

Chlorine Residual

VT WSMD Wastewater Program Lab Manual Section #9

Table of Contents

Chlorine Residual	2
Background	2
Methods of Measurement.....	2
Interferences.....	4
Sampling.....	4
DPD Colorimetric Method.....	4
Equipment.....	4
Reagents.....	5
Procedure (DPD Colorimetric Method).....	5
DPD Ferrous Titrimetric Method	6
Equipment.....	6
Reagents.....	7
0.100N (Stock) Potassium Dichromate ($K_2Cr_2O_7$) Solution	7
0.025N (Working) Potassium Dichromate ($K_2Cr_2O_7$) Solution	7
0.0282N Standard Ferrous Ammonium Sulfate (FAS) Titrant.....	7
Phosphate Buffer Solution	7
N,N-Diethyl-P-Phenylenediamine (DPD) Indicator Solution	7
Concentrated Sulfuric Acid, H_2SO_4 (36N)	7
Ferroin Indicator in Dropping Bottle.....	7
Potassium Iodide (KI) Crystals.....	7
Chlorine Demand Free Water	7
FAS Standardization Procedure	8
DPD Titrimetric Procedure	9
Chlorine DPD Titrimetric Method Troubleshooting Guide	10
Quality Control for the DPD (FAS) Titrimetric Method	11
Reporting Chlorine (DPD Titrimetric) Data	12
References	12

Chlorine Residual

Background

Chlorine (Cl_2) has been used for many years as a disinfection agent to destroy disease-causing microorganisms (pathogens). It is a very powerful oxidizing agent making it an excellent disinfectant, particularly effective against many bacteria, viruses, and protozoa. It is also very toxic to organisms in the receiving water. The kill of the microorganisms is proportional to the contact time and the concentration of the chlorine. When chlorine is added to wastewater, either as chlorine gas or as hypochlorite, it hydrolyzes and produces free chlorine. Free chlorine readily combines with various substances such as ammonia, iron, manganese, and some organic components.

When ammonia is present (as is the case in treated wastewater) the free available chlorine combines with it to form chloramines which are combined available chlorine. Chloramines are also disinfectants but are some 100 times less effective than free chlorine. The relative amounts of free and combined chlorine present will depend on the amount of nitrogen present, the pH, the temperature, and the amount of chlorine added. In most wastewater there is very little free chlorine left because of the small amounts of chlorine added relative to the amount of ammonia and other materials present.

Over-chlorination is to be avoided for a number of reasons; it is very expensive, it is harmful to aquatic life, and toxic compounds may form. It is important to measure the chlorine residual to maintain a balance between these disadvantages and the benefit of disinfection. The total chlorine residual should be kept as low as possible while maintaining a coliform/*E. coli* count within permitted conditions.

Methods of Measurement

EPA approved methods for the analysis of residual chlorine include the amperometric method, the iodometric method, the selective ion electrode method, and the DPD (N,N-diethyl-p-phenylenediamine) method. The high level iodometric methods are only good for measuring chlorine concentrations greater than 1 mg/L. Most Vermont wastewater permits require limits much less than 1 mg/L.

The low level amperometric method is actually more accurate than all other methods for measuring lower concentrations of TRC but it is more difficult than the colorimetric methods and requires greater skill and much greater maintenance. The electrodes must be kept very clean and free of any films or contaminants and the stirring of the sample must be kept slow enough so as not to allow loss of chlorine. For analysis of (TRC) Total Residual Chlorine concentrations of less than 0.2 mg/L the low-level amperometric or ultra-low level colorimetric methods should be used. **Links for HACH® low and ultra-low colorimetric methods are included at the end of the section**

Note: For industrial wastes you must choose a method that is not prone to interference by metals. The amperometric method is not effective in effluents containing certain analytes, such as silver, copper, cyanide, iron, nitrite and oxidized manganese. There are often complex anions in industrial wastes that can interfere with this method of analysis.

Instructions for the proper calibration of the amperometric meter are included with each specific probe.

Results using the DPD method may be obtained using either endpoint titration or by spectrophotometer. The DPD kits using powder pillows and a small "color wheel" comparator are EPA

Chlorine Residual

approved for drinking water only. They are not approved for the analysis of chlorine in wastewater! Even though this may seem unfair, there is a very logical reason for it. Whereas drinking water is usually clear and colorless, this does not always hold true for wastewater effluent. It is the color and turbidity of the wastewater that interfere with the comparative method of chlorine analysis, causing the method to be deemed unacceptable for wastewater samples. The kit may be used for quick spot-checks but the reported daily tests must be performed using an approved method!

The good news is that there are now very “simple to use” kits for Cl_2 analysis that include either a spectrophotometer or filter photometer. The use of these kits in Cl_2 analysis is perfectly acceptable.

Procedure 4500-C1 G (“DPD Colorimetric Method”) in 23rd Edition, Standard Methods for the Examination of Water and Wastewater states that the required apparatus includes either:

- a. Spectrophotometer, for use at a wavelength of 515 nm and providing a light path of 1 cm or longer, or
- b. Filter photometer, equipped with a filter having maximum transmission in the wavelength range of 490 to 530 and providing a light path of 1 cm or longer.

This **colorimetric** method is based on the same principles as the DPD titrimetric method. That is, under acidic conditions chlorine reacts with DPD indicator to form a red colored complex. Then instead of titrating with Ferrous Ammonium Sulfate as in the titrimetric method, the sample is placed in a test tube or photometer cell and the chlorine content is measured with a spectrophotometer or photometer. The analytical procedure will be described later in this section.

The **amperometric** method for chlorine analysis is the standard against which all other methods are compared. However, the equipment necessary for this method is expensive. This method also requires more operator skills than any of the other methods. Basically, the procedure consists of titrating the sample with a standard phenylarsine oxide (PAO) solution while observing current changes on the titrator meter. As the current changes get smaller and smaller, less and less titrant is added until the needle ceases to move. The amount of titrant is then read and recorded. When 0.00564N PAO is used as titrant in a 200 mL sample, each mL of titrant is equal to 1 mg/Liter chlorine. Because each meter is somewhat different, it is important to follow the manufacturer’s instructions for your specific meter. For further information you might refer to the Apparatus Section of the Amperometric Titration Method in 23rd Edition “Standard Methods”. This analytical procedure will be described later in this section.

The **iodometric** method is suitable for the determination of chlorine residual in wastewater. However, for concentration less than one (1) mg/L the iodometric method might be less sensitive than required for permit compliance. This method uses back titration to arrive at the chlorine concentrations. First, a known excess volume of a standard thiosulfate solution is added to the sample. This thiosulfate reacts with the chlorine present. The excess thiosulfate is then titrated with a standard iodate solution to its endpoint. The chlorine residual can be calculated by subtracting the amount of iodate solution used from the amount of thiosulfate solution added originally. (This gives you the amount of thiosulfate solution that reacted with the chlorine. The ratio of reacted thiosulfate (mL) to chlorine in mg/L is 1:1. Example: If two mL iodate solutions are used, the chlorine residual would be recorded at two mg/L). Since there is no laboratory in Vermont known to be using this method the procedure will not be

Chlorine Residual

included in this manual. The procedure may be found in the 23rd Edition, "Standard Methods" 4500-Cl G Iodometric Electrode Technique on pages 13 -14 (Section 4500-Cl:I)

The **selective ion electrode** method is a very simple method for chlorine residual analysis. However, the equipment necessary to perform the analysis can be very expensive and must be calibrated daily with freshly prepared standards.

Interferences

ALL methods for analysis of Total Chlorine depends on stoichiometric production of iodine in waters containing reducing substances may not be analyzed accidentally by these methods.

Color, turbidity, and certain metals like manganese interfere with all colorimetric analyses.

Sampling

Residual chlorine is subject to dissipation by exposure to sunlight, exchange of gasses with the atmosphere and reactions with compounds in the wastewater over time. For this reason, chlorine residual samples must be analyzed immediately. The sample should be taken gently into a 300 mL amber or opaque DO bottle filled to the top the stopper inserted and the bottle shielded from the sunlight.

There is a maximum hold time of 15 minutes for the Total Chlorine analysis but the closer to "IMMEDIATELY" the analysis is performed the better.

Samples for Cl₂ analysis cannot be stored or sent off to another lab for analysis!!!

DPD Colorimetric Method

Equipment

- Spectrophotometer with a light path of 1 cm or longer - capable of providing a wavelength of 515 nm.
- **OR**
- Filter Photometer - with a light path of 1 cm or longer and a filter with maximum transmission in the wavelength range of 490-530 nm
- Colorimeter/fixed photometer – same as for filter photometer

SAMPLE TYPE: Grab

CONTAINER: Glass or Plastic (Polyethylene or Equivalent) amber or opaque

PRESERVATIVE: None. Analyze immediately – absolute max hold time 15 minutes

SAMPLE VOLUME: As appropriate for instrument used

*If the Total Residual Chlorine exceeds 4mg/l, the sample should be diluted with chlorine demand-free water.

*For measurement of chlorine residual below 0.1 mg/L the light path length of whatever equipment is used must be between 5 – 10 cm.

Reagents

DPD Total Chlorine Reagent Powder Pillows (or DPD Total Chlorine Reagent Aluminum Packets, recommended):

Preparing DPD reagents yourself is not recommended due to time and safety considerations

Phosphate Buffer Solution: Dissolve 24 grams anhydrous disodium hydrogen phosphate, Na_2HPO_4 and 46 grams anhydrous potassium dihydrogen phosphate, KH_2PO_4 , in distilled water. Combine this solution with 100 mL distilled water in which 0.8 grams disodium ethylenediamine tetraacetate dihydrate, also called (ETDA), has been dissolved. Dilute to one liter with distilled water and add 0.02 g mercuric chloride (HgCl_2) to prevent mold growth, and to prevent interference in the free available chlorine test caused by any trace amounts of iodide in the reagents. (HgCl_2 is toxic.)

N,N-Diethyl-P-Phenylenediamine (DPD) Indicator Solution: Dissolve 1 g DPD Oxalate or 1.5 g DPD sulfate pentahydrate or 1.1 g anhydrous DPD sulfate in chlorine-free distilled water containing 8 mL of 1+3 sulfuric acid (25% solution) and 0.2 g disodium ethylenediamine tetraacetate dihydrate (EDTA). Make up to one liter, store in a brown glass-stoppered bottle, and discard when discolored.

Potassium Iodide (KI) Crystals

Purchase dry (anhydrous) crystals.

Procedure (DPD Colorimetric Method)

- 1) Add the contents of one DPD Total Residual Chlorine reagent powder pillow or aluminum packet - make sure to use the designated volume of sample for the pillow or packet used. (Some are designed for use with 10 or 25 mL samples.)
- 2) Wait at least three (3) minutes but not more than six minutes.
- 3) Follow instructions for the specific meter you are using for analysis.

With kind permission from the HACH company I have included the DPD colorimetric method from the Hach user manual for the DR 300 chlorine colorimeter. At the time this manual is being written the colorimetric method using some form of "pocket colorimeter" or spectrophotometer is by far the most common method for analysis of Total Residual Chlorine.

Both the low range and high range methods are included in the user manual. Most, if not all, Vermont WWTF operators/technicians may need to use the LOW Range method as the permit limits for chlorine residual are already as low as 0.02 mg/l in some cases. The high range method is only capable of reading results to 0.1 mg/l CL_2 . Use of both is consistent with Standard Method 4500.CL-G

*There are a few simple steps that if followed religiously will help ensure good results.

1. ALWAYS rinse the sample cell AND THE CAP with distilled water after use – Before use rinse the sample cell to the cap with the sample!!

Chlorine Residual

2. Wipe all fingerprints, moisture, condensation, and other debris off the outside of the sample cell with a KimWipe before placing it into the colorimeter.
3. Always place the sample cell into the colorimeter the same way. For example: Each sample cell has a diamond imprinted on the sample cell – Make sure the diamond is facing the same direction every time. Most operators prefer to face the diamond toward the front.

The Low range method requires the use of a reagent blank. All reagents have color! That is, the reagent itself can account for a reading of 0 - 0.5 mg/L!! It is very important to determine the “amount” or intensity of the color in the DPD reagent. We find that by using a reagent blank *(the reagent blank consists of pure distilled water). The instrument is zeroed using distilled water just as if this were the sample. After zeroing, a reagent packet is added to the distilled water/sample, the cell is inverted to mix, wait three to six minutes, and then read the result. This result can then be subtracted from the sample result.

For example:

Blank (distilled water) is zeroed

Reagent is added and the result is 0.03 mg/L

Sample is then analyzed yielding a result of 0.09 mg/L – The reagent blank result is subtracted from the sample result.

$0.09 \text{ mg/L} - 0.03 \text{ mg/L} = .06 \text{ mg/L}$

This reagent blank can be subtracted from all sample results obtained from that batch of reagents. The analyst must re-establish the reagent blank every time a new batch /lot of reagents is used.

DPD Ferrous Titrimetric Method

Equipment

- 10 mL automatic burette and/or 50 mL burette 10 mL volumetric pipet
- 2 - 250 mL Erlenmeyer flasks 100 mL graduated pipet
- 2 - 5 mL graduated pipets 500 mL Erlenmeyer flask
- various glassware for reagent preparation

SAMPLE TYPE: Grab

CONTAINERS: Glass or plastic

PRESERVATIVE: None – Analyze immediately

Reagents

0.100N (Stock) Potassium Dichromate ($K_2Cr_2O_7$) Solution

Dissolve 4.904 grams of anhydrous potassium dichromate ($K_2Cr_2O_7$) into 600 mL distilled water. Dilute to 1,000 mL with distilled water.

0.025N (Working) Potassium Dichromate ($K_2Cr_2O_7$) Solution

Pipette 25.00 mL of the 0.1N potassium dichromate solution into a 100 mL volumetric flask Dilute to 100 mL with distilled water. This solution is used to standardize the standard FAS solution.

0.0282N Standard Ferrous Ammonium Sulfate (FAS) Titrant

Dissolve 11.106 g ferrous ammonium sulfate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, in distilled water containing one mL of 1+3 sulfuric acid (25% solution) and make up to one liter with freshly boiled and cooled distilled water. This primary standard may be used for six months.

Instructions for the standardization of this FAS concentration to prepare the 0.00282N working solution are included at the end of "Reagents" section.

Phosphate Buffer Solution

Dissolve 24 grams anhydrous disodium hydrogen phosphate, Na_2HPO_4 , and 46 grams anhydrous potassium dihydrogen phosphate, KH_2PO_4 , in distilled water. Combine this solution with 100 mL distilled water in which 0.8 grams disodium ethylenediamine tetraacetate dihydrate, also called (ETDA), has been dissolved. Dilute to one liter with distilled water and add 0.02 g mercuric chloride ($HgCl_2$) to prevent mold growth, and to prevent interference in the free available chlorine test caused by any trace amounts of iodide in the reagents. ($HgCl_2$ is toxic.)

N,N-Diethyl-P-Phenylenediamine (DPD) Indicator Solution

Dissolve 1 g DPD Oxalate or 1.5 g DPD sulfate pentahydrate or 1.1 g anhydrous DPD sulfate in chlorine-free distilled water containing eight (8) mL of 1+3 sulfuric acid (25% solution) and 0.2 g disodium ethylenediamine tetraacetate dihydrate (EDTA). Make up to one liter, store in a brown glass-stoppered bottle, and discard when discolored. (The buffer and indicator are commercially available as a combined reagent in a stable powder form). It is advisable to purchase this reagent in ready-made form.

Concentrated Sulfuric Acid, H_2SO_4 (36N)

Ferroun Indicator in Dropping Bottle

Potassium Iodide (KI) Crystals

Chlorine Demand Free Water

Add sufficient chlorine to high quality distilled water to give five mg/L free chlorine. Let sit for two days. If the distilled **water** was of sufficient quality, there should be at least two mg/L free chlorine still present after standing for two days. At this **point**, remove the remaining chlorine by setting it in the sunlight or under an ultraviolet lamp until all traces of chlorine are gone. The 23rd Edition of Standard Method's for the Examination of Water and Wastewater offers suggestions on storage of this water.

Chlorine Residual

FAS Standardization Procedure

Standardize the 0.0282 N FAS by the following procedure which should be run in duplicate:

- 1) Pipet 10.00 mL 0.025 N potassium dichromate ($K_2Cr_2O_7$) into a 250 mL Erlenmeyer flask. Use a volumetric pipet to measure out exactly 10.00 mL potassium dichromate.
- 2) Add approximately 90 mL distilled water.
- 3) Add approximately 25 mL concentrated sulfuric acid SLOWLY.
- 4) Cool to room temperature in a cool water bath.
- 5) Add three (3) drops ferroin indicator.
- 6) Titrate with 0.0282 N FAS from yellow, through green to aqua to the red-brown endpoint.
- 7) Record milliliters (mL) of FAS used.

The burette reading is then plugged into the equation:

$$\text{Normality (N) FAS stock solution} = \frac{0.25 \text{ N } K_2Cr_2O_7}{\text{mL FAS used}}$$

The resulting N of stock FAS is used in the following equation to yield the mL of stock FAS to be diluted in a 200 mL volumetric flask to make the working strength 0.00282 N:

$$\text{Volume to use (mL)} * \text{N of FAS stock solution} = 200 \text{ mL} * 0.00282 \text{ N FAS working solution}$$

$$\text{Volume to use (mL)} = \frac{0.564}{\text{N of FAS stock solution}}$$

The working strength solution is made up and used for one (1) week to a month at the longest.

Example: The standardization procedure is performed with the stock FAS solution and 8.8 mL are used in the titration.

$$\text{N of FAS stock solution} = \frac{0.25 \text{ N } K_2Cr_2O_7}{8.80 \text{ mL}} = 0.0284 \text{ N FAS stock solution}$$

The volume of the stock solution to be diluted to 200 mL is now calculated:

$$\text{Volume to use (mL)} = \frac{0.564}{0.0284 \text{ N FAS stock solution}} = 19.86 \text{ mL}$$

Using a burette, measure the volume of stock solution indicated (in this example, 19.86 mL or 19.85 mL) into a 200 mL volumetric flask. Add distilled water up to the 200 mL line, cap, and mix.

This is the 0.00282 N FAS solution to use for the daily chlorine residual measurements during the coming week.

DPD Titrimetric Procedure

- 1) Pipet 5 mL each of the phosphate buffer and the DPD indicator solutions into the 500 mL Erlenmeyer flask. Mix by swirling.
- 2) Add 100 mL of freshly collected sample.

Perform STEP 3 ONLY IF free chlorine residual determination is desired. If only total chlorine residual is desired, omit Step 3 and go from Step 2 to Step 4.

- 3) Titrate immediately with 0.00282 N FAS until pink color disappears. Read burette and record as free chlorine residual. Do not re-zero (refill) burette.
- 4) Add approximately one gram potassium iodide, KI, crystals, mix and time for two minutes. The solution should turn pink again.
- 5) Titrate, with FAS, the new pink color until it disappears/is clear.
- 6) Read the burette and record this reading as total chlorine residual, in mg/L. NOTE: The total chlorine reading.
- 7) Should the sample return to a pink color, allow another two minutes and titrate to the colorless endpoint. This is the total chlorine residual.

If you get a high free chlorine residual, chances are that there was a small amount of KI left in the titration flask and what you actually have is some total residual showing up as free because of it. It is a good idea to rinse the flask several times with distilled water to help alleviate this problem.

Example: 1 mL of titrant is used to titrate for free chlorine. Then an additional 3 mL of titrant is needed to obtain the clear endpoint after the addition of the KI crystals the results would be recorded as:

Free CL₂ = 1 mg/L

Total CL₂ = 4 mg/L

Chlorine DPD Titrimetric Method Troubleshooting Guide

PROBLEM	MOST LIKELY CAUSE	SOLUTION
Reagents turn pink before sample is added	Contaminated glassware	Rinse glassware thoroughly with distilled water. Rerun analysis.
	Reagents (DPD indicator) contaminated or has passed expiration date	Prepare fresh DPD indicator solution
Unreasonably low result (end point is reached with first drop of titrant even though you are sure the residual is quite high.)	Using "stock" 0.0282N FAS as opposed to proper "working" concentration of .00282N FAS	Use proper concentration of FAS-Retest
A strange orange color is produced instead of a pink color.	Possibly manganese contamination	Add 0.5mL sodium arsenite solution or 0.5 mL thioacetanide to sample before adding DPD indicator solution
To prepare sodium arsenite solution: Dissolve 5.0 g NaAsO₂ in distilled water and dilute to one liter.		
Unusually high Cl ₂ result	pH of sample is too high causing dissolved oxygen to give color	Adjust sample pH to approximately 6.5
Pink color keeps coming back seconds after titrating to clear endpoint	You didn't wait the required two (2) minutes after adding the KI crystals before titrating the sample	Wait a full two (2) minutes
	High concentration of contaminants (ammonia) from ambient air are getting into the sample	Take precaution to avoid airborne contaminants

Quality Control for the DPD (FAS) Titrimetric Method

Document the Following (Included but not limited to):

Supply Water Quality

- Chlorine and Ammonia Free
- No Chlorine Demand
- Conductivity <10 micro siemens

Sampling

- Grab:
 - Exact time and Date Sampled
 - Exact time and Date Analyzed
- Volume – X mL
- Location – Be Exact

Glassware

- Washed (phosphate free detergent) & rinsed thoroughly (distilled water)
- Rinse with sample material, discard and refill

Reagents

- NIST Traceability (Hach, Fisher, etc)*
- Preparation, Standardization & Expiration Dates (documented in reagent log, on a bench sheet, or wherever QC data are kept)

Replication/Duplication

- once every 10 samples- once/week is typical

*SUGGESTED – may become mandatory in the future

Reporting Chlorine (DPD Titrimetric) Data

Total Chlorine (DPD Titrimetric) Bench Sheet
ANALYST:
SAMPLE TIME and DATE:
SAMPLE LOCATION:
ANALYSIS TIME and DATE:
SAMPLE VOLUME:
BURET READING START:
BURET READING AT ENDPOINT:
TOTAL CHLORINE RESULT: -Report result to one digit beyond the decimal point.

References

Hach® page with interesting general information regarding chlorine analysis

[Chlorine - Water Quality Parameter Overview and Products | Hach](#)

Hach's® colorimetric Low range Total Chlorine analysis. This analysis is for Total Chlorine in the range of 0.2-2.0 mg/L

[DOC316.53.01450_4ed \(1\).pdf](#)

Hach® ultra-low range total chlorine analysis. This method is for analysis of Total Chlorine in the range of 2 to 500 micrograms/liter or 0.02 to 0.5milligrams/liter . Note: special flow cells are required to use the DR300 colorimeter for this analysis.

[DOC086.53.01000.book\(DOC316.53.01032.fm\) \(azdhs.gov\)](#)