

***CHLORINE
RESIDUAL
(CL₂)***

CHLORINE RESIDUAL

Background

Chlorine (CL_2) has been used for many years as a disinfection agent, to destroy disease-causing microorganisms (pathogens). The kill of the microorganisms is proportional to the contact time and the concentration of the chlorine. When either chlorine gas or hypochlorite is added to water it hydrolyzes, that is, combines with water and produces free chlorine. This is a very powerful disinfectant and very reactive, so much so that it readily combines with various substances as soon as it enters the wastewater stream. When ammonia is present, as is the case in 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 would be kept as low as possible while maintaining a coliform 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 method.

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 approved for drinking water only. They are generally not approved for the analysis of chlorine in wastewater! Even though this may seem unfair, there is actually 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 Colormetric Method") in 18th 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 **colormetric** method is based on the same principles as the DPD titrimetric method. That is under acidic condition 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 colorimetrically 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. The equipment necessary for this method however 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 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 concentrations less than one (1) mg/l the iodometric method might be less sensitive than desired. 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 (mls) to chlorine in mg/l is 1:1. Example: If two mls iodate solutions are used, the chlorine residual would be recorded as two mg/l). Since there is no laboratory in Vermont known to be using this method the procedure will not be included in this manual. The procedure may be found in 18th Edition, "Standard Methods" on pages 4-38 and 4-39.

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.

Instructions for the proper calibration of the meter are included with each specific probe. Basically, calibration is usually achieved using a 1:500 dilution of a bleach, establishing a chart, then performing a one point calibration on a daily basis.

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 DO bottle to the neck, the stopper inserted and the bottle shielded from sunlight.

DPD FERROUS TITRIMETRIC METHOD

Equipment

10 ml automatic buret and/or 50 ml buret
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 ($K_2Cr_2O_7$)

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

0.025N (WORKING) POTASSIUM DICHROMATE ($K_2Cr_2O_7$)

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

STANDARD F.A.S. TITRANT 0.0282N

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 F.A.S. 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, H₂SO₄ (36N)

FERROIN INDICATOR in dropping bottle

POTASSIUM IODIDE CRYSTALS (KI)

CHLORINE-DEMAND-FREE WATER

Add sufficient chlorine to high quality distilled water to give five mg/L free chlorine. Let set 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 17th Edition of Standard Methods for the Examination of Water and Wastewater (page 4-52) offers suggestions on storage of this water.

F.A.S. Standardization Procedure

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

- 1) Pipet 10.00 mls potassium dichromate, 0.025 N K₂Cr₂O₇, into a 250 ml Erlenmeyer. Use a volumetric pipet to measure out exactly 10.00 mls potassium dichromate).
- 2) Add approximately 90 mls distilled water.
- 3) Add approximately 25 mls 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 (mls) of FAS used.

The buret reading is then plugged into the equation:

$$N(\text{Normality}) \text{ of FAS} = \frac{0.25}{\text{mls of FAS used}}$$

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

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

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 8.80 mls are used in the titration.

$$\begin{aligned} N \text{ of FAS} &= \frac{0.25}{8.80 \text{ mls}} \\ &= 0.0284 \text{ N} \end{aligned}$$

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

$$\begin{aligned} \text{Volume to use} &= \frac{0.564}{0.0284} \\ &= 19.86 \text{ mls} \end{aligned}$$

Using a buret, measure the volume of stock solution indicated (in this example, 19.86 mls or 19.85 mls) 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.

Procedure (DPD Titrimetric)

The procedure for the actual chlorine residual measurement is as follows:

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

(Perform STEP 3 ONLY IF free chlorine residual determination is desired.)

- 3) Titrate immediately with 0.00282 N FAS until pink color disappears. Read buret and record as free chlorine residual. Do not re-zero (refill) buret.

If only total chlorine residual is desired, omit Step 3 and go from Step 2 to Step 4.

- 4) Add approximately one gram potassium iodide, KI, crystals, mix and time for two minutes.
- 5) Titrate, with FAS, the new pink color until it disappears.
- 6) Read the buret 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 mls of titrant is needed to obtain the clear endpoint after the addition of the KI crystals the results would be recorded as:

Free CL_2 = 1 mg/L

Total CL_2 = 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 0.5 ml sodium arsenite solution <u>or</u> 0.5 ml thioacetamide 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

***Supply Water Quality**

- Chlorine and Ammonia Free
- No Chlorine Demand
- Conductivity

Sampling

- Grab - Exact Time and Date Sampled
- Exact Time and Date Analyzed
- Volume - 100 mls
- Location - Be Exact

Glassware

- Washed & Rinsed thoroughly
- Rinse with sample material, discard and refill

Reagents

- NIST Traceability (Hach, Fisher, etc.)
- Preparation, Standardization & Expiration Dates

* SUGGESTED - may become mandatory in the future.

REPORTING CHLORINE (DPD Titrimetric) DATA

<p style="text-align: center;">Total Chlorine (DPD Titrimetric) Bench Sheet</p>
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.

THE DPD COLORIMETRIC METHOD

Equipment

Spectrophotometer with a light path of 1 cm or longer - capable of providing a wave length 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.

SAMPLE TYPE: Grab
CONTAINER: Glass or Plastic (Polyethylene or Equivalent)
PRESERVATIVE: NONE Analyze immediately
SAMPLE VOLUME: As appropriate for instrument used
* If the Total Residual Chlorine exceeds 4 mg/L, the sample should be diluted with chlorine demand-free water.

NOTE: The Hach DR100 has been approved by US EPA for the determination of chlorine residuals ≥ 0.1 mg/L.

* 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 aluminum packets)

OR, To prepare reagents yourself:

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 CRYSTALS

Purchase dry crystals.

Procedure (DPD Colorimetric Method) - Using your own reagents -

- 1) Pipet 5 mls each of the phosphate buffer and the DPD indicator solutions into an adequate container and mix by swirling.
- 2) Add 100 mls of freshly collected sample.
- 3) Add one gram potassium iodide and let stand for at least three minutes (no more than six minutes).

OR, using powder pillows

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.) Wait at least three (3) minutes but not more than six minutes. Then:

If using a Bausch and Lomb Spec 20

- 1) Adjust the wave length to 520 nm.
- 2) Adjust the zero control to read 0% transmittance. Make sure sample compartment cover is on.
- 3) Pour untreated sample into a test tube, place the tube into the sample compartment, and adjust the Full Scale Control to obtain a reading of 100% transmittance. This is the blank.
- 4) Pour a portion of the sample to which the reagents were added into a test tube. Place the tube into the sample compartment and read the result in percent transmittance. To **convert** percent transmittance to mg/L total chlorine refer to the table of "Concentration in mg/L free chlorine vs. Percent transmittance".

Concentration in mg/l free chlorine vs. Percent transmittance

TENS
%T

%T UNITS

	0	1	2	3	4	5	6	7	8	9
10	4.00	3.84	3.68	3.54	3.42	3.30	3.18	3.08	2.98	2.88
20	2.80	2.71	2.63	2.55	2.48	2.41	2.34	2.28	2.21	2.15
30	2.09	2.04	1.98	1.93	1.88	1.82	1.78	1.73	1.68	1.64
40	1.59	1.55	1.51	1.47	1.43	1.39	1.35	1.31	1.28	1.24
50	1.20	1.17	1.14	1.10	1.07	1.04	1.01	0.98	0.95	0.92
60	0.89	0.86	0.83	0.80	0.78	0.75	0.72	0.70	0.67	0.74
70	0.62	0.60	0.57	0.56	0.52	0.50	0.48	0.46	0.43	0.41
80	0.39	0.37	0.34	0.32	0.30	0.28	0.26	0.24	0.22	0.20
90	0.18	0.16	0.14	0.13	0.11	0.09	0.07	0.05	0.04	0.02

Table taken from page 2-29, Procedures, Chemical Lists and Glassware for Water and Wastewater Analysis, 2nd Edition, Hach Chemical Company

If using Bausch and Lomb Mini Spectronic 20

- 1) Adjust the wavelength to 520 nm
- 2) Use the one-half inch adaptor with insert. Place the opaque rod into the sample compartment and adjust the zero control to read 0% transmittance.
- 3) Pour untreated sample into a 25 ml cell and place the cell into the sample compartment, adjust the full scale control for a reading of 100% transmittance.
- 4) Pour a portion of the sample to which the reagents were added into a 25 ml cell. Place the cell into the sample compartment and read % transmittance. To convert percent (%) transmittance to mg/L Total Chlorine, refer to the table of "Concentration in mg/L free chlorine vs. Percent transmittance."

If using the Hach pocket colorimeter (fixed photometer) or DR100 refer to the instructions provided with these instruments for proper procedures.

The Hach DR-100 has an internal standard curve. This allows samples analyzed via this instrument to be read directly. Good laboratory practice requires routinely checking the instrument's response with a known chlorine residual standard (minimum frequency once per week or once every 10 analyses, whichever comes first but preferably every time the analysis is performed).

When using an instrument that does not already have an internal standard curve, a standard curve **MUST** be developed using known concentration of chlorine or potassium permanganate solution.

Chlorine Standards

Chlorine standards can be purchased from Hach chemical company or other companies or prepared in the laboratory. It is highly recommended that NIST traceable standards be purchased.

**CHLORINE - DPD Colorimetric Method
TROUBLESHOOTING GUIDE**

PROBLEM	MOST LIKELY CAUSE	SOLUTION
Strange; Dark color is produced-very high residual	Possible Chromate contamination	Use the thioacetamide blank correction (CAUTION: This solution is a suspected carcinogen) Instructions for preparation can be found in 18th Edition "Standard Methods" page 4-44
Unusually high residual	Contaminated glassware	Rinse glassware thoroughly with distilled then with a portion of the material to be sampled. Reanalyze: Zero instrument with untreated sample
Instrument flashes strange numbers ex.-888888	<p>Chlorine Residual higher than equipment range</p> <p>Instrument not properly zeroed</p> <p>Low battery/power</p>	<p>Dilute sample and reanalyze</p> <p>Use untreated sample to zero instrument</p> <p>Replace power supply; recalibrate and reanalyze</p>

**Quality Control for
TOTAL CHLORINE (DPD COLORIMETRIC)**

Document

***Supply Water Quality**

- Chlorine and ammonia free
- No chlorine demand
- Conductivity

Sampling

Grab - Exact time and date sampled

Exact time and date analyzed

NO HOLD TIME

Volume - Dependent upon spectrophotometer cell size and concentration - Diluted?

Location

Glassware

- Thoroughly washed and rinsed
- Rinse with sample material - discard - refill
- Use separate glassware and cells for free & total chlorine determination

Equipment

Type - DR100, Mini Spec 20, etc.

Wavelength used-530 nm

Light path

Range capabilities

Reagents

NIST traceability

Preparation and Expiration dates

Calibration

Date and Time

Minimum Frequency

- For instruments without internal standard curve - Daily

- For instruments with internal standard curve - Weekly

Reagents Used

Concentration used

Results - calibration curve (if required)

Duplication Schedule (10% min)

* Control Charts

* - Suggested QC at this time - May become mandatory in the future.

REPORTING TOTAL CHLORINE (DPD COLORIMETRIC)

<p>Total Chlorine Residual (DPD Colorimetric) Bench Sheet</p>
<p>ANALYST:</p>
<p>SAMPLE TIME and DATE:</p>
<p>SAMPLE LOCATION:</p>
<p>ANALYSIS TIME and DATE:</p>
<p>SAMPLE VOLUME:</p>
<p>INSTRUMENT CALIBRATION DATE:</p>
<p>STANDARD RESULTS FROM INSTRUMENT % absorbance, etc:</p>
<p>STANDARD RESULTS FROM STANDARD CURVE (if not direct read):</p>
<p>SAMPLE RESULT FROM INSTRUMENT:</p>
<p>SAMPLE RESULT FROM STANDARD CURVE:</p>

**AMPEROMETRIC METHOD
FOR THE ANALYSIS OF CHLORINE RESIDUAL**

Equipment

1 amperometric titrator
1 250 ml graduated cylinder
1 250 ml beaker
1 buret

Reagents

0.00564 N PHENYLARSINE OXIDE SOLUTION. PAO

Dissolve about 0.8 grams phenylarsine oxide powder into 150 mls of 0.3N NaOH solution. When this has settled, decant 110 mls into 800 mls distilled water. Mix thoroughly. Adjust this solution to a pH of 6 to 7 with 6N HCL. Then dilute to 950 mls with distilled water.

CAUTION! Poison, suspected carcinogen.

PHOSPHATE BUFFER SOLUTION. pH 7

Dissolve 25.4 grams anhydrous KH_2PO_4 and 34.1 g anhydrous Na_2HPO_4 in 800 mls distilled water. Add 2 mls sodium hypochlorite solution containing 1% chlorine. Mix thoroughly. Protect this solution from sunlight for two (2) days. Qualitatively determine presence of free chlorine then expose the solution to sunlight (or ultraviolet lamp) until no total chlorine remains (determine this by adding KI and measuring total chlorine with one of the colorimetric tests). Dilute to one liter. Filter if necessary.

POTASSIUM IODIDE SOLUTION

Dissolve 50 grams KI and dilute to one liter with freshly boiled and cooled distilled water. Refrigerate in an amber glass-stoppered bottle. If the solution taints yellow, discard.

ACETATE BUFFER SOLUTION. pH 4

Dissolve 146 grams of anhydrous $\text{NaC}_2\text{H}_3\text{O}_2$ **OR** 243 grams $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$, in 400 mls distilled water. Add 480 grams of concentrated acetic acid and dilute to one-liter with chlorine-demand free water.

Procedure

- 1) Pour 200 ml sample into beaker. (When expected CL_2 residual is less than 2 mg/l.) If expected level is higher, use 100 ml or proportionately less.
- 2) If necessary, adjust pH to 6.5-7.5 by adding 1 ml phosphate buffer.
- 3) Titrate with 0.00564N PAO solution until needle movement ceases. This gives you the free CL_2 residual.)
- 4) Add 1.00 ml potassium iodide (KI) solution and 1 ml acetate buffer solution, in that order. Continue titrating with PAO solution to the endpoint (as above). If the titration was continued without refilling the buret, this will represent the total chlorine residual.

Calculation

mg Cl as $CL_2/L = A \times 200/ml$ sample

A = volume of phenylarsine oxide solution used in titration (in mls)

**TOTAL CHLORINE RESIDUAL
(Amperometric Titration)
TROUBLESHOOTING GUIDE**

PROBLEM	MOST LIKELY CAUSE	SOLUTION
Lower than expected CL_2 results	Stirring mechanism is over-agitating the sample causing volatilization of the chlorine	Slow the stirring action to a constant but not too violent speed
Reaction time is longer than usual	pH of sample is greater than 7.5 Sample temperature is very low	Buffer sample to pH 7.0 or less Allow the reaction to be completed. Record results. Precision of results is not affected
Endpoint is not clear cut. Needle seems to keep moving a little bit with each addition of titrant	Dirty or contaminated platinum electrode Salt bridge is partially plugged	Clean with mild abrasive Clean salt bridge rejuvenate sodium chloride solution Keep solution surrounding the reference electrode free of contamination. Ensure an adequate supply of undissolved salt to the reference electrode at all times

**Quality Control for
TOTAL CHLORINE ANALYSIS (Amperometric Titration)**

Document

***Supply Water Quality**

- Chlorine and Ammonia Free
- No Chlorine Demand
- Conductivity

Sampling

Grab - Exact Time and Date Sampled
Exact Time and Date Analyzed
NO HOLD TIME
Volume - $CL_2 < 2 \text{ mg/L} = 200 \text{ mls}$
 $CL_2 > 2 \text{ mg/L} = 100 \text{ mls or less}$
Location - Be exact

Glassware

Washed and rinsed thoroughly
Rinsed with sample material, discarded, refilled

Reagents

NIST Traceability
Preparation, Standardization and Expiration Dates

Equipment

Type - Fisher, etc.
Calibration -
Date and Time
Reagents Used
Concentrations
Instrument Results

Duplication Schedule

10% minimum

* Control Charts

* Suggested QA - May become mandatory in the future

REPORTING TOTAL CHLORINE RESIDUAL (Amperometric Titration)

Total Chlorine Residual (Amperometric Titration) Bench Sheet
ANALYST:
SAMPLE TIME and DATE:
SAMPLE LOCATION:
ANALYSIS TIME and DATE:
SAMPLE VOLUME:
INSTRUMENT CALIBRATION DATE: RESULTS: INITIALS OF ANALYST:
REAGENT PREPARATION AND EXPIRATION DATE:
SAMPLE TEMPERATURE:
SAMPLE pH:

References

The DPD Ferrous Titrimetric Method (#4500-CL F) can be found on page 4-43 in the 18th Edition of Standard Methods for the Examination of Water and Wastewater. Pages 4-54 to 4-57 in the 17th Edition of Standard Methods for the Examination of Water and Wastewater and on pages 47-50 in the Simplified Laboratory Procedures for Wastewater Examination, Third Edition, WPCF 1985.

Instructions for the preparation of these standards, as well as, details of making the calibration curve can be found on page 4-46 of the 18th Edition Standard Methods For The Analysis of Water and Wastewater.

The DPD colorimetric method (#4500-C1 G) can be found on page 4-45 in the 18th Edition of Standard Methods for the Examination of Water and Wastewater or in EPA Storet No. 50060, Method #330.5.

The amperometric titration method can be found on page 4-41 in the 18th Edition of Standard Methods for the Examination of Water and Wastewater.