

Current Technology of
Chlorine Analysis
for Water and Wastewater

Technical Information Series — Booklet No.17
By **Danial L. Harp**

In memory of
Clifford C. Hach

(1919 – 1990)

inventor, mentor, leader and, foremost,
dedicated chemist

Current Technology of Chlorine Analysis for Water and Wastewater

Table of Contents	Page
1. Overview of Chlorine Chemistry in Water Treatment	1
2. Analytical Methods for Chlorine and Chloramines	2
a. DPD Colorimetric Method	2
b. DPD Titration Method	5
c. Iodometric Titration Method.....	6
d. Amperometric Titration Methods	6
e. Other Analytical Methods:	8
Orthotolidine.....	8
Syringaldazine (FACTS)	9
Electrode	9
3. Method Interferences and Sources of Errors	11
a. Sampling Considerations	11
b. Interferences Common to All Chlorine Methods	11
Other Disinfectants.....	11
Manganese Compounds.....	12
Organic Chloramines	12
Bromides in Chlorinated Waters	12
c. Errors Common to Total Chlorine Determinations	12
d. Interferences in the DPD Methods.....	13
Calibration Non-Linearity	13
Precautions in Using Permanganate as an Equivalent Standard	13
Monochloramine Interference in the Free Chlorine Test	15
Stability of the Colored Reaction Product	16
Compensation for Sample Color and Turbidity	16
e. Interferences in the Amperometric Titration Methods	17
Deposition on Electrode Surfaces	17
Manganese Interference	17
Nitrite Interference	17
Choice of Reductant.....	19
Effect of Iodine Demand on End Point Determinations	19
Order of Reagent Addition.....	20
4. Method Comparisons and Performance Evaluations	21
a. Field Kit or Laboratory Comparisons	21
b. Performance Evaluations of Residual Chlorine Process Analyzers	23
5. Selection of the Appropriate Testing System	24
a. Field Testing	24
b. Laboratory Testing	25
c. On-line Automated Testing.....	26
6. Conclusions	27
References	29
Acknowledgements	30

1. Overview of Chlorine Chemistry in Water Treatment

Chlorination of public water supplies has been practiced for almost 100 years in the United States. Although the pros and cons of disinfection with chlorine have been extensively debated, it remains the most widely used chemical for disinfection of water in the U.S.

Comprehensive information explaining chlorine chemistry in water treatment is available in several excellent references describing chlorination and disinfection practices. (See Ref. 1.1 - 1.4). An overview emphasizing general chemistry of chlorine disinfection will be presented here.

Chlorine usually is added to water as the gaseous form or as sodium or calcium hypochlorite. Chlorine gas rapidly hydrolyzes to hypochlorous acid according to the following equation:



Similarly, aqueous solutions of sodium or calcium hypochlorite will hydrolyze according to:



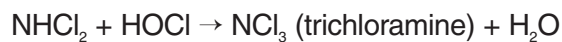
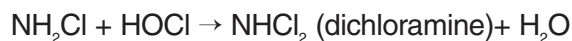
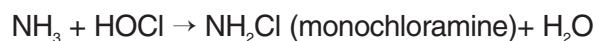
The two chemical species formed by chlorine in water, hypochlorous acid (HOCl) and hypochlorite ion (OCl^-), are commonly referred to as “free available” chlorine. Hypochlorous acid is a weak acid and will disassociate according to:



In waters with pH between 6.5 and 8.5, the reaction is incomplete and both species (HOCl and OCl^-) will be present. Hypochlorous acid is the more germicidal of the two.

A relatively strong oxidizing agent, chlorine can react with a wide variety of compounds. Of particular importance in disinfection is the chlorine reaction with nitrogenous compounds—such as ammonia, nitrites and amino acids.

Ammonia, commonly present in natural waters, will react with hypochlorous acid or hypochlorite ion to form monochloramine, dichloramine and trichloramine, depending on several factors such as pH and temperature. Typical reactions follow:



Known as “break-point” reactions, they are important in water disinfection. The chloramines are potent biocides but not as effective as hypochlorous acid or the hypochlorite ion.

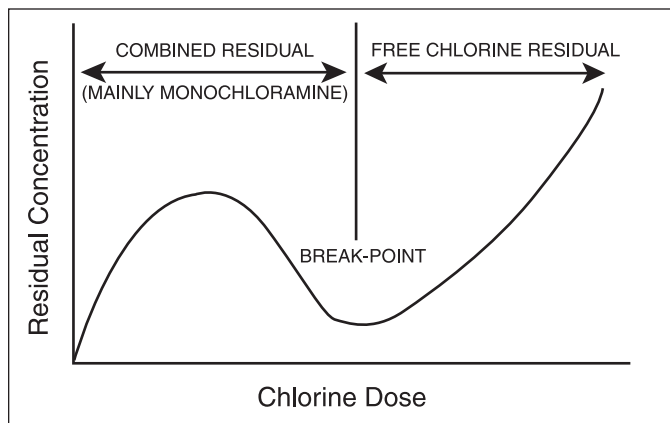


Figure 1.1: Typical Break-point Chlorination Curve

Chlorination of water to the extent that all ammonia is converted to either trichloramine or oxidized to nitrogen or other gases is referred to as “break-point chlorination.”

Figure 1.1 shows a typical break-point chlorination curve. Prior to the break point, “combined” chlorine (monochloramine plus dichloramine) predominates. In disinfection systems in which chloramination is practiced, the goal is to remain at the peak of the curve prior to the break point. If the amount of unreacted ammonia is minimized, monochloramine will be the predominant chloramine.

After the break point, free chlorine (hypochlorous acid plus hypochlorite) is the dominant disinfectant. Typically, the free chlorine residual is adjusted to maintain a minimum level of 0.2 mg/L Cl_2 throughout the distribution system.

The importance of break-point chlorination lies in the control of taste and odor and increased germicidal efficiency. The killing power of chlorine on the right side of the break point is 25 times higher than that of the left side (*Ref. 1.1*). Hence, the presence of a free chlorine residual is an indicator of adequate disinfection. The shape of the break-point curve is very dependent on contact time, water temperature, concentrations of ammonia and chlorine, and pH.

The use of monochloramine as an alternate disinfectant for drinking water has received attention lately due to concern about the possible formation of chlorinated by-products when using free chlorine disinfection. Considerable debate continues about the merits of chloramination disinfection. The reader is referred to White's handbook (*Ref. 1.1*) for an animated discussion of the pros and cons of chloramination practices in drinking water treatment.

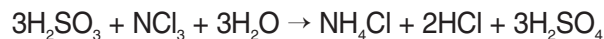
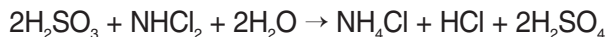
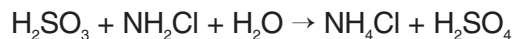
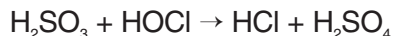
In chloramination disinfection, monochloramine is formed from the reaction of anhydrous ammonia and hypochlorous acid. In general, ammonia is added first to avoid formation of chlorinated organic compounds, which can exhibit objectionable taste and odors. Hach offers a method specific for inorganic monochloramine disinfectant in the presence of organic chloramines (*Ref. 1.2*).

Throughout the U.S. Today, wastewater effluents are chlorinated to kill pathogens and then dechlorinated before discharge. This common practice resulted from several comprehensive studies (*Ref. 1.5*) which quantified the toxicity of chlorinated effluents on aquatic life. The amount of total residual chlorine in the final effluent is regulated by a National Pollutant Discharge Elimination System (NPDES) permit. Typical permit limits for total residual chlorine (TRC) in the final effluent range from 0.002 to 0.050 milligram per liter (mg/L). To the chlorination-dechlorination practitioner, this level translates to zero mg/L TRC.

Dechlorination by sulfur dioxide (SO₂) is the most common process to meet zero TRC effluent limits. Sodium bisulfite and sodium metabisulfite also have been used for chemical dechlorination. In the dechlorination process using SO₂, sulfurous acid is formed first:



Sulfurous acid then reacts with the various chlorine residual species:



It is common practice to overdose the sulfur dioxide to maintain a level up to 5 mg/L SO₂ in the effluent. This ensures the reduction of all chlorine residual species.

2. Analytical Methods for Chlorine and Chloramines

2a. DPD Colorimetric Method

The DPD (N, N-diethyl-p-phenylenediamine) method for residual chlorine was first introduced by Palin in 1957 (*Ref. 2.1*). Over the years it has become the most widely used method for determining free and total chlorine in water and wastewater. Hach Company introduced its first chlorine test kit based on the DPD chemistry in 1973.

The chemical basis for the DPD chlorine reaction is depicted in **Figure 2.1**. The DPD amine is oxidized by chlorine 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. DPD can be further oxidized to 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.

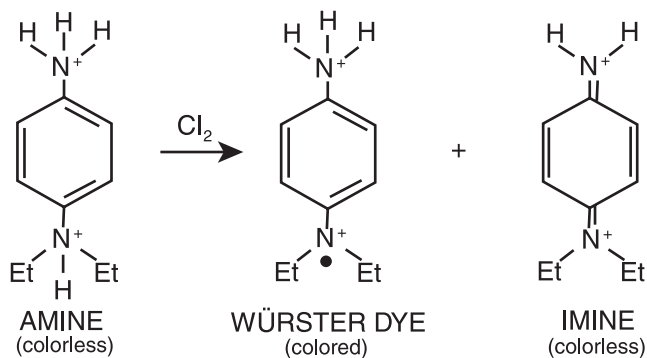


Figure 2.1: DPD-Chlorine Reaction Products

The DPD Würster dye color has been measured photometrically at wavelengths ranging from 490 to 555 nanometers (nm). The absorption spectrum (**Figure 2.2**) indicates a doublet peak with maxima at 512 and 553 nm. For maximum sensitivity, absorption measurements can be made between 510 and 515 nm. Hach Company has selected 530 nm as the measuring wavelength for most of its DPD systems. This “saddle” between the peaks minimizes any variation in wavelength accuracy between instruments and extends the working range of the test on some instruments.

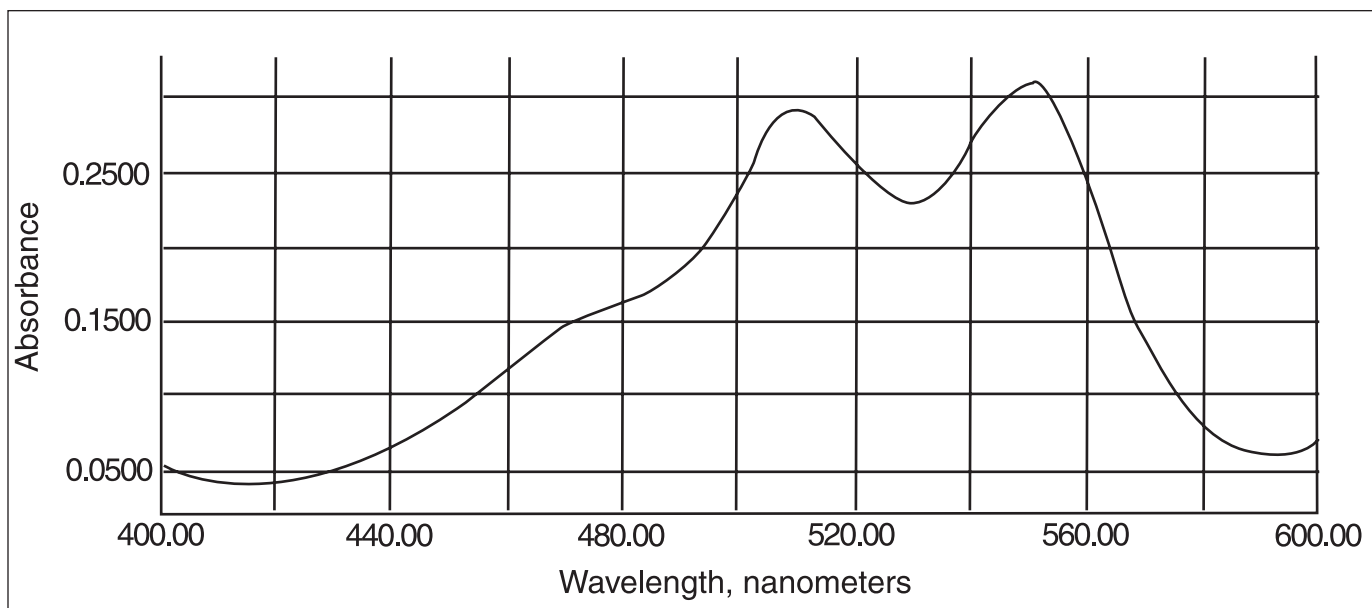
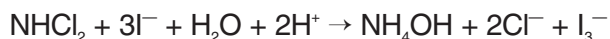
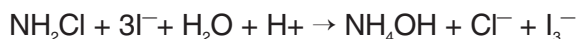


Figure 2.2: Absorption Spectrum - DPD Würster Compound

Monochloramine and dichloramine are slow to react directly with DPD at a near neutral pH. To quantify these species, the test is performed under slightly acidic conditions in the presence of iodide ion. The iodide reacts with the chloramines to form iodine as the triiodide ion (I_3^-):



The triiodide, in turn, reacts with DPD, forming the Würster oxidation product. There is very little confirmed evidence that trichloramine species can be quantified when using iodide with DPD (Ref. 2.2).

In practice, only a trace of iodide is required at pH 6.2-6.5 to resolve monochloramine. *Standard Methods for the Examination of Water and Wastewater* (Ref. 2.3) stipulates the addition of approximately 0.1 mg of potassium iodide to a 10-mL sample to determine monochloramine. By adding excess potassium iodide (an additional 0.1 gram or more per 10-mL sample), dichloramine is included. It is not entirely clear at what level of iodide the dichloramine fraction begins to intrude into the monochloramine results.

Two “standard” DPD colorimetric methods generally are recognized in the international community. These are the *Standard Methods* 4500-Cl G and International Organization for Standardization (ISO) Method 7393/2 (Ref. 2.4). The ISO method has been adopted by most of the members of the European Union. Germany’s DIN

Standard 38 408 G4 for free and total chlorine is modeled after ISO 7393/2. **Table 2.1** shows the main differences between Standard Methods 4500-Cl G and ISO 7393/2.

Both *Standard Methods* and ISO procedures call for liquid DPD reagents prepared from DPD sulfate or DPD oxalate salts. Liquid DPD reagents, inherently unstable, are subject to oxidation from either atmospheric oxygen or dissolved oxygen present in the preparation water. It has been shown that the oxidation of DPD by oxygen is pH-dependent (Ref. 2.5). The liquid DPD formulations attempt to retard oxidation by lowering the pH of the indicator reagent.

The liquid formulations also incorporate disodium ethylenediamine tetraacetate (Na_2EDTA) in order to “retard deterioration due to oxidation and, in the test itself, provide suppression of dissolved oxygen errors by preventing trace metal catalysis” (Ref. 2.6). The practice of adding Na_2EDTA to the DPD indicator reagent is questionable because of the low solubility of EDTA in dilute acid solutions.

Standard Methods and ISO procedures both use phosphate buffers to adjust the sample pH to between 6.2 and 6.5. The slightly acidic pH is preferred to quantitatively resolve the chloramine species and to minimize interferences. Phosphate buffers, however, do not work in hard or brackish waters. Calcium and magnesium ions in the sample will precipitate the phosphate and destroy the buffering capacity (Ref. 2.7). Because aqueous phosphate solutions are excellent growth media for biological growth, highly toxic mercuric chloride is added to preserve the reagent.

	Standard Methods	ISO 7393/2
Test Range	0.01 - 4 mg/L as chlorine	0.03 - 5 mg/L as chlorine
Apparatus	Spectrophotometer: 515 nm Filter Photometer: 490 - 530 nm	Spectrophotometer: 515 nm Discontinuous wavelength close to 510 nm Comparator with glass color standards
Reagents	DPD sulfate or DPD oxalate (Final SM and ISO formulations are equivalent) (Both SM and ISO state combined powder formulations are acceptable)	DPD sulfate
Calibration	Permanganate dilutions: 515 nm	Iodine dilutions generated from iodate+ acid pH adjusted prior to additions of mixed reagent
Procedure	10-mL sample to 0.5 mL each reagent (or increase volumes proportionally) TRC: ab. 0.2 gm KI /10-mL sample	100-mL sample added to 5.0 mL each reagent TRC: ab. 1 gm KI /100 mL
Correction for Mn7⁺	arsenite + buffer to sample, then DPD	arsenite to sample, then add to DPD + buffer
Reporting	expressed as mg/L chlorine	expressed as mmoles/L chlorine

Table 2.1: Differences Between *Standard Methods 4500-CI G* and *ISO 7393/2*

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

Hach's buffer component makes use of a carboxylate-phosphate system which works extremely well in high hardness and brackish water samples. Up to 1000 mg/L CaCO₃ hardness can be tolerated with either the free or total chlorine powder formulations. Mercuric salts are not used in any of Hach Company DPD formulations.

Hach Company's DPD powder reagents are quite stable when protected from moisture, light and temperature extremes. Excellent reagent stability is achieved by sealing the reagent in unit-dose foil pouches. AccuVac® DPD reagent ampuls are air-evacuated and hence are protected from oxidation and moisture. It is recommended that all DPD reagents, both liquids and powders, be stored between 10 to 25 °C (50 to 77° F) for greatest stability.

Hach Company has produced a stable liquid DPD reagent. The DPD Indicator Solution for Ultra Low Range (ULR) Chlorine, Cat. No. 24932, is sealed in a unit-dose ampule under argon gas. The use for this reagent is in trace determinations of total chlorine in water and wastewaters. Liquid reagents are preferred for trace levels of chlorine — less than 20 micrograms per liter (µg/L). Powdered reagents typically leave a very small

undissolved residue when added to the water sample. Although the resulting turbidity is not evident visually, it may be sufficient to interfere in trace colorimetric measurements. Shelf studies indicate the ULR-DPD reagent exhibits no loss in sensitivity to chlorine over a one-year period (*Ref 2.8*).

For trace determinations of chlorine, purity of the buffer and iodide components are critical. 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 useless in samples containing hardness. Liquid phosphate buffers can contain insoluble impurities or microbiological growth which may cause turbidity when added to the sample. Iodide often contains iodine or iodate impurities which react directly with the DPD indicator. Exposure to oxygen and light will gradually oxidize iodide to triiodide even in the solid state.

A stable liquid buffer/iodide reagent developed by Hach is suitable for trace chlorine analysis. The ULR Chlorine Buffer, Cat. No. 24931, is specially treated to remove any chlorine demand from its components. Iodide in the reagent is controlled to minimize oxidation impurities. The ULR Chlorine Buffer is packaged under argon in a light-protected, unit-dose ampule.

Another important consideration for trace analytical measurements is the "reagent blank." This is the amount of interference due to 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 indicator with chlorine. When the DPD reagent is added to the sample containing chlorine, the

amount of color measured will be the sum of the reaction product of DPD-Cl₂ and the added oxidized DPD. For trace analysis, the reagent blank contribution must be accurately known.

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. If a relatively strong reducing agent such as sulfite or ferrous ammonium sulfate were added to the sample, it would reverse any colored DPD Würster dye present in the indicator reagent to the free amine, thereby preventing reagent blank compensation.

Hach Company has developed a procedure to determine the reagent blank for the ULR-DPD method. The procedure dechlorinates the sample without affecting the color contributed by the indicator reagent. In the reagent blank compensation procedure, a non-reducing 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. The resulting color is used to correct the sample analysis results. Consistent reagent blank values, equivalent to less than 3 µg/L chlorine, are obtained when using the ULR-DPD reagents.

When using Hach Company’s method for ULR total chlorine testing, chlorine residuals as low as 2 µg/L can be determined (*Ref. 2.8*). This level of detection was determined using the U.S. Environmental Protection Agency (USEPA) procedure for estimating the method detection limit (MDL) (*Ref. 2.9*). The upper range for the test is 500 µg/L as Cl₂.

Monitoring uses for the ULR-DPD method for total chlorine include dechlorination of feedwater to reverse osmosis membranes or ion-exchange resins, make-up water for the pharmaceutical and beverage industries, and in wastewater treated to meet NPDES requirements. The ULR-DPD method is USEPA-accepted for total chlorine determinations in drinking water and wastewaters.

2b. DPD Titration Method

The DPD titration method is based on the same chemistry as the DPD colorimetric method – in that DPD is oxidized by chlorine (or iodine in the case of chloramines) to the magenta-color species. The red color then is titrated with a ferrous reducing agent to the colorless end point. The reaction chemistry is depicted in **Figure 2.3**.

Standard Methods and ISO DPD titration procedures both use the same buffer and indicator reagent

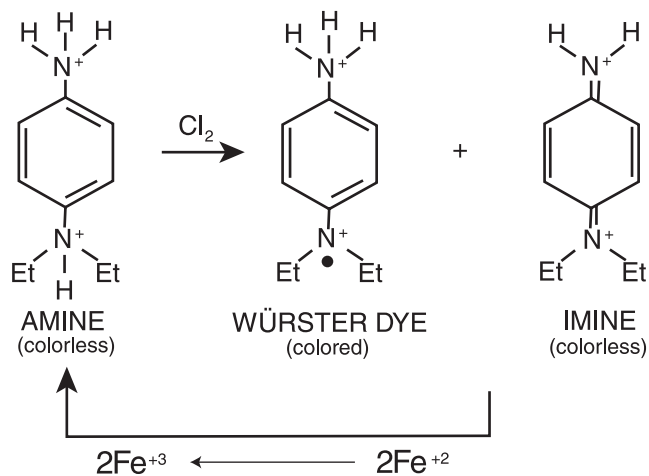


Figure 2.3: Chemistry of DPD-FAS Titration

formulations as those specified in the referenced DPD colorimetric methods. Hence, the inherent problems of reagent instability and buffering of hard water samples cited above also are applicable to the reference titration procedures.

The ferrous iron titrant reagent used in the Standard Methods and ISO DPD titration methods is prepared from ferrous ammonium sulfate. This titrant solution is very unstable, susceptible to oxidation, and must be frequently standardized against standard potassium dichromate. The titrant generally is used for only one month.

Hach Company has improved the ferrous titrant solution by using a primary standard ferrous ethylenediammonium sulfate (Oesper’s reagent) salt under oxygen-free conditions. The titrant is sealed in Digital Titrator cartridges after preparation to a 0.00564 N (normality) concentration using de-oxygenated water. With minimal exposure to oxygen due to the packaging, the Ferrous Ethylenediammonium Sulfate (FEAS) Titrant, Cat. No. 22923, exhibits excellent shelf stability (greater than six months) compared to that of the reference method formulations.

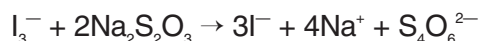
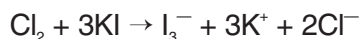
In Hach Company’s DPD titration method, a DPD Free or Total Chlorine Reagent Powder Pillow is added to 25 mL of sample. After full development of the Würster dye, the reacted sample is titrated to the colorless end point using FEAS with the Digital Titrator. The number of digits required to the end point is divided by 100 to obtain the mg/L chlorine.

For most samples, there is no clear advantage to using the DPD titration method over Hach’s DPD colorimetric method. In fact, there may be several disadvantages. First, the titration procedure requires additional time to perform. In the case of possible monochloramine

intrusion into free chlorine (see **Section 3d**), the additional time required for a free chlorine titration may lead to errors. Accurate measurement of sample volume for the titration is essential. To achieve accuracy, a pipet must be used – a procedure which can lead to loss of volatile chlorine species. The visual estimation of the titration end point is imprecise compared to the measurement of color obtained by using a colorimeter or spectrophotometer.

2c. Iodometric Titration

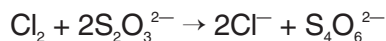
The starch-iodide titration method, one of the oldest methods for determining chlorine, is very non-specific for oxidants and generally is used for total chlorine testing at levels above 1 mg/L Cl₂. The method is based on reaction with thiosulfate solution:



The end point of the titration is indicated by the disappearance of the blue-colored, starch-iodide complex. The titration usually is performed at a sample pH between 3-4.

Research by Hatch and Yang (*Ref. 2.10*) has shown sample temperatures above 20 °C can produce significant errors if starch is used as the titration end-point indicator. Their studies indicate the release of triiodide from the starch helix is temperature-dependent. For maximum accuracy, iodometric titrations using starch indicator should be performed at sample temperatures less than 20 °C (68° F).

A “back titration” is recommended for waters containing potential chemical interferences. In this case, a known amount of thiosulfate is added in excess of the chlorine in the sample. The amount of unreacted thiosulfate is titrated with a standard iodine solution. Then, the total chlorine is calculated, based on the thiosulfate equivalency in the sample. The chemical reactions are:

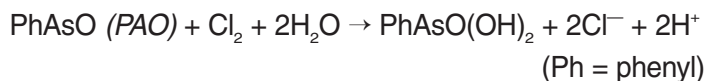


Hach Company offers several total chlorine systems using the iodometric titration method. Typically, the application range is from 1 to 70,000 mg/L chlorine. Hach Company’s iodometric procedures are used to assay chlorine in commercial bleach solutions and in chlorinated wastewaters.

2d. Amperometric Titration Methods

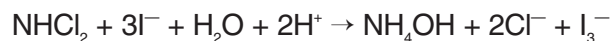
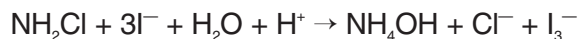
Amperometry is an electrochemical technique that applies a small electrical voltage across two electrodes and measures the change in current resulting from chemical reactions taking place. Amperometric titration measures the current change as a function of titrant added. Typical amperometric titration instrumentation includes a probe or cell containing dual platinum electrodes (biamperometric) or two dissimilar electrodes (for example, silver/platinum), a microampere meter and a titrant-dispensation device.

In the amperometric determination of free chlorine, chlorine is titrated with a standard reducing agent such as thiosulfate or phenylarsine oxide (PAO) at pH 7. A small potential is applied across the electrodes before the titration begins. Current cannot flow between the electrodes unless two substances are present — one that can be oxidized at the anode and another that can be reduced at the cathode. During the course of the titration, chlorine is reduced at the cathode to chloride (Cl⁻) from the reaction with PAO. PAO is oxidized from the +3 to the +5 oxidation state at the anode:

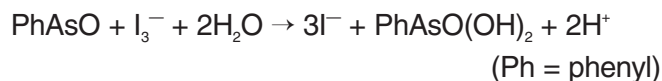


As long as the oxidant (free chlorine) is present in the titrated sample, a current flows through the cell. When all of the oxidant is reacted, the rate of current change is zero, signalling the end point of the titration. After the end point is reached, the solution cannot conduct current even though excess PAO is added. The amount of PAO used at the titration end point is proportional to the chlorine concentration in the sample.

In the case of chloramine determination, the pH is lowered to 4 and potassium iodide is added to convert the chloramine species to an equivalent amount of triiodide ion:



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



Standard Methods (Ref. 2.11) differentiates between monochloramine and dichloramine by performing the monochloramine titration in the presence of potassium iodide at pH 7. After titration, the pH is lowered to 4, additional iodide is added, and the titration is continued to resolve the dichloramine fraction. Because an amperometric titration typically must be “over-shot” to determine the end point, the volume of titrant must be corrected for the over-shot increment. This practice leads to some ambiguity in the determination of monochloramine and dichloramine fractions, especially when present at low concentrations.

The direct amperometric titration of chlorine or chloramines with a standard reducing agent is known as a “forward” titration. Back titration with an amperometric end point also is used widely for the determination of total chlorine in water. The amperometric back titration is essentially the back iodometric titration method with an amperometric, rather than a visual, end-point detection.

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 reductant.

(2) Since the end point is reversed, there is less interference from iodine-demand substances in the sample. The back amperometric end point is signaled when free iodine (triiodide ion) is present — as indicated by a current flow between the electrodes.

Amperometric titrations require a higher level of skill and care than the colorimetric methods for chlorine analysis. *Standard Methods* states the amperometric method “is the standard of comparison for the determination of free or combined chlorine” (*Ref. 2.12*). However, the amperometric method is no longer accepted by ISO for the determination of chlorine species (*Ref. 2.13*). There is considerable conflicting information about interferences with amperometric methods for chlorine in treated wastewater and effluents (**see Section 3e.**).

Hach Company offers both forward and backward amperometric methods for determination of free and total chlorine in water. Hach’s AutoCat 9000 Amperometric Titrator (**Figure 2.4**) is based on a bi-amperometric system that uses a dual platinum electrode (DPE) probe. The AutoCat software controls the delivery of titrant from a glass burette driven by a step motor. The step motor requires 18,000 individual steps to deliver the full 5.0 mL of titrant that it contains. This allows a volume resolution of 0.0003 mL per step.



Figure 2.4: Hach Company’s AutoCAT 9000 Amperometric Titrator

A glass buret also may be used to dispense the titrant. Drawbacks of using a buret include the fragility of the glassware and the relatively large dispensation. Even when a Class A 5-mL buret is used, dispensation of one small droplet of 0.00564 N PAO could relate to as much as 20 µg/L Cl₂ in a forward titration using 200 mL of sample.

Typical titration plots for Hach's AutoCat 9000 forward and back amperometric procedures are shown in **Figures 2.5 and 2.6**. The end point can be determined manually or automatically. In a manual end-point determination, the analyst uses cursors to select a linear region on each side of the end point. Then the instrument calculates and places least-squares regression lines at each point. The intersection of the two best lines through the points is the end point. In an automatic end

point determination, the instrument searches for a pair of intersecting lines that best fit the titration curve. The end point is derived from the intersection of the two points.

A comparison of currently available commercial amperometric systems shows lower detection levels are possible with the AutoCAT 9000 because of micro-dispensation and automatic determination of the endpoint. Method detection limits for the total chlorine forward titration are 0.0012 mg/L (1.2 µg/L) Cl₂ and 0.0051 mg/L (5.1 µg/L) for the back titration.

Hach Company's amperometric titration methods meet the testing requirements for measuring chlorine according to the U.S. National Drinking Water Act Regulations as well as the NPDES compliance monitoring programs.

For a comprehensive review of analytical methods which have been used to determine chlorine in water, the reader is referred to the *American Water Works Association's Disinfectant Residual Measurement Methods (Ref. 2.2)*. A review of other methods which have been commonly used in the water treatment industry follows.

2e. Other Common Analytical Methods

Orthotolidine Method

The orthotolidine (OT) method for chlorine was first reported by Ellms and Hauser (*Ref. 2.14*). The method has been modified several times to overcome stability problems and interferences related to monochloramine breakthrough in the free chlorine procedure.

The orthotolidine method was dropped from the 14th edition of *Standard Methods* after the results of two round-robin studies (*Refs. 2.15, 2.16*) were released. 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 (*Refs. 2.17, 2.18*) 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.

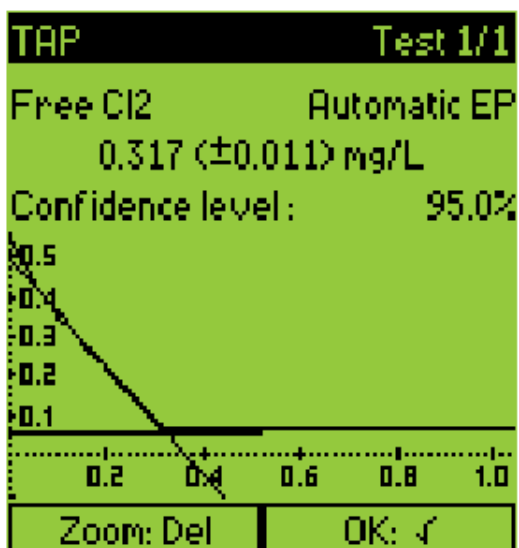


Figure 2.5: Forward Amperometric Titration Plot

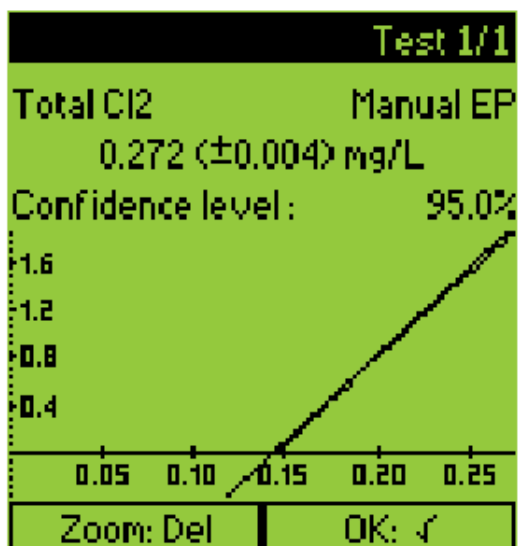
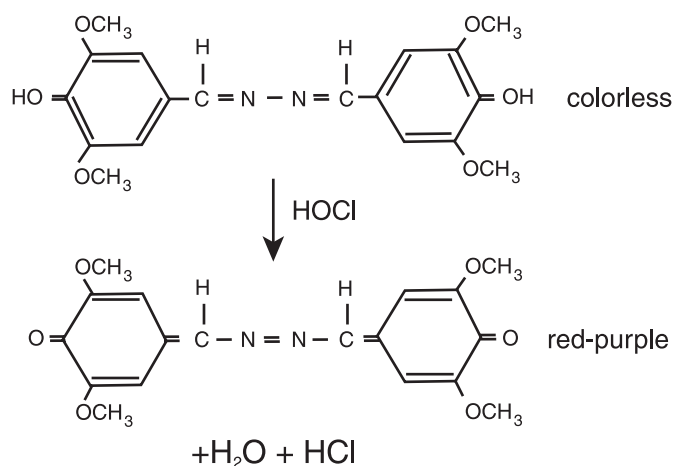


Figure 2.6: Back Amperometric Titration Plot

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 Cl₂. The test has been adapted to the determination of total chlorine as well as other oxidants (Ref. 2.19).

The FACTS method has been reported to be specific for free chlorine, with little interference from manganese (+4) and monochloramine. A Standard Method procedure (Ref. 2.20) for free chlorine determinations, it is not recognized by the ISO.

Major disadvantages of the FACTS method are the insolubility of the indicator and its product, storage of the indicator solution, and a variable sensitivity to chlorine. The syringaldazine indicator is prepared in 2-propanol, in which it has limited solubility. It is necessary to gently heat and use ultrasonic agitation for several hours to dissolve syringaldazine in the 2-propanol. Also, the 2-propanol must be distilled to remove unidentified impurities which exert a chlorine demand.

Hach Company research shows a FACTS indicator solution with consistent sensitivity to chlorine is difficult to produce, even with distillation of the 2-propanol. Also, if heat is excessive in preparation of the indicator solution, degradation of the syringaldazine can occur, resulting in decreased sensitivity. *Standard Methods* allows an

alternate procedure to remove the chlorine demand by chlorinating the alcohol and dechlorinating by exposure to sunlight or ultraviolet (UV) light. This procedure is not recommended, due to the flammability of 2-propanol.

Although not addressed in the *Standard Methods* procedure, syringaldazine indicator solutions cannot be stored in plastic containers. The solvent apparently leaches out impurities in the resin, resulting in a chlorine demand in the indicator. For greatest stability, the syringaldazine reagent should be stored in an amber glass-stoppered bottle protected from heat and UV light.

Another problem with the FACTS procedure is fading of the oxidized (colored) species. This is due, in part, to the relative insolubility of the product when diluted by the aqueous sample. Chiswell and O'Halloran (Ref. 2.21) reported the FACTS method is unsuitable for free chlorine testing due to the instability of the oxidized reaction product. Increasing the propanol concentration did not significantly improve the solubility of the oxidation product. Also, the product decomposes rapidly if the test pH falls out of the range of 6.5 to 6.8.

The *Standard Methods* procedure calls for a phosphate buffer to control the sample pH at 6.6. Hach Company's research has shown that sample hardness at levels as low as 200 mg/L CaCO₃ will have an appreciable effect on the stability of the colored product. Precipitation of calcium phosphate destroys the buffer capacity, with a resulting test pH lower than 6.5. At this pH, color fading is appreciable and color measurements must be made at standardized intervals. A maleic-hydroxide buffer system is an alternative for hard water applications but does not work well with samples with high alkalinity.

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

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 electrode 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 (I_2Cl^-) 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. Because the electrode will sense any oxidant capable of oxidizing iodide, species such as manganese, iodate, bromine, cupric and chlor-oxy 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 Cl_2) total oxidant can be achieved (Ref. 2.22), 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 (Ref. 2.23) 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. Wilde concluded the DPD method (using a Hach DR 100 Colorimeter Kit) is the recommended method for future monitoring at SRS due to its simplicity and suitability for both field and laboratory measurements.

Table 2.2 lists the common methods used for analysis of free or total chlorine disinfectants in water. Comparisons are shown for the analysis range, published detection or quantification limits, estimated precision and skill level required to perform the tests.

Method	Analysis Range (mg/L)	DL* (mg/L)	Estimated Precision (% RSD [†])	Application	Skill Level [‡]
DPD Colorimetric	0-5	0.005	1-2%	Free and Total	1
ULR-DPD Colorimetric	0-0.500	0.002	5-6%	Total	2
DPD Titration	0-3	0.018	2-7%	Free and Total	2
Iodometric	up to 4%	1	NR	Total Oxidants	2
Amperometric Titration					
Forward	up to 10	0.0012	1-2%	Free and Total	3
Back	0.006-1.00	0.0051	2-4%	Total	3
FACTS	0-10	0.1	10%	Free	1
Electrode	0-1	0.05	10%	Total Oxidants	2

* Minimum or Estimated Detection Level
[†] % Relative Standard Deviation
[‡] 1 = minimal training, 2 = moderately skilled with method, 3 = experienced
 NR = not reported

Table 2.2: Comparison of Common Analytical Methods for Free and Total Chlorine in Water

3. Method Interferences and Sources of Errors

3a. Sampling Considerations

A 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 very low. It readily reacts with various inorganic compounds and 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 (*Ref. 3.1*).

Ideally, samples should be analyzed 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. Plastic sample containers should be avoided because they might exert an appreciable chlorine demand. Clean glass sample containers should be pretreated by soaking in a dilute bleach solution (1 mL commercial bleach solution to 1 liter of water) for at least one hour. After soaking, they should be rinsed thoroughly with deionized or distilled water or the sample. Another treatment is required only occasionally if sample containers are rinsed with deionized or distilled water after use.

Do not use the same sample containers for free and total chlorine analysis. If trace iodide (from the total chlorine reagent) is carried over into the free chlorine determination, monochloramine will interfere in the free chlorine test. Ideally, separate and dedicated sample containers would be used for free and total chlorine determinations. A pre-treated BOD bottle, with ground glass stopper, makes an ideal sample container for chlorine analysis. For on-site determinations using Hach DPD colorimetric procedures, the one-inch square or cylindrical DR cell serves as an excellent sampler.

Avoid excess agitation and exposure to sunlight when sampling. Allow several volumes of the container to overflow and cap the sample container to eliminate head space above the sample. 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 Ampuls, collect sample in a wide-mouth container, such as a beaker, rinsing several times with sample. Proceed with the analysis immediately.

If the iodometric back-titration methods (either visual or amperometric end point) are used for total chlorine determinations, 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 standard thiosulfate or PAO, 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, 200 mL of sample are measured and carefully transferred to the sample container and swirled to mix.

The delay between sample fixing and analysis should be minimized (usually less than one hour) to prevent bacterial decomposition of excess thiosulfate (or PAO) in the sample. It is important that the entire contents of the sample container be transferred to the analysis glassware used in the titration.

3b. 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. It should be emphasized that each of the chlorine methods is based on the total oxidizing capacity of the sample being analyzed and is readily subject to interferences from other oxidizing agents. Generally, all the accepted methods for chlorine are subject to potential interferences from particles, color, inorganic and organic compounds, and buffer capacity in the sample. Unfortunately, there is no “ideal” method for chlorine analysis which is specific and selective for the free chlorine and chloramine species.

Other Disinfectants

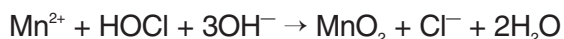
In general, all of the common chlorine methods will detect other oxidants used as disinfectants — such as chlorine dioxide (ClO_2), ozone (O_3), bromine (Br_2), hydrogen peroxide (H_2O_2), and disinfectant by-products such as chlorite and chlorate — if present in large amounts. In the free chlorine determinations, these oxidants, in sufficient concentration, can react directly with the colorimetric indicator or 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. Hach Company 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 extra required 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 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:



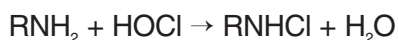
Apparently, chloramines will not oxidize manganous compounds. Oxidized manganese will react directly with the DPD indicator. It is claimed that Mn (+4) does not interfere in the FACTS method at a 1.0 mg/L level (*Ref. 3.2*). At 2.6 mg/L Mn (+4), interference is noted after five minutes with the FACTS test. Oxidized manganese (+4 to +7) also will interfere in the amperometric titration for free chlorine.

Iodide can be oxidized by Mn (+4 to +7) to I_2 , 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 (*Ref. 3.3*).

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. Unfortunately, alternative reducing agents, such as PAO, thiosulfate, or ferrous salt, cannot be used because they also will reduce Mn (+7).

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:



where R = the organic moiety

Typical organic nitrogen compounds would include common amino acids and heterocyclic bases. Free chlorine reacts quickly with these types of compounds to form non-germicidal organic chloramines.

Published studies (*Refs. 3.4, 3.5*) have concluded that certain organic chloramines, especially N-chlorinated

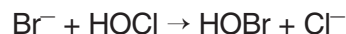
amino acids and N-chlorinated heterocyclic compounds, will interfere with all the common analytical methods for free chlorine. However, chlorinated amino acids do not appear to interfere in the free chlorine DPD and FACTS methods.

White (*Ref. 3.6*) has contested the validity of organic chloramine interference in the amperometric titration method. Based on his observations and surveys of wastewater disinfection systems, he contends that organic chloramines will be detected only as the dichloramine fraction when titrated in a forward amperometric titration.

At this time, the interference of organic chloramines in the free chlorine tests must be considered conditional, pending additional research.

Bromide in Chlorinated Waters

Sea water 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:



This reaction is irreversible and the product will interfere with all common analytical procedures for free chlorine.

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.

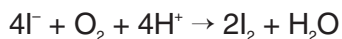
It should be noted that bromide, when present in a chlorinated sample, forms a disinfectant (hypobromite and/or bromoamines) and, technically, the analytical results would indicate the total oxidizing capacity of the sample.

3c. Errors Common to Total Chlorine Determinations

All of the common total chlorine methods are based on the oxidation of iodide to triiodide ion. There are several potential sources of errors related to the iodide/triiodide reaction. They include:

- 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 reagent is subject to air oxidation by the reaction:



The reaction is accelerated by decreasing pH, light and traces of metal ions. 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 (*Ref. 3.7*). An EPRI recommendation stipulates KI solutions be prepared fresh daily and stored in the dark.

Alkaline iodide solutions apparently are much more stable to oxidation than at neutral or low pH. A trace amount of base (e.g., sodium hydroxide) should be added to stock iodide reagent solutions for best stability.

Volatilization of free iodine from the reaction of oxidant with iodide is diminished somewhat in that excess iodide is present in the sample. In the presence of excess iodide, the less volatile triiodide ion forms. According to EPRI, the error due to iodine volatilization will likely be only a small percent (*Ref. 3.8*). The speed of the analysis also is a determinant for minimizing iodine loss by volatilization.

The purity of the 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 or chloramines or the indicator reagent itself. Even solid potassium iodide can be oxidized provided sufficient exposure to oxygen and ultraviolet 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 I_2 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 (*Ref. 3.9*). This is one reason for the traditional preference of the back-titration methods for total chlorine in sewage treatment plant effluents.

3d. Interferences in the DPD Methods

Calibration Non-Linearity

As stated in **Section 2a.**, 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 and results in apparent “fading” of the colored solution. It is necessary that the DPD: oxidant ratio remain high to minimize fading of the resulting color.

The non-linearity of the DPD colorimetric method calibration using the *Standard Methods* procedure has been reported by Gordon and co-workers (*Ref. 3.10*) and confirmed by Hach Company chemists. 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 Company also has confirmed the non-linearity of the *Standard Methods* procedure using free chlorine standards.

The non-linearity of the *Standard Methods* calibration (**Figure 3.1**) 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, less active DPD free amine is available to react with sample chlorine, thereby shifting the DPD:oxidant ratio. This would lead to increasing non-linearity at the higher chlorine levels as the DPD reagent solution ages and becomes oxidized.

Hach Company has optimized its DPD reagent formulations to obtain a linear response to chlorine over the test range. Hach DPD reagents are controlled to assure linearity over the specified range. Because Hach DPD powdered formulations offer superior stability over the liquid reagent formulations, a reproducible and linear response to chlorine will be obtained for a longer period of time.

It should be noted that 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.

Precautions Using Permanganate as an Equivalent Standard

Dilute solutions of potassium permanganate are used in *Standard Methods* as equivalent standards for establishing a chlorine calibration. It should be emphasized that permanganate is a stronger oxidant than chlorine and certain precautions on its use and storage should be acknowledged. As noted by Gordon, et al. (*Ref. 3-10*), permanganate oxidizes DPD to both the colored

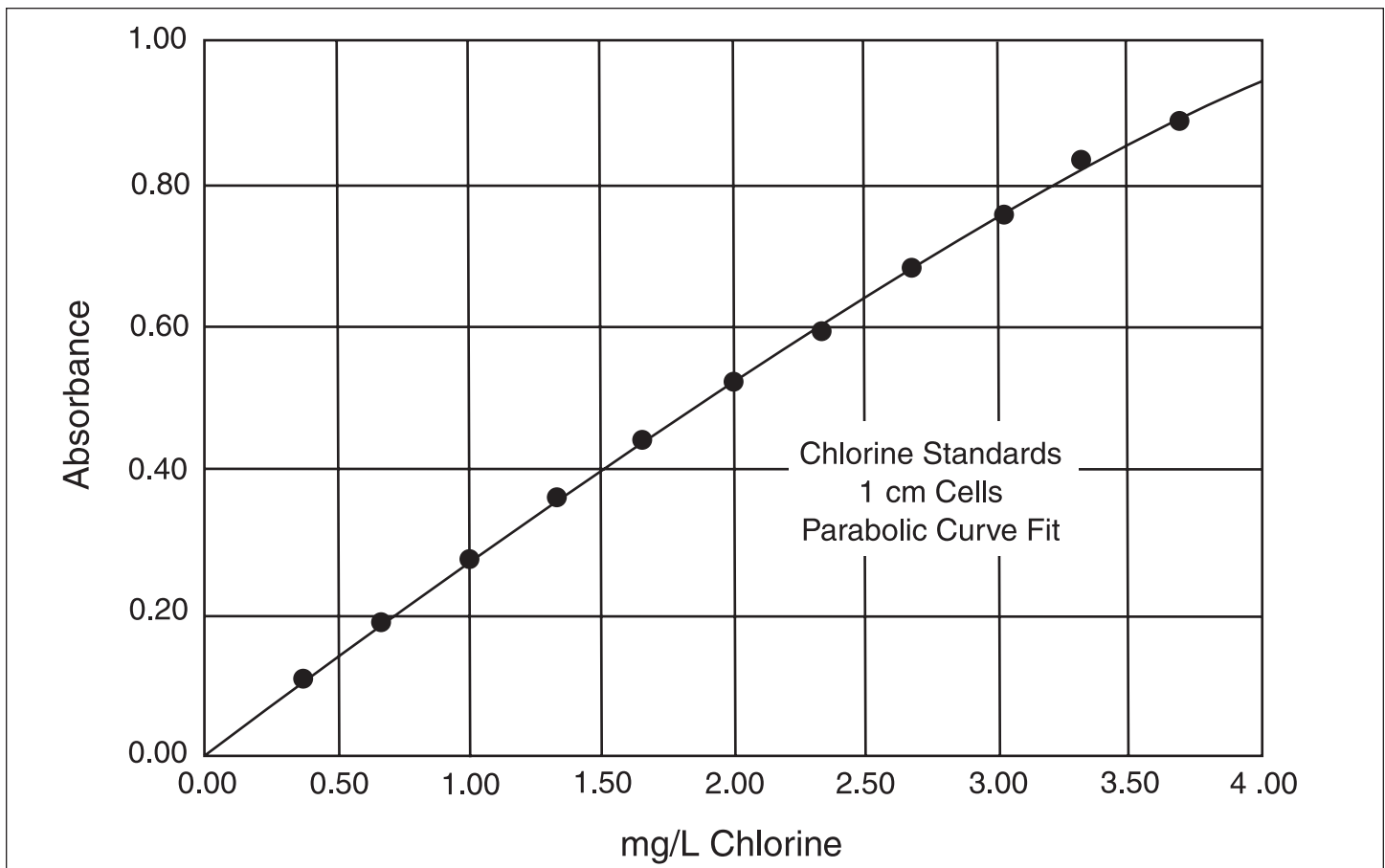


Figure 3.1: *Standard Methods Calibration - DPD Colorimetric Method*

and colorless oxidation product. Hach Company researchers have noted the order of adding reagent to sample also 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 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, if the free chlorine DPD indicator/buffer reagent is placed in the sample cell and permanganate is added to it, 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. **Table 3.1** shows 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.

It should be noted that the "order of addition" effect has been noted only when using permanganate standards. This effect has not been noted when dilute chlorine standards were used.

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

1. Glassware used in the preparation and dilution of permanganate solutions should be treated with chromic acid cleaning solution to remove any organic contamination. Then glassware should then be rinsed copiously with pure water, which is low in organics.
2. 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 (*Ref. 3.11*). Dilution water for permanganate should never be stored in plastic containers or exposed to airborne contamination. The stock solution should be standardized routinely with dried sodium oxalate (*Ref. 3.12*).
3. Dilute equivalent standards are not stable and should be prepared as needed. Never store dilute permanganate in plastic containers.

Equivalent mg/L Cl ₂	Reagent-to-Sample		Sample-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 Company's DPD Free Chlorine Powder Pillows, Cat. No. 14070, and DR 3000 Spectrometer with pre-programmed calibrations

Table 3.1 Order of Sample-to-Reagent Addition Using Permanganate Equivalent Standards

Because of these constraints, Hach Company does not recommend the use of permanganate equivalent standards with Hach DPD reagents. Alternatively, Hach Company recommends the standard additions technique using Chlorine Voluette® Standards for routine verification of pre-programmed calibrations.

The Chlorine Voluette standards are pure aqueous free chlorine standards prepared in two ranges — 20 - 30 mg/L or 50 - 75 mg/L chlorine. The actual value is provided for each lot of standards. Hach Company research has shown that the ampuled chlorine standards exhibit excellent stability, when stored at temperatures between 2 to 8 °C (33 to 47° F).

A simple procedure is used to verify the accuracy of the chlorine calibration. For example:

- a) Snap the top off a Chlorine 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. The exact value depends on the Voluette concentration. Check the certificate enclosed with the Voluette Ampules for this value.

Refer to Hach Company's *Water Analysis Handbook* (Ref. 3.13) for more information on the standard additions technique for verification of accuracy.

Monochloramine Interference in the Free Chlorine Test

There is considerable controversy about monochloramine interference in the free chlorine DPD test. Some studies (Ref. 3.14) have indicated the percent interference in the free chlorine results can vary from 2.6 to 6.0%, depending on the monochloramine concentration and sample temperature.

The amount of monochloramine must be substantial in comparison to the free chlorine concentration to indicate an interference in the DPD colorimetric free chlorine determination. The reaction of DPD with free chlorine is rapid. If the color is measured within one minute, the monochloramine breakthrough will be minimal. A concentration of 3.0 mg/L monochloramine (as Cl₂) will cause an increase of less than 0.1 mg/L free chlorine when using Hach DPD colorimetric tests.

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 of free chlorine in the presence of more than 0.5 mg/L chloramines.

Hach Company does not recommend the use of thioacetamide in the free chlorine DPD titration or colorimetric methods for two reasons:

1. Thioacetamide has been shown to be 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? To date, no independent validation or optimization has been conducted with the thioacetamide modification procedure.

If free chlorine is to be tested in the presence of a significant amount of monochloramine, the free chlorine DPD colorimetric test is the recommended procedure.

Some published reports (*Refs. 3.15, 3.16*) indicate mercuric chloride, added to the *Standard Methods* liquid phosphate buffer, has an inhibitory effect on monochloramine breakthrough in the DPD free chlorine determination. The mercuric salt may scavenge trace iodide, thereby minimizing monochloramine oxidation. Here again, because this phenomenon is not completely understood and because of the toxicity of mercury salts, Hach Company does not recommend or use mercury in any of its DPD reagent formulations.

Stability of the Colored Reaction Product

The colored product formed on reaction of DPD with chlorine (or iodine in the total chlorine test) at neutral pH is a relatively stable, cationic free radical (*Ref. 3.17*). Continued oxidation of the free radical will develop the unstable colorless imine compound and result in apparent fading of the reacted sample color over time. The potential for the free radical to polymerize and form insoluble products also has been cited as a possibility for reaction product instability (*Ref. 3.18*). When limiting the oxidation of DPD to the Würster dye stage, it is important to optimize and control the ratio of indicator to oxidant. A large excess of indicator should be avoided because this would contribute to the reagent blank and possible monochloramine breakthrough.

Dissolved oxygen in the sample can promote additional oxidation of the DPD colored product. Trace metals in the sample and exposure to light may catalyze the oxidation (*Ref. 3.19*). Controlling the test pH is important because the reaction rate of DPD with oxygen is pH-dependent. Ideally, the reaction pH should be lowered if controlled oxidation is the primary concern. Other factors, such as the presence of nitrites, must be considered. Nitrites can occur under certain anaerobic conditions, and their interference will increase with decreasing pH. Hach Company has found that a reaction pH controlled within the range of 6.0 to 6.8 appears optimum for water and wastewater analysis with minimum interference from dissolved oxygen or nitrites present in the sample.

Sufficient color development time is necessary to resolve dichloramines at cold sample temperatures. Conversely, longer waiting times can result in color fading due to further oxidation, polymerization or side reactions of the free radical. For successful testing, especially in treated effluents, strict adherence to the development time is necessary. Three to six minutes of development time are sufficient to resolve all chloramine forms without significant error from competing reactions.

Compensation for Sample Color and Turbidity

One critical problem when applying colorimetric procedures to treated wastewaters is interference from turbidity and color in the water. For certain parameters, a preliminary filtration can be performed to remove particulate matter from the sample. The residual sample color is "zeroed" at the measuring wavelength with the color-measuring instrument.

Standard Methods compensates for sample color and turbidity simply by zeroing the photometer with sample (*Ref. 3.20*). This is appropriate for most colorimetric testing. When testing for trace levels of total chlorine in treated wastewater using Hach Company's ULR-DPD procedure, fine particulate matter may cause a "noise" level of up to ± 0.010 absorbance (using a 1" pathlength 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. Adsorption of the hypochlorite ion on, or reaction with, certain filter material also can lead to chlorine loss during the filtering process.

Hach Company studies indicate if the 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. Some membrane filter compositions have a surface charge that would exclude using them. The selection of filter porosity also is critical in terms of adequate removal of the particle sizes that could interfere at the absorption wavelength.

In the ULR-DPD Total Chlorine procedure for treated wastewater, sample turbidity is removed, using a syringe filter apparatus 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.

3e. Interferences in the Amperometric Methods

Standard Methods states the amperometric method “is the method of choice because it is not subject to interference from color, turbidity, iron, 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:

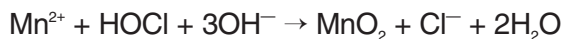
Deposition on Electrode Surfaces

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.

For Hach Company’s dual platinum electrodes (DPE), regular cleaning and conditioning are necessary to remove any oxidation of the metal surfaces and to sensitize the electrodes to chlorine. Cleaning involves soaking the electrode surfaces with a 1:1 Nitric Acid Solution for a short period of time and then rinsing the probe repeatedly with distilled or deionized water. The cleaned probe is stabilized by soaking the platinum electrodes in chlorinated tap water or a dilute (1-5 mg/L chlorine) solution of commercial bleach, while stirring. Allow at least 10 minutes for probe stabilization in the chlorinated water. Performing a couple of test titrations with chlorine or iodine standards prior to actual sample titration will further stabilize the probe. The frequency and quality of samples titrated will dictate the need for probe cleaning and conditioning.

Manganese Interference

There is a certain ambiguity in the literature concerning manganese interference in the forward and back amperometric titrations for chlorine. As explained in **Section 3.b**, if the sample contains free chlorine, any soluble manganese will be oxidized:



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

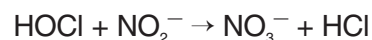
Nitrite can exist as a transitory compound in certain waters, due to the biological oxidation of ammonia:



There is conflicting information about the interference of nitrites in either the forward or backward amperometric methods for total chlorine. According to *Standard Methods*, nitrites do not interfere in the forward titration methods (Ref. 3.22). *Standard Methods* section 4500-Cl Cb., the Iodometric Method II, states that nitrite interference can be minimized by buffering to pH 4.0 before addition of iodide. It also states that interference from more than 0.2 mg/L of nitrites can be controlled by the use of a phosphoric acid-sulfamic acid reagent. This reagent is used in conjunction with iodate as titrant because higher acidity is required to liberate free iodine.

White (Ref. 3.23) indicates nitrites can oxidize KI to iodine, similar to the reaction of KI with chlorine or chloramines. The reaction of KI with nitrite apparently is accelerated by acidity, especially when the pH is less than 4. White recommends the addition of sulfamic acid to the sample containing nitrites and allowing it to stand for 10 minutes prior to the addition of standard reducing agent. This procedure does not, however, address the possible loss of chloramines or side reactions during the delay period.

Hach Company researchers, using the forward- and back-titration procedures, have investigated the effect of nitrites in the determination of monochloramine. Monochloramine was selected since it is slow to react with nitrites (Ref. 3.24) and represents the primary disinfectant form in treated wastewater. Free chlorine has been shown to react directly with nitrites (Ref. 3.25) according to:



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, then pH 4 buffer (iodine as titrant)
4. Back titration, excess PAO, buffer, then KI (iodine as titrant)
5. Back titration, excess PAO, KI, then H₃PO₄/sulfamic acid (iodate as titrant)
6. Back titration, excess PAO, H₃PO₄/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 (Cl₂). 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 **Figure 3.2**.

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 - 50 mg/L, will 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 Company studies, however, indicate nitrite as low as 5 mg/L will “break through” within 30 seconds after addition of the KI and acid mixture.

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, indicating 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

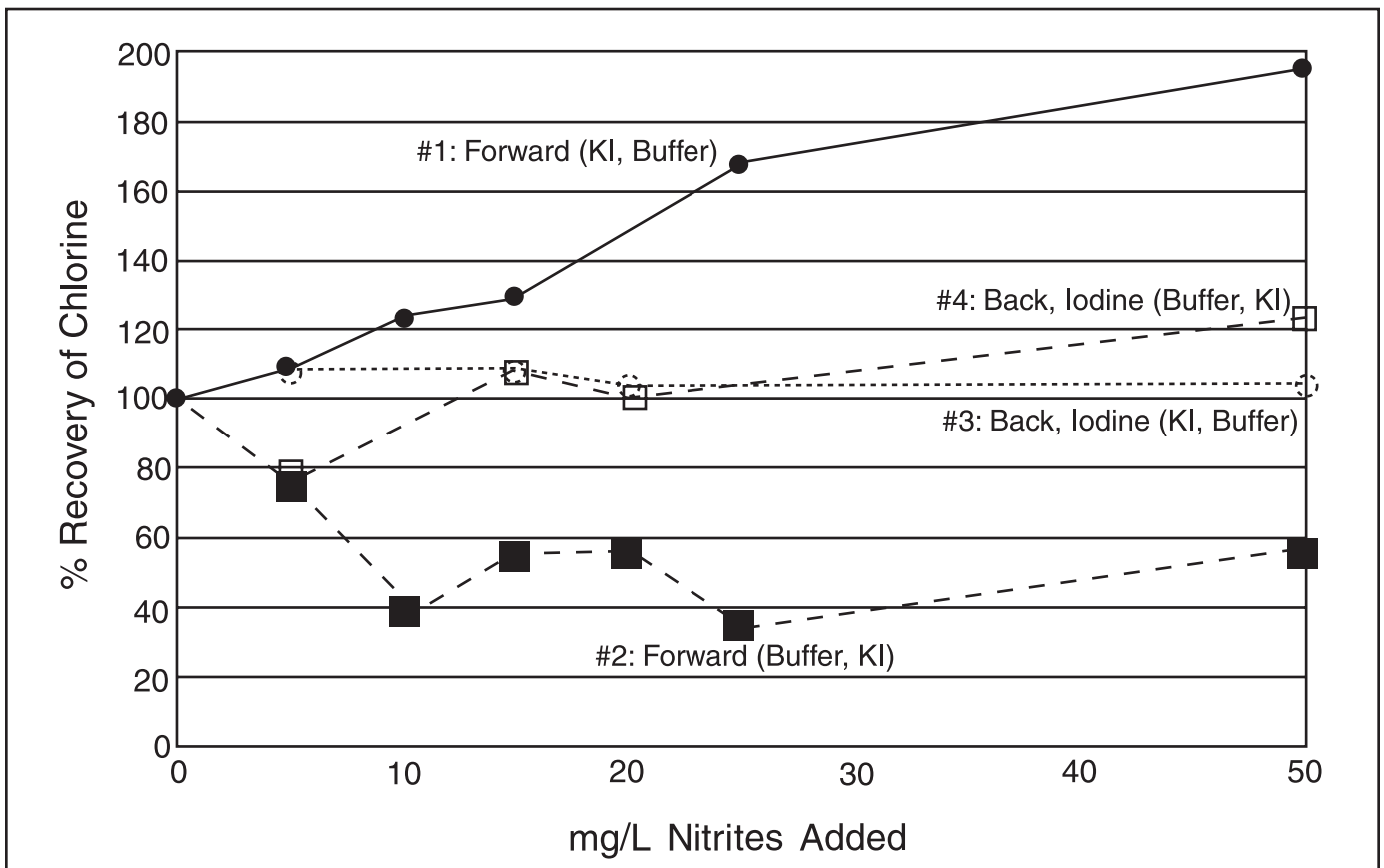


Figure 3.2: Nitrite Interference in Amperometric Chlorine Methods

the amperometric titration of total chlorine in treated wastewaters, agricultural waters and industrial discharges.

Hach Company has developed a convenient amperometric back-titration procedure using Standard Iodine Titrant, 0.0282 N. Hach Company researchers have investigated the factors which affect stability of dilute aqueous triiodide (I_3^-) solutions. A standard iodine titrant, which is stable for months when stored at moderate temperatures, is now available. With micro-dispensation of the titrant and automatic determination of the titration end point, total chlorine levels as low as 1.2 $\mu\text{g/L}$ can be detected.

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. This is shown comparatively in **Figure 3.3**. The titration

plots show the titration of an 82 $\mu\text{g/L}$ 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 a certain amount of uncertainty when determining the end point graphically (as indicated in **Figure 3.3a**). The use of PAO gives a relative sharper end-point determination (**Figure 3.3b**).

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.

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.

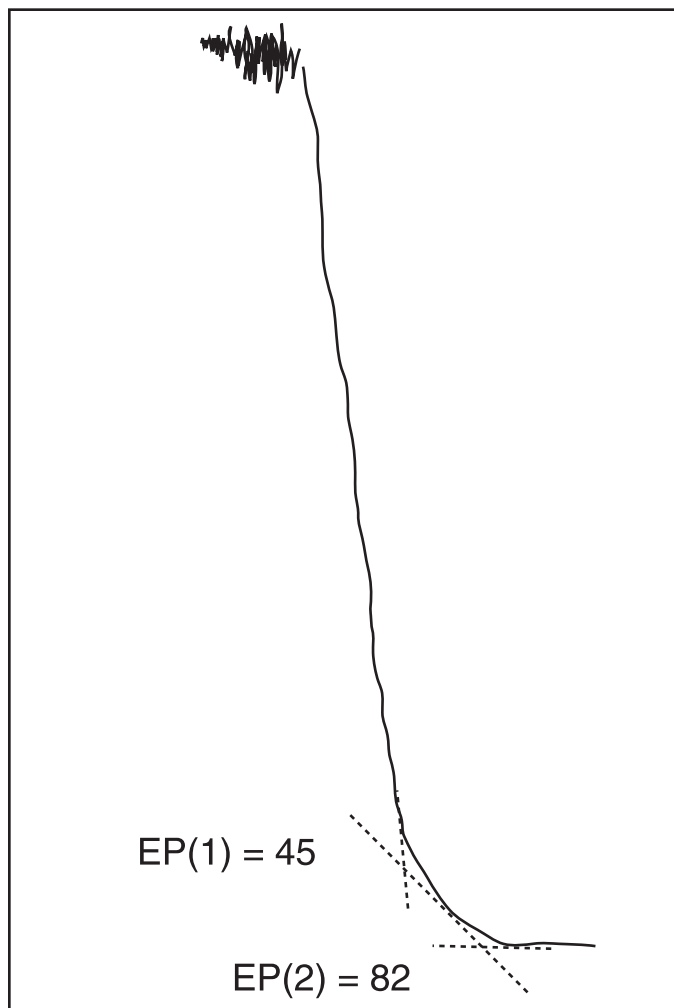


Figure 3.3a: Thiosulfate as Titrant

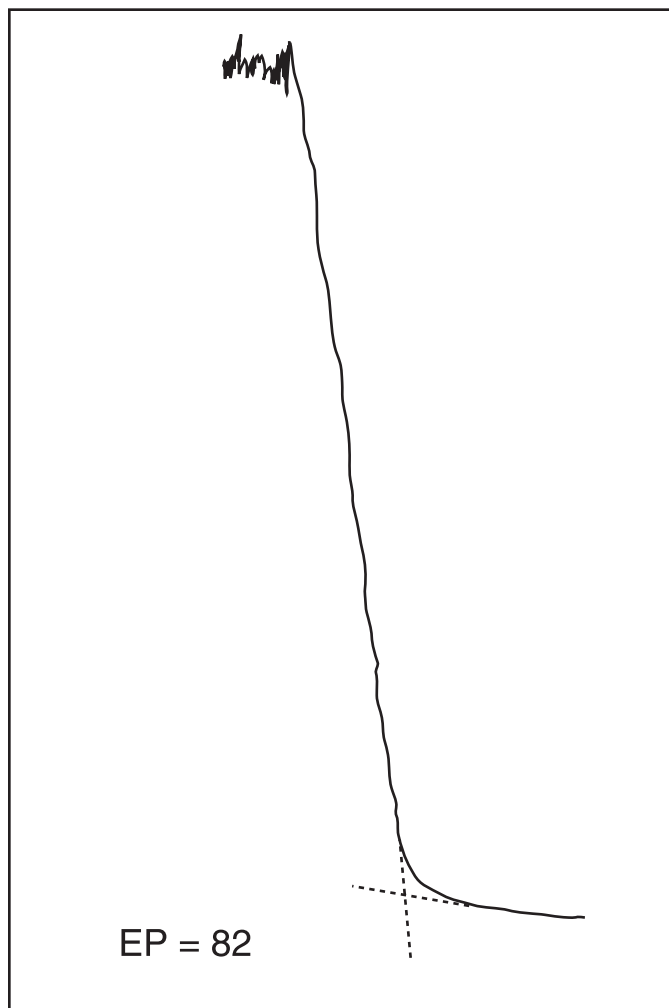


Figure 3.3b: PAO as Titrant

An example of this effect is shown in **Figure 3.4**. If the sample contains suspended particles, generated 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, some difficulty will be encountered in achieving an accurate estimation of the end point. Continuing the titration to obtain several readings after the end point will help in the interpolation of the two intersecting lines. Also, 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

The measurement of chlorine in saline and estuary water or sea water is exceedingly difficult with any of the available analytical methods. There is a certain amount of 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.

It should be emphasized that the chemistry of chlorine in sea water is exceedingly complex. Saline waters usually contain an appreciable chlorine demand, due in part to oxidation of carbon and nitrogen-containing compounds. Bromide, usually present in sea water, will oxidize to 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 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 oxidant concentration may be underestimated.

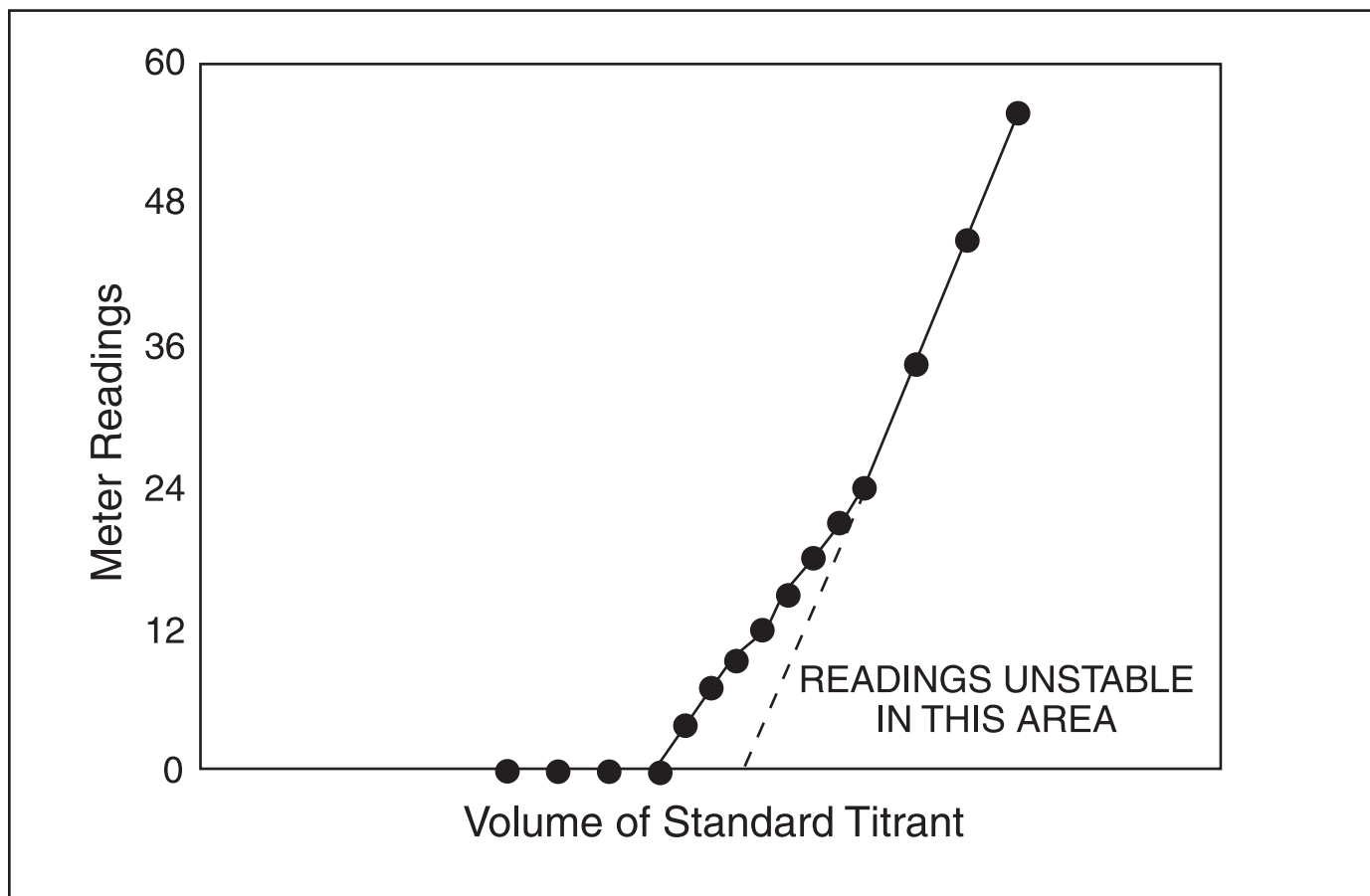


Figure 3.4: Iodine Demand - Back Titration

4. Method Comparisons and Performance Evaluations

Several comparative studies of the analytical methods for chlorine analyses have been published. For a comprehensive survey of laboratory method comparisons, see AWWA's *Disinfectant Residual Measurement Methods* (Ref. 4.1). A summary of published studies which have compared the Hach DPD method of analyses to other chlorine methods appears below. A note of caution is advised in the interpretation of early method comparison studies because the technology has improved over the years.

4a. Field Kit and Laboratory Comparisons

1978: USEPA-EMSL Report EPA 600/4-78-019

“Comparison of Methods for the Determination of Total Available Residual Chlorine in Various Sample Matrices” by Daniel F. Bender

This study compared 10 methods for the measurement of total chlorine in various matrices. Three versions of the DPD colorimetric method were used: the *Standard Methods* 409F, Hach Company's CN-66 visual comparator, and the Bausch & Lomb's Mini Spec 20 Kit. The samples studied were: spiked distilled water, river water, sewage plant influent and effluent, and unspiked tap water.

The iodometric forward titration (IFT) was chosen arbitrarily as the reference method. The accuracy of each method was expressed as percent recovery of total chlorine compared to the IFT method. Precision was established from the relative standard deviation (%RSD) derived from replicate analyses at a certain concentration.

During this study, Hach Company's CN-66 produced unacceptably high recovery (134%) in drinking water and low recovery (52%) in river water matrix, but only slightly high results (105-109%) in distilled water and sewage effluent matrices, compared to the IFT method. Turbidity and deep straw color of the sewage influent sample prevented it from being tested by the comparator.

Precision for the CN-66 was “remarkable” (3-5% RSD), considering a comparator was used.

1991: *Water Resources*, Volume 25, No. 10, p. 1303-1305

“Comparison of Three Methods for Measuring Residual Chlorine” by Edward W. Wilde

Results obtained when using a Hach Company DR 100 Colorimeter for total residual chlorine were compared to results obtained from a Fisher chlorine amperometric

titrator and an Orion ion selective electrode (ISE) on standard solutions and cooling water samples at the Savannah River Site nuclear facility.

Testing of chlorine standards prepared in high purity water showed no statistically significant difference among the three analysis methods. In contrast, the results on unchlorinated, chlorinated and chlorinated/dechlorinated cooling water samples indicated that the measurements with the Hach DR 100 did not differ significantly from measurements obtained with the amperometric titration method. Measurements made with the ISE method, however, were significantly lower than those made with the DPD and amperometric methods.

The author concluded the DPD method using Hach Company's DR 100 is the most appropriate technique for future monitoring of residual chlorine at the Savannah River Site. Simplicity and suitability for both field and laboratory measurements were determining factors.

1993: *Water Environment Research*, Volume 65, No. 3, p. 205-212

“Comparison of Free and Total Chlorine Measurement Methods in Municipal Wastewater” by James Derrigan, Li-Yin Lin, and James Jensen

In this study, four titrimetric methods for total chlorine (iodometric with starch end point, forward amperometric, back amperometric, and DPD titrimetric) were compared in testing chlorinated municipal wastewater samples. In addition, on-site measurements were made using an unspecified Hach Company test kit based on the DPD colorimetric method.

Cross comparisons of the data from all the methods on six samples collected from the chlorine contact basin indicated the plant readings with the on-site DPD colorimetric kit compared favorably with the laboratory results. Although the study was limited in the comparison of Hach Company's DPD method with the *Standard Methods* titrimetric procedures for chlorine, the authors concluded the on-site DPD colorimetric readings were in agreement with results obtained with the forward and back amperometric titration methods.

1993: Proceedings of the 66th Water Environment Federation Conference "Application of the DPD Colorimetric Method for Measuring Trace Residual Chlorine" Paper AC93-059-002, by Danial L. Harp

Hach Company's ultra-low range chlorine DPD (ULR-DPD) method was compared to the Standard Methods back amperometric titration method (4500-Cl-C) using iodine titrant on nine geographically dispersed samples. Treated wastewater samples 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 blowdown and manufacturing wastes.

Samples were treated with a suitable amount of hypochlorite to satisfy any chlorine demand. While samples were aging in the dark under nitrogen gas, chlorine was added to obtain a total chlorine residual

between 5 - 400 $\mu\text{g/L}$. Aliquots were drawn at varying concentration levels and tested by both the ULR-DPD and back amperometric methods. At least eight data pairs (ULR-DPD vs. Amperometric) were obtained for each sample within the 5 - 400 $\mu\text{g/L}$ chlorine range.

In addition, a small amount of known hypochlorite addition (a "spike") was added to a second aliquot of each sample and tested by the two analysis methods. This provided an estimate of the accuracy of the methods, as percent recovery of the spike.

Figure 4.1 shows 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 back amperometric method within this concentration range.

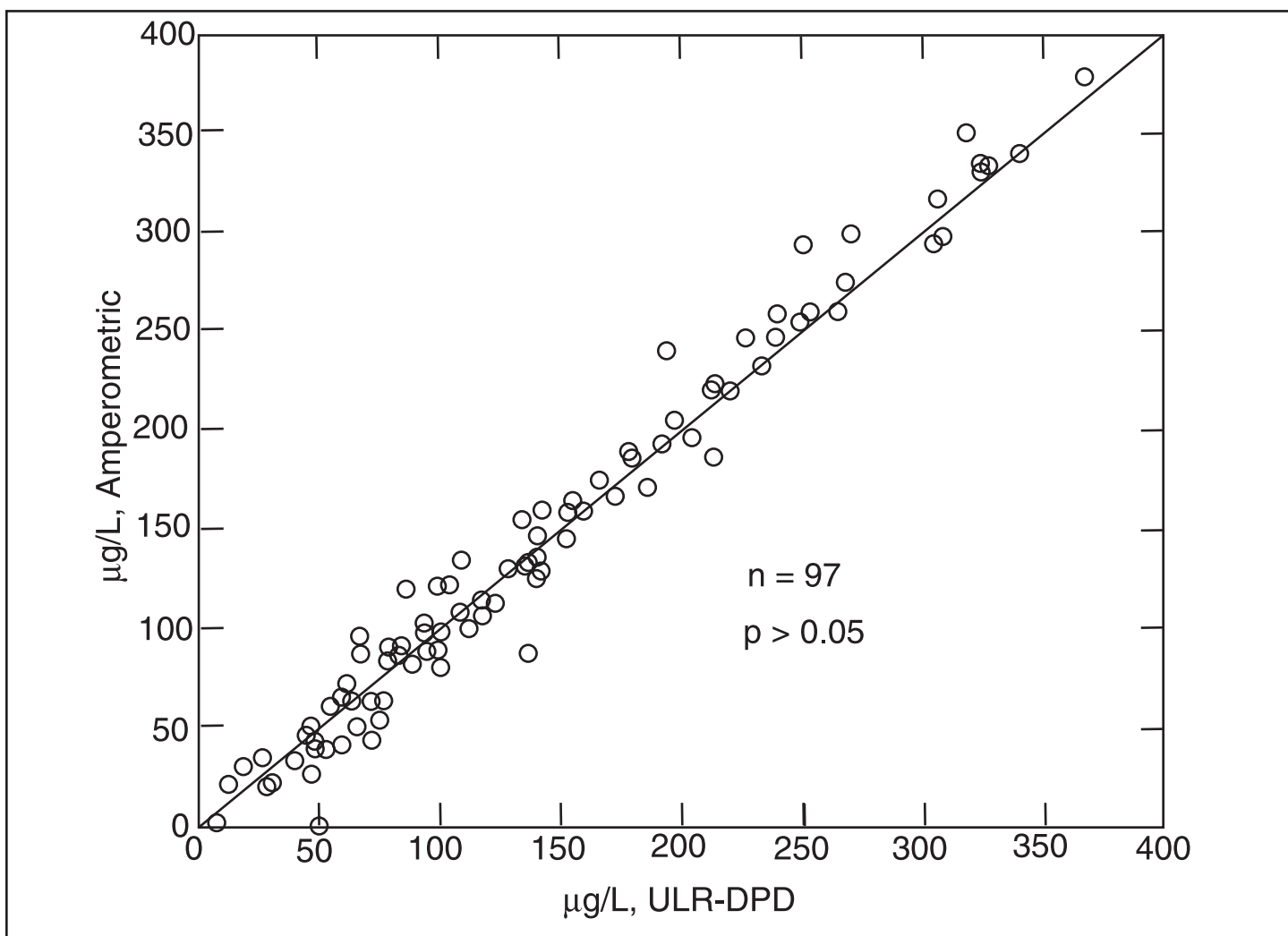


Figure 4.1: Method Comparison Data: Ultra-low Range Chlorine Methods

The percent recoveries obtained from the spiked sample data ranged from 82.8 to 97.8% (mean = 90.5%) for the ULR-DPD method and 92.5 to 136.6% (mean = 112.0%) for the back amperometric method.

4b. Performance Evaluations of Process Analyzers for Residual Chlorine

The Water and Wastewater Instrumentation Testing Association (ITA, formerly known as Instrument Testing Service) has conducted two comprehensive evaluations of residual chlorine analyzers (*Refs. 4.2, 4.3*). ITA is a non-profit association set up to perform independent testing and evaluation of instrumentation used in the water and wastewater treatment industries.

The initial ITA effort was the assessment of total residual chlorine (TRC) analyzers, performed during 1983-1984. The testing program included bench analysis of on-line TRC analyzers under controlled conditions and field testing at a wastewater treatment site in Ontario, Canada. Bench testing was performed on four different analyzers: two based on amperometric detection, one based on potentiometry, and Hach Company's Pump Colorimeter™ Analyzer (PCA), based on the DPD colorimetric analysis. The bench testing program involved a series of tests to evaluate the mechanical and electrical components of the instruments and instrument performance under standard conditions.

Three analyzers representing amperometric, potentiometric and colorimetric detection were used for field testing. Protocol for the field evaluation included long-term performance, calibration, response time, interferences and general design factors. The DPD colorimetric method was selected as the reference laboratory test method for TRC in the analyzer evaluations.

The bench-test results demonstrated the adequacy of the electrical and mechanical components of the instruments. In general, the instruments performed per specification during the bench wet tests. Hach Company's PCA showed relative insensitivity to either sample temperature or ambient temperature fluctuations. The minimum detectable limit was determined to be 0.009 mg/L as Cl₂ for the PCA.

Field testing results indicated the PCA's accuracy, response time and recovery time were relatively unaffected by continuous exposure to wastewater after 60 days of exposure. The PCA was the only analyzer not requiring maintenance beyond routine calibration and reagent replacement during the evaluation period.

The ITA research group concluded the Hach Company Pump Colorimeter Analyzer overall “exhibited accepted accuracy over its normal operating range, and accuracy and response were unaffected by exposure to wastewater or by temperature changes.”

A second, more detailed evaluation of residual chlorine analyzers was conducted by the ITA during 1989. In this study, both free and total residual chlorine analyzers were tested. Six different manufacturers' on-line chlorine analyzers were tested on the bench and in the field. The analyzer types included three based on amperometry, one with a polarographic probe, one with an iodine ion-selective electrode, and Hach's CL17 free and total chlorine analyzers, based on DPD colorimetry.

The bench tests assessed reproducibility, response, noise, calibration, detection limit and temperature effects under controlled conditions. Field tests consisted of operating the free chlorine analyzers at an operating drinking water treatment plant and the total chlorine analyzers at a wastewater treatment plant for a period of 45 days. Accuracy of the analyzers was judged in the field twice daily by comparisons to laboratory results. In addition to quantitative tests, each instrument was subjected to a qualitative analysis to assess operational and maintenance performance in the field.

The CL17 analyzers exhibited good accuracy and reproducibility with little temperature effects. In addition, the instrument indicated one of the lowest detectable concentration levels of all analyzers tested at 0.013 mg/L Cl₂. The total chlorine CL17 showed the least interference when compared to the other commercial chlorine analyzers.

Relatively high maintenance (40 events) was required for the total chlorine CL17 during the field testing. This was due to sample line blockage, sample strainer cleaning, sample line tubing replacement and sample cell cleaning. Since the ITA evaluation, Hach Company has developed a self-cleaning Y-strainer designed for use with the CL17 analyzer. The strainer has since been shown to reduce maintenance requirements significantly in wastewater applications.

Complete test results for the bench and field evaluations of Hach Company's CL17 analyzers along with evaluations of competitor chlorine analyzers can be found in ITA's report, “*Performance Evaluation of Residual Chlorine Analyzers for Water and Wastewater Treatment Applications*,” Report CH-1 (*Ref. 4.3*).

5. Selection of the Appropriate Testing System

The selection of an analytical system for chlorine testing will depend on several factors and situations. For example, if chlorine testing is performed to meet regulatory compliance, the selected method must be acceptable to the regulatory agency. Under certain situations, the use of visual field test kits will provide acceptable results. Some situations require near continuous analyses using a process analyzer. The following will provide guidance in selection of the most appropriate chlorine test system for a particular situation.

5a. Field Testing

Test kits using color comparators or colorimeters based on the DPD colorimetric method are ideal for measuring free or total chlorine in water on site. **Table 5.1** compares the Hach Company DPD platforms designed for field testing.

Many of the visual comparator DPD kits are used for public and private swimming pools, aquariums, small and large industrial processes and small potable water treatment systems. These types of systems typically screen or check for maintenance of a chlorine residual. High degrees of accuracy and precision are not required and a visual color match is sufficient for estimation of the chlorine level. Color matching can be in the form of incremental steps, as in the Color Cube, or in the form of a continuous gradient, as in the Color Disc.

Test kits for measuring residual chlorine following the DPD methodology are recommended by the World Health Organization (WHO) in guidelines to small community supply systems (*Ref. 5.1*).

In recent years, the concept of on-site testing with a small, portable colorimeter has matured. Colorimeters eliminate the human errors associated with color matching. Hach Company pioneered this concept with the introduction of the DR and DREL portable colorimeters for chlorine testing in the 1960s. The first hand-held colorimeter for chlorine testing, the DR 100, was introduced by Hach Company in 1980. With the advent of accurate digital electronics, portable colorimeters have become more compact, durable and versatile. Examples of the latest technology trend include the Pocket Colorimeter™, the DR/800 Portable Colorimeter and the DR/2500 Spectrophotometer.

Most of the testing platforms listed in **Table 5.1** are acceptable for testing free chlorine or chloramines in potable water. Most potable water supplies are low in color and turbidity and show little chemical interference in the DPD method.

Many water utilities have scattered chlorination stations throughout their distribution systems. The best choices for this case would be a CN-70, a CN-80 or an AccuVac color disc test kit, or a portable photometer system such as the Chlorine Pocket Colorimeter. If additional parameters are tested at the chlorinating sites, a CEL/800 or DR/2400 Portable Spectrophotometer should be considered.

Many states regulations allow the use of DPD visual comparator kits in fulfillment of residual chlorine reporting requirements under the Safe Drinking Water Act. Local or state regulatory agencies should be contacted for specific information on the procedures and equipment specified for chlorine testing in each area.

DPD test kits and photometer systems are used routinely for monitoring free and combined chlorine residuals in treated wastewaters. If the wastewater is highly colored,

Type of Measurement	Platform	Product Examples	Test Ranges* (mg/L)
Visual Comparison	Color Cube	DPD Color Cube	0-2.5
	Color Disc	CN-66 test kit	0-3.5
		CN-70 test kit	0-0.7, 0-3.5
		AccuVac® Reagent Ampul	0-2.5
Colorimeter	Pocket Colorimeter	Pocket Colorimeter Cl ₂ Kit	0-2.0, 0-4.5(T)
	DR/800	CEL/800 Lab	0-2.0(F), 0-3.5(T)
Spectrophotometer	DR/2400	DR/2400 Portable Spectrophotometer	0-2.0, 0-5, 0-10
Titration	Digital Titrator	DPD-FEAS	0-3.0

* applies to both "free" and "total" unless otherwise noted
(F) = Free Chlorine
(T) = Total Chlorine

Table 5.1 Hach Company Field Testing Systems for Chlorine

it may be more practical to use the DPD-FEAS or iodometric titration methods with the Digital Titrator for field testing. If final dechlorinated effluent is tested, the ULR-DPD procedure for total chlorine can be used in conjunction with the portable DR/2400 Spectrophotometer for on-site testing. Hach Company's DPD chemistry is accepted by the USEPA for total chlorine testing under the NPDES program. Local or state regulatory agencies should be contacted for specific area information about total chlorine testing requirements for permitted discharge waters in that area.

Each of the visual comparators and the field instruments use the same proven Hach Company DPD colorimetric chemistry for chlorine testing. The amount of reagent fill per package (pillow, ampule, or container) is adjusted for the sample volume used — usually based on 5-, 10- or 25-mL sample sizes. The concentration range can be extended by varying the sample cell pathlength and adjusting the reagent to sample ratio. For example, in the CN-70 and CN-80 color disc kits, the sensitivity can be increased by using length-wise viewing.

5b. Laboratory Testing

Ideally, samples for chlorine analysis should be tested on site, as described in Section 3a. But if sample holding times allow, the best accuracy and precision for chlorine analysis are obtained with laboratory analyses. Laboratory methods for free and total chlorine include the DPD method — using a spectrophotometer, the amperometric titration methods and the titration methods with a visual colorimetric end point.

The DPD method using Hach Company's DPD pillows and a DR/2500 or DR/4000 Spectrophotometer is recommended for routine laboratory testing of free and

total chlorine residuals. The linear range for the spectrophotometers is 0-10.0 mg/L Cl₂. Higher levels of chlorine can be determined by dilution of the sample with chlorine-demand-free water. When samples are diluted, some loss of chlorine may occur. **Figure 5.1** illustrates a decision-tree for selecting the proper chlorine test.

The spectrophotometer procedures use a standard 10- or 25-mL sample size. Alternatively, reagents packaged into AccuVac™ Ampuls can be used for carrying out the chemistry and measuring the color with a spectrophotometer and special cell adapter.

The patented (Ref. 5.2) Ultra-Low Range DPD (ULR-DPD) colorimetric method for total chlorine uses a flow cell with either a DR/2500 or DR/4000 Spectrophotometer. The "Pour-Thru" cell eliminates optical errors caused by using discrete sample cells and contributes to accurate measurements of low color absorption. A filter assembly is required for highly turbid samples. For maximum sensitivity, the color measurements are made either at 510 or 515 nm.

The range for the ULR-DPD method is 0-500 µg/L chlorine with a method detection limit (MDL) of 2 µg/L. The ULR-DPD method is accepted by the USEPA for reporting purposes under the Safe Drinking Water act and the NPDES permit program.

Hach Company offers several procedures using Hach's AutoCat™ 9000. Procedures are available for total chlorine forward titration, range 0.0012 - 5.000 mg/L Cl₂, total chlorine back titration, range 0.0052 - 5.000 mg/L Cl₂, and free chlorine, range 0.100-5.000 mg/L Cl₂. Ranges can be extended by sample dilution. All of Hach Company's amperometric titration procedures are based on *Standard Methods* 4500-Cl or USEPA Method 330.

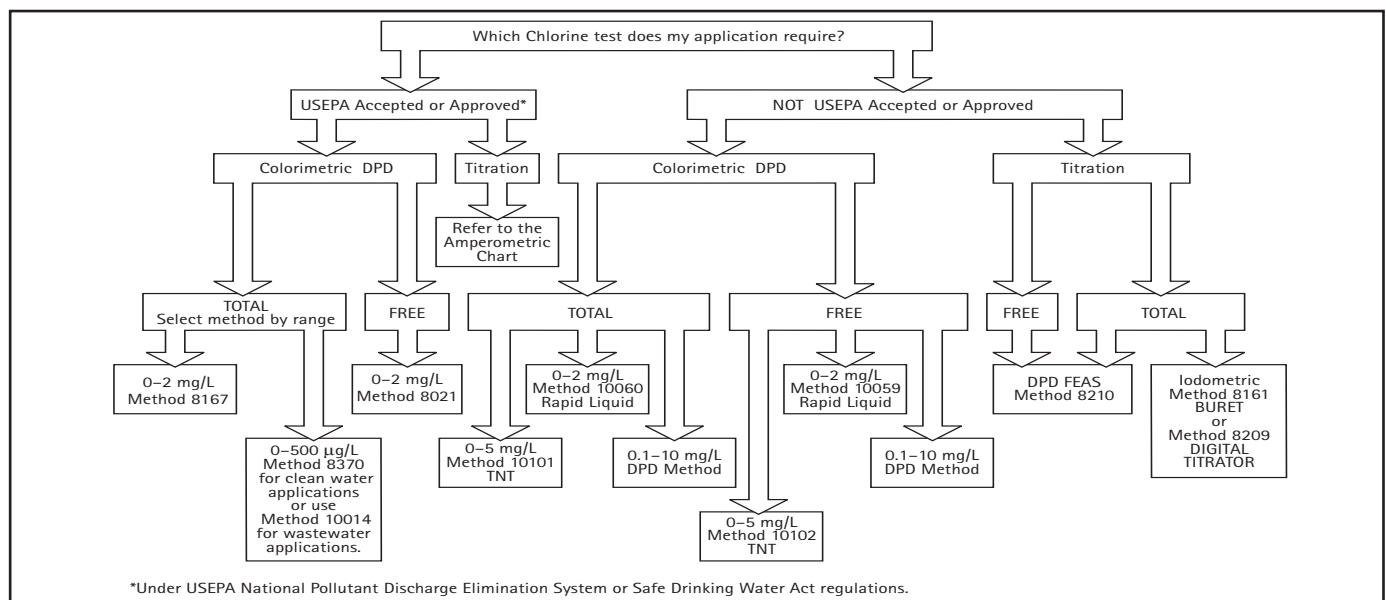


Figure 5.1: Selection of the Correct Amperometric Titration Procedure



Figure 5.2: CL17 Chlorine Analyzer

Hach Company titration methods for chlorine also include the iodometric method using sodium thiosulfate as titrant and the DPD titration method using ferrous ethylenediammonium sulfate (FEAS) as titrant. In these procedures, the titration end point is indicated by a visual color change.

5c. On-line Automated Testing

The Surface Water Treatment Rule issued by the USEPA (Ref. 5.3) requires that residual chlorine be monitored continuously on distributed water for systems serving more than 3300 persons. The CL17 Chlorine Analyzer (Figure 5.2) is used extensively at the point of distribution to ensure adequate chlorine residuals. The CL17 Analyzer also is used in cooling water treatment to prevent bio-fouling, in reverse osmosis systems to protect membranes, and in wastewater treatment to ensure regulatory compliance.

The analyzer is equipped with a two-reagent system based on the DPD chemistry. The DPD Indicator is prepared by adding the powdered DPD reagent salt to the acidic indicator solution. The powder readily dissolves in the solution and the mixed solution is stable for at least two months. Great care is exercised in manufacturing the DPD reagents to ensure the DPD Indicator Solution does not contain impurities which can promote oxidation of ionic DPD. After dissolution, the DPD Indicator Reagent Solution is free of insolubles which can exhibit a reagent blank or plug reagent tubing.

The buffer solution for the total chlorine CL17 Analyzer is a citrate-type which also contains iodide. The Free Chlorine Buffer Reagent is a maleate-type buffer.

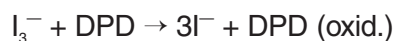
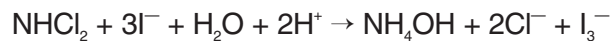
The buffer reagent and its complementary indicator reagent are added in equal volumes to a captured portion of sample. Pre-mixing the two reagents before introduction to the sample is important. This is accomplished by incorporating a “T” union in the reagent feed lines prior to the colorimeter block.

The operation cycle of the CL17 Analyzer is summarized as follows:

1. Sample inlet line of the pump/valve module is opened, allowing pressurized sample to flush sample tubing and the colorimeter sample cell.
2. Sample inlet is closed, leaving fresh sample in the cell. Cell volume is controlled by an overflow weir.
3. As sample inlet line closes, reagent lines open, allowing buffer and indicator solutions to fill tubing in the pump/valve module.
4. Reference measurement of untreated sample (a sample blank) is made prior to reagent addition. This compensates for sample color and turbidity.
5. Reagent outlet block opens, allowing precise volumes of buffer and indicator to blend and enter the colorimeter cell to mix with sample.
6. After about a one-minute delay for full development of color, measurement of the magenta color is taken at 510 nm (the sample measurement).
7. Concentration (as mg/L chlorine) is calculated by the log of the ratio of reference measurement to sample measurement, and then displayed.

The cycle sequence is repeated every 2.5 minutes.

For the on-line determination of total chlorine, the color development time required has been shortened by varying the test acidity and increasing the iodide concentration in the sample. Consider the reaction chemistry of dichloramine:



The rate of the first reaction is much slower than the rate of the second. The speed of the dichloramine-iodide reaction can be increased by increasing the iodide addition and/or adjusting the acidity. Acidity cannot be significantly increased, however, because of increased nitrite interference at a lower reaction pH.

Hach Company chemists have optimized the analyzer reagent formulations to quantitatively measure 5 mg/L dichloramine (as Cl₂) at cold sample temperatures without nitrite interference and within the one-minute color-development time.

6. Conclusions

Currently, no “ideal” method exists for quantifying chlorine and chloramines in water. All common methods of chlorine analyses display some lack of specificity and are not adequately selective to be completely free of interferences.

Fourteen conceptual qualities of an “ideal” method for chlorine analyses were presented in AWWA’s Disinfectant Residual Measurement Methods (Ref 6.1). The 14 qualities are:

1. Being method specific to the actual species (e.g., free chlorine = HOCl + OCl⁻).
2. Possessing a selectivity of at least 500 times over possible interferences.
3. A detection limit of 1 ppb as Cl₂.
4. Precision of ± 0.1% or better.
5. Accuracy of ± 0.5% or better.
6. A linear working range of four orders of magnitude.
7. Performance with any sample matrix.
8. No requirement for sample dilution to minimize interferences.
9. Working in both batch and automated modes.
10. Maximum sensitivity with traditional laboratory instruments.
11. No specialized skills required to perform the test.
12. Reagent stability in excess of one year.
13. Performance of the test within one minute.
14. Being cost-effective.

An arbitrary rating of the common chlorine analytical methods — based on the author’s expertise with each method — was conducted. The information appears in **Table 6.1**. Five of the analytical methods are Hach

AWWA Quality Concept	DPD Color.	DPD Titration	Iodometric Titration	Amper. Forward	Amper. Back	FACTS	Electrode
1. Specificity	7	5	2	6	2	8	2
2. Selectivity	7	7	4	5	6	7	6
3. 1 ppb MDL	9	5	1	7	7	3	6
4. 0.2 % Precision	7	5	3	7	1	2	2
5. 1 % Accuracy	8	7	5	7	6	5	5
6. 4 Orders Linear Range	6	7	9	8	7	8	9
7. Any Sample Matrix	8	7	7	4	7	6	3
8. No Dilution Required	7	8	6	8	8	8	7
9. Can Automate	9	3	3	2	2	4	6
10. Traditional Instruments	9	9	9	4	4	9	5
11. No Special Skills	9	8	8	2	1	8	6
12. Stable Reagents	9	5	4	5	4	3	4
13. Fast Procedure	8	5	5	3	2	6	3
14. Cost Effective	9	7	6	4	3	6	3
TOTAL SCORE	112	88	72	72	60	83	67
<p>“1” = does not meet quality concepty “10” = meets quality concepts fully</p>							

Table 6.1 Ratings of Common Chlorine Analytical Methods vs. the “Ideal” Method

Company modifications (DPD colorimetric, DPD titrimetric, iodometric titration, and forward and back amperometric titrations). The FACTS method and the iodine electrode method were based on experience with *Standard Methods* methodologies.

A sliding scale was used in the ratings. On the scale, “10” means the method meets the quality concept of the “ideal” method completely and “1” means the method does not meet the concept at all. Each concept was weighed equally. The methods were judged versus each of the 14 ideal method concepts and the ratings were tallied. **Table 6.1** shows the results of the ratings.

As subjectively indicated in **Table 6.1**, Hach’s DPD colorimetric method is closer to the conceptual “ideal” method than any of the other common chlorine analytical methods. Most of the limitations associated with the traditional DPD chemistry (e.g., calibration linearity, reagent stability, reaction product stability, etc.) have been addressed sufficiently in Hach Company’s procedures and reagent formulations. Hach versions of the DPD chemistry have been successful in several studies under various conditions.

Although the amperometric titration method generally is perceived as the “referee” method for chlorine determinations in North America, it has been shown that several sources of error can occur when using this method unless precautions are taken. Contrary to the notion that the amperometric method is free of most common interferences, several poorly documented interferences have been identified. The amperometric method requires much greater skill to perform and a thorough understanding of the nature of the sample to be tested.

Even with these limitations, in the hands of a skilled operator and with thorough knowledge of the sample to be tested, the amperometric procedures can provide accurate and precise data. Because the amperometric methods are not easily adapted to the field, some trade-off in precision and accuracy can be expected due to analyte loss or changes to the sample during the holding period. In view of the relative instability of chlorine and chloramines in aqueous solutions and the availability of accurate digital titrators, colorimeters and portable spectrophotometers, on-site testing for chlorine is preferable.

Considering these factors and Hach Company’s versions of the DPD chemistry, one can be assured of the most reliable, accurate and precise data available with on-site testing using portable instrumentation. Many would consider this as the “ideal” system for routine chlorine measurements.

References:

- 1.1 White, G. C.; *Handbook of Chlorination and Alternative Disinfectants*, 3rd ed.; Van Nostrand Reinhold, New York, 1992.
- 1.2 Harp, D.L.; *A Specific and Effective Method for Controlling Chloramination of Waters*. Hach Company, 2000.
- 1.3 *Manual of Water Chlorination Principles and Practices*; American Water Works Association, 1973.
- 1.4 *Wastewater Disinfection*, Manual of Practice FD-10; Water Pollution Control Federation, 1986.
- 1.5 For a review, see Brungs, W.A.; *Jour. Water Pollution Control Fed.*; 45, 2180 (1973).
- 2.1 Palin, A. T.; *Jour. Am. Water Works Assoc.*; 49, 873 (1957).
- 2.2 Gordon, G.; Cooper, W.; Rice, R.; and Pacey, G.; *Disinfectant Residual Measurement Methods*, 2nd. ed.; AWWA Research Foundation and American Water Works Association, 1992, p. 62.
- 2.3 *Standard Methods for the Examination of Water and Wastewater*; 18th ed., American Public Health Association, American Water Works Association, and Water Environment Federation, 1992, Method 4500-Cl G., p. 4-46.
- 2.4 "International Organization for Standardization, Water Quality"; *ISO Standard 7393-2*:1985.
- 2.5 Cooper, W.; Roscher, N.; and Slifker, R.; *Jour. Am. Water Works Assoc.*; 74; 362 (1982).
- 2.6 *Standard Methods for the Examination of Water and Wastewater*; 18th ed.; op. cit., Method 4500-Cl Ed., p. 4-44.
- 2.7 Sengupta, C.; "Survey of Chlorine Analytical Methods Suitable for the Power Industry"; EPRI Report EA-929, October 1978, p. 5-22.
- 2.8 Harp, D.; "Application of the DPD Colorimetric Method for Measuring Trace Total Residual Chlorine"; Proceedings of the 66th Annual Conference and Exposition, Water Environment Federation, paper AC93-059-002, 1993.
- 2.9 Title 40, *Congressional Federal Register*; Appendix B, Section 136, 7-1-94.
- 2.10 Hatch, G.; Yang, V.; *Jour. Am. Water Works Assoc.*; 75, 154 (1983).
- 2.11 *Standard Methods for the Examination of Water and Wastewater*; 18th ed.; op. cit., Method 4500-Cl D., p. 4-42.
- 2.12 *Standard Methods for the Examination of Water and Wastewater*; 18th ed.; op. cit., Method 4500-Cl D., p. 4-36.
- 2.13 Gordon, G.; et al.; *Disinfectant Residual Measurement Methods*; op. cit.; p. 115.
- 2.14 Ellms, J.; Hauser, S.; *Jour. Ind. Eng. Chem.*; 5, 915 (1913).
- 2.15 "Water Chlorine (Residual) No. 1"; Analytical Reference Service Report No. 35, United States Environmental Protection Agency, Cincinnati, Ohio, 1969.
- 2.16 "Water Chlorine (Residual) No. 2"; Analytical Reference Service Report No. 40, United States Environmental Protection Agency, Cincinnati, Ohio, 1971.
- 2.17 Tompkins, J.; Tsai, C.; *Trans. Am. Fish. Soc.*; 105, 313 (1976).
- 2.18 Fava, J.; Tsai, C.; *Trans. Am. Fish. Soc.*; 105, 430 (1976).
- 2.19 Leiberman, J.; Roscher, N.; Meier, E.; and Cooper, W.; *Environ. Sci. Tech.*, 14, 1395 (1980).
- 2.20 *Standard Methods for the Examination of Water and Wastewater*; 18th ed.; op. cit., Method 4500-Cl H., p. 4-47.
- 2.21 Chiswell, B.; O'Halloran, K.; *Anal. Chim. Acta*, 248, 519 (1991).
- 2.22 Dimmock, N.; Midgley, D.; *Talanta*, 29, 557 (1982).
- 2.23 Wilde, E.; *Wat. Resources*, 25, 1303 (1991).
- 3.1 Jolley, R.; Brungs, W.; Cotruvo, J.; Cumming, R.; Mattice, J.; Jacobs, V.; *Water Chlorination: Environmental Impact and Health Effects*, Volume 4; Book 1; Chemistry and Water Treatment; Ann Arbor Science; 1983; p. 33.
- 3.2 Cooper, W.; Sorber, C.; Meirer, E.; *Jour. Am. Water Works Assoc.*; 67; 34 (1975).
- 3.3 Bongers, L.; O'Connor, T.; and Burton, D.; "Bromide Chloride -- An Alternate to Chlorine for Fouling Control in Condenser Cooling Systems"; EPA 600/7-77-053; United States Environmental Protection Agency; 1977.
- 3.4 Morris, J.; Ram, N.; Baum, B.; Wajon, E.; "Formation and Significance of N-Chloro Compounds in Water Supplies"; EPA 500/2-80-031; United States Environmental Protection Agency; 1980.
- 3.5 Wajon, J.; Morris, J.; *Environ. International*; 3; 41 (1980).
- 3.6 White, G. C., *Handbook of Chlorination and Alternative Disinfectants*; op. cit.; p. 287.

3.7 Sengupta, C.; "Survey of Chlorine Analytical Methods Suitable for the Power Industry"; op. cit.; p. 3-9.

3.8 *ibid.*; p. 3-12.

3.9 *ibid.*; p. 3-15.

3.10 Gordon, G.; Sweetin, D.; Smith, K.; Pacey, G.; *Talanta*; 38, 145 (1991).

3.11 ASTM D1193-77: "Standard Specification for Reagent Water"; Annual Book of ASTM Standards; American Society for Testing and Materials; 1994.

3.12 Vogel, A.; *A Textbook of Quantitative Inorganic Analysis*; 3rd ed.; Longmans Publishing; 1961.

3.13 Hach Company; *Water Analysis Handbook*; 2nd ed.; 1992; Section I.

3.14 Gordon, G.; et al.; *Disinfectant Residual Measurement Methods*; op. cit.; Table 2.10.

3.15 Strupler, N.; *J. Inst. Water Eng. and Sci.*; 39; 134 (1985).

3.16 Whittle, G.; "New Methods for the Colorimetric Determination of Halogen Residuals"; Ph.D. Dissertation; University of Florida; 1966.

3.17 Michaelis, L.; *J. Am. Chem. Soc.*; 53; 2953 (1931).

3.18 Jaffari, G.; Nunn, A.; *J. Chem. Soc.*; 93, 823 (1971).

3.19 *Standard Methods for the Examination of Water and Wastewater*; 18th ed.; op. cit., Method 4500-Cl A.

3.20 *ibid.*; Method 4500-Cl G.b.

3.21 *ibid.*; Method 4500-Cl A.b.

3.22 *ibid.*; Method 4500-Cl D.b.

3.23 White, G. C., *Handbook of Chlorination and Alternative Disinfectants*; op. cit.; p. 227.

3.24 Margerum, D.; Schurter, L.; Hobson, J.; Moore, E.; *Environ. Sci. Technol.*; 28; 331 (1994).

3.25 White, G.C., *Handbook of Chlorination and Alternative Disinfectants*; op. cit.; p. 226.

4.1 Gordon, G.; et al.; *Disinfectant Residual Measurement Methods*; op. cit.; Chap. 2, Sec. VIII.

4.2 Instrumentation Testing Service, Inc.; "Evaluation Report, Hach Model 31300 Total Chlorine Pump-Colorimeter Analyzer"; Report 84-3; 1983.

4.3 The Water and Wastewater Instrumentation Testing Association; "Performance Evaluation of Residual Chlorine Analyzers for Water and Wastewater Treatment Applications"; Report CH-1; 1990.

5.1 World Health Organization; "Guidelines for Drinking Water Quality, Vol. 3: Small Community Supplies"; 1993; Chap. 6.

5.2 U.S. Patent No. 5,362,650; *Ultra-low Range Chlorine Determination*; Inventor: Danial L. Harp; Assignee: Hach Company; Nov. 8, 1994.

5.3 Title 40, *Congressional Federal Register*, Ch. 1, Section 141.74, 7-1-92.

6.1 Gordon, G.; et al.; *Disinfectant Residual Measurement Methods*; op. cit.; p. 33-35.

Trademarks

The following are trademarks of Hach Company:

AccuVac®

AutoCat™

Pocket Colorimeter™

TenSette®

Voluette®

Acknowledgements

The author expresses appreciation to the following, for proofing the manuscript and for their kind encouragement:

Lee Cooper

Marge Hale

Starla Harp

Tim Holtz

Tom Haukebo

Bob Klein

Sharon Sloat

Pat Wiese

