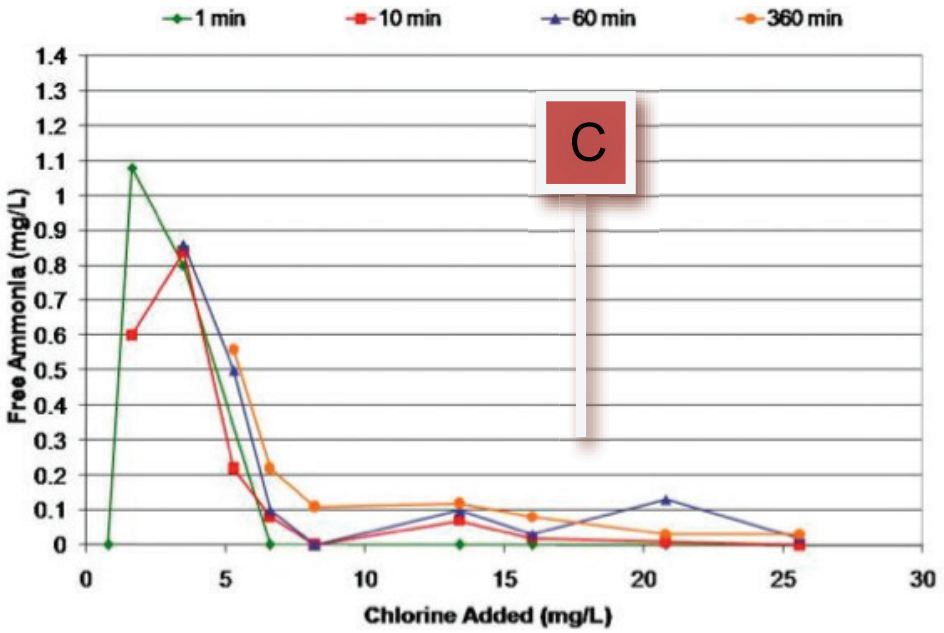

Figure 7: Free ammonia vs. chlorine added.
Used with permission of the Golden State Water Company

Nitrification

Nitrification occurs in a water system using chloramination when favorable conditions of time, temperature, pH and availability of ammonia combine to permit certain organisms to flourish. Organisms including Nitrosomonas, Nitrosococcus and Nitrosospira assist the following reaction where ammonia is oxidized to form nitrite:

$$NH_3 + O_2 \longleftrightarrow NO_2^- + 3H^+ + 2^{e-}$$

Organisms such as Nitrobacter, Nitrospina, Nitrococcus and Nitrospira continue the reaction converting nitrite to nitrate:

$$NO_2^- + H_2O \longleftrightarrow NO_3^- + 2H^+ + 2^{e-}$$

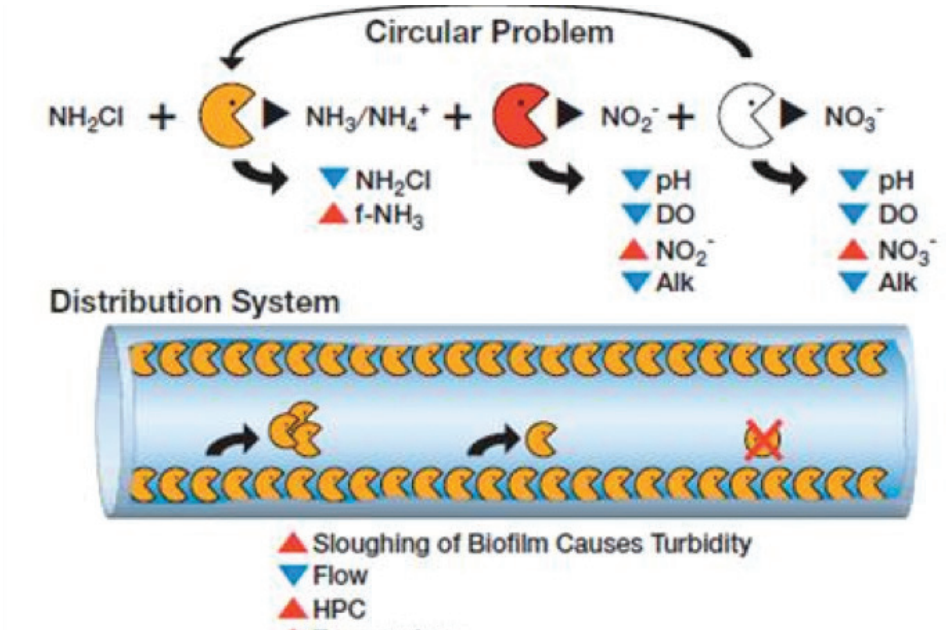

Figure 8: Nitrification, a circular problem.

Effect of Temperature on Nitrification

Various references provide slightly different guidance on the temperature ranges that are favorable or unfavorable for occurrence of nitrification. The figure below offers a general guideline.

32˚F	50˚F	77˚F	80 100˚ F	104˚F 122˚F
Nitrification ceases	Nitrification slows	Favorable for nitrification	Most favorable for nitrification	Nitrification slows and ceases
0˚C	10˚C	25˚C	26 39˚ C	40˚C 50˚C

Figure 9: Effect of temperature in nitrification

Effect of pH on Nitrification

Researchers have observed varying effects of pH on nitrification. Some have observed nitrification at pH as high as 9.7. Others have observed pH greater than 9 inhibits nitrification. There is little variation, however, in observing that nitrification is possible over a very wide pH range. It encompasses the pH range in most potable water systems. The figure below provides a general guide.

Nitrosomonas	Activity pH range	6.5 - 9
	Optimal pH range	7.0 - 8.0
Nitrobacter	Activity pH range	6.5 - 9
	Optimal pH range	7.5 - 8.0

Source: Nitrification, Office of Water, Office of Ground Water and Drinking Water, Distribution System issue paper, U.S. EPA, August 15, 2002

Figure 10: Effect of pH on nitrification

Oxidation of ammonia to nitrite during nitrification requires (consumes) 7.2 mg/L as $CaCO_3$ of alkalinity for each 1 mg/L of ammonia. Additional alkalinity is consumed in conversion of nitrite to nitrate. In low alkalinity water (less than 30 mg/L as $CaCO_3$) this may lead to a decrease in pH. The decrease in pH then may have other consequences including:

- Increasing the rate of nitrification
- Contributing to increased corrosion in the distribution system
- Possibly increase the leaching of lead and/or copper thus having a negative impact on the utility's compliance with the Lead and Copper Rule (in the United States)

Even when the alkalinity (buffer capacity of the water) is sufficiently high so that pH is not significantly affected by onset of nitrification, it is still important to measure and monitor pH in the distribution system. Measurement of pH is important for corrosion control and for calculation of CT values. Change in pH may signal other problems in a water system such as an introduction of foreign material into the water due to a system malfunction, a main break, backflow, or deliberate contamination.

Observed parameter		Possible signals of onset of nitrification
pH		▼
Dissolved Oxygen (DO) Approximately 4.6 mg/L of oxygen are required to oxidize 1 mg/L of NH_3-N to NO_3^--N		▼
Alkalinity Approximately 7.2 mg of alkalinity as $CaCO_3$ is required to oxidize 1 mg/L of NH_3-N to NO_2^--N		▼
Monochloramine Residual		▼
Free Ammonia	As monochloramine reverts to free ammonia and chlorine, free ammonia will initially increase then to be consumed as it is converted to nitrite.	▲ ▼
Water Age		▲
Water Temperature		▲
Nitrite		▲
Nitrate		▲
Heterotrophic Plate Counts (HPC) and/or ATP		▲
Sloughing of biofilm increases customer turbidity complaints		▲
Increase of biofilm reduces pipe flow (increases friction). This can be detected by HPC or ATP analysis.		▲

Decrease ▼

Increase ▲

Figure 11: Parameters associated with possible onset of nitrification

Responding to onset of nitrification can be difficult. There is no single correct response. The correct response varies based on water quality and the resources at hand. The following figure contains some possible corrective measures.

Common Possible Corrective Actions	Possible steps to consider	Discussion
pH	▲	If the alkalinity of the water is relatively high, this may not be practical
Dissolved Oxygen (DO)	▲	Aerate by use of an aerator or improved circulation in a storage tank
Monochloramine Residual	▲	Increase residual and operate chloramination closer to 5:1 Cl_2: N ratio if practical
Free Ammonia	▼	Operate chloramination closer to 5:1 Cl_2: N ratio when practical
Water Age	▼	Improve circulation in storage tanks, increase flushing, decrease storage capacity

Decrease ▼

Increase ▲

Figure 12: Possible corrective actions for nitrification

A combination of tactics typically is necessary to control nitrification. Certainly, the best practice is to work diligently to minimize the opportunity for nitrification to occur, including:

- Maintain very low free ammonia residual.
- Attempt to limit water age.
- Ensure water storage tanks and reservoirs properly circulate.

Analytical Tools for Monitoring for Nitrification

Analyte	Laboratory tools available	Online tools available
Chlorine residual	Laboratory and portable colorimeters and spectrophotometers and reagents for free and total residual chlorine	Colorimetric Analyzer or amperometric probes for free or total residual chlorine.
Monochloramine residual	Laboratory and portable colorimeters and spectrophotometers and reagents for monochloramine residual	Ammonia/Monochloramine Analyzer for monochloramine, free and total Ammonia
Free and total ammonia*	Laboratory and portable colorimeters and spectrophotometers and reagents for free and total ammonia	Ammonia/Monochloramine Analyzer for monochloramine, free and total Ammonia
pH	Laboratory and portable pH meters** and electrodes	pH probes and controllers***
Dissolved Oxygen	Laboratory and portable meters* and electrodes	DO probes and controllers***
Temperature	Included as part of all pH and DO probes for laboratory, portable or online use	
Alkalinity	Laboratory and portable titration with the Digital Titrator	Alkalinity Analyzer
Nitrite	Laboratory and portable colorimeters and spectrophotometers with the Diazotization method	Scanning UV sensors
Nitrate	Laboratory and portable colorimeters and spectrophotometers with the cadmium reduction or Dimethylphenol methods, or Nitrate ISE*	Nitrate probe and scanning UV sensors
Adenosine Triphosphate (ATP)	Apparatus, reagents and luminometer	EZ-series ATP analyzer
Heterotrophic plate counts (HPC)	Media, plates and apparatus	N/A
Nitrifying bacteria	NB BART™ # for nitrifying bacteria	N/A

** Nessler and Salicylate methods are available for total ammonia. Hach recommends the Salicylate method.*
*** The HQd family of meters permit use of a number of Hach's smart sensors including probes for pH, conductivity, DO and many ion selective electrodes including nitrate.*
**** Select from the Hach family of sc controllers including the single or dual sensor input sc200 or up to 8 sensor input sc1000*
 # BART is a trademark and patented product of Droycon Bioconcepts, Inc.

Figure 13: Analytical tools for monitoring nitrification

Analytical Laboratory Methods for Measurement of Chlorine Residuals

There are many possible methods for determination of chlorine residual. Only two analytical laboratory methods are widely used for day-to-day operational use, the DPD method and amperometric titration. The table below summarizes basic information about these methods.

Method*	Analysis Range, mg/L	Estimated Precision**	Application	Technician Skill Level***
DPD				
Colorimetric	0 - 5	1-2%	Free and Total	1
Ultralow Range Colorimetric	0 - 0.500	5-6%	Total	2
FEAS Titration	0 - 3	2-7%	Free and Total	2
Amperometric Titration				
Forward Titration	Up to 10	1-2%	Free and Total	3
Back Titration	0.006 - 1.00	15%	Total	3

** See Appendix A for details about orthotolidine and syringaldazine (FACTS) methods. These methods are infrequently used*
*** %Relative Standard Deviation*
**** Technician skill level: 1-Minimal training 2-Moderately skilled with the method*
3- Experienced with the method

Figure 14: Comparison of DPD and amperometric laboratory methods for free and total chlorine

DPD Colorimetric and Titrimetric Methods

Dr. Thomas Palin introduced the DPD (N, N-diethyl-p-phenylenediamine) method for residual chlorine in 1957. Over the years it has become the most widely used method for determining free and total chlorine in water and wastewater. Hach introduced its first chlorine test kit based on the DPD chemistry in 1973.

Liquid vs. Powdered Reagents

Procedures published in widely used method manuals (i.e. Standard Methods) call for liquid DPD reagents prepared from DPD sulfate or DPD oxalate salts.

- Liquid DPD reagents are subject to oxidation from either atmospheric oxygen or dissolved oxygen present in the preparation water. Oxidation of DPD by oxygen is pH dependent (Standard Methods, 20th ed.). The liquid DPD formulations attempt to retard oxidation by lowering the pH of the indicator reagent.
- The liquid formulations incorporate disodium ethylenediamine tetraacetate (Na2EDTA) in order to "retard deterioration due to oxidation and, in the test itself, provide suppression of dissolved oxygen errors by preventing trace metal catalysis" (Standard Methods, 20th ed.).
- Phosphate buffers used in Standard Methods adjust the sample pH to between 6.2 - 6.5. The slightly acidic pH is preferred to resolve the chloramine species quantitatively and to minimize interferences. Phosphate buffers, however, do not perform well in hard or brackish waters. Calcium and magnesium ions in the sample will precipitate the phosphate and destroy the buffering capacity (Sengupta). Because aqueous phosphate solutions are excellent growth media for microorganisms, highly toxic mercuric chloride is added to preserve the reagent.

Hach DPD powder formulations overcome the disadvantages of using liquid reagents. Hach's DPD indicator and buffer, combined in powder form, minimize degradation by oxidation and microbial action. Hach's DPD powder indicator does not exist in an ionized state thus is not subject to air oxidation as is liquid DPD reagent. The combined reagents are formulated to prevent metal-catalyzed oxidation.

Hach's buffer makes use of a carboxylate-phosphate system that works extremely well in high hardness and brackish water samples. The reagents can tolerate up to 1000 mg/L as $CaCO_3$ hardness with either the free or total chlorine powder formulations. Hach DPD formulations do not contain mercuric salts.

Hach's DPD powder PermaChem® Reagents are quite stable when protected from temperature extremes. Excellent reagent stability is achieved by sealing the reagent in unit-dose foil pouches that protect them from exposure to air, moisture and light. The DPD powdered reagents are also available in AccuVac® DPD reagent ampules.

The ampules are air evacuated to protect reagents from oxidation and moisture. Storage containers protect the reagents from exposure to sunlight. Storage containers should be kept closed between uses to protect the ampules from light. All of Hach's DPD reagents, both liquids and powders, should be stored between 10 to 25 °C (50-77 °F) for greatest stability.

Hach uses liquid formulations for the CL17 on-line chlorine analyzer and for Hach's Ultralow Range DPD method, described below. One can use the CL17 liquid reagents in the laboratory.

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Hach uses liquid formulations for the CL17 on-line chlorine analyzer[4] and for Hach's Ultralow Range DPD method, described below. One can use the CL17 liquid reagents in the laboratory.

DPD Colorimetric Method

The following figure depicts reaction of chlorine with DPD. Chlorine oxidizes the DPD amine to two oxidation products.

At a near neutral pH, the primary oxidation product is a semi-quinoid cationic compound known as a Würster dye. This relatively stable free radical species accounts for the magenta color in the DPD colorimetric test. Continued oxidization forms a relatively unstable, colorless imine compound. When DPD reacts with small amounts of chlorine at a near neutral pH, the Würster dye is the principal oxidation product. At higher oxidant levels, the formation of the unstable colorless imine is favored resulting in apparent "fading" of the colored solution.

The absorption spectrum of the DPD Würster dye indicates a doublet peak with maxima at 512 and 553 nm.

Hach uses 530 nm as the measuring wavelength for most of its laboratory DPD systems. This relatively broad "saddle" between the peaks minimizes any variation in wavelength accuracy among different instruments and extends the working range of the test on some instruments. It also permits accurate measurements with an inexpensive colorimeter. The Ultralow Range method uses a wavelength of 515 nm. The relatively steep slope at 515 nm makes it necessary to use a spectrophotometer for the Ultralow Range method. The CL17 Analyzer operates at a wavelength of 510 nm.

Figure 15: Foil packaged DPD free chlorine reagent

Figure 16: Chlorine residual AccuVac Ampules

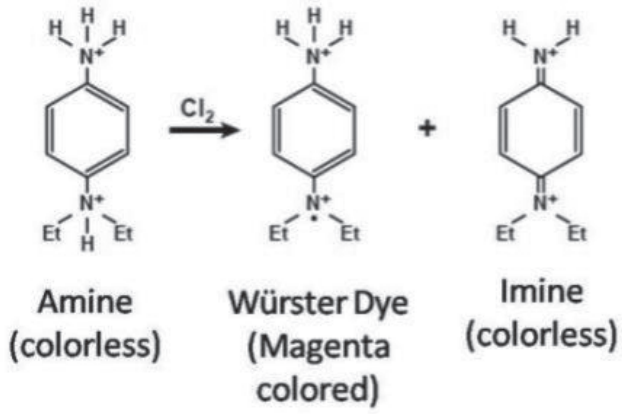


Figure 17: DPD-chlorine reaction products

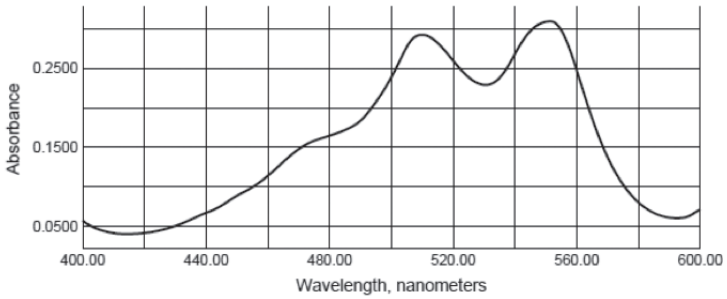


Figure 18: Absorption spectrum DPD Würster compound

[4]*The DPD powdered indicator and the liquid solvent for the indicator are kept separate and mixed immediately prior to use. Therefore, the reagent stability is not affected.*

DPD Titration Method

The DPD titration method uses a ferrous reducing agent as the titrant solution. DPD is oxidized by chlorine (or iodine in the case of chloramines) to the magenta-color species. The solution then is titrated to a colorless end-point. The titrant typically used is a solution of ferrous ammonium sulfate (FAS), $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$. FAS titrant solution is unstable (typically one month shelf life). FAS is subject to oxidation and requires frequent standardization against a potassium dichromate solution.

Hach suggests the use of ferrous ethylenediammonium sulfate, FEAS, $FeC_2H_4(NH_3)_2(SO_4)_2 \cdot 4H_2O$ (Oesper's reagent) for the titrant. Hach prepares the FEAS titrant and packages it in a sealed Digital Titrator Cartridge thus preventing its exposure to air. Hach's preparation and packaging of the reagent provides a shelf life of up to six months.

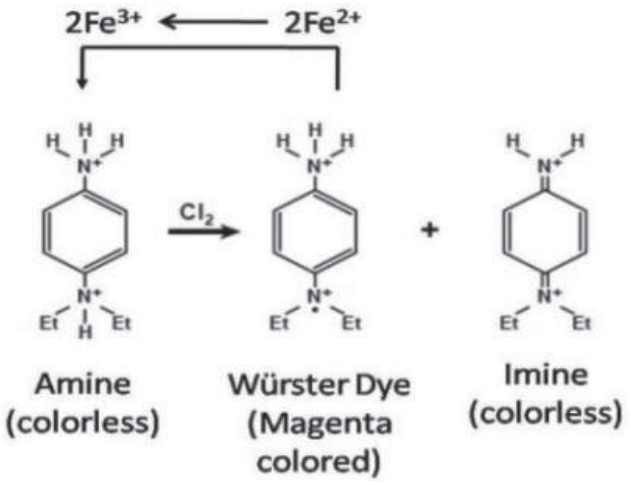


Figure 19: DPD-FAS or DPD-FEAS titration

DPD Ultralow Range Colorimetric Method

Hach has developed a stable liquid DPD reagent system (U.S. Patent No. 5,362,650) for use in determination of ultralow range (ULR) levels of total residual chlorine. This reagent is for use in trace determinations of total chlorine in water and wastewater. Liquid reagents are preferred for trace levels of chlorine less than 20 µg/l (ppb).

Trace determination of chlorine requires high purity buffer and indicator components. Powdered DPD reagents typically leave a very small amount of undissolved residue when added to the water sample. Although the resulting turbidity is insignificant in normal measurements, it may be sufficient to interfere in trace colorimetric measurements.

Organic buffer impurities can exhibit a "chlorine demand" when added to a sample containing trace amounts of chlorine. As stated previously, phosphate buffers generally are problematic in samples containing hardness. Liquid phosphate buffers can contain insoluble impurities or microbiological growths that may cause turbidity when added to the sample. Iodide often contains iodine or iodate impurities that react directly with the DPD indicator. Exposure to oxygen and light will gradually convert iodide to triiodide ion even in the solid state.

Hach's ULR reagents address these problems. The specially compounded ULR Chlorine Buffer is free from any chlorine demand. Careful preparation of Iodide-containing reagent minimizes oxidation impurities. The ULR Chlorine Buffer and ULR DPD Indicator solutions are sealed in unit-dose ampules under argon gas. An amber glass ampule is used for the buffer solution. Both solutions should be protected from ambient light during storage.

Shelf life studies indicate the ULR-DPD reagents exhibit no loss in sensitivity to chlorine over a one-year period when properly stored.

Another important consideration for trace analytical measurements is the "reagent blank." Reagent blank is the amount of interference contributed only by the addition of the reagents. In the DPD colorimetric test for chlorine, oxidation of the DPD indicator gives the same colored Würster dye product as the reaction of the DPD indicator with chlorine.

Figure 20: Ampuled reagents for the Hach ultralow range chlorine residual test

When DPD reagent is added to a sample containing chlorine, the absorbance measured will be the sum of the DPD-chlorine reaction product and the oxidized DPD (reagent blank value). Contribution of the reagent blank is insignificant for higher range (mg/L) measurements. However, one must accurately compensate for reagent blank when making trace (µg/l) measurements.

Ideally, the amount of color due to the reagent addition can be determined by using a sample known to contain no oxidant. Unfortunately, a truly "oxidant-free" sample does not exist.

Hach's procedure to determine the reagent blank value for the ULR-DPD method uses dechlorinated sample without affecting the color contributed by the indicator reagent.

In the reagent blank compensation procedure,

- An agent is added to the sample to remove free and combined chlorine.
- Next, indicator and buffer reagents are added to the dechlorinated sample, following the normal test procedure.
- Measure the resulting absorbance and then use it to correct the actual sample analysis results.

Consistent reagent blank values, equivalent to less than 3 µg/l chlorine, are obtained when using the ULR-DPD reagents. Using Hach's method for ULR total chlorine testing, chlorine residuals as low as 2 µg/l can be determined. This level of detection was determined using the U.S. Environmental Protection Agency (USEPA) procedure for estimating the method detection limit (MDL, Title 40, and Congressional Federal Register; Appendix B, Section 136, 7-1-94.).

The upper range for the test is 500 µg/l (0.5 mg/L) as Cl2. Monitoring applications for the total residual chlorine ULR-DPD method include dechlorination of feed water to reverse osmosis membranes or ion-exchange resins, make-up water for the pharmaceutical and beverage industries, and wastewater discharge to meet NPDES requirements.

In 1993, a number of tests were completed comparing Hach's ultra-low range chlorine DPD (ULR-DPD) method to the Standard Methods back amperometric titration method (4500-Cl-C.) using iodine titrant. Treated wastewater samples (see Compensation for Sample Color and Turbidity, below) were obtained from large and small publicly owned treatment works, an electric utility, a national security installation, an inorganic chemical manufacturer and an organic chemical manufacturer. The samples represented diverse matrices of domestic sewage effluents, cooling water, boiler blow down and manufacturing wastes.

Chlorine demand of the samples was satisfied with a suitable amount of hypochlorite. While aging in the dark under nitrogen gas, the samples were chlorinated to obtain total chlorine residual between 5 and 400 µg/l. Aliquots were tested by both the ULR-DPD and amperometric back-titration methods. At least eight data pairs (ULR-DPD vs. amperometric) were collected for each sample within the 5 - 400 µg/l chlorine range. In addition, a second aliquot of each sample was tested by the two analysis methods after being treated with small amount of known hypochlorite addition (a "spike"). This provided an estimate of the accuracy of the methods, as percent recovery of the spike.

The figure illustrates the results of the method comparison study of all paired data. The 45 °- line represents "ideal" correlation between the two analytical methods. Statistical evaluation of the data, using analysis of variance and a paired-t test at a 95% confidence level, indicated measurements made with the ULR-DPD method did not differ significantly from measurements made with the amperometric method within this concentration range.

The ULR-DPD method is USEPA accepted for total chlorine determinations in drinking water and wastewater.

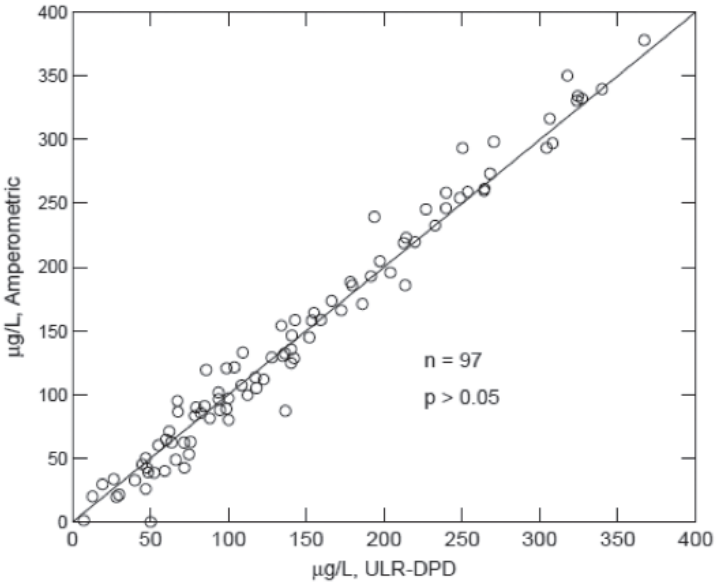


Figure 21: Comparison of Hach's ULR total chlorine residual method with amperometric titration

Indophenol Method for Monochloramine in Water and Wastewater

Water systems practicing chloramination and wastewater facilities need to measure monochloramine. It has been common practice to attempt to estimate monochloramine by simply measuring free and total residual chlorine and then assuming the difference is monochloramine. That approach is a very inaccurate. Numerous reference texts including Standard Methods, 20th ed., 5th ed. of White's book and the Hach WAH contain instructions for measuring and speciation of free, total residual chlorine, and mono-, di-, tri-chloramines. However, these procedures are very technique dependent and time consuming. For chloramination, the primary specie of interest is monochloramine; therefore, Hach chemists developed a simple method for determining monochloramine.

Hach methods for monochloramine include methods 10200 for Water and 10172 for wastewater (U.S. Patent 6,315,950). The method is based on the indophenol chemistry for determining ammonia. The test is specific for monochloramine, without interference from organic or inorganic amines, dichloramine, free chlorine, organic chloramines, nitrites or manganese.

Chemical Reactions

Monochloramine reacts with a substituted phenate to form a quinone imine intermediate. In the presence of a cyanoferrate, the intermediate couples with excess phenate to form a green-colored indophenol compound. The amount of indophenol formed is proportional to concentration of monochloramine in the sample.

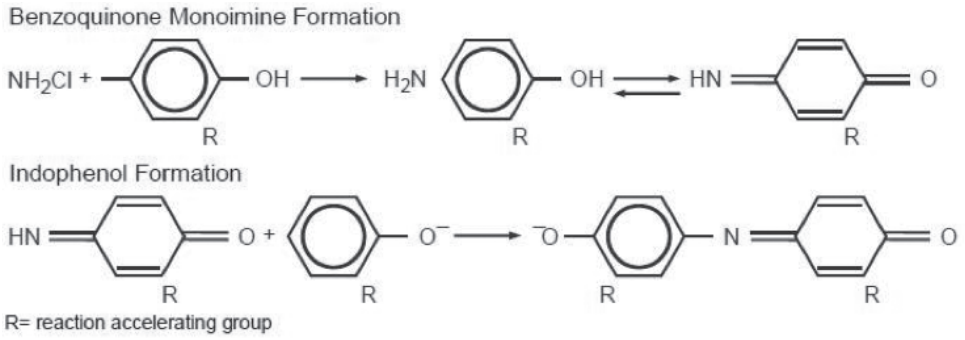


Figure 22: Indophenol formation for determination of monochloramine

Controlling the chloramination process to produce predominately monochloramine necessitates control of ammonia to assure the ratio Cl2:N is less than 5:1. Design of the indophenol test permits determination of free ammonia as well so the analyst can assure free ammonia is greater than zero.

Indophenol Free Chlorine Method

Chloramine, manganese and chromium are positive interferences in the DPD method. The procedure for addressing these interferences in the DPD method is time consuming and sometimes impossible.

Hach developed the Indophenol method 10241 for determining free chlorine residual (U.S. Patent No. 2009/0320570). The method determines free chlorine concentrations without interference from manganese, chromium or chloramines. Only two reagents are required.

The Indophenol free chlorine method eliminates the standard practice of adding sodium arsenite (and the resulting waste) to correct for manganese or chromium interference in the DPD free chlorine method. This "green" alternative method requires no pretreatment steps.

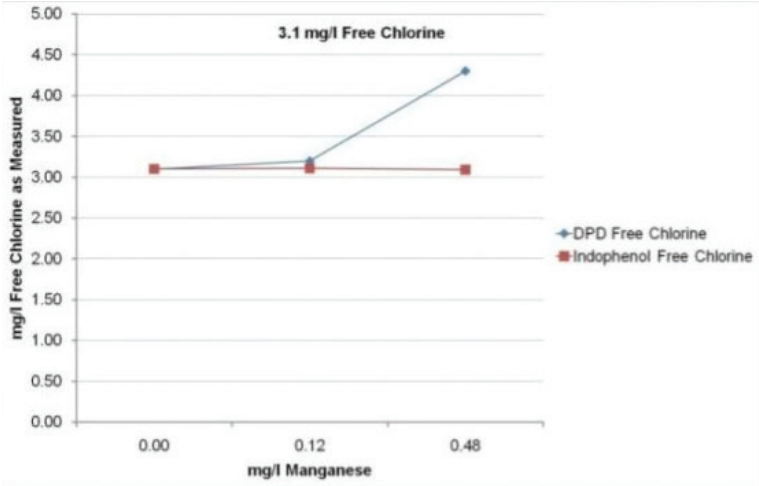


Figure 23: Comparison of DPD vs. indophenol for free residual chlorine at 3.1 mg/L in the presence of manganese.

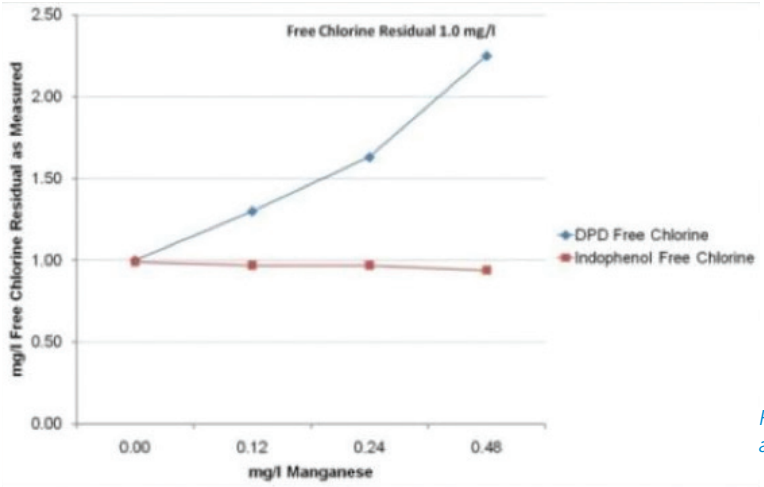


Figure 24: Comparison of DPD vs. indophenol for free residual chlorine at 1 mg/L in the presence of manganese.

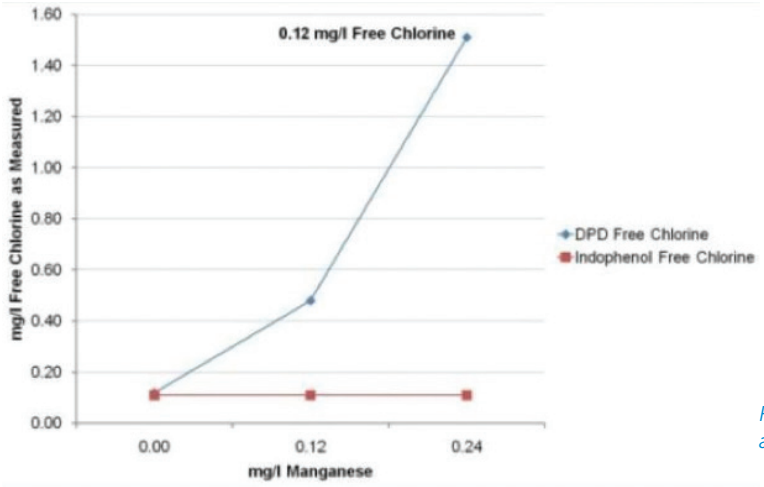


Figure 25: Comparison of DPD vs. indophenol for free residual chlorine at 0.12 mg/L in the presence of manganese.

Chloramines break through and cause high results in a DPD free chlorine determination. The level of breakthrough is dependent on chloramine type, concentration as well as sample pH and temperature. One often observes the presence of chloramines as a slow steadily increasing free chlorine value. The current guidance for analysts using DPD is to read the chlorine as soon as possible (within one minute) to minimize the interference. Indophenol method 10241 for free chlorine eliminates chloramine interference.

Site ID	DPD Test Method		Indophenol Test Method		
	Free Chlorine Residual	Total Chlorine Residual	Free Chlorine Residual	Monochloramine Residual	Free Ammonia
1	0.18	1.77	0.00	1.53	0.07
2	0.06	2.02	0.00	1.93	0.12
3	0.02	1.57	0.00	1.42	0.09
4	0.16	1.86	0.00	1.66	0.18
5	0.01	2.11	0.02	1.91	0.04
6	0.02	0.99	0.00	0.64	0.17
7	0.21	1.92	0.03	1.74	0.10

Figure 26: Chloramine interference in the DPD free chlorine test vs. indophenol free chlorine test

Method Description

- Collect a sample and split into two portions, a sample and a blank.
- Treat one portion, the blank, with addition of Monochlor F Reagent.
- To the second portion, add Freechlor F Reagent Solution. The free chlorine in this portion is converted immediately to monochloramine.
- The developed color in both portions is measured with a colorimeter or spectrophotometer.
- Subtracting the blank value from the sample value provides the concentration of free residual chlorine.
- mg/L sample portion - mg/L blank portion = mg/L free residual chlorine

Color development time of five minutes or longer is necessary depending upon sample temperature. This time may be of concern but it requires less time than the dechlorination procedure using sodium arsenite and the DPD method. The range of the method is 0.04 4.50 mg/L as Cl_2.

Iodometric Titration

The starch-iodide titration method, one of the oldest methods for determining chlorine, is very non-specific for oxidants and generally used for total residual chlorine testing at levels above 1 mg/L Cl_2. Hach uses iodometric procedures to determine chlorine in commercial bleach solutions and in chlorinated wastewaters. Several total chlorine test systems using the iodometric titration method are available with ranges as high as a 15% chlorine solution.

In the iodometric titration method, after addition of potassium iodide (KI) to the sample, chlorine reacts with the KI to produce Iodine[5]. The iodine then reacts with sodium thiosulfate (Na2S2O3) titrant solution. Starch is used as an indicator:

$$Cl_2 + 3KI \rightarrow I_3^- + 3K^+ + 2Cl^-$$

$$I_3^- + 2Na_2S_2O_3 \rightarrow I_3^- + 4Na^+ + S_4O_6^{2-}$$

The endpoint of the titration corresponds to the disappearance of the blue-colored, starch-iodide complex. The pH range for the titration is usually 3-4. Research by Hatch and Yang determined that sample temperatures above 20 °C could introduce significant errors in the iodometric titration. Thus, it is advisable to conduct iodometric titrations at a sample temperature less than 20 °C (68 °F).

Back-titration for samples containing potential chemical interferences is recommended. In this case, add a known amount of thiosulfate in excess to the chlorine in the sample. The amount of unreacted thiosulfate is titrated with a standard iodine solution. The total chlorine, based on the thiosulfate equivalency in the sample, is then calculated. The chemical reactions are:

$$Cl_2 + 2S_2O_32^- \rightarrow 2Cl^- + S_4O_6^{2-}$$

$$I_3^- + 2S_2O_3^{2-} \text{ (excess)} \rightarrow I_3^- + S_4O_6^{2-}$$

[5]*Molecular iodine (I_2) in aqueous solution is typically present as a triiodide ion I_3^-.*

Amperometric Titration Methods

Amperometry is an electrochemical technique that applies a small electrical voltage across two electrodes and measures the change in current resulting from the chemical reactions taking place. Amperometric titration measures the current change as a function of titrant added. Typical amperometric titration instrumentation includes a probe or cell containing dual platinum electrodes (bi-amperometric) or two dissimilar electrodes (for example, silver/platinum), a microampere meter and a titrant-dispensation device. Sodium thiosulfate or phenylarsine oxide (PAO) titrants may be used. The figure below illustrates PAO (b) is typically preferred as it provides a sharper endpoint than thiosulfate (a).

There are applications for both forward and back-titrations. Forward titration describes a process of adding a standard reducing titrant solution to the sample until a defined endpoint is reached. Back-titration describes a process where a sample is 'fixed' by adding excess reducing agent and then the excess is titrated to an endpoint.

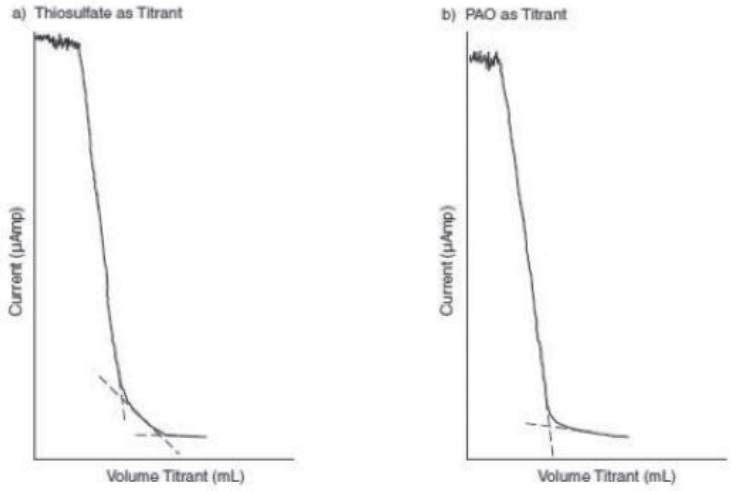


Figure 27: Thiosulfate vs. PAO titrant for amperometric titration

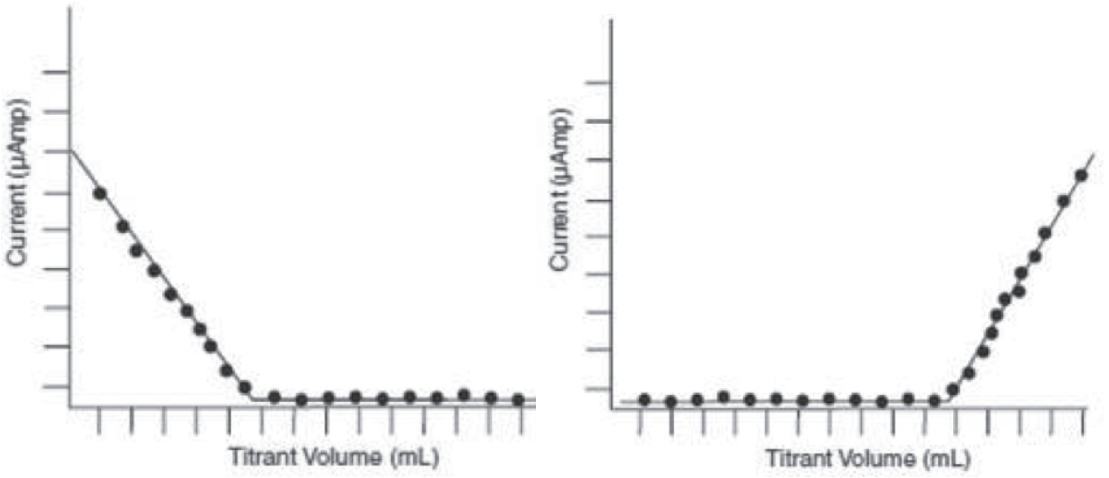


Figure 28: Forward titration (left), back-titration (right)

Amperometric Titration for Free Residual Chlorine

Free residual chlorine determination using forward amperometric titration involves titration with a standard reducing agent such as phenylarsine oxide (PAO) at pH 7. A small potential is applied across the electrodes before the titration begins. An electrical current cannot flow between the electrodes unless two substances are present — one is oxidized at the anode and another reduced at the cathode. During the course of the titration, free chlorine is reduced at the cathode to chloride (Cl^-) from the reaction with PAO titrant. Arsenic (As) in the PAO is oxidized from the +3 to the +5 at the anode:

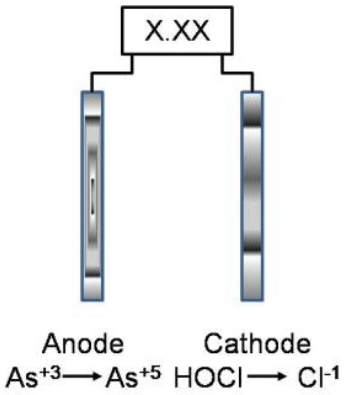


Figure 29: Amperometric forward titration for free residual chlorine

$$PhAsO + HOCl + H_2O \rightarrow PhAsO(OH)_2 + H^+ + Cl^-$$

$$PhAsO + OCl^- + 2H_2O \rightarrow PhAsO(OH)_2 + H_2O + Cl^-$$

Or

$$PhAsO + Cl_2 + 2H_2O \rightarrow PhAsO(OH)_2 + 2H^+ + 2Cl^-$$

(Ph = $C_6H_5^-$, phenyl)

As long as the oxidant (free chlorine) is present in the titrated sample, current flows through the cell. When all of the oxidant is reacted, the rate of current change is zero, signaling the endpoint of the titration. After reaching the endpoint, the solution cannot conduct electrical current even though addition of PAO continues. The amount of PAO used at the titration endpoint is proportional to the chlorine concentration in the sample. The key is accurately determining when the electrical current is zero.

Amperometric Titration for Combined and Total Residual Chlorine

In the case of chloramine (monochloramine and dichloramine) determination, the pH is lowered to 4 and potassium iodide is added to convert the chloramine species to an equivalent amount of triiodide ion (I_3^-):

$$NH_2Cl + I_3^- + H_2O + H^+ \rightarrow NH_4OH + I_3^- + Cl^-$$

$$NHCl_2 + I_3^- + 2H^+ + H_2O \rightarrow NH_4OH + I_3^- + 2Cl^-$$

The triiodide is titrated with PAO with the current change measured amperometrically:

$$PhAsO + I_3^- + 2H_2O \rightarrow PhAsO(OH)_2 + 2H^+ + I_3^-$$

One can determine monochloramine and dichloramine separately by performing a sequential titration.

- First, in the presence of potassium iodide at pH 7, titrate to determine monochloramine. The amount of titrant required is recorded.
- Determine dichloramine by lowering the pH to 4 and more add iodide. Continue titration to resolve the dichloramine fraction.

Titrant must be added in slight excess ("over-shot") to assure the endpoint has been reached. One must account for excess volume of titrant. This practice leads to some ambiguity in the determination of monochloramine and dichloramine fractions, especially when determining low concentrations.

Total residual chlorine concentration can be measured by sequential titration.

- First, the free chlorine residual is determined as above.
- Then potassium iodide, KI is added and the pH adjusted to 4. The titration is resumed. Total residual chlorine then is the total amount of PAO titrant used in both steps.
- If total residual chlorine is the only interest, treat the sample immediately with KI, adjust the pH to about pH 4 and then titrate with PAO until there is zero change in the current flow.

Some users attempt to determine the endpoint by simple visual observation of the current flow to determine the zero endpoint. Determining the endpoint graphically is more accurate and precise.

Back-titration for Total Chlorine

Back-titration is widely used for the determination of total chlorine in water. The amperometric back-titration method has been popular in wastewater laboratories for two reasons:

1. The sample chlorine can be "fixed" at the sampling site with the addition of excess reducing agent (reductant).
2. There is less interference from iodine-demand substances in the sample. Beginning of current flow between the electrodes corresponds to the presence of free iodine (triiodide ion, I_3^-) and signals the endpoint of the amperometric back-titration procedure.

Amperometric titrations require a higher level of skills and care than the colorimetric methods for chlorine analysis. Some references consider the amperometric method to be the standard of comparison for determining free or total chlorine. There is considerable conflicting information about interferences in treated wastewater and effluents (see Interferences in the Amperometric Methods, below).

Most conventional amperometric titration systems rely on the technician to determine visually the titration endpoint by observing changes in a digital or analog meter. In either case the operator, through observation of the meter's display is supposed to judge when the current flow exactly reaches zero in forward titrations or becomes positive in back-titrations.

Hach offers the AT1000 Titrator whereby the instrument's microprocessor continuously monitors the titration. The unit collects and plots multiple points before and after the endpoint is reached. The microprocessor calculates the exact endpoint.

Figure 30: AT1000 Automatic Titrator

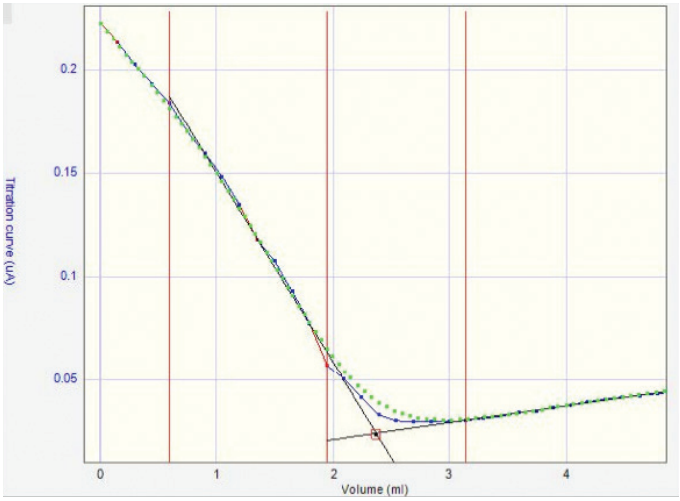


Figure 31: Typical forward titration for free residual chlorine when using the Hach AT1000 Titrator

Use of Standards and Devices for Method Accuracy and Performance Verification

Standards are required to establish accuracy of any analytical method.

If standards are not used, inconsistent results can leave the analyst wondering about the accuracy of the instrument, reagent, and technique. Knowing that standard results are correct can help in many ways:

- Use standards to establish the entire test system is functioning correctly before spending time and reagents testing actual samples.
- Use standards to help evaluate and improve the skills and techniques of the analyst.
- Use standards to provide proof of accuracy for regulatory compliance or customers.
- Use standards to compare performance between two instruments, for example, a laboratory spectrophotometer with an online chlorine analyzer. If readings from an on-line chlorine analyzer and laboratory instrument do not match, the analyst should run a standard to troubleshoot and determine whether the error is in the laboratory or with the on-line instrument. However, the first step should be to ensure the laboratory and on-line analyzers are using exactly the same sample!

Running a standard solution may not provide an answer to a measurement problem, but it narrows down the troubleshooting options in an otherwise complicated situation. For more information about use of standards and quality control, the booklet, An Introduction to Standards and Quality Control for the Laboratory, is available for download at www.Hach.com.

Low Level Chlorine Standards for Method Verification

When using standards for method verification, one performs an analysis of a standard at a similar concentration to that of a typical sample. However, such a procedure is not always feasible. Such is the case with low-range chlorine analysis.

For verification of low range chlorine analysis, Hach recommends the preparation of chlorine standard solutions at concentrations no lower than 0.10 mg/L.

It is important to understand the practical limitations of preparing a low-level chlorine standard. Some of the potential error sources in the preparation of a low concentration chlorine standard solution include:

1. Dilution Water - The dilution water used to prepare a chlorine standard must be chlorine-demand free. For accurate results, the water used to prepare a chlorine dilution should be 18 mega ohm, organic free (<20 µg/l of total organic carbon), amine and aldehyde free, and sterile (this can be achieved by filtration through a 0.2 µm filter). One may follow the procedure in Standard Methods, 20th ed., method 2350B to determine chlorine demand of the dilution water.
2. Atmospheric Exposure - To avoid oxidation and loss of chlorine, low-level chlorine standards must be prepared under a high-purity inert gas headspace. Nitrogen and argon are acceptable gases to use in this application. Avoid contact with atmospheric gases, ammonia vapors and exposure to ambient light.
3. Containers - The containers in which chlorine standards are prepared and handled will affect accuracy. It is important that all containers be chlorine-demand free. Avoid plastic containers as they can leach organics into water and be a source of chlorine demand. Glass, Teflon, and PET are preferred materials for wetted parts of the system. Pretreat all parts for chlorine demand by soaking in a dilute bleach solution (5 drops of commercial bleach per liter of water) followed by rinsing with copious amounts of chlorine-demand-free deionized water. Avoid amber glass containers.
4. pH - The solution pH also affects the stability of a prepared chlorine standard solution. Chlorine is more stable as hypochlorite ion (pH greater than 9) than as hypochlorous acid. Chlorine standard solutions prepared in deionized water are typically less than pH 9. Thus, the prepared standard solution is unstable and must be prepared immediately prior to analysis.
5. Equivalent Standards - With the many potential sources of error in the preparation of chlorine standard solutions, it may be tempting to prepare a chlorine equivalent standard from potassium permanganate. Hach does not recommend the use of permanganate standards for chlorine verification. Precautions Using Permanganate as an Equivalent Standard, below, contains more detailed information.

The many sources of potential error mean that the actual concentration of the standard solution may not match the theoretical calculated concentration of the standard. The actual concentration of the prepared chlorine standard used for verification should be determined through a separate reference method, such as amperometric titration.

Amperometric titration is a method that is traceable to a primary standard. The PAO titrant is traceable to arsenic trioxide, a primary standard. Use an instrument such as the AutoCAT 9000 Amperometric Titrator to standardize PAO versus arsenic trioxide. A certificate of analysis for the PAO titrant is also available for download from www.hach.com.

Additionally, the calibration curves for colorimetric chlorine analyses programmed into Hach colorimeters and spectrophotometers are the result of multiple standards (referenced to amperometric titration) analyzed with multiple lots of reagent. Verification of the method with chlorine standards is recommended, adjustment of the existing calibration curve or recalibration of the instruments is not recommended.

Standard additions (sample spike) is another method for verification. Procedures for standard additions are published in the "Accuracy Check, Standard Additions Method" section of many Hach procedures or in the Hach Water Analysis Handbook. Chlorinated wastewater or tap water should be dechlorinated by exposure to ultraviolet light UV, prior to the addition of a chlorine spike. Chemical methods of dechlorinating cannot be used, as any residual of the dechlorinating agent would interfere with the spike.

Hach recommends the standard additions technique using Chlorine PourRite® Ampule Standards or Voluette® Ampuled Standards[6] for routine verification of pre-programmed calibrations.

[6] *PourRite Ampuled Standard, 2 ml each, 20/pkg; Voluette Ampuled Standard, 10ml each, 16/pkg*

Figure 32: PourRite (left) and Voluette Ampule Chlorine Standard Solutions

The Chlorine ampuled standards are pure aqueous free chlorine solutions prepared in two ranges, 25 30 mg/L (PourRite ampules) or, 50 75 mg/L chlorine (PourRite or Voluette ampules). The actual value is provided for each lot of standards. Hach research has shown that the ampuled chlorine standards exhibit excellent stability, when stored at temperatures between 2 to 8 °C (33 to 47 °F.). Use a simple procedure to verify the accuracy of the chlorine calibration. For example:

a) Snap the top off a Chlorine PourRite or Voluette Ampule Standard Solution.

b) Use the TenSette® Pipet to add 0.1, 0.2 and 0.3 ml of standard to three 25-ml samples. Swirl gently to mix.

c) Analyze each sample immediately per the Hach DPD colorimetric procedures.

d) Each 0.1 ml of standard will cause an incremental increase in chlorine content. The exact value depends on the actual concentration.

Check the certificate enclosed with the ampules for this value. Refer to Hach's Water Analysis Handbook, for more information on the standard additions technique for verification of accuracy.

If you have any questions or concerns regarding the preparation of chlorine standard solutions for method verification, contact Hach Technical Support at 1-800-227-4224 or email techhelp@hach.com.

Precautions Using Permanganate as an Equivalent Standard

Standard Methods, 20th ed., contains instructions for using dilute solutions of potassium permanganate as equivalent standards for establishing a chlorine calibration. As noted by Gordon, et al. permanganate oxidizes DPD to both the colored and colorless oxidation product.

Hach researchers have noted the order of adding reagent to sample will affect the ratio of oxidized DPD products. For example, if the permanganate equivalent standard is placed in a container (such as a DR sample cell) and the free chlorine reagent is added to it, the oxidant is in excess during the addition process. Therefore, more of the colorless imine product can form, resulting in less color in the test.

Conversely, adding free chlorine DPD indicator/buffer reagent in the sample cell and then the permanganate solution, the DPD indicator remains in excess, with proper formation of the colored product. In practical terms, the differences between reagent-to-sample and sample-to-reagent additions using permanganate standards and Hach's DPD reagent are relatively small.

Equivalent mg/L Cl_2	Reagent added to sample		Sample added to reagent		Difference	
	Abs	Conc. mg/L	Abs	Conc. mg/L	Abs	Conc. mg/L
0.20	0.108	0.20	0.109	0.21	0.001	0.01
0.50	0.271	0.51	0.271	0.51	0.000	0.00
0.80	0.427	0.80	0.432	0.81	0.005	0.01
1.00	0.530	0.99	0.543	1.02	0.013	0.03
1.20	0.613	1.15	0.632	1.19	0.019	0.04
1.40	0.727	1.36	0.743	1.39	0.016	0.03
1.50	0.764	1.43	0.791	1.49	0.027	0.06
1.60	0.815	1.53	0.834	1.57	0.019	0.04
1.80	0.920	1.73	0.928	1.74	0.008	0.01
			Mean Difference		0.012	0.03
			Standard Deviation		0.009	0.02
			Range		0.027	0.06

Using Hach's DPD Free Chlorine Powder Pillows, Cat. No. 14070, and using a Hach DR 3000 Spectrophotometer with pre-programmed calibrations. 1995

Figure 33: Order of sample-to-reagent addition using permanganate equivalent standards.

The figure above illustrates the differences obtained over a series of permanganate standards in the range of 0.2-1.8 mg/L as chlorine. The average difference between the two addition techniques was 0.03 mg/L as chlorine. The greatest discrepancies were noted at concentrations greater than 1.0 mg/L. The "order of addition" effect has been noted only when using permanganate.

A few precautions in the preparation and use of permanganate standards are:

- Glassware used in the preparation and dilution of permanganate solutions should be treated with chromic acid cleaning solution to remove any organic contamination. Then rinse the glassware copiously with low-organics water.
- Water used for dilution of stock permanganate solution should be low in organics and should exceed American Society for Testing and Standards (ASTM) Type I quality specifications. Dilution water for permanganate should never be stored in plastic containers or exposed to airborne contamination. Standardize the stock solution routinely with dried sodium oxalate (Vogel).
- Dilute equivalent standards are not stable and should be prepared as needed. Never store dilute permanganate in plastic containers.

Because of these constraints, Hach does not recommend the use of permanganate equivalent standards with Hach DPD reagents.

Use of Spec✔™ Color Standards

Hach manufactures Spec✔ Color Standards for use in rapid method performance checks. The standards are a gel colored to simulate specific concentrations. Three sets are available for the DPD chlorine measurement.

Each set includes three different color standards and a blank. Spec✔ Color Standards can be used with all Hach colorimeters and spectrophotometers.

Figure 34: Spec✔ Color Standards for DPD-chlorine

Method	Concentration		
DPD Chlorine	Low range 0-2 mg/L Cl_2	Mid range 0-4 mg/L Cl_2	High range 0-6.5 mg/L Cl_2
Indophenol method for ammonia/monochloramine	Free ammonia (0 - 0.50 mg/L NH_3-N), Monochloramine (0 - 4.5 mg/L Cl_2)		
Ozone	0-0.75 mg/L O_3		
Fluoride	0-2.00 mg/L F^-		

Figure 35: Spec✔ Color Standards

Method Interferences and Sources of Errors

Sampling Considerations

Perhaps the most common source of error in testing for chlorine in water is the failure to obtain a representative sample. Because free chlorine is a strong oxidizing agent, its stability in natural waters is relatively low. Chlorine readily reacts with various inorganic compounds. It will slowly oxidize organic compounds.

Various factors, including reactant concentrations, pH, temperature, salinity and sunlight, influence the decomposition of free chlorine in water. Monochloramine, on the other hand, is much more persistent in the environment. Typically, the decay rate of monochloramine is tenfold slower than the decay of free chlorine in natural waters (Jolly, et.al.).

Ideally, analyze samples for chlorine on site. If sampling from a tap, allow water to flow at least five minutes before sampling to ensure a representative sample.

- Sample containers should be pretreated to remove any chlorine demand. A pre-treated glass BOD bottle, with ground glass stopper, makes an ideal sample container for chlorine analysis. Avoid plastic sample containers because they might exert an appreciable chlorine demand.
- Pretreat clean glass sample containers by soaking in a dilute bleach solution (1 ml commercial bleach solution to 1 liter of water) for at least one hour. After soaking, rinse them thoroughly with deionized or distilled water or the sample. Another such treatment is required only occasionally if sample containers are always rinsed with deionized or distilled water after each use.
- Ideally, separate and dedicated sample containers should be used for free and total chlorine determinations. Trace iodide (from the total chlorine reagent) may be carried over into the free chlorine determination. Monochloramine will interfere in the free chlorine test.
- Avoid excess agitation and exposure to sunlight and high temperatures when sampling. Allow several volumes of the container to overflow and cap the sample container to eliminate head space above the sample
- For on-site determinations using Hach DPD colorimetric procedures, the one-inch square or cylindrical DR cell serves as an excellent sampler.
- If sampling with the DR cell, rinse the cell with several volumes of sample; then carefully fill to the 25-mL (or 10-mL) mark.
- For AccuVac ampules, collect sample in a wide-mouth container, such as a beaker, rinsing several times with sample. Immerse the ampule as illustrated at right and snap off the neck allowing it to fill. Proceed with the analysis immediately.

Figure 36: Filling an AccuVac Ampule

- If the iodometric back-titration methods are used for total chlorine analyses, the sample can be "fixed" on site. This involves the addition of a precise amount of standard reducing agent to the sample at the collection site. The fixing procedure calls for the addition of 1.00 ml 0.00564 N PAO or standard thiosulfate, potassium iodide, and 1.0 ml pH 4 Acetate Buffer into a clean, dry glass container with a capacity of at least 250 ml (such as a BOD bottle).
  - At the sampling site, collect 200 ml of sample with the sample container and swirl to mix.
  - Minimize the delay between sample fixing and analysis (usually less than one hour) to prevent bacterial decomposition of PAO (or thiosulfate) excess in the sample.
  - It is important to transfer the entire contents of the sample container to the analysis glassware used in the titration.

Interferences Common to All Chlorine Methods

All of the common analytical methods for chlorine or chloramines in water are based on chemical oxidation-reduction reactions. Each of the chlorine methods depends on the total oxidizing capacity of the sample being analyzed and is readily subject to interferences from oxidizing agents other than chlorine. Generally, all of the accepted methods for chlorine are subject to potential interferences from particles (turbidity), color, inorganic and organic compounds, and buffering capacity (acidity or alkalinity) of the sample. There is no 'ideal' method for chlorine analysis, which is specific and selective for the free chlorine and/or chloramine species.

Other Disinfectants

In general, all of the common chlorine methods will detect other oxidants used as disinfectants — such as chlorine dioxide (ClO_2), ozone (O_3), bromine (Br_2), hydrogen peroxide (H_2O_2), permanganate and disinfectant byproducts such as chlorite and chlorate — if present in sufficient amounts. In the free chlorine determinations, these oxidants can react directly with the colorimetric indicator or they will be reduced with thiosulfate or PAO in the titration method. Each of these oxidants will oxidize iodide to iodine to a certain degree, thereby interfering in the total chlorine determination. On the other hand, this interference makes it possible to use total chlorine methods for determination of TRO (total residual oxidant) concentration, as it is required in some applications (e.g. seawater-based treatments).

Hach has developed methods based on standard chlorine chemistries for Br_2, I_2 and H_2O_2. Analytical methods that attempt to distinguish between combinations of oxidants try to convert all oxidants, except the analyte, to a non-reactive form. In reality, the required additional manipulations may mean some loss of the analyte, due to the extra time involved or changes of reaction conditions for the test.

Manganese Compounds

Manganese is the 2nd most abundant metal (12th most abundant element) on earth and estimated to be present at nuisance levels in nearly 70% of water supplies. Manganese can exist in oxidation states of +2 through +7. The higher oxidation states, typically +3 to +7, will interfere with all the common chlorine methods. Free chlorine reacts to oxidize soluble manganese compounds. For example:

$$Mn^{2+} + HOCl + 3OH^- \longrightarrow MnO_2 + Cl^- + 2H_2O$$

Apparently, chloramines will not oxidize manganous compounds. Oxidized manganese will react directly with the DPD indicator. It is claimed that Mn^{4+} does not interfere in the FACTS method at a 1.0 mg/L level (Cooper, et.al.). At 2.6 mg/L Mn^{4+}, interference has been observed after five minutes with the FACTS test. Oxidized manganese (+4 to +7) will also interfere in the amperometric titration method for free chlorine. Iodide can be oxidized by manganese (+4 to +7) to I2, which will interfere in both the colorimetric and titrimetric methods for total chlorine. The interference of oxidized manganese in back-titration methods appears to be a function of iodide concentration and the test pH (Bongers, et.al.).

Manganese interference is so common that test instructions for Hach's laboratory and portable DPD test procedures contain instructions for compensating for manganese interference. The customary procedure to compensate for manganese interference in the DPD methods is to first dechlorinate the sample with sodium arsenite, which does not affect the manganese, and then proceed with the test. The result obtained with the dechlorinated sample is subtracted from the normal test result to obtain the correct chlorine concentration.

Hach suggests use of the Indophenol Free Chlorine Method (Method 10241) for Use in Waters Containing Manganese or Chloramines (see above) as a simpler alternative to measurement of free residual chlorine without interference due to manganese.

Compensating for Manganese, Oxidized (Mn^{4+}, Mn^{7+}) or Chromium, Oxidized (Cr^{6+})
1. Collect a portion of sample and split it into two 10 ml samples, test portion 1 for chlorine following the normal test procedure. Treat portion 2 as follows:
2. Adjust sample pH to 6–7.
3. Add 3 drops Potassium Iodide (30-g/l) to a 10-mL sample.
4. Mix and wait one minute
5. Add 3 drops Sodium Arsenite 1 (5-g/l) and mix.
6. Analyze 10 ml of the treated sample as described in the procedure.
7. Subtract the result from this test portion from the result obtained from the untreated portion (1) to obtain the correct chlorine concentration: mg/L (portion 1) - mg/L(portion 2) = Correct mg/L chlorine concentration

Figure 37: Typical procedure for compensating for manganese or chromium interference in chlorine residual testing.

Organic Chloramines

There is considerable debate over the interference of organic chloramine compounds with the cited free chlorine tests. Organic nitrogen compounds can combine with chlorine analogous to the reaction with ammonia:

$$RNH_2 + HOCl \longrightarrow RNHCl + H_2O$$

where R = the organic moiety.

Typical organic nitrogen compounds would include common amines, amino acids and heterocyclic bases. Free chlorine reacts quickly with these types of compounds to form non-germicidal organic chloramines. While formation of organic chloramines may be more common in wastewater effluent, organic nitrogen is typically absent or in very low levels in drinking water supplies. Still, studies have indicated possible interference from organic chloramines with analytical methods for free and total chlorine.

In general, methods that determine free chlorine and monochloramine at neutral pH values (6-7), including the amperometric method (forward titration), the DPD methods, and the FACTS method, are not very susceptible to interference from organic nitrogen. Methods that include dichloramine and those that use acidic conditions (pH 4 or lower) to determine free or combined chlorine, such as the standard back titration method, the orthotolidine method, the LCV method and the MO method are vulnerable to interference by organic chloramines. (White, 5th ed., p 184.)

Bromide in Chlorinated Waters

Seawater and estuary water may contain natural levels of bromide ions up to 65 mg/L. The addition of chlorine to waters containing bromide will produce hypobromous acid and hypobromite ion:

$$Br^- + HOCl \longrightarrow HOBr + Cl^-$$

This reaction is irreversible and the product will interfere with all common free residual chlorine analytical procedures. If ammonia is present in the sample, HOBr will react with ammonia forming bromamines. Bromamines will react with iodide reagent analogously to the chloramine reaction, indicating a positive interference in the total chlorine test. Bromide, when present in a chlorinated sample, forms a disinfectant (hypobromite and/or bromamines) and, technically, the analytical results would indicate the total oxidizing capacity of the sample. In this case, the analyte termed Total Residual Oxidant (TRO) and its concentration is reported as ppm (mg/L) of chlorine or bromine.

Errors Common to Total Chlorine Determinations

All of the common total chlorine methods are based on the oxidation of iodide to iodine (triiodide ion) followed by determination of its concentration. There are several potential sources of errors related to the iodide/iodine reaction, including:

- Air oxidation of the iodide reagent
- Volatilization of produced iodine
- Iodine or iodate contamination in the iodide reagent
- Consumption of triiodide by sample components

Potassium iodide (KI) reagent is subject to air oxidation by the reaction:

$$4I^- + O_2 + 4H^+ \longrightarrow 2I_2 + H_2O$$

Decreasing the pH and traces of metal ions will accelerate the reaction. Iodide reagent solutions are quite susceptible to oxidation from exposure to light and oxygen. Research sponsored by the Electric Power Research Institute (EPRI) has shown an amount of oxidant equivalent to 1 mg/L chlorine can be generated in one day in a 0.1 M (molar) KI stock solution (Sengupta). Providing alkaline conditions improves stability of KI solutions. It is prudent to prepare or purchase the solutions in small quantities, store the solutions in amber containers, and protect them from direct sunlight and temperature extremes. It also is important to complete the analysis quickly to minimize iodine loss by volatilization.

The purity of potassium iodide is critical when measuring total chlorine at trace levels. The iodide should be free of iodine or iodate, which can react directly with chlorine, chloramines or the indicator reagent itself. Even solid potassium iodide can be oxidized provided sufficient exposure to oxygen and ultraviolet light occurs.

Adsorption of the produced iodine on suspended particles can be a serious problem in muddy or highly organic-rich waters. A perfect example of this type of adsorption is the blue complex formed between I2 and starch, the visual indicator for the iodometric titration method. In addition to adsorption, iodine can react with organic matter to form carbon-iodine bonds (Sengupta). This is one reason for the traditional preference of the back-titration method for total chlorine in wastewater.

Interferences in the DPD Methods

Calibration Non-Linearity

The reaction of chlorine with DPD results in two oxidation products: the colored Würster dye and the colorless imine. The proportion of colored to colorless product is related to the ratio of DPD indicator to oxidant. When DPD reacts with small amounts of chlorine, the Würster dye product is favored. At higher oxidant levels, the formation of the unstable, colorless imine is favored—resulting in apparent "fading" of the colored solution. It is necessary that the ratio DPD to oxidant remain high to minimize fading of the resulting color.

Gordon, et.al. (Talanta) reported the non-linearity of the DPD colorimetric method calibration using the Standard Methods procedure.

The concentration range is stated to be 0 4.0 mg/L Cl_2, using either chlorine standards or secondary standards made from potassium permanganate. Gordon reported the Standard Methods procedure using permanganate exhibited a non-linear response above 1.0 mg/L equivalent chlorine. Hach also has confirmed the non-linearity of the Standard Methods procedure using free chlorine standards.

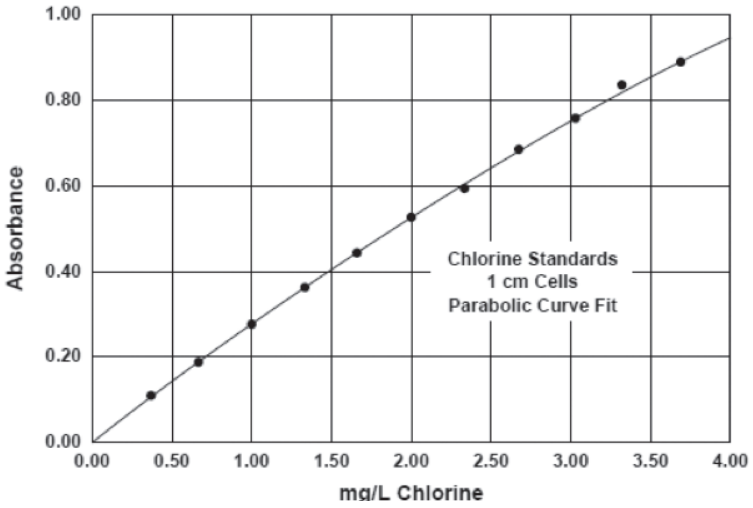


Figure 38: Standard Method Calibration DPD Colorimetric Method

The non-linearity of the Standard Methods calibration is attributed to the increased formation of the colorless imine product at higher oxidant concentration.

In the Standard Methods formulation the amount of DPD added to the sample is insufficient to optimize the oxidation to the Würster product stage. The instability of the liquid DPD reagent is also a contributing factor to the non-linear chlorine calibration. As the DPD indicator solution ages, there is less of the active DPD amine form available to react with sample chlorine, thereby shifting the ratio of DPD to oxidant. Changing the ratio of DPD to oxidant leads to increasing non-linearity at the higher chlorine levels as the DPD reagent solution ages and becomes oxidized. Hach DPD reagents maintain a higher ratio of indicator to oxidant and therefore do not suffer the same nonlinearity as the Standard Methods formulations.

Hach DPD powdered formulations offer superior stability over the liquid reagent formulations; therefore, a reproducible and linear response to chlorine will be obtained for a longer period of time. In the DPD titration method both DPD oxidation products are titrated by the ferrous titrant. As a result, the titration method does not suffer from the "color fading" phenomenon.

Monochloramine Interference in the Free Chlorine Test

There is considerable controversy about monochloramine interference in the free chlorine DPD test. Monochloramine breakthrough is more of a problem in the DPD titrimetric method for free chlorine because of the additional time necessary to perform the test. Standard Methods recommends the use of thioacetamide to, "completely stop further reaction with combined chlorine in the free chlorine test." The thioacetamide modification is recommended for the DPD titration method for free chlorine, if chloramines are 0.5 mg/L or greater.

Hach does not recommend the use of thioacetamide in the free chlorine DPD measurements for two reasons:

1. Thioacetamide is a toxin and confirmed carcinogen.
2. The reaction of thioacetamide to prevent oxidation of DPD by monochloramine is not thoroughly understood. It is not clear if thioacetamide reduces DPD oxidized by monochloramine or just reduces the combined chlorine. If it does reduce the oxidized DPD, why does it not reduce DPD oxidized by free chlorine?

Other references cite use of mercuric salt to aid in inhibiting monochloramine interference. Hach does not use or recommend use of mercuric salts.

Hach suggests use of the Indophenol Free Chlorine Method (Method 10241) to prevent interference from manganese, chromium or chloramines as a simpler and safer alternative use of thioacetamide or mercuric salts. (See Indophenol Free Chlorine Method for Use in Waters Containing Manganese, Chromium or Chloramines, above.)

Compensation for Sample Color and Turbidity

One critical problem, especially when applying colorimetric procedures to treated wastewaters, is interference from turbidity and color in the water. Preliminary filtration can be performed to remove particulate matter from the sample for certain parameters. The residual sample color is "zeroed" at the measurement wavelength with the colorimeter. In many instances, sample color and turbidity can be compensated for by simply zeroing the photometer with the sample blank prior to reagent addition. This is appropriate for most colorimetric testing.

When testing for trace levels of total chlorine in treated wastewater using Hach's ULR-DPD procedure, fine particulate matter may cause a "noise" level of up to ± 0.010 absorbance (using a 1"- path length cell). This level of variation is unacceptable when measuring trace color developed from the reaction of DPD with low concentrations of total chlorine. Preliminary filtration of the water sample is not appropriate when testing for chlorine. Whether or not chlorine loss occurs during the sample filtration depends on the predominant chlorine species present in the sample and the nature of the filter media. Some loss can be attributed to the relative volatility and instability of chlorine compounds in natural waters. Certain filter materials also can lead to chlorine loss during the filtering process due to adsorption of the hypochlorite ions or existing chlorine demand.

Hach studies indicate if filtration is performed after the development of the colored product (a post filtration), removal of interfering sample turbidity can be accomplished without concern for chlorine loss. The selection of the filter media is important because the Würster dye product is a positively charged ion. Membrane filter compositions having a surface charge cannot be used. The selection of filter porosity also is critical in terms of adequate removal of the particle sizes that could interfere at the absorption wavelength.

Figure 39: Oriflo™ Filter Apparatus and glass fiber filters

In the ULR-DPD Total Chlorine procedure for treated wastewater, sample turbidity is removed, using a syringe filter apparatus (Oriflo™ Filter Apparatus, U.S. Patent # 5549816) with a special inert 3-micron filter. A preliminary filtration is performed on the sample to zero the photometer. A second portion of sample is reacted with the reagents and a filtration is performed on the reacted sample. When the post filtration procedure is used, the net absorbance is adequately corrected for sample color and turbidity.

Interferences in the Amperometric Titration Methods

Standard Methods states the amperometric titration method "is the method of choice because it is not subject to interference from color, turbidity, iron, and manganese or nitrite nitrogen" (Ref. 3.21). In reality, several of these factors do affect the determination of chlorine species when using amperometric methods. A brief review of some of the common sources of errors encountered with real world samples follows.

Deposition on Electrode Surfaces: Clean and regularly conditioned electrodes are necessary for sharp amperometric titration end points. Because the electrodes contact the sample, certain species in the sample may plate out or coat the electrode's metallic surface. Metallic ions such as copper (+2), silver (+1) and iron (+3) have been reported as either interferences in the forward amperometric method or may diminish the electrode response. In some waters, foaming or oily surface-active agents will coat the metallic electrodes, resulting in decreased sensitivity. Follow instructions from the manufacturer for maintaining the electrode surfaces.

Manganese Interference: There is a certain ambiguity in the literature concerning manganese interference in the amperometric forward and back-titration for chlorine. As discussed above, if the sample contains free chlorine, any soluble manganese will be oxidized:

$$Mn^{2+} + HOCl + 3OH^- \longrightarrow MnO_2 + Cl^- + 2H_2O$$

The oxidized forms of manganese (+4 to +7) will titrate with phenylarsine oxide (PAO) in the forward titration procedure for free chlorine. Oxidized forms of manganese will react with iodide at pH 4, producing iodine, which titrates with PAO, causing an interference.

Nitrite Interference: Nitrite can exist as a transitory compound in certain waters, due to the biological oxidation of ammonia:

$$2NH_4^+ + 3O_2 \longrightarrow 2NO_2^- + 4H^+ + 2H_2O$$

There is conflicting information about the interference of nitrites in either the forward or backward amperometric titration methods for total chlorine. Nitrites are seldom significant in drinking water applications. Nitrite interference may go unnoticed in wastewater measurements.

According to Standard Methods, 20th ed. nitrites do not interfere in the forward titration methods (4500-Cl D, pg 4-59). In section 4500-Cl C.1b, states that nitrite interference can be minimized by buffering to pH 4.0 before addition of iodide. It indicates interference from more than 0.2 mg/L of nitrites can be controlled by the use of a phosphoric acid-sulfamic acid reagent.

Hach researchers have investigated the effect of nitrites in the determination of monochloramine using the forward- and back-titration procedures. Monochloramine was selected since it is slow to react with nitrites (Margerum, D, et. al.) and represents the primary disinfectant form in treated wastewater. Free chlorine has been shown to react directly with nitrites (White, 3rd, ed., pg 226):

$$HOCl + NO_2^- \longrightarrow NO_3^- + HCl$$

To investigate the effect of nitrites on the determination of low concentrations of monochloramine, six variations in the amperometric procedures were studied:

1. Forward titration with KI added first, then pH 4 buffer (PAO as titrant)
2. Forward titration with buffer added first, then KI (PAO as titrant)
3. Back-titration, excess PAO, KI, and then pH 4 buffer (iodine as titrant)
4. Back-titration, excess PAO, buffer, and then KI (iodine as titrant)
5. Back-titration, excess PAO, KI, then H3PO4/sulfamic acid (iodate as titrant)
6. Back-titration, excess PAO, H_3PO_4/sulfamic acid, then KI (iodate as titrant).

No. 1, No. 3 and No. 5 follow the Standard Methods procedures for forward titration, back-titration with iodine, and back-titration with iodate, respectively. The testing for No. 1 through No. 4 was performed at pH 4, because this is the pH used to speciate "total" chlorine. All of the titration end-points were determined amperometrically.

A monochloramine standard was prepared in the range of 70 to 80 µg/l (Cl_2). Small portions of a stock nitrite standard, equivalent to the addition of 0 to 50 mg/L nitrites, were added to 200 ml of the monochloramine standard. Analyses were performed in triplicate according to the sequences listed above. Mean percentage recoveries as a function of nitrite concentration are shown graphically in the following figure:

In variations No. 5 and No. 6, with the addition of nitrite to the chlorine standard, a large amount of iodine was generated almost instantaneously after the addition of the reagents. This suggested that nitrites, at concentrations between 5 and 50 mg/L, would react readily with iodide at the lower pH, even in the presence of excess reductant and sulfamic acid. Standard Methods directs the analyst to "titrate immediately" with iodate. Hach studies, however, indicate nitrite as low as 5 mg/L will "breakthrough" (interfere) within 30 seconds after addition of the KI and acid mixture.

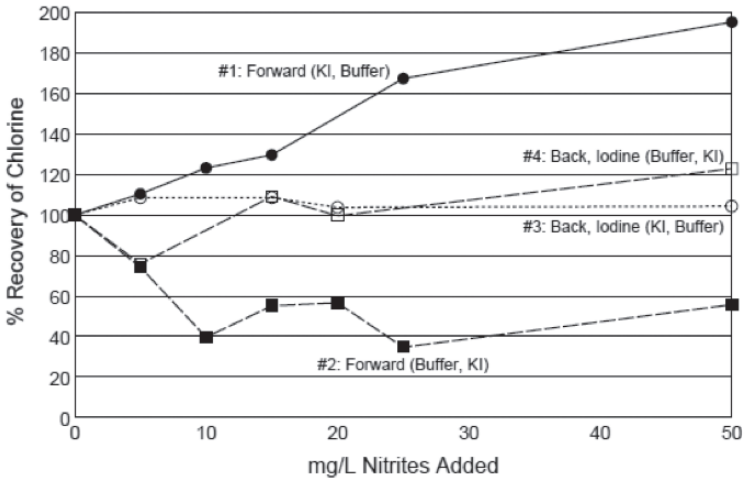


Figure 40: Nitrite interference in amperometric chlorine methods

In the forward titrations (No. 1 and No. 2), nitrites seem to indicate either a positive or negative interference depending on the order of reagent addition. If iodide is added to the sample prior to pH 4 buffer, the error increases as a function of nitrite concentration. If buffer is added prior to the iodide, a large negative error, independent of the nitrite level, occurs.

The preferred procedure, with the least interference from nitrites, is the back-titration at pH 4, using standard iodine titrant, (No. 3 and No. 4). The iodometric procedure in which KI is added first, then buffer, seems to provide the least amount of variation with increasing amounts of nitrites. This procedure is recommended for the amperometric titration of total chlorine in treated wastewaters, agricultural waters and industrial discharges.

Choice of Reductant

In the forward amperometric titration method, it is important that only phenylarsine oxide (PAO) be used as the titrant when measuring total chlorine. PAO will give sharper end points than standard thiosulfate at pH 4.0.

The titration plots show the titration of an 82 µg/l monochloramine standard, using a continuous titrant feed of: a) standard thiosulfate and b) standard PAO. The rate of reaction of generated triiodide with thiosulfate evidently changes as the end point is approached. This can lead to uncertainty when determining the endpoint graphically. PAO gives a relative sharper end-point determination. In the case of the amperometric back-titration method, the addition of either excess PAO or thiosulfate is acceptable. The titration end-points for both reductants are equivalent when standard iodine is the titrant.

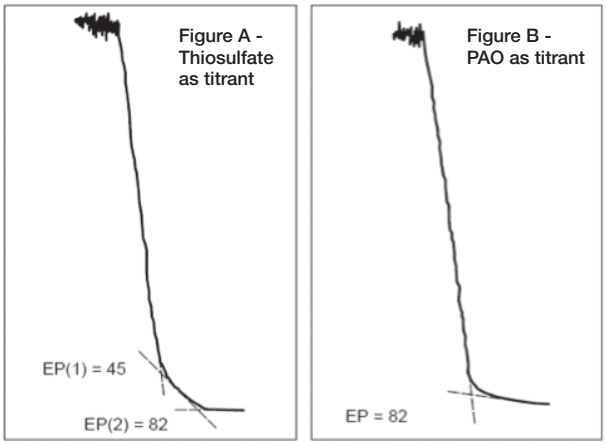


Figure 41: Comparison of thiosulfate and PAO as titrants

Effect of Iodine Demand on End Point Determinations

Certain samples containing organic compounds may exhibit an iodine demand that can shift the titration end-point, even when a back-titration procedure is used.

If the sample contains suspended particles, iodine will adsorb readily onto the particles, resulting in a shift of the current readings. In addition to adsorption, iodine can react with dissolved organic matter in the sample forming carbon-iodine bonds. For samples containing appreciable iodine demand, it may be difficult to achieve an accurate estimation of the endpoint. Continuing the titration to obtain several readings after the endpoint will help determine the intersection of the two lines. In addition, the speed at which the titration is performed will be a factor in minimizing iodine demand and identifying the actual end point. Dilution of the sample with chlorine demand-free water also will minimize iodine demand, although with a certain sacrifice in sensitivity.

Order of Reagent Addition for Saline Water or Seawater

The chemistry of chlorine in seawater is complex. Measurement of chlorine in saline and estuary water or seawater is exceedingly difficult with any of the available analytical methods. There is conflicting information in the literature pertaining to the amperometric determination of total chlorine in salt water. Several studies have indicated the order of KI and buffer reagent addition may cause underestimation of the total chlorine concentration when determined amperometrically. Saline waters usually contain an appreciable chlorine demand, due in part to oxidation of carbon and nitrogen-containing compounds. Bromide, usually present in seawater, will oxidize to hypobromous acid and hypobromite when chlorine is added.

Furthermore, the concentration of chlorine-containing and secondary oxidants produced by chlorination are dependent on the characteristics of the water being chlorinated, such as bromide concentration, salinity, organic load, water temperature and incident sunlight. There is general consensus that iodide reagent should be added before or simultaneously with the pH 4 buffer in the amperometric determination for "total chlorine" in saline waters. If the saline sample is buffered prior to addition of the iodide, the total residual oxidant (TRO) concentration may be underestimated.

Comparing Portable and Laboratory Measurements

A variety of chlorine test platforms is available for the laboratory and for portable use in the field. The most practical field method for chlorine residual is the DPD colorimetric method. Whether used in the laboratory or in a field environment, the reagents are the same. The variables determining accuracy of field/portable measurement compared to a laboratory result are:

Figure 42: Color Comparator test kit for chlorine residual

Figure 43: Hach DR300 Colorimeter

Figure 44: Hach DR6000 UV-Vis Spectrophotometer

- When comparing a laboratory result to a portable result the sample must be as close as practical to be the same sample. With an analyte as reactive and volatile as chlorine, it is unlikely one can obtain a grab sample on site then transport a portion to the laboratory and expect the results to be comparable to measurements made on site. Even when a sample is 'fixed' as described above for amperometric back-titration, some uncertainty will result from the transport and delay in measurement.
- The sampling point must be clean and free from contamination.
- Remove aerators and screens prior to sampling.
- Allow the sample line to run for at least five minutes to ensure the sample is representative of the process.
- Choice of measurement platform
  - Test strips and Visual color comparison Test strips and visual color comparators should be avoided when making measurement for regulatory reporting or other instances when a good degree of accuracy is desired for the following reasons:
  - Judgment of the color that develops is dependent on the individual analyst's ability to judge subtle differences in color.
  - The apparent color or intensity of color can vary with light source. Whether a test strip or color comparator is viewed in bright sunlight, heavy overcast, fluorescent lamps, mercury vapor lamps, etc. will change the result of the visual color judgment.
  - Visual comparator kits and test strips may be appropriate for non-regulatory reporting such as pools and spas or other chlorine concentration measurement where a high level of accuracy is not required.
- A photometer (colorimeter or spectrophotometer) should be used when a better degree of accuracy and precision is needed than can be achieved with visual methods. Photometers can range in price from a few hundred dollars to several thousand dollars. For purposes of measurement of chlorine residual greater than approximately 0.05 mg/L to second decimal place accuracy, an inexpensive handheld, portable colorimeter is just as reliable as a much more expensive laboratory spectrophotometer provided the instrument is maintained in good condition. It is prudent to check periodically the handheld portable instrument with standards to verify performance. It is good practice to do the same with expensive laboratory spectrophotometers.
- Another way to conduct colorimetric chlorine measurements is provided by SL1000 - portable parallel analyzer (PPA), which uses prefabricated plastic sticks called Chemkeys bearing all necessary chemicals on them and serving as lab-on-chip, essentially. The PPA draws sample through Chemkeys and determine analyte concentration inside each Chemkey. Up to four analyses can be conducted simultaneously and two additional e-chem analyses can be performed with available electrodes (Fig. 45). The SL1000 eliminates sample preparation phase and thus minimizes user's influence over the analysis results. For example, four critical prameters for chloramination monitoring and control can be analyzed simultaneously - Total Chlorine, Monochloramine, Free Ammonia, and either Total Ammonia or Free Chlorine in a matter of 8 minutes. In addition, an important measurement of the sample pH can be conducted at the same time, so the results would present a complete snapshot of the process with accuracy very adequate for portable instrumentation suitable for field use.
- For measurement of very low residuals (i.e. use of the ULR-DPD method) one should use a laboratory spectrophotometer and work in the laboratory environment. While Hach manufactures portable instrumentation suitable for the ULR-DPD method, it is very difficult in the field to control variables when one is trying to measure concentrations of 20 µg/l or less.

Working in the laboratory provides the ability to:

- Control interferences and perform other quality control measures.
- Protect reagents from temperature extremes and direct sunlight.
- Maintain cleanliness of apparatus and instruments.
- Use standards and standard additions to verify performance.

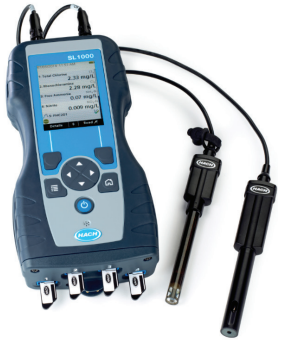


Figure 45: Hach SL1000

Continuous On-line Measurement of Chlorine Residual

The two most common methods for on-line (process) chlorine analysis are colorimetric and amperometric detection. DPD colorimetric analysis is a method based on N,N-Diethyl-p-Phenylenediamine (DPD) reaction with active halogens and amperometric probes use electrochemical determination of chlorine based on redox processes occurring at the electrodes. See Appendix A for discussion of potentiometric instruments.

Figure 46: CL17sc Chlorine Analyzer

Another method currently used for chlorine monitoring is ORP oxidation-reduction potential. This is not a primary method for measuring concentration of chlorine, because it is neither selective nor specific to the analyte. Since there are primary methods available for measuring chlorine, it is usually not justified to substitute the analysis with a secondary trending technique. In some cases, the ORP may provide an additional value and there is more information available in the references at the end of this document.

Colorimetric DPD Process Chlorine Analyzer

An online chlorine residual analyzer based on DPD colorimetric measurement as used in Hach CL17 or CL17sc analyzer, is appealing because the majority of water and wastewater utilities and many industrial sites use the laboratory DPD colorimetric method. Having the same basic measurement technology in laboratory, portable and online configurations permits good comparison between the laboratory and process measurements. This is especially true when it becomes necessary to check or validate performance of the on-line instrument. It is always prudent to check the performance of any on-line instrument periodically against a laboratory method.

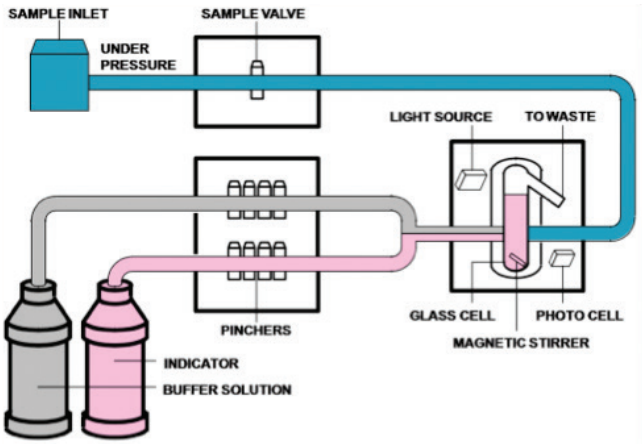


Figure 47: CL17 and CL17sc Flow Path Diagram

The same characteristics of the DPD method that make it easy and reliable for laboratory and portable testing apply also to on-line measurement. Use of a buffer to control pH during sample measurement makes the method largely independent of fluctuations in sample pH. In addition, DPD indicator and buffer reagents prepared with stringent quality controls provide stability for long-term use in an on-line analyzer.

The Hach CL17 Chlorine Analyzer utilizes the DPD colorimetric method. The analyzer can be configured for either free residual chlorine or total residual chlorine analysis by simply installing the proper reagents. No other change to the instrument is necessary.

The analyzer completes a sample analysis every 2.5 minutes. The sample is fed into the colorimeter's measuring cell. The sample blank absorbance is measured first.

Measurement of sample blank absorbance allows compensation for turbidity or natural color in the sample, and provides an automatic zero reference point. Reagent addition follows after zero is set.

A linear peristaltic pump/valve module controls the flow of incoming sample and injects metered volumes of the buffer and indicator reagents during the 2.5-minute measurement cycle.

The pump/valve module uses a motor-driven cam to operate pinch blocks that squeeze special thick-walled tubing against a fixed plate. The cycle operates as follows:

- The sample inlet line opens allowing sample under pressure to flush sample tubing and the colorimeter sample cell. The sample inlet line is closed, leaving fresh sample in the cell.
- A measurement of untreated sample makes an average reference measurement prior to reagent addition i.e. the zero value is determined thus compensating for background color and/or turbidity.
- Reagent lines open, allowing buffer and indicator solutions to enter the colorimeter cell to mix with the sample.

- After mixing the solution with a stir bar and an additional delay to ensure full color development, a measurement is made to determine the chlorine concentration.

The sequence repeats every 2.5 minutes. The chemistry used is based on the EPA specified laboratory method with adjustments made to the buffers to permit either free residual chlorine or total residual chlorine analysis within the 2.5 minute cycle time.

CL17 Waste Discharge Analysis

The waste stream generated by the DPD-based analyzers might be of concern, as discharge from all analyzers should be. Hach conducted a comprehensive analysis of the discharge generated by the Hach CL17 analyzer by far the most popular on-line chlorine analytical system. Hach collected the samples for multiple analyses. Two independent consulting laboratories were employed to complete the analyses. Due to the absence of federal regulations (RCRA) for this kind of discharge, the analyses were performed in

SAMPLE ID	ANALYTE	METHOD	RESULT	UNITS	MDL[a]	MCL (DW)[6]	CAS
TC	Bis (2-ethylhexyl) phthalate [DEHP]	M8270C GC/MS	12	µg/l	4	6	117-81-7
TC	Chloroform	M8260B GC/MS	15.7	µg/l	0.5	80	67-66-3
TC	Aluminum, total	M200.8 ICP-MS	5	µg/l	1	50-200b	7429-90-5
TC	Boron (dissolved)	EPA-6010B	0.043	mg/L	0.006	1c	7439-92-1
TC	Potassium, total	M200.7 ICP	3.2	mg/L	0.3	NA	7440-09-7
TC	Sodium, total	M200.7 ICP	13.1	mg/L	0.3	20d	7440-23-5
TC	Zinc, total	M200.8 ICP-MS	3	µg/l	2	5000b	7440-66-6
FC	Chloroform	EPA8260B GC/MS	5.1	µg/l	0.5	80	67-66-3
FC	Al (dissolved)	EPA6010B ICP	20	µg/l	10	50-200b	7429-90-5
FC	Zn (dissolved)	EPA6010B ICP	5	µg/l	2	5000b	7440-66-6
DIW	Chloroform	EPA8260B GC/MS	13.9	µg/l	0.5	80	67-66-3
DIW	Zn (dissolved)	EPA6010B ICP	4	µg/l	2	5000b	7440-66-6

[a] Method Detection Limit; [b] Secondary DW Regulations; [c] Lifetime level (Health Advisory) [d] DW advisory, health-based value

Figure 48: Summary of CL17 Discharge Analysis

accordance with the EPA methods[7] to identify compounds regulated for Drinking Water and the results were compared with Maximum Contamination Levels (MCL) listed for those chemicals. In order to identify chemicals produced by the reagents and analyzer, additional analyses of the sample matrix and pure reagents also were conducted. Obviously, comparison to drinking water standards is a very stringent test to apply to a discharge sample that is wastewater. The following table contains a summary of the test results.

The experiment was conducted on the most common configuration of the CL17 analyzer involving a standpipe providing steady sample flow/pressure to the analyzer. The test was conducted with two analyzers one with Free Residual Chlorine reagents and another with Total Residual Chlorine reagents. Two different laboratories conducted the analyses on the discharge samples. As seen in the data, the analyses identified only one regulated compound that exceeded the limits for DW samples– DEHP, which is a common plasticizer leaching out of various polymeric materials (pipes, tubing, etc.). The compound, identified only in the discharge of the CL17 equipped with Total Chlorine reagents, but not with the Free Chlorine reagents, was of concern. After additional testing, the source of DEHP was found to be a plastic drain tube, which is not a supplied analyzer accessory.

DPD reagent, also found in the discharge, is not reportable according to the current EPA methods and regulations; therefore, it did not appear on the official laboratory reports. The studies confirm Hach's CL17 Chlorine Analyzer produces no regulated compound at concentrations exceeding the federal drinking water regulations when used with Hach's manufactured reagents.

Amperometric Sensors

Amperometry is an electrochemical technique that measures the change in electrical current resulting from chemical reactions taking place at the electrodes as a function of the analyte concentration. A typical amperometric sensor consists of two dissimilar electrodes an anode and a cathode (i.e. silver/platinum or copper/gold). Some designs cover the electrode with a membrane; others do not have a membrane.

Sensors with a membrane provide better selectivity during the analysis. Additionally, a small electrical voltage applied across the electrode provides greater sensor stability and minimizes interferences. The applied voltage also permits use of a smaller electrode area, thus a smaller sensor.

[7]Clean Water Act Methods of Interest Approved for use at 40 CFR 136 http://www.epa.gov/waterscience/methods/method/) and Drinking Water Standards and Health Advisories (2006 Ed.) United States Environmental Protection Agency http://www.epa.gov/waterscience/criteria/drinking/dwstandards.pdf)

When no membrane is used, the system is termed bare-electrode amperometric and in the case of no applied voltage, the system is termed galvanic.

From a technical standpoint, many electrochemical methods fall under the amperometric measurement category, including bare-electrode (open-cell) and galvanic systems. These are sometimes are incorrectly referred to as polarographic. The polarographic method involves a dripping mercury electrode and therefore this name is not applicable to the sensors as described above.

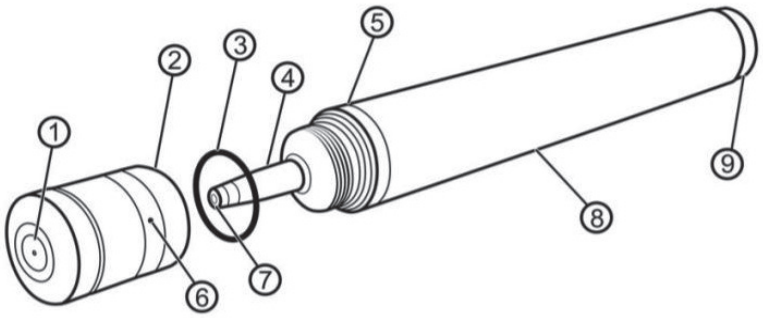
Below is a general representation of the oxidation-reduction reaction taking place in the amperometric system:

Cathode (working electrode):

$$HOCl + H^+ + 2\bar{e} \longrightarrow Cl^- + H_2O \text{ (reduction of hypochlorous acid)}$$

Anode (reference electrode):

$$Cl^- + Me \longrightarrow MeCl + \bar{e} \text{ (oxidation of anodic material, where Me = metal)}$$



1 Polymeric Membrane	4 Reference Electrode	7 Working Electrode
2 Membrane Cap	5 Counter Electrode	8 Sensor Body with Electronics Inside
3 O-Ring 14 x 1.8mm	6 Vent Hole Covered by Rubber Band	9 Transparent Window for Diagnostic LEDs

Figure 49: Diagram of Hach's 3-Electrode Amperometric Chlorine Probe

The anode may be composed of two parts - a reference and an auxiliary (or counter) electrode making the measurement more stable. Such systems are termed three-electrode sensors. The following diagram illustrates the general construction of the three-electrode amperometric sensor (probe) used by Hach.

On-line amperometric sensors and laboratory amperometric titration are different measurement technologies and should not be confused as being the same. Additionally, the DPD methodology and amperometric titration are standard measurement methods that provide adequate accuracy throughout the entire measurement range. In contrast, on-line amperometric sensors are designed mainly for process control and, usually, provide adequate accuracy around the calibrated set point (normally, within ± 1-2 mg/L or ~20% of the set point).

This calibration dependency of the on-line amperometric sensors is a fundamental difference between on-line amperometric and colorimetric technology. The amperometric method consumes the anodic material and electrolyte. The colorimetric method consumes only reagents. This difference provides full understanding of the calibration dependency of the amperometric sensors. Amperometric sensor performance is dependent upon shape and mass of the electrodes, which change (they are being consumed) while in operation. In order to compensate for the changes, one must conduct sensor calibration and recalibration on a regular basis.

Other factors usually influencing amperometric sensors include fluctuation in sample flow and pressure; presence of air bubbles; fouling of bare sensor or the membrane by solids, iron or manganese; membrane delamination; and perhaps the most important, sample pH.

Flow and Pressure Usually, amperometric sensors , especially membrane-covered, require a flow-through cell. The redox (oxidation/reduction) reaction relies on stable equilibrium (mass transfer process) across the membrane. The sample flow rate and pressure must be consistent as the sample passes the membrane. Fluctuations in flow or pressure may easily contribute in variations of the readings and therefore poor accuracy. One can see these factors play a crucial role in attempting direct sensor insertion in a pressurized sample flow (in-pipe mounting).

The following figure demonstrates the effect of flow changes on an amperometric probe with a constant chlorine concentration of approximately 2 mg/L.

In some cases, amperometric sensors have been mounted in-pipe[8] with no flow cell to condition the sample and it has been reported that the sensor's accuracy is completely lost if the sample pressure changes more than ± 5 psi. In any membrane-based measurement system, varying sample pressure will change the thickness of the micron-sized electrolyte layer between the membrane and electrode surface leading to erratic responses.

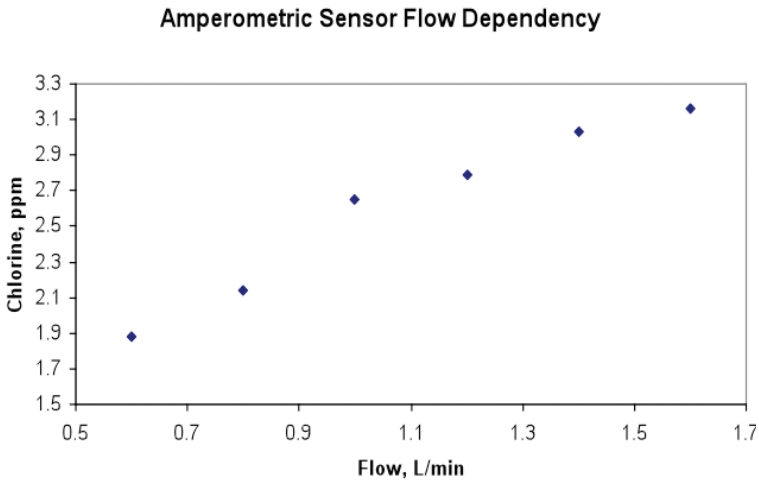


Figure 50: Effect of Flow Rate on an Amperometric Sensor

Loss of Flow A properly designed flow cell should prevent the membrane surface from drying out in case of loss of the sample flow. If the on-line sensor loses sample and the membrane dries out or if the minimum flow requirement is not maintained, calibration will be lost and then sensor re-conditioning in the sample stream followed by re-calibration is required.

Air Bubbles Amperometric chlorine sensors are relatively intolerant of air bubbles on the probe membrane or surface of bare electrodes. Air bubbles that collect on membrane inhibit chlorine from easily passing through into the electrolyte. Therefore, the flow cell design for probes should discourage accumulation of air bubbles.

Membrane Fouling The presence of high solids, iron or manganese, or other substances can foul membranes affecting the passage of chlorine species through the membrane into the electrolyte inside the probe.

The membranes outer coating can also delaminate under influence of harsh water conditions, which will diminish the performance. Examples of effects of high iron content in the water and delaminated membranes can be seen in the following photo array.

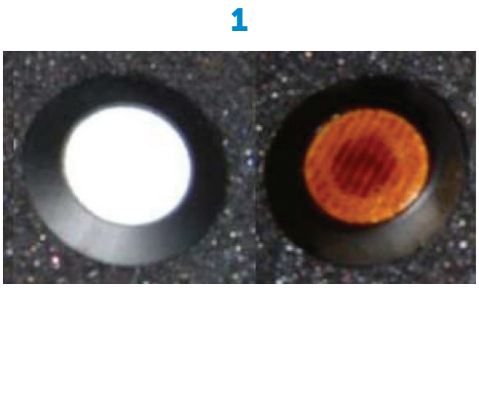


Figure 51: Amperometric probe membranes demonstrating iron fouling and delamination

Photo 1, on the left, is a new membrane and on the right is a membrane removed from service after just 30 days in water containing high iron content.

Photo 2, good membrane. Photos labeled 3 are examples of partial (top) and complete (bottom right) delamination of the membrane coating.

[8] *Several considerations should be studied before attempting to install a chlorine or other sensor directly into a pipe for potable water monitoring; including but not limited to, NSF International approval for the device; safety and ease of inserting/withdrawing the sensor for maintenance; dynamic and static pressure and velocity extremes that may be encountered.*

Effect of pH on Amperometric Measurements For free residual chlorine applications, a pH of ~ 5.0 to 7.0 is the ideal operation range for an amperometric sensor because of the high percentage of hypochlorous acid (HOCl) (>80%) in the sample and the shape of the free chlorine dissociation curve in this range. The pH can move within this range and the chlorine concentration can drift without significantly diminishing the accuracy of the instrument. This pH range, however, is not typically present in drinking water applications

A pH of ~ 7.0 to 8.0 is typically the normal operating range for most drinking water facilities. The HOCl concentration is much lower versus the OCl^- (hypochlorite ion) in this range. Amperometric free chlorine sensors directly measure only HOCl, not OCl^- or Cl_2, so any change in pH within this range will substantially affect the accuracy of the on-line unit.

In contrast, the DPD method is equally sensitive to all species present. Moreover, the pH of the reaction is controlled in the DPD method because the sample is buffered during on-line measurement.

At a pH 8.0 or greater (often the operating range for facilities experiencing problems with DBPs), the HOCl part of free chlorine concentration is very low (<20%), therefore accuracy of the amperometric probe may suffer significantly with even slight changes in sample pH.

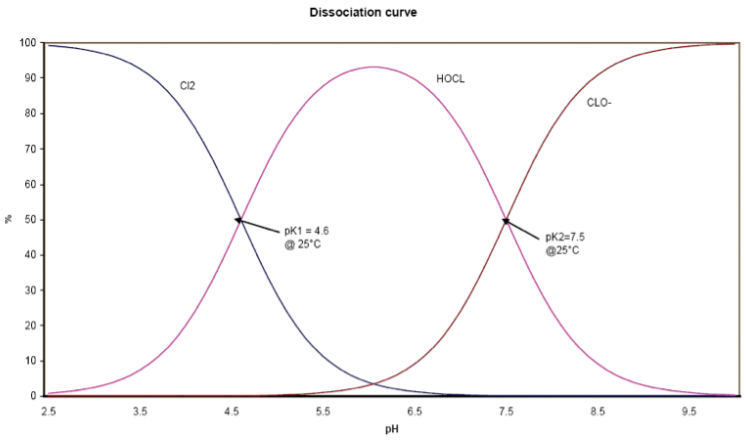


Figure 52: Hypochlorous Acid Dissociation Curve vs. pH

pH	CL17, mg/L	Avg. Amperometric, Chlorine, mg/L	Difference
8.44	0.99	1.00	1.1%
7.85	0.99	1.06	6.5%
7.21	0.99	1.12	13%
6.80	0.99	1.24	25%
6.48	1.00	1.38	39%
6.01	1.01	1.55	54%
8.42	1.00	1.01	0.36%

Figure 53: DPD vs. Amperometric probe as pH is varied. (Average for 5 amperometric probes (calibrated in 1 mg/L chlorine sample at pH = 8.4)

Internal/External pH Compensation for Amperometric Probes
Change in pH affects all types of amperometric chlorine analyzers. Many manufactures claim that the probes can accurately measure chlorine in the presence of minor pH fluctuations. In reality, the probes always experience some signal loss due to variations in the sample pH. One manufacturer claims that the signal loss is 5% per every unit of pH change over 7.0, however, a more common 10% change should be expected.

Adding a third electrode (3-electrode design) can increase stability and pH variations can be tolerated up to pH 8 or even 9 with some additional efforts, such as internal pH compensation as employed in Hach CLF10 and CLT10 analyzers. In this case, a buffered filling solution (electrolyte) helps to convert free chlorine species into hypochlorous acid, which becomes the only substance reacting with electrodes. However, to ensure the best accuracy, at sample pH greater than 8.5 (certainly at pH > 9.0) one should consider external pH adjustment with either an acid (e.g. acetic acid) or CO_2 gas.

In external pH compensation applications, a buffer from an external reservoir is added to the sample to adjust and control sample pH. The buffer may be as simple as vinegar or as complex as necessary to provide additional benefits. Although this approach provides improved accuracy, the on-line instrumentation often loses its “reagent-less” appeal due to additional ongoing buffer (reagent) expenses and waste stream containing chemicals.

Some manufacturers add pH probes to the amperometric chlorine analyzer to provide feedback to the unit. The pH measurement is used to compensate for the ratio of hypochlorous acid and hypochlorite ion. By measuring the pH of the water, the software in the analyzer attempts to correct for fluctuations in the pH and maintain an accurate chlorine reading. The degree to which this scheme can successfully correct for pH changes depends on the manufacturer, on the membrane material and the implemented algorithm. Some manufacturers claim that with such compensation the chlorine measurement can be conducted up to pH 7.5, while others claim they can make the correction up to 8.0 or even higher. It is important to note that just because an analyzer has a pH input, it does not always mean that the pH probe is providing feedback to correct the chlorine measurement.

Hach is not convinced this approach works very well and hence has elected not to employ such pH compensation. As explained above, Hach has chosen for the CLF10 and CLT10 analyzers to provide an input for pH, but do not attempt any mathematical compensation for variations in pH.

Whether using open cell or probe style amperometric analyzers to measure free or total residual chlorine, pH is a major variable. When the pH of the sample can be maintained at a stable value and without fluctuation, it may not be necessary to add acid or carbon dioxide to the sample. However, if a change in pH were to occur, the signal generated by the sensor would be reduced and an error would be introduced into the measurement. It is always advisable to monitor pH of the sample alongside the chlorine probe. When pH is highly variable or exceeds pH 9, it is advisable to acidify the sample externally (using an acid or CO_2 gas) to maintain a stable pH in the range of pH 4.5 - 6, even in the case of internal pH compensation.

Temperature Effect/Calibration Requirements for Amperometric Probes

Amperometric sensors are always sensitive to temperature changes. Two areas affected by temperature are the membrane permeability rate and the pH compensation, when it is done by calculation. No mathematical algorithm can accurately reflect all changes in the water matrix and the response of chlorine to those changes.

Response of an amperometric chlorine sensor to temperature change vs. DPD readings is demonstrated in the figure. The downward trend of the DPD measurements reflects normal loss of chlorine from the solution at elevated temperature.

In addition, any essential changes to the water sample matrix may require recalibration of the amperometric sensor. When the water characteristics are constantly changing, this will often require weekly and sometimes daily calibration of the amperometric instrument to retain overall accuracy. In contrast, DPD technology does not require calibration due to the established proportionality between chlorine concentration and light absorbance.

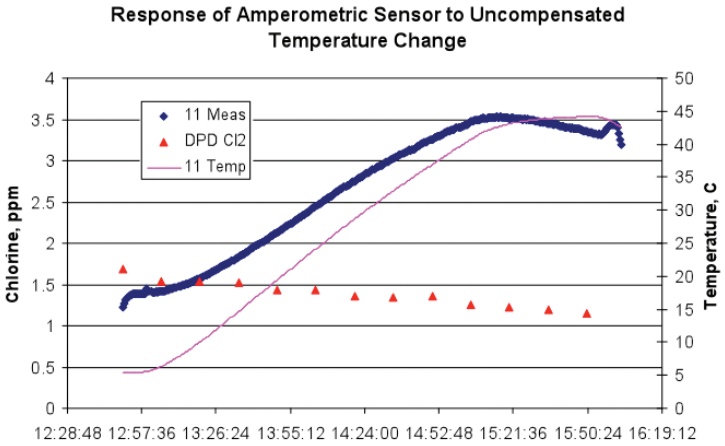


Figure 54: Temperature Effect on an Amperometric Sensor

Modern amperometric analyzers automatically compensate chlorine measurements for sample temperature fluctuations. However, the chlorine sensors may not display the sample temperature. A separate temperature sensor or an optional pH probe equipped with temperature sensor is needed to display sample temperature on the controller. In the case of CLF10 and CLT 10 analyzers, all three measurements (chlorine concentration, pH, and temperature) will be displayed on the controller when the optional pH probe is added. The common controller (sc200, or sc1000) provides easy management of the instrument in all configurations (calibration, data logging, etc.) and various external communication options (e.g. with SCADA, PLC's, etc.)

As was mentioned above, unlike colorimetric analyzers, the amperometric instruments do require calibration, simply because their performance is based on consumption of electrodes and electrolyte in addition to all the other factors. Usually, the calibration consists of two points zero and process.

The zero calibration may present the biggest challenge, especially with older 2-electrode systems. The best and most accurate zero calibration requires the operator to introduce a dechlorinated sample into the measuring cell or probe flow through cell. Because background matrices need to be accounted for in the calibration, DI or distilled water should not be used to perform the zero, or any other calibration.

Dechlorination of sample is the first step in the process. The second step is to introduce the zero water into the analyzer at the same rate that the sample normally flows through the cell.

Providing zero-chlorine sample water to the sample line is not always easy and can require an external pump or large quantities in a gravity feed configuration. Some installations actually run a parallel sample through a dechlorinating filter and then into the analyzer to produce zero water. A valve isolates the sample from flowing directly into the analyzer, and routes the sample through the filter before entering the measuring cell when a zero calibration is needed. After the zero calibration is completed, the technicians collect a manual grab sample and test it with a colorimeter or spectrophotometer to determine the chlorine residual. The value obtained with the grab sample is entered into the online analyzer to complete the calibration procedure.

Another method of zeroing an amperometric analyzer is to perform an electronic or electrical zero. Essentially, the analyzer simulates a zero current through the electrodes and stores the reading in the software. An electronic zero is convenient and compensates for electrical noise in the hardware, however it does not compensate for background interferences in the water.

Since the 3-electrode sensors are considerably more stable against the interferences, the electrical zero calibration is preferable for the instruments employing such sensors, including the Hach CLF10 and CLT10 analyzers.

Open-Cell Chlorine Amperometric Technologies

Amperometric technology does not rely on the use of reagents to condition the sample or create a reaction, but may require the use of acids or carbon dioxide gas to establish and control the pH of the sample. When total chlorine is being measured potassium iodide and acid or CO_2 gas may be added to the sample stream.

Typically, two electrodes, a gold cathode and copper anode, are used to generate a small electrical current proportional to the chlorine residual in the sample. As chlorine passes the electrodes, the sacrificial copper electrode gives off electrons creating an electrical current flow in the measuring cell.

The amperometric cell can be an open design where the gold and copper electrodes are situated in a non-pressurized sampling chamber. If no external voltage is applied across the two electrodes such a sensor is usually referred to as galvanic.

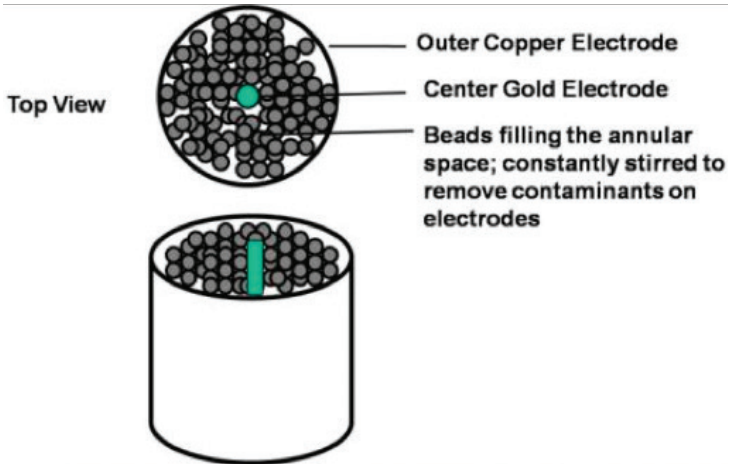


Figure 55: Open-cell amperometric sensor illustration

The sample pH must be in the range of pH 4.5 - 6.0 for such systems to operate properly. Acid addition is typically the method used to adjust and control the sample pH; however, CO_2 gas can also be used. When acid is used, some manufacturers recommend a buffer of glacial acetic acid and sodium acetate, and others recommend vinegar. It is important to follow manufacturer's instructions. When configured to measure total residual chlorine, potassium iodide (KI) must also be added to the sample. When acids are used for pH adjustment, the KI may be added to the buffer or vinegar. Once KI is added to the buffer or vinegar it is not stable for long periods. When vinegar is used, the stability may be only a week. When the glacial acetic acid/sodium acetate buffer is used, the solution with KI may be stable for up to 2 weeks. Consult the manufacturer about stability of the solutions containing KI.

There are other designs for a bare-electrode amperometric systems currently available. The manufacturers are trying to accommodate their sensors to changing water conditions and electrodes fouling with varying degree of success. The current designs usually place the electrodes in a flow cell and add a pH probe to monitor and compensate for changing acidity/alkalinity of the water sample.

In addition to maintaining a stable pH, the rate of flow through the cell must be maintained at a constant level to ensure measurement accuracy. The cell must also be kept clean to maintain a stable signal proportional to the chlorine content in the water.

To keep the cell and electrodes clean, some means is typically provided to remove corrosion products and other deposits. Some style open-cell amperometric chlorine analyzers employ a system of rotating spheres, up to 200, that rotate around the two electrodes. The spheres scour the electrodes and remove bio-fouling or oxides that can accumulate on the electrodes. Other designs may employ use of a wiper or sand to keep the electrodes clean. The most advanced designs employ electrochemical means for automated cleaning of the electrodes.

Hach manufactured and offered an open cell on-line instrument for many years, but no longer offers this configuration as we believe the DPD colorimetric or probe-style amperometric sensors are superior technologies.

CLF10 and CLT10 Amperometric Probe Chlorine Residual Analyzers

The membrane-type amperometric probes containing electrolyte solution and the electrodes, separated from the process by a hydrophobic membrane, are usually selective for chlorine species and do not require addition of external acids or potassium iodide (KI, for total chlorine residual). The separation of the analytical system with a membrane, especially along with a 3-electrode design, helps to ensure better stability of the readings and provides less susceptibility to contamination and interference. The electrolyte can provide additional capabilities, especially for total chlorine analysis.

Available for either free, CLF10, or total residual chlorine, CLT10, the Hach amperometric chlorine analyzers use a 3-electrode sensor and a proprietary filling solution (electrolyte) to compensate for pH fluctuations from 4 to 9.

An optional pH electrode (shown to the right of chlorine sensor) can be used to independently monitor sample pH and provides additional means of troubleshooting. For example, the pH measurements are used by the software to determine whether the electrolyte has lost its strength and then to alert the operator of the need to replace the electrolyte. This feature is called CAL WATCH.

Figure 56: Hach CL10 Amperometric Chlorine Analyzer

CAL WATCH monitors the deviations of chorine concentration and/or pH readings from the previously calibrated level. If the deviations exceed the preset levels, a warning or alarm is displayed. If chlorine concentration changes as pH swings (especially decreases as pH increases), it is normally an indication of worn-out electrolyte and therefore the user can be warned to replace it. The CAL WATCH feature is completely user-configurable and can be set to activate and deactivate an alarm automatically based on the process realities and the user preferences.

The CLF10sc and CLT10sc are identical instruments except for the sensors (probes), which are interchangeable and electrolyte that is specific to the sensor type. Thus, the instrument can be easily reconfigured in the field from free to total chlorine or vice versa if needed. The total chlorine sensor is designed to measure all types of chlorine species. However, the free chlorine sensor may experience interference from the combined chlorine species, primarily monochloramine. The free chlorine sensors will better withstand pH fluctuations that are more common in such applications.

Limitations of online measurement instruments

Currently, no "ideal" method exists for quantifying chlorine and chloramines in water. All common methods of chlorine analysis display some lack of specificity and are not adequately selective to be completely free of interferences. However, most of the limitations associated with the traditional DPD chemistry (e.g., calibration linearity, reagent stability, reaction product stability, etc.) have been addressed sufficiently through procedures and reagent formulation since the first Hach chlorine test kit based on the DPD chemistry was introduced in 1973. On the other hand, new methods including the online amperometric chlorine determination should be characterized very thoroughly from the interference standpoint. Once there is a complete understanding of those methods, especially in terms of the application specifics, they can be successfully used for online chlorine monitoring and may provide additional benefits to users.

Several interferences have been identified that can present limitations when amperometric sensors are used for continuous on-line process measurements. Some of the more noted variables providing interference are based on sample and sampling environments with changing chlorine concentration, pH, temperature, sample flow, and pressure. Other variables are application-based involving ease of use, sensor fouling, interferences and calibration. In contrast, the EPA-approved DPD colorimetric method (SM 4500G) is independent of temperature, pH, and sample flow/pressure fluctuations.

Both colorimetric and amperometric methods suffer from interferences due to presence of some specific compounds. For example, there is well-known positive interference of DPD analysis to the presence of chromium and manganese species in water. Chemically, the amperometric method is more tolerant of this interference, however amperometric sensors are more prone to fouling with the presence of iron or manganese in the sample (as well as in the presence of high turbidity), and this will result in increased cleaning and calibration frequency.

Steps to Selecting an Online Measurement Technology

Prior to choosing an online chlorine analyzer, the application should be evaluated to define what technology will be most suitable - DPD or amperometric. Utilization of amperometric technology requires much better understanding of the nature of the sample to be tested and the application realities, making it difficult to perform consistently well. It is perceived that amperometric sensors designed for process control may work well in applications where chlorine concentration, sample flow, pressure, temperature and pH are stable, i.e. ground water monitoring, or in certain distribution systems. Nevertheless, this is a perception only, because, even in such applications chlorine concentration may change over time, length of distribution system, and nature of the sample matrix; therefore trade-offs in precision and accuracy can be expected.

Amperometric (e.g. Hach CLF10 sc or CLT10 sc)	Colorimetric (e.g. Hach CL17 and CL17 sc)
Pros • Fast response to changes in Cl_2 concentration • Reagentless • No reagents in the waste stream • Range from 0 to 20 mg/L	**Pros** • Accuracy (no calibration needed) • Unattended operation for up to 30 days • Results independent of changes in sample pH, temperature, Cl_2 concentration, etc • Can be used for dechlorination applications approaching zero chlorine
Cons • Greater interference from sample pH, temperature, pressure, Cl_2 concentration • Cannot be used to monitor zero chlorine. Some measurable chlorine must be present to maintain proper sensor functionality	**Cons** • Reagents and waste stream management • Range of 0-5 mg/L (10 for CL17sc) • Must maintain flow to the instrument in specified range

Figure 57: Pros and Cons of CLF10 or CLT10 and the CL17 Analyzers

In view of the relative instability of chlorine and chloramines in aqueous solutions, especially in many process applications, as well as the associated dynamic water conditions of these processes, on-line chlorine measurement using the DPD is usually suitable for most applications.

The process of making the right choice starts with moving through the following simple steps, each of those is referred to in the guide (Fig. 58) on page 46.

Step 1.
Look at the instrument's specified chlorine measurement range and sample pH range to make your initial decision. If the simple comparison of main specifications such as measurement range is not enough to choose, proceed to the next step.

Step 2.
Consider each technology's key differentiators to determine which technology is preferred for your application.

Step 3.
Consider the additional detailed specifications to understand nuances important to determine the suitability.

Step 4.
Finally, consider the keys to application success to make sure that your preferred instrument is right for your application.

When you answered all questions presented in the Step 4, the picture should become clear on what technology is better for your application.

	CL17sc Free or Total Chlorine	CLF10sc Free, CLT10 sc Total
The Online Chlorine Monitoring Instrumentation Selection Guide		
1. Basic Specifications		
Chlorine Concentration Range	0 - 10 mg/L	0 - 20 mg/L
Sample pH range (w/o buffering)	NA	pH 4 - 9
2. Key Differentiators		
Sample pH, chlorine concentration, temp, flow and/or pressure changes	No impact on readings	Readings may be impacted. Adjustment to calibration may be needed.
Calibration	Calibration not needed (unless required by regulatory agency)	Required. Frequency based upon the application.
Routine Maintenance	Tubing and stir bar replacement every 6 months	Membrane and electrolyte replacement every 3-6 months (frequency depends on application)
Reagents	Reagent replacement every 30 days	NA
Reagent Waste Stream	Yes	No
Regulatory Method	SM 4500 CLG, 40CFR 141.74 or EPA Method 334.0	Only EPA Method 334.0
Multi-parameter	Chlorine and Flow. Other parameters can be added to the sc-controller	Optional pH and Temperature. Other parameters can be added to the sc-controller.
3. Instrument Specifications		
Accuracy	±0.04 or 5%, whichever is greater, ±10% above 5 mg/L	CLF10sc: ±3% at pH<7.2 (±0.2 pH unit), ±10% at a pH<8.5 (±0.5 pH unit) CLT10sc: ±10% at a pH<8.5 (±0.5 pH unit)
Limit of Detection (LOD)	30 ppb	30 ppb
Response Time	Batch analysis, 150 seconds	Continuous, CLF10sc T_{90} = 140s, CLT10sc T_{90} = 100s
Technology	DPD Colorimetric Method	Amperometric Method
Automated Cleaning	No	Yes, optional
4. Keys to Application Success		
Appropriate Applications (Requirements)	• Must be able to replace reagents monthly • Must have a system to manage the waste stream (if required)	• Must have uninterrupted sample flow • Must have uninterrupted power • Sample pH should be stable within +/- 0.5 pH unit from the average value • Chlorine concentration should be stable within +/- 20% from the average value

Figure 58: Selection Guide of CLF10 or CLT10 and the CL17sc Analyzer

Several major conclusions leading to defining the preferred method for online chlorine monitoring may be made based on the guide above by analyzing the differences in specification for these two methods. For example, complex accuracy specifications established for the amperometric instruments clearly indicate dependency of the readings on pH of the sample, even in the case of available pH compensation.

Limit of Detection (LOD or MDL - method detection limit) is a qualitative parameter showing a borderline between detectable and undetectable concentration of the analyte. The interpretation of this parameter is simple: analyte is present in the sample only at the reading above the LOD. While the amperometric and colorimetric analyzers appear to have a similar LOD, they may not be equally suited to measuring very low levels of chlorine residual.

If no positive interferences are present, and the chlorine is in fact zero, the colorimetric analyzer may display a zero value and thus it may be used in dechlorination applications. However, an amperometric sensor must continuously see the analyte (chlorine) or it will lose calibration. Hence, if chlorine residual will approach levels at LOD or less and effectively reach zero chlorine, an amperometric sensor may not be a good choice. If the sensor "sees" no chlorine for an extended period, it will lose sensitivity to chlorine. This phenomenon is sometimes called "sleeping sensor" and the amperometric probe must be recalibrated to restore accuracy after chlorine feed is restored.

However, the most difficult specification to understand may be the response time, expressed in number of seconds to detect a certain level of the chlorine concentration when it has changed in the sample.

In Hach instrumentation it is either 100% for a batch method or 90% (T_{90}) for continuous analysis, assuming the chlorine concentration has reached its final level and is not changing anymore at the time the reading is recorded. In order to explain this difference, results of calculations conducted for the two types of analyzers were plotted against each other and the resulting graphs are presented in the figure.

Data presented in this figure illustrate that absolute accuracy of the response to a change in chlorine concentration is reached at approximately the same time by either instrument (CLF10sc and CL17sc). However, the amperometric instrument starts providing the response nearly instantaneously and therefore it can be configured for much tighter control of the chemical pumps*. Moreover, if the sample was taken by the CL17 (or CL17sc) a little earlier than the dosage change happened, the accurate concentration reading becomes available only after two cycles of measurement. This situation displays one advantage of the continuous amperometric technology over DPD-based batch analysis.

The CL10sc and CL17sc have the capability for signal averaging which can be useful to avoid false positive responses. However, this feature, when activated, will extend the time for reacting to changes in the chlorine concentration should they happen. With an equal amount of signal averaging programmed into the two styles of instrumentation, the amperometric probe will still provide faster response.*

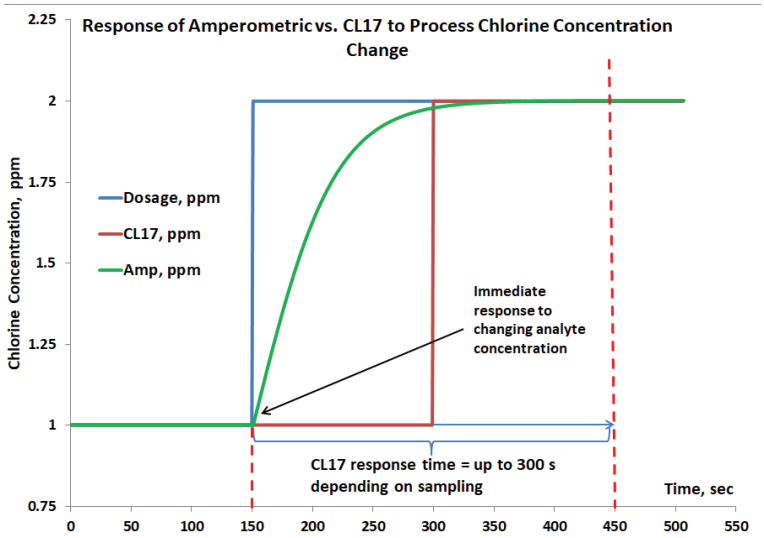


Figure 59: Graphical expression of calculated responses of the CL17 vs. amperometric probe

One should resist the temptation to react too quickly to apparent changes in concentration. Chemical feed systems, including chlorination, will perform best when controlled at nearly constant feed rates paced to the flow. Reacting too quickly to measured changes in concentration can lead to undesirable cyclic operation of a chemical feed system. Taken in this light, while it is certainly true the amperometric platform can provide more rapid updates of measured chlorine residual, it is not necessarily a good idea to act on such rapid changes. In this regard, the signal averaging function plays an important role in minimizing the potential for changes that are too rapid and too frequent. When one carefully considers all the process control variables, the apparent advantage in response time between the amperometric platform and the CL17 analyzer may become much less important.

*It may not be beneficial for process control and there is usually a delay introduced via a PLC to avoid pump oscillation.

Continuous On-line Measurement of Chloramination

Figure 60: 5500sc AMC

The 5500sc Ammonia/Monochloramine Analyzer (5500sc AMC) uses the modified Phenate approach optimized for stability, dynamic range, and fast reaction time. The chemistry is very similar to that used for the laboratory indophenol method for monochloramine and free ammonia.

To increase monitoring frequency, the analyzer uses two colorimeters, one for monochloramine and another for total ammonia. Both colorimeters operate at a wavelength of 650 nm. Monochloramine and ammonia are measured simultaneously and the values updated every 4.5 minutes.

To measure monochloramine, a buffer and indicator are added to the sample in the colorimeter. Thus, the colorimeter also serves as a reactor maintaining constant elevated temperature of the reaction. The indicator forms a green color when monochloramine is present and this color intensity is proportional to monochloramine concentration.

Total ammonia is determined in much the same way. However, besides the buffer and indicator, an excess of hypochlorite at a high pH is added to convert any free ammonia present in the sample to monochloramine. The remainder of the analysis is identical to the monochloramine method. The total ammonia result indicates the combination of any monochloramine initially present in the sample and any monochloramine formed from free ammonia. Maintaining the proper pH speeds up the reaction and prevents the formation of dichloramine even when excess chlorine is present.

After completing each cycle, the free ammonia and the chlorine to nitrogen ratio is calculated and the results are displayed for all four parameters determined for each of two samples (optional 2-channel configuration).

If the total ammonia and monochloramine values are equal (indicating no free ammonia is present) the analyzer defaults to "99999" for the ratio, indicating a potential overfeed of chlorine.

The analyzer auto-calibrates using factory formulated and made ammonia standards. It treats these known concentration standards the same as a sample. The analyzer determines if the absorbance of the standards is within the proper range. If not, it warns of the potential degradation of a reagent. The reagent most susceptible to degradation is Reagent 3 (the hypochlorite solution) because it is highly reactive and light sensitive. Typical shelf life for unopened Reagent 3 is six months. Failure to protect it from light may lead to faster degradation.

This analyzer has many options and features that are well described in corresponding manuals and this brief recap above is only to explain the method employed by the instrument and provide some insight into its performance.

Comparison of On-line to Grab Sample Measurements

It is always prudent to compare the results of analysis from an on-line instrument to a laboratory measurement. For chlorine measurement it is necessary to perform the grab sample analysis on site with portable instrumentation, most frequently with the DPD method.

When conducting comparison of grab samples to the on-line instrument one must:

1. Ensure the exact same sample is being measured. If no Grab Sample feature provided by the analyzer, the best location to draw a grab sample from is either the effluent of the on-line instrument (separate from one containing reagent discharge, if applicable), or via a three-way valve in the sample line immediately before the entrance to the process analyzer.
2. Ensure all possible sources of interference are known and compensated for in the grab sample analysis.
3. Remember that expected difference between the readings of two instruments should be within a sum of their accuracies as specified by the manufacturer. If each method/instrument has its accuracy of +/-5%, then the expected window is 10% between the readings. E.g. if a process analyzer reads 2.2 ppm and a grab sample analysis returns 2.0 or 2.4 - all results are within the expected accuracy window, being 0.2 ppm (10%) of the reading.

USEPA Method 334 indicates that measurements from an online chlorine analyzer must be within 15% of the grab sample measurement. If the variance exceeds 15% then Method 334 says the online instrument must be recalibrated. However, before

recalibration, one should check again to be certain the portable instrument is accurate, samples being compared are exactly the same and that all interferences are accounted for. Interferences may include manganese, chromium and naturally occurring ammonia or organic compounds from NOM (naturally occurring organic matter). The sample flow, condition of the on-line instrument for reagents, cleanliness of the sample cell or amperometric probe, etc. should also be check and corrected as needed.

Sometimes, ground water is only chlorinated and then discharged into the distribution system with no other treatment or measurement. While this approach is legitimate, it may present some unforeseen situations if the ground water contains elevated amounts of naturally occurring ammonia, NOM, or iron and manganese. Then a problem may occur when an amperometric chlorine analyzer is used for monitoring of the sample. The interferences listed above can cause a skewed calibration of the amperometric chlorine probe which could result in the amperometric analyzer reporting inaccurate chlorine values. This presents a substantial risk, especially if the amperometric chlorine analyzer is reporting values that are higher than the actual chlorine concentration in the sample.

In wastewater dechlorination applications similar situation may occur due to the presence of organic chloramines in the water, which would cause positive interference to DPD analysis and not to the amperometric method. In both situations, the operations happen in low chlorine conditions and this would cause the calibration failure, because the correction factor at low concentration is higher than can be accepted by the CL10sc analyzer. An attempt to introduce too high a calibration factor will lead to rejection of the calibration value by the analytical system and an error message. Amperometric sensors are not a good choice for dechlorination systems because, as noted above, they must continually "see" some level of chlorine to maintain sensitivity to the analyte.

The rule of thumb in such situations is to evaluate all possible components of the calibration/verification process, the reference method and instrument, the sample matrix influence (potential interference), and the on-line analyzer, prior to making any conclusion.

Acknowledgements

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Appendix A: Other Analytical Methods

Orthotolidine Method

The orthotolidine (OT) method for chlorine was first reported by Ellms and Hauser. The orthotolidine method was dropped from the 14th edition of Standard Methods after the results of two round-robin studies were released ("Water Chlorine (Residual) No. 1"; Analytical Reference Service Report No. 35, United States Environmental Protection Agency, Cincinnati, Ohio, 1969. And, "Water Chlorine (Residual) No. 2"; Analytical Reference Service Report No. 40, United States Environmental Protection Agency, Cincinnati, Ohio, 1971.).

Both studies indicated the OT method gave poor accuracy and precision and a high overall error in comparison with the other chlorine methods. Two aquatic toxicity studies (Tompkins, J.; et.al.). And Fava, J, et. al.), compared the DPD colorimetric, amperometric titration and orthotolidine methods for determining chlorine residuals. In both studies, the OT method gave lower values at all concentrations of total chlorine relative to the other two methods. Because of relatively poor accuracy and precision and a lack of specificity, the orthotolidine method generally is not accepted in the United States and most developed countries. Usage of this method is mainly confined to low-cost pool testing applications. Hach does not provide a testing platform for use of OT. Hach also does not recommend its use even for pool testing applications.

Syringaldazine (FACTS) Method

This method is based on the reaction of 3,5- dimethyl-4-hydroxybenzaldazine (syringaldazine) with free chlorine on a 1:1 basis:

The product is a red-purple compound with a absorption maximum at 530 nm. The published method generally is known as the FACTS method (free available chlorine testing with syringaldazine). The application range is reported as 0.1-10 mg/L Cl_2. The test has been adapted to the determination of total chlorine as well as other oxidants (Leiberman). The FACTS method has been reported to be specific for free chlorine, with little interference from manganese (+4) and monochloramine. (Standard Methods, 20th ed.)

Due to the difficulties of non-reproducible indicator solutions, inadequate buffer capacity with certain samples, and color fading, Hach does not offer a free chlorine test based on the FACTS method.

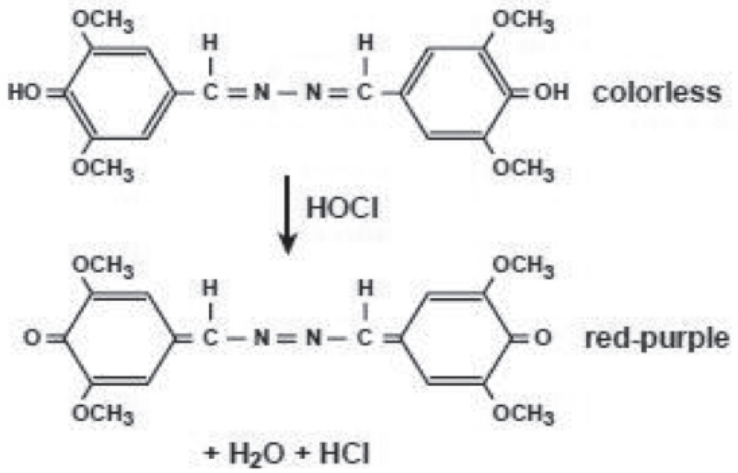


Figure 61: Reaction of syringaldazine with free chlorine

Potentiometric Electrode Method

The electrode method is based on the potentiometric measurement of free iodine produced when iodide is added to an acidic sample containing an oxidant. The method is analogous to the iodometric titration method in that total oxidant is measured and speciation of disinfectants residuals is not possible.

The method is based on the Nernst equation:

$E = E_o + [2.303RT/2F] \log [I_2]/[I^-]$

Where:
E = measured potential
E_o = standard potential
2.3 RT/2F = Nernst constant
$[I_2]$ = iodine concentration
$[I^-]$ = iodide concentration

In practice, a platinum/iodide electrode pair is used in combination with a millivolt (pH) meter.

The iodide ion-specific electrode (ISE) serves as the reference electrode. A constant excess of iodide (I^-) is required in the measured sample. This is necessary to "fix" the concentration of triiodide (I_3^-) formed, so free iodine (I_2) can be measured. It is important that the same amount of iodide is added to both calibration standards and the sample.

The electrode method suffers from several interferences. Chloride ion can form the iodine-chloride complex (I2Cl–) which is not sensed by the electrode. Organics in the water sample can react with the free iodine released during the procedure, yielding low readings. The electrode will sense any oxidant capable of oxidizing iodide. Hence, species such as manganese, iodate, bromine and cupric will interfere. As with all ISE procedures, accurate compensation for sample temperature is necessary.

Although it is claimed that a MDL of 5 µg/l (as Cl2) total oxidant can be achieved (Dimmock), this involves tightly controlled conditions in the non-linear area of the electrode response. The procedure requires at least two minutes under constant stirring for a complete response. Considering the volatility of chlorine and iodine in natural waters, a practical level of detection using the electrode method is closer to 50 µg/l. Wilde (Wat. Resources, 25, 1303) compared the electrode method to the forward amperometric method and the DPD colorimetric method on standards and cooling water samples for total residual chlorine at the Savannah River Site (SRS). Standard testing with high purity water dosed with chlorine showed no statistical difference among the three methods. However, measurements made with the electrode on cooling water samples were significantly lower than those obtained with the other two methods were. Wilde concluded the DPD method (using a Hach Colorimeter Kit) is the recommended method for future monitoring at SRS due to its simplicity and suitability for both field and laboratory measurements.

Appendix B: Calculation of CT Values

The intent of this discussion is to provide cursory information about calculation of CT. Enforcement of disinfection rules and establishment of measurement criteria may vary from State to State. The reader should always consult with local regulatory officials regarding monitoring requirements and interpretation of regulations.

Definition of CT

CT is an expression of the concentration of a chemical disinfectant, C in mg/L, multiplied by the contact time, T in minutes. The unit of measure for CT then is (mg-min)/l. Most primacy agencies enforce disinfection rules based on calculation of CT.

Emphasis on expression and use of CT became common in the drinking water field during the late 1970's to mid 1980's. However it was first suggested as a public health tool in the early 1900's. Increased use of CT in the drinking water field was largely prompted by waterborne disease outbreaks caused by two troublesome protozoa, *Giardia lamblia* (causes Giardiasis) and *Cryptosporidium parvum* (causes Cryptosporidiosis). Both of these organisms and their cysts (oocysts) can cause severe diarrhea leading to dehydration. Persons with weakened immune systems or those who are otherwise susceptible can experience more serious health problems including death. Several outbreaks of Giardiasis in the mid to late 1970's spurred more emphasis on the use of CT to measure/monitor disinfection.

Over one hundred people died as the result of a Cryptosporidiosis outbreak in Milwaukee, Wisconsin in 1993. Thousands of people became ill. The outbreak is to date the largest waterborne disease outbreak recorded in the United States.

One should note hand to mouth transfer of cysts due to contact with fecal matter from wild or domestic animals (or other infected humans), not drinking water, is the most common mode of transmission of these diseases.

Disinfection Strategies

Drinking water disinfection and disinfection strategies depend on recognition and, where possible, control of a number of variables. First, recall one should not consider disinfection as resulting only from application of a single chemical (chlorine, ozone) or physical (high heat) step in the process. The entire water treatment process contributes to disinfection (the multiple barrier approach) and thus must be considered. Physical barriers such as infiltration schemes (river bank filtration), coagulation, flocculation, sedimentation and filtration, and membranes all contribute to removal of pathogenic organisms and hence are part of the disinfection process. Clear wells, storage reservoirs and transmission pipes prior to the first customer provide contact time for the disinfectant and thus are part of the disinfection process.

[9] *Wilde specifically referenced the Hach DR100 Colorimeter that is no longer available. The Hach Pocket Colorimeter II is the direct replacement.*

Whether disinfection is effective depends on:

- Kind and concentration of organism to be removed, inactivated or destroyed
- Kind and concentration of chemical disinfectant
- Kind and effectiveness of other treatment techniques/processes
- Water temperature
- pH
- Time contact time; how long the chemical disinfectant is in contact with the water prior to the first use of the water by a consumer.

Figure 62: Variables affecting effectiveness of disinfection

US EPA rules established under the Safe Drinking Water Act (SDWA); Long Term 1 Enhanced Surface Water Treatment Rule, LT1ESWTR; Long Term 2 Enhanced Surface Water Treatment Rule, LT2ESWTR; and the Ground Water Rule all address to some extent the importance of considering the six variables listed above.

Kind and Concentration of Organisms Addressed

U.S. EPA rules and regulations specifically address the coliform group (Total Coliform Rule), *Giardia lamblia*, *Cryptosporidia* and viruses. Note that only the species, *lamblia* is addressed for the genus *Giardia*. While all members of the genus *Cryptosporidia* are addressed, not just the species *parvum*.

Treatment requirements for these organisms are expressed in terms of log removal (see Understanding Log Removal, below).

Requirements for *Giardia* and Viruses

Requirements for removal of *Giardia* and viruses are set out in the Surface Water Treatment Rule as summarized in the table below. The rule requires a minimum 3-log (99.9%) removal/inactivation of *Giardia* and 4-log (99.99%) removal/inactivation of viruses. Note the caveat that the stated "expected removals" are in a "well operated" plant. Different primacy agencies may adopt different criteria for "well operated."

	Excepted Log Removals in Well Operated Plant		**Recommended Disinfection (Log Reduction)**	
Filtration type	*Giardia*	Viruses	*Giardia*	Viruses
Conventional	2.5	2.0	0.5	2.0
Direct	2.0	1.0	1.0	3.0
Slow Sand	2.0	2.0	1.0	2.0
Diatomaceous Earth	2.0	1.0	1.0	3.0

Figure 63: SWTR Allowed removal credit for treatment and disinfection in combination

Requirements for *Cryptosporidium* under LT2ESWTR

LT2ESWTR (Federal Register Vol. 71, No. 3 Thursday, January 5, 2006 Rules and Regulations) requires certain treatment and CT values based on whether or not the system is filtered and on the concentration of cysts (oocysts). The requirements for filtered systems are summarized in the tables below from the Federal Register:

If your *Cryptosporidium* concentration (oocysts/l) is...[1]	Your bin classification is...	And if you use the following filtration treatment in full compliance with existing regulations, then your additional treatment requirements are...			
		Conventional filtration	Direct filtration	Slow sand or diatomaceous earth filtration	Alternative filtration technologies
< 0.075	1	No additional treatment	No additional treatment	No additional treatment	No additional treatment
>0.075 < 1.0	2	1-log treatment[2]	1.5-log treatment[2]	1-log treatment[2]	As determined by the State[2,4]
> 1.0 and < 3.0	3	2-log treatment[3]	2.5-log treatment[3]	2-log treatment[3]	As determined by the State[3,6]
> 3.0	4	2.5-log treatment[3]	3-log treatment[3]	2.5-log treatment[3]	2.5-log treatment[3,6]

[1] 40 CFR 141.710 and 40 CFR 141.711

[2] Systems may use any technology or combination of technologies from the microbial toolbox.

[3] Systems must achieve at least 1-log of the required treatment using ozone, chlorine dioxide, UV, membranes, bag filtration, cartridge filtration or band filtration.

[4] Total *Cryptosporidium* removal and inactivation must be at least 4.0 logs.

[5] Total *Cryptosporidium* removal and inactivation must be at least 5.0 logs.

[6] Total *Cryptosporidium* removal and inactivation must be at least 5.5 logs.

Source: Long Term 2 Enhanced Surface Water Treatment Rule Toolbox Guidance Manual, United States Office of Water Environmental, US EPA, April 2010.

Figure 64: Bin classification and additional treatment requirements for filtered systems

Unfiltered systems must meet a variety of criteria. A summary of some of the important information follows:

Average *Cryptosporidium* concentration (oocysts/l)	Additional *Cryptosporidium* inactivation requirements
≤ 0.01	2-log[1]
> 0.01	3-log[1]

[1]Overall disinfection requirements must be met with a minimum of two disinfectants

Unfiltered systems must use chlorine dioxide, ozone, or UV to meet the *Cryptosporidium* inactivation requirements and must meet overall disinfection requirements (i.e., *Cryptosporidium*, *Giardia*, and virus inactivation) with a minimum of two disinfectants [40 CFR 141.712 (d)]. Each of the two disinfectants must achieve by itself the total inactivation required for one of the three pathogen types.

Figure 65: LT2ESWTR Treatment requirements for unfiltered systems

Summary of Microbial Toolbox Options

The LT2ESWTR requires systems to use one or more of the microbial toolbox options described in Table 1.3 (40 CFR 141.722). Components of the toolbox include watershed control programs, alternative sources, pretreatment process, additional filtration barriers, inactivation technologies, and enhanced plant performance. The intent of the toolbox is to provide systems with flexibility in selecting cost-effective LT2ESWTR compliance strategies.

In most cases, systems will receive presumptive log credit for a toolbox option by demonstrating compliance with required design and implementation criteria. The demonstration of performance option allows States to approve a treatment credit greater than the presumptive log credit based on a site-specific or technology-specific demonstration of performance (40 CFR 141.727(c)).

Systems may use a combination of toolbox options to achieve the required log treatment. For example, a conventional filtration system assigned to Bin 3, requiring an additional 2 log treatment, can implement ozone with a contact time and concentration yielding 1.5 log credits and achieve the requirements for combined filter performance, thus receiving an additional 0.5 log credit for a total of 2 log credit.

Toolbox Option	*Cryptosporidium* Treatment Credit with Design and Implementation Criteria
Source Toolbox Components	
Watershed control program	0.5 log credit for State approved program comprised of EPA specified elements. Specific criteria are in 40 CFR 141.725(a)..
Alternative source/ intake management	No presumptive credit. Systems may conduct simultaneous monitoring for LT2ESWTR bin classification at alternative intake locations or under alternative intake management strategies.
Pre-Filtration Toolbox Components	
Bank filtration	0.5 log credit for 25 foot setback; 1.0 log credit for 50 foot setback. Aquifer must be unconsolidated sand containing at least 10% fines. Average turbidity in wells must be <1 NTU. Systems with existing wells must monitor well effluent to determine bin classification and are not eligible for presumptive credit. See 40 CFR 141.726(c).
Presedimentation basin with coagulation	0.5 log credit for new basins with continuous operation and coagulant addition. Basins must achieve 0.5 log turbidity reduction based on the monthly mean of daily measurements in 11 of the 12 previous months. All flow must pass through basins. Systems with existing pre-sedimentation basins must monitor after basins to determine bin classification and are not eligible for presumptive credit.
Two-stage lime softening	0.5 log credit for two-stage softening with coagulant addition. Coagulant must be present in both clarifiers and includes metal salts, polymers, lime, or magnesium precipitation. Both clarifiers must treat 100% of flow.
Treatment Performance Toolbox Components	
Combined filter performance	0.5 log credit for combined filter effluent turbidity ≤ 0.15 NTU in 95% of samples each month.
Individual filter performance	1.0 log credit for individual filter effluent turbidity # 0.1 NTU in 95% of daily maximum samples each month (excluding 15 minutes following backwash) and no filter >0.3 NTU in two consecutive measurements taken 15 minutes apart. See 40 CFR 141.727(b). See Chapter 7.
Demonstration of performance	Credit based on a demonstration to the State through State-approved protocol. See 40 CFR 141.727(c).
Additional Filtration Toolbox Components	
Bag filters	1 log credit with demonstration of at least 2 log removal efficiency in challenge test; Specific criteria are in 40 CFR 141.728(a).
Cartridge filters	2 log credit with demonstration of at least 3 log removal efficiency in challenge test; Specific criteria are in 40 CFR 141.728(a).
Membrane filtration	Log removal credit up to the lower value of the removal efficiency demonstrated during the challenge test if verified by direct integrity testing. See 40 CFR 141.728(b). See the Guidance Manual for Membrane Filtration.
Second stage filtration	0.5 log credit for a second separate filtration stage; treatment train must include coagulation prior to first filter. No presumptive credit for roughing filters. See 40 CFR 141.728(c).
Slow sand filters	2.5 log credit for second separate filtration process. No disinfectant residual present in influent. See 40 CFR 141.728(d).
Inactivation Toolbox Components	
Chlorine dioxide	Log credit based on demonstration of compliance with CT tables. See 40 CFR 141.729(b
Ozone	Log credit based on demonstration of compliance with CT tables. See 40 CFR 141.729(c).
UV	Log credit based on demonstration of compliance with UV dose table; reactor testing required to establish validated operating conditions. See 40 CFR

Figure 66: Microbial tool box options

Determining CT Requirements

From the previous discussion one can see how water sources, kind and concentration of organisms, and treatment techniques all factor into the disinfection process and what sort of 'credit' is applicable to a particular factor. The final question is, just how does calculation of CT play into all of this. To determine CT requirements one must first measure to determine the chlorine residual, sample temperature and sample pH. One then can refer to tables to determine what contact time T is needed. The requirement for *Giardia* and *Cryptosporidium* must be determined separately.

Determination of the required CT requires certain information to be known prior to beginning calculation including the disinfectant being used, disinfectant residual and temperature. Then one refers to a table of values (see below).

For example, if the temperature is 5° C, the pH is 7.5, and the free chlorine residual is 1.6 mg/L, then a CT of 192 mg-min/l is required to achieve 3-log inactivation (CT3-log) of *Giardia*. The treatment system includes granular media filtration meeting turbidity of < 0.1 NTU on combined filter effluent 95% of the time.

Chlorine Concentration (mg/L)	Temperature<5°C							Temperature=5°C							Temperature=10°C						
	pH							pH							pH						
	<=6.0	6.5	7.0	7.5	8.0	8.5	9.0	<=6.0	6.5	7.0	7.5	8.0	8.5	9.0	<=6.0	6.5	7.0	7.5	8.0	8.5	9.0
<=0.4	137	163	19	23	277	329	390	97	11	13	166	198	236	279	73	88	104	12	149	177	209
0.6	141	169	20	23	286	342	407	100	12	14	171	204	244	291	75	90	107	12	153	183	218
0.8	145	172	20	24	295	354	422	103	12	14	175	210	252	301	78	92	110	13	158	189	226
1	148	176	21	25	304	365	437	105	12	14	179	216	260	312	79	94	112	13	162	195	234
1.2	152	180	21	25	313	376	451	107	12	15	183	221	267	320	80	95	114	13	166	200	240
1.4	155	184	22	26	321	387	464	109	13	15	187	227	274	329	82	98	118	14	170	206	247
1.6	157	189	22	27	329	397	477	111	13	15	192	232	281	337	83	99	119	14	174	211	253
1.8	162	193	23	27	338	407	489	114	13	16	196	238	287	345	86	10	122	14	179	215	259
2	165	197	23	28	346	417	500	116	13	16	200	243	294	353	87	10	124	15	182	221	265
2.2	169	201	24	29	353	426	511	118	14	16	204	248	300	361	89	10	127	15	186	225	271
2.4	172	205	24	29	361	435	522	120	14	17	209	253	306	368	90	10	129	15	190	230	276
2.6	175	209	25	30	368	444	533	122	14	17	213	258	312	375	92	11	131	16	194	234	281
2.8	178	213	25	31	375	452	543	124	14	17	217	263	318	382	93	11	134	16	197	239	287
3	181	217	26	31	382	460	552	126	15	18	221	268	324	389	95	11	137	16	201	243	292

Chlorine Concentration (mg/L)	Temperature=15°C							Temperature=20°C							Temperature=25°C						
	pH							pH							pH						
	<=6.0	6.5	7.0	7.	8.0	8.5	9.0	<=6.	6.5	7.0	7.5	8.0	8.5	9.0	<=6.0	6.5	7.0	7.5	8.0	8.5	9.0
<=0.4	49	59	70	83	99	118	140	36	44	52	62	74	89	105	24	29	35	42	50	59	70
0.6	50	60	72	86	102	122	146	38	45	54	64	77	92	109	25	30	36	43	51	61	73
0.8	52	61	73	88	105	126	151	39	46	55	66	79	95	113	26	31	37	44	53	63	75
1	53	63	75	90	108	130	156	39	47	56	67	81	98	117	26	31	37	45	54	65	78
1.2	54	64	76	92	111	134	160	40	48	57	69	83	100	120	27	32	38	46	55	67	80
1.4	55	65	78	94	114	137	165	41	49	58	70	85	103	123	27	33	39	47	57	69	82
1.6	56	66	79	96	116	141	169	42	50	59	72	87	105	126	28	33	40	48	58	70	84
1.8	57	68	81	98	119	144	173	43	51	61	74	89	108	129	29	34	41	49	60	72	86
2	58	69	83	10	122	147	177	44	52	62	75	91	110	132	29	35	41	50	61	74	89
2.2	59	70	85	10	124	150	181	44	53	63	77	93	113	135	30	35	42	51	62	75	90
2.4	60	72	86	10	127	153	184	45	54	65	78	95	115	139	30	36	43	52	63	77	92
2.6	61	73	88	10	129	156	188	46	55	66	80	97	117	141	31	37	44	53	65	78	94
2.8	62	74	89	10	132	159	191	47	56	67	81	99	119	143	31	37	45	54	66	80	96
3	63	76	91	11	134	162	195	47	57	68	83	101	122	146	32	38	46	55	67	81	97

Figure 67: Required CT Values (mg-min/L) for 3-log Inactivation of Giardia *Cysts by Free Chlorine, pH 6.0-9.0*

Then, compare that to the actual CT if one has calculated the detention time to be 100 minutes (see **Calculating Detention Time**, below). The calculated CT would be: CT_{calc} = 1.6 mg/L X 100 min. or 160 mg-min./l. Thus, the current system is not enough to meet the required CT.

Giardia inactivation with the current scheme is short of the requirement. Calculate how much additional 'credit' is needed by the following calculation:

For *Giardia* inactivation: = 3 X ($CT_{calc}/CT_{3\text{-log}}$) = 3 X (160/192) = 2.5 log removal.

So, in this example, either through additional detention time, additional chlorine or an additional treatment technique, the system needs to provide an additional 0.5-log of credit.

But notice the treatment plant includes filtration and according to the table in figure 2, filtration provides a 'credit" of 2.5 logs. Therefore, this entire treatment system is providing 5-log removal of *Giardia*: 2.5-log from free chlorine and the detention time plus 2.5-log from filtration.

If one was determining virus inactivation the equation would be:

4-log virus inactivation = 4 X (($CT_{calc}/CT_{4\text{-log}}$)

A similar calculation is used for calculation of *Cryptosporidium* inactivation.

The Entire Treatment System is Important

As this example illustrates, calculation of CT is relatively straight forward. Determining how the treatment system complies with log removal requirements requires documenting the contribution of each portion of the treatment system.

In most cases, the worst case scenarios are assumed:

- Peak hourly flow, Q, in gallons per minute.
- Temperature at the sampling point
- pH at the sampling point
- Type of disinfectant used
- Residual disinfectant concentration (C) at the sample point
- Detention time created by basins/piping/unit process (T). Note the volume used for calculation must be the minimum working volume not the design capacity. (see Calculating Detention Time, below)
- Baffle factor (see Baffling Factor, below)

Document each part (unit process) of the treatment and also the amount of log credit the process provides. Constructing a table such as follows may be useful.

City of Anywhere Process Inventory

Unit Process	Log Credit for *Giardia*	Log Credit for *Crypto*	Log Credit for Viruses
Approved watershed control program		0.5	
River bank infiltration gallery 50 ft set back		1.0	
Ozonation		0.5	
Conventional filtration	2.5	0.5	2.0

Detention Time Inventory

Device	Capacity	DT at max flow total	Baffling Factor	DT (min) at Max flow (13,888 gal./min) w baffling factor
36" transmission main from CW to 8 MG tank, 3 miles long	837,083 gallons	60.3	1.0	60.3 min
0.2 MG CW	200,000	14.4 min.	0.1	1.4
8 MG tank	8,000,000	576 min	0.1	57.6

Figure 68: Unit Process Inventory for Log Credit

Understanding Log Removal

The terms log removal and log credits are widely used to express performance of various treatment processes. The terms can be somewhat confusing. A logarithm is the exponent to which a number is raised for a particular number base, in the 10-base counting system (log_{10}) it is the exponent to which 10 is raised. The log removal calculation is straight forward: log_{10} (Influent/effluent) which can also be calculated as log_{10} (influent) log_{10} (effluent). (Recall from algebra, log (a/b) = log a log b.)

Percent Removal	Decimal equivalent	Log Removal
68.4	0.684	0.5
90	0.90	1
99	0.99	2
99.684	0.99684	2.5
99.9	0.999	3
99.968	0.99968	3.5
99.99	0.9999	4
99.9968	0.999968	4.5
99.9990	0.99999	5
99.99968	0.999997	5.5
99.99990	0.999999	6

Figure 69: Percent vs. Log Removal

For example, if a raw water has 16,000 particles/ml >2µm

16,000 = 1.6 X 10^4, or log_{10} 16,000 = 4.204, or 16,000 = $10^{4.204}$

If after filtration the water has 16 particles/ml >2µm,
Then there was a 3 log removal (10^3) –the decimal moved to the left 3 places.

Or, 99.9 % of the particles (16,000-16/16,000 = 0.999 or 99.9%)

If the effluent counts were 123, then the log removal would be log10 (16,000/123) or log10 (16,000) log_{10} (123) = 2.114.
% = 100 10(2-log value) so, percent = 100 10(2-2.114)=100 .769
Or 99.23 %

For some treatment processes, it is problematic to express results in terms of log removal. When monitoring membranes with a particle counter, permeate (effluent) may approach zero particle counts. As the permeate approaches zero particle counts log (influent/effluent) becomes undefined division by zero. Rearranging the expression to log (influent) log (effluent) does not solve the problem. There is no exponent to which any number can be raised which will yield zero. Log (0) is undefined. Hence if the effluent approaches zero, it is best to express the removal as a percent removal.

Likewise, for some applications expression as a percent is problematic.

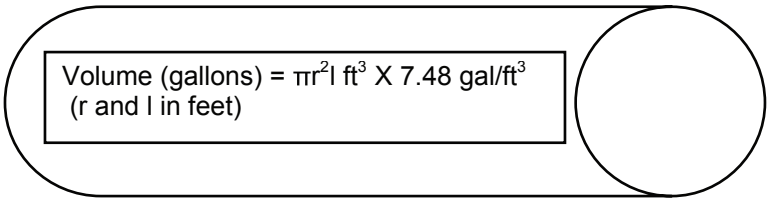
For drinking water applications a variety of rules apply which stipulate a certain minimum removal of problem organisms, i.e. "4-log removal of viruses." Why couldn't the rule just say 99.99%? Well, it could except it would actually make calculation more difficult.

The same rules that stipulate removal also stipulate blanket 'credits' for certain treatment techniques. A particular utility may receive filtration a credit of 2.5 log removal (99.68%); riverbank filtration may provide another 0.5 log (68.4%) of credit. So, how close is this to the required 4 log removal? Well, adding the two log removal values together, one gets 3.0 log removal (99.9%). But one cannot add the percentage values in the same way (if one tries to add the equivalent percentages one gets1.681 or 168.1 percent!). It is much more convenient to express these sorts of requirements as a log removal.

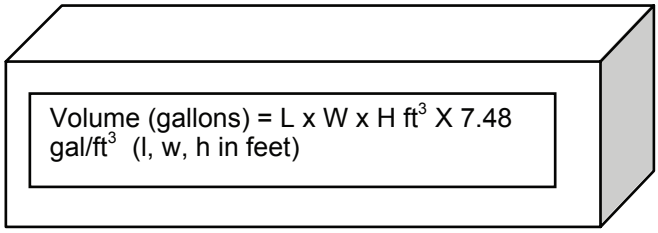
Calculating Detention Time

Peak hourly flow, temperature, pH and residual concentration should all be known from previous measurements. The baffling factor will be obtained from a reference table (see below). Only the detention time requires calculation prior to determining CT. The simplest way to think of detention time is to rephrase it as "how long will it take to fill?"

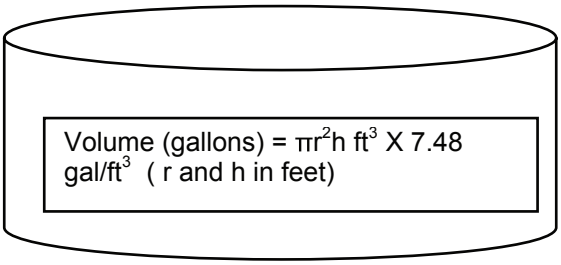
For a pipe:



For a rectangular basin:



For a circular tank:



Note: For a storage tank/reservoir/basin the height or depth MUST be the minimum active level. That is, what is the operational minimum level the tank is permitted to drop to during normal operations on the peak hour of the day? So, if the maximum water depth (height) is 20 ft but the minimum level is 12 feet, then 12 feet must be used in calculation of detention time, T for CT

Detention Time = Volume (gallons)/flow (gallons/min) or gallons x min. /gallons = minutes.

Baffling Factor

Finally, one must consider how well baffled the pipe/basin/reservoir is. That is, does a certain volume of water travel through the device as a plug flow (first in, first out) or can the flow short circuit? The following table should be used to account for baffling.

Baffling Conditions	Baffling Factor	Baffling Description
Unbaffled (mixed flow)	0.1	None, agitate basin, very low length to width ratio, high inlet and outlet flow velocities. Can be approximately achieved in flash mix tank.
Poor	.0.3	Single or multiple unbaffled inlets and outlets, no intra-basin baffles
Average	0.5	Baffled inlet or outlet with some intra-basin baffles
Superior	0.7	Perforated inlet baffle, serpentine or perforated intra-basin baffles, outlet weir or perforated launders
Perfect (plug flow)	1.0	Very high length to width ration (pipeline flow), perforated inlet, outlet and intrabasin baffles

Figure 70: Table of Baffling factors

Actual Detention Time = Calculated Detention Time X Baffling Factor

For example, if a circular basin is 20 feet high, 60 feet in diameter with a minimum working level of 12 feet, the detention time at a flow of 5000 gallons/min. is 50.7 minutes (Vol. in gal. = ϖr2h X 7.48=253,661 gallons. Detention time = volume/flow = 50.7 minutes.)

But, if the basin is unbaffled, then,

Actual Detention Time = 50.7 minutes X 0.1 or 5.1 minutes!

Use Hach WIMS to Calculate CT

For users of Hach Water Information Management Solutions (Hach WIMS) calculation of CT is very easy. Data needed are extracted from HACH WIMS and all calculations performed! That's it! CT tables for *Giardia*, *Cryptosporidium* and viruses are built in. Tables of other information needed such as in figure 9 are created in HACH WIMS by the user. Then when it's time for the CT calculations, a few clicks in HACH WIMS and it's done. A drinking water customer purchasing HACH WIMS for the first time or performing an upgrade can simply tell the Hach WIMS contact they want to do CT and the HACH WIMS person will assist them is seeing the system is properly set up. The following link provides a detailed description of CT calculations within HACH WIMS (hold Ctrl and click on the link).
http://www.opssys.com/instantkb/article.aspx?id=10095&query=CT+Calculations.

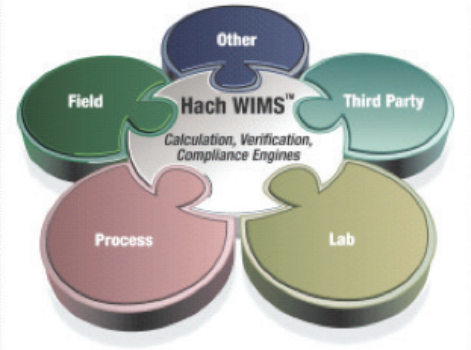


Figure 71: Hach WIMS

EPA Automated CT Calculation Tools Available

Two tools are available from USEPA for calculating CT. Two Excel workbooks, a short form and a long form are available to speed calculation and also to keep track of CT requirements. Both can be downloaded from the websites indicated. The workbooks also contain detailed instructions for their use.

The Short Form is intended for simple systems with a single disinfection stage; basically, chemical disinfection only: chloramines, chlorine, and ozone or chlorine dioxide. Once the starting date baffling factor, disinfectant type is selected and the residual, pH, temperature, flow and volume are entered, the balance of the sheet self calculates.
http://www.epa.gov/safewater/mdbp/lt1/xls/profile_benchmark_calculator_short.xls.

The long form is similar except a complex chain of treatment processes can be accommodated:
http://www.epa.gov/safewater/mdbp/lt1/xls/profile_benchmark_calculator_long.xls

Appendix C: Plumbing Sample to a Process Analyzer

If the sample is not right, the analysis is wrong!

1. Is the sample well mixed and representative?

a. Any chemical addition which can affect the measurement should be added far enough ahead of the sample point that it is well mixed and in solution. For example, if pH is to be measured after lime is added for pH adjustment, the measurement needs to be made downstream that all the lime is in solution.

b. If a chemical addition will interfere with measurement of the parameter of interest the sample should be drawn before the point of chemical addition. For example, suspended lime particles can cause positive error in particle count measurements following filtration. Measure particle counts in filter effluent prior to lime addition.

2. Where possible avoid turbulent flow conditions i.e. sample locations near valves, ells, tees, flanges. Turbulent flow conditions may dislodge scale, introduce severe entrained air and cause other sample anomalies that will lead to inaccurate measurement.

Keep it short, keep it simple, and don't delay

The instrument should be located as close as is practical to the sample location. If the sample to be measured is in the pipe gallery, then the instrument should be there too! Avoid piping sample long distances. Exceptions to the 'keep it short' rule include

- Do not mount instruments in locations where the environment will be hostile to the function and life of the instrument, i.e. areas with corrosive gases or strong electromagnetic fields.
- Do not mount instruments in locations that are hazardous or difficult to access for operations and maintenance personnel. All instruments require periodic maintenance. If instruments are difficult or hazardous to access to perform required maintenance, they won't be maintained and they won't work!
- Use sample lines that are corrosion resistant, small diameter and maintain high sample velocity.

Where possible use opaque, black plastic or metallic pipe/tubing compatible with the sample to be measured. The sample line must be opaque to block all light thus discouraging growth of biofilm. Avoid use of copper pipe or copper tubing.

Use the smallest diameter tubing that will deliver adequate volume and maintain high velocity. Select small diameter sample line to minimize the volume contained in the sample line and to maintain a high velocity. Maintaining high velocity in the tubing will discourage accumulation of biofilm and solids, which will affect accuracy.

Don't delay Keep it short, keep it simple, maintain high velocity.

Sample Delay in minutes per Foot of Sample Line (neglecting friction loss which will further increase the delay)

Sample Flow Rate, ml/min	Sample Flow Rate, gal/min	Copper Tubing (Nominal size, ID)			Sch 40 PVC (Nominal size, ID)		
		1/4", 0.315	3/8", 0.43	1/2", 0.545	1/4", 0.364	3/8", 0.493	1/2", 0.602
300	0.08	0.051	0.095	0.153	0.068	0.125	0.186
500	0.13	0.031	0.057	0.092	0.041	0.075	0.112
750	0.20	0.020	0.038	0.061	0.027	0.050	0.075
1000	0.26	0.015	0.029	0.046	0.020	0.038	0.056
1500	0.40	0.010	0.019	0.031	0.014	0.025	0.037
2000	0.53	0.008	0.014	0.023	0.010	0.019	0.028
3785	1.00	0.004	0.008	0.012	0.005	0.010	0.015
		Sch 80 PVC (Nominal size, ID)			Tygon Tubing (Nominal size, ID)		
		1/4"	3/8"	1/2", 0.562	1/4", 0.125	3/8", 0.25	1/2", 0.375
300	0.08	NA	NA	0.162	0.008	0.032	0.072
500	0.13	NA	NA	0.097	0.005	0.019	0.043
750	0.20	NA	NA	0.065	0.003	0.013	0.029
1000	0.26	NA	NA	0.049	0.002	0.010	0.022
1500	0.40	NA	NA	0.032	0.002	0.006	0.014
2000	0.53	NA	NA	0.024	0.001	0.005	0.011
3785	1.00	NA	NA	0.013	0.001	0.003	0.006

Do not mix and match plumbing fittings!

Do not connect to a steel pipe with a galvanized nipple, connected to a brass valve that will then connect to a copper sample line before getting to the analyzer. This scenario is all too common and creates a galvanic corrosion cell at every point of contact between dissimilar metals. It can result in sample line failure and corrosion products that interfere with sample measurement.

Use resistant materials where ever practical with minimal changes in the composition of materials of the plumbing fittings. Preferably, install corrosion-resistant metal or plastic materials.

Use resistant materials where ever practical with minimal changes in the composition of materials of the plumbing fittings. Preferably, install corrosion-resistant metal or plastic materials.

Provide proper flow control

Controlling flow and pressure is important for all measurements, critical for others. Instruments such as amperometric chlorine analyzers, particle counters and turbidimeters are very sensitive to changes in flow and pressure. Valves so many choices. Ball valves, needle valves, gate valves, globe valves.

- Needle valves avoid. Needle valves often cause sampling difficulty.
  - Can easily become clogged with sample debris and/or corrosion products from sample plumbing.
  - Rapid velocity changes around a needle valve can cause entrained air bubbles in the sample.
- Use a rotameter to measure flow if you wish. They are simple, easy to install and provide sufficient accuracy.
  - Do not use rotameters with integral needle valves for flow control.
  - Install a globe valve with a rotameter to set the proper flow.
- Use ball and gate valves for on/off control. Ball and gate valves are commonly used to throttle (control) flow. Ball valves are convenient in that they are normally ¼ turn from closed to open making operation fast and easy.
- Globe valves are designed to control flow.

Make the correct sample tap

Make the correct sample tap to avoid errors in measurement. Do use an existing sample tap only because it already exists. If an existing sample tap does not satisfy the following criteria, make a new tap.

- If, as with chlorine, the purpose of the measurement is to monitor chemical dose or residual, sample at a point where the sample to be monitored is well mixed. Ideally, provide an in pipe static mixer between the point of chemical injection and sampling.
- Avoid sampling from the top or bottom of a pipe.
  - Sampling from the top will often result in problems with air in the sample.
  - Sampling from the bottom will be non-representative due to solids that will inevitably accumulate at the bottom of the pipe.
- Typically it is best to sample from the side of a pipe ± 45°.
- It is desirable to sample from the middle of the pipe rather than from the edge, especially on larger diameter pipe (say, 6" diameter or larger). Samples drawn from the edge of a pipe can be non-representative due to fouling from sediment/biofilm accumulated on the wall of the pipe.
- Sample probes or sample quills are available from a number of manufacturers. Some of these are fixed in place, others are retractable. The probes/quills are available in a variety of materials. Some quills have multiple ports so the sample is a cross section of the pipe rather than one point a feature which may be desirable in some instances, especially larger diameter pipes.

Figure 72: Sample Quill

Sample Pumping

Avoid pumping sample where possible. Pumping can change the sample by entraining air, changing sample temperature (thus changing solubility of some substances) contributing corrosion products and/or changing the nature (i.e. size or shape) of suspended material.

When pumping is unavoidable:

- Avoid pumps that cause pulsation (diaphragm, piston, and peristaltic pumps). Pulsations can cause measurement irregularity. If unavoidable, use a pulse dampener after the pump.
- Centrifugal pumps are typically preferred to positive displacement pumps for providing samples to analyzers due to lower cost and centrifugal pumps are easier to throttle (control flow and pressure).
- Select a pump with components compatible with the sample. A pump with all composite (nonmetallic) wetted parts is desirable. Pumps with metallic wetted parts can create measurement errors by introducing corrosion products.
- Avoid excessive suction lift. At sea level an ideal pump has a maximum lift of about 34 feet. Considering pump efficiencies, and other factors, even at sea level the practical suction lift is only about 25 feet. At a mile above sea level (Denver, Co) the practical lift is only about 21 feet. Pump manufacturers will typically specify the maximum lift for their pump. Operating a pump near suction lift design limits will cause cavitation and other problems. The suction side of a centrifugal pump should not be restricted the valve on the suction side should always be fully open. Where suction lift is too great, one should consider a submersible pump.

When good sampling practices are not followed, do not blame inaccurate measurement on the instrument! If the sample is not right, the analysis is not right!

Appendix D: Feeding Ammonia for Chloramination

Several different compounds are commonly used to add ammonia to water for the purpose of chloramination

Compound	Chemical formula	Form	Percent Purity/ Solution Strength	Molecular Weight (mass)	Percent Composition as Nitrogen	Pounds Nitrogen per Pound or gallon of compound
Anhydrous Ammonia	NH_3	Compressed liquefied gas	100%	17	82.35% as N	0.82#/pound of NH_3
Ammonium Sulfate	$(NH_4)_2SO_4$	Granular or powder	99%	132	21.21% as N	27#/pound of Ammonium Sulfate
Liquid Ammonium Sulfate (LAS)	$(NH_4)_2SO_4$	Liquid	40% (specific gravity 1.216-1.228)	132	21.21% as N	0.84#/gallon of LAS
Aqua Ammonia	NH_4OH	Liquid	19% (typical, specific gravity 0.897)	111	12.61% as N	0.94#/gallon of Aqua Ammonia

Figure 73: Ammonia compounds used for chloramination

Example Calculation: Using Liquid Ammonium Sulfate (LAS)

Most suppliers of LAS provide a 38-40% aqueous solution of ammonium sulfate, $(NH_4)_2SO_4$. Each gallon of LAS has a specific gravity from 1.216 to 1.228 or 10.15 to 10.25 #/gallon and thus is typically 10% as ammonia (NH_3). For coarse control, see step one above; we can simplify this using the approximation that LAS is 10#/gallon. Since LAS is 10% **as ammonia**, each gallon (10#) contains approximately 1# of ammonia or **0.84# as N**:

Percent Composition of Ammonium Sulfate $(NH_4)_2SO_4$

Element	Atomic Weight	x	Number of Atoms	=	Weight (Mass)
Nitrogen	14		2		28
Hydrogen	1		8		8
Sulfur	32		1		32
Oxygen	16		4		64
Total					132
Portion that is ammonium (2N + 8H)					36
% ammonium NH_4					27%
Portion that is nitrogen (2N)					28
% N					21%

Typical LAS Solution		Density 10#/gal.		40% $(NH_4)_2SO_4$ by weight		10% NH_3
# N	=	10# solution	x	0.4 # $(NH_4)_2SO_4$	x	0.21# N
Gal LAS 40% solution of $(NH_4)_2SO_4$		Gal LAS		1# solution		1 # $(NH_4)_2SO_4$

# N	=	0.84# N
Gal LAS (40% solution)		Gal of LAS

Or, a 40% solution of LAS has a weight of 10#/gallon and contains 0.84# as N.

Example: If the expected chlorine feed rate is 4 #/hour, how much LAS should be fed per hour to achieve an approximate ratio of 4.5:1 (chlorine: nitrogen)

Gal of LAS assumes a 40%solution of $(NH_4)_2SO_4$	=	4# Cl_2	x	1# N	x	1 Gal. LAS
hr		hr		4.5# Cl_2		0.84# N

Gal. of LAS	=	1.1 Gal. LAS
hr		hr

If aqua ammonia (ammonium hydroxide), granular ammonium sulfate or anhydrous ammonia is being used, use a similar procedure as above to calculate the correct dosage rate.

Simple Steps to controlling chlorine and ammonia for chloramination

1. Measure total ammonia with a Hach test kit (#5870040 Pocket Colorimeter II) or lab methods, for example the salicylate method, to detect/control the ammonia feed rate. This might be considered as a coarse control to monitor the ammonia feed rate.
2. Measure monochloramine and free ammonia with Hach's monochloramine/free ammonia kit (#5870026 Pocket Colorimeter II) or lab methods. This we can refer to as a fine control. Fine control is used to adjust the chlorine to ammonia ratio to achieve chloramination with monochloramine keep free ammonia greater than but close to zero.
    a. If one has too much free ammonia, either slightly increase the chlorine feed or decrease the ammonia feed.
    b. If one has too little free ammonia, either increase ammonia feed or decrease chlorine feed.
    c. Typically one should change only one variable. That is, one should set either ammonia or chlorine feed rate and vary the other one. Different utilities will have their own preference as to which one to fix and which one to vary. This preference will be based on consulting advice, chemical feed schemes and other operational considerations.
3. For fine control measure monochloramine and free ammonia using Hach's test kit or lab methods. Is the free ammonia close to but greater than zero (many operators find operating in a range of 0.05 to 0.1 mg/L NH3 N is a good range)? If yes, great! If free ammonia is zero, decrease chlorine feed (or increase ammonia feed) until a slightly positive free ammonia is obtained. Remember, it is best to fix one variable and make changes with only one.

Stability of Ammonia and Bleach Solutions

Solutions of aqua ammonia are relatively unstable and may deteriorate over time. It is prudent to check solution concentration after preparation or when a commercially prepared solution is delivered. Check the solution weekly and adjust the chemical dose accordingly. Hach offers an acid-base titration procedure for determining the strength of aqua ammonia solutions. Hach recommends setting the aqua ammonia feed rate based on this titration procedure and not on the certificate of analysis that is typically based on the specific gravity of the solution.

Similarly, commercial bleach, solutions of sodium hypochlorite, is typically available as a 12% solution. Hypochlorite solutions, as aqua ammonia, are not stable. Shipments should be tested upon delivery and again about once per week.

Chlorine bleach and aqua ammonia solutions should be stored in a well ventilated, temperature controlled environment with no direct sunlight.

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HACH World Headquarters: Loveland, Colorado USA

United States:	800-227-4224 tel	970-669-2932 fax	orders@hach.com
Outside United States:	970-669-3050 tel	970-461-3939 fax	int@hach.com

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