

An Amperometric Titration Procedure for the Determination of Total Chlorine Concentrations in Natural Waters*

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Abstract

The US Environmental Protection Agency (US EPA) water quality criteria and several states' water quality standards for chlorine residual in aquatic systems range from 3 to 10 µg/L. These concentrations are considerably below the detection limits for chlorine residual measurements made using conventional equipment normally present in domestic water treatment plant (WWTP) laboratories. An analytical procedure has been developed for the determination of low-level chlorine concentrations using standard water and wastewater amperometric titration equipment such as the Wallace and Tiernan amperometric titrator. The authors evaluated used this procedure for measuring chlorine concentrations in WWTP effluents and in rivers downstream from the WWTP outfalls. The key modifications made for this procedure were: the use of a more dilute phenylarsine oxide, and endpoint detection by plotting titrant volume versus current. This procedure has been found to be reliable over the range of 3 to 1000 µg/L.

Introduction

The authors conducted series of field investigations of chlorine persistence in waters downstream of wastewater treatment plants in several Colorado Front Range rivers. They found, however, that analytical procedures conventionally used for chlorine residuals were unreliable in low ranges that are of significance to aquatic life in receiving waters. Therefore, they developed an analytical procedure for the determination of low-level chlorine concentrations using standard water and wastewater amperometric titration equipment. This procedure is a modification of the Section 409C Amperometric Titration Method presented in APHA et al. "Standard Methods¹." The authors used the modified procedure for measuring chlorine concentration in municipal wastewater treatment plant (WWTP) effluents and in rivers downstream from the WWTP outfalls. The detailed analytical procedure and the experience of the authors in applying this procedure are discussed in this paper.

Background

The determination of chlorine residuals is important in both the water and wastewater fields. In the water field, it is normally free available chlorine (hypochlorous acid and hypochlorite ion, the distribution of which depends largely on pH), that is determined. In the wastewater field, analyses are generally made for total residual chlorine, which consists primarily of free chlorine and chloramines (also called combined chlorine). In chlorinated WWTP effluents and in waterbodies receiving those effluents, essentially all of the chlorine is present as combined chlorine.

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Several studies have been conducted to evaluate the suitability of various test kit procedures for determining free available chlorine. Guter et al.² concluded that the DPD procedure was accurate and precise over a range of pH values and temperatures, and that syringaldazine, leuco crystal violet and SNORT were suitable for free chlorine determinations. Those researchers used iodometric and amperometric titration procedures as reference methods with which to compare the results obtained using the procedures being evaluated.

Cooper et al.³ and Meier et al.⁴ concluded that a modification of the syringaldazine procedure, termed FACTS, was the best method for free available chlorine determination. In contrast with the results of Guter et al.³, those researchers concluded that all other test kit procedures, including DPD, were not suitably specific for free available chlorine.

Some procedures used for free chlorine measurements are also used for total chlorine determinations, with appropriate modifications. However, the chemistry involved in the determination of total chlorine differs from that involved in measuring free available chlorine. Therefore, procedures suitable for free chlorine determination are not necessarily acceptable for measurements of total chlorine residual.

It appears that DPD colorimetric determination and amperometric titration as described in Standard Methods¹ are the procedures most commonly used for routine measurement of total chlorine. Few studies have been conducted to evaluate these or other total residual chlorine measurement techniques. Bender⁵ studied approximately 10 test procedures and found that results using the DPD colorimetric procedure were consistently higher than those using amperometric titration. Brooks and Seegert⁶ described an amperometric titration procedure employing a recording polarograph and microburette, which was reported to be accurate and free from interference. That procedure requires equipment not normally available in a wastewater treatment plant laboratory.

The reliability of the DPD colorimetric method for free chlorine has been increasingly questioned in recent years.⁷ The suitability of that procedure for accurate total chlorine determinations appears to the authors to be questionable, as well. Amperometric titration as described in Standard Methods¹ cannot be used to measure total chlorine concentrations less than about 0.05 mg/L, which is at least an order of magnitude greater than levels of concern in natural waters for potential toxicity to aquatic organisms. A reliable, simple procedure for low-level total chlorine determinations is clearly needed.

Analytical Procedure

Section 409C of Standard Methods¹ includes a General Discussion section on amperometric titration for the determination of chlorine in aqueous solutions. That discussion is applicable to the procedure used by the authors. Also included in Standard Methods¹ is a section concerning the titration apparatus. Basically, the titration equipment consists of a buret capable of accurately delivering 0.01 mL of titrant, a sample cup, and a stirring device in which is housed a platinum electrode and a KCl reference electrode. Several companies manufacture amperometric titrators that fit this general description. The experience of the senior author is that some of the commercial titrators are less suitable than others, primarily because of the small surface area of

some of the electrodes employed. A Wallace and Tiernan amperometric titrator was used by the authors in developing and applying the procedure described below.

Reagents

a. *Chlorine-free water*. Only distilled or demineralized water that is free of chlorine should be used in preparing reagents. Chlorine-free water may be prepared by passing distilled or demineralized water through a suitable activated carbon filter adsorption column. The water may be tested for the presence of chlorine by titrating a sample as described in the Procedure section of this paper. Any deflection in the meter upon the addition of PAO titrant indicates the presence of chlorine or other oxidants that would interfere in the titration procedure.

b. *Standard phenylarsine oxide (PAO)*, 0.00564 N. See Standard Methods¹ Section 409B, paragraph 3a.

Standardization – Dilute 50.00 mL of freshly prepared 0.0002256 N potassium biniodate to 200 mL in chlorine-free water. Add approximately 1.5 g KI and stir to dissolve. Add 1 mL acetate buffer and allow to stand in the dark for 6 minutes. Titrate using the amperometric titrator and determine the equivalence point as detailed in the Procedure section. If the standard PAO is 0.00564 N, exactly 2.00 mL of PAO will be required to reach the equivalence point.

c. *Phenylarsine oxide titrant*, 0.000564 N. Dilute 10.00 mL of 0.00564 N PAO to 100.0 mL in chlorine-free water.

Standardization – Dilute 5.00 mL of 0.0002256 N potassium biniodate to 200 mL with chlorine-free water. Add approximately 1.5 g KI and stir to dissolve. Add 1 mL acetate buffer and allow to stand in the dark for 6 minutes. Titrate using the amperometric titrator and determine the equivalence point as detailed in the Procedure section below. If the PAO titrant is 0.000564 N, exactly 2.00 mL of PAO will be required to reach the equivalence point.

d. *Potassium biniodate*, 0.0002256 N. Dissolve 0.7332 g reagent grade $\text{KH}(\text{IO}_3)_2$ in 500 mL chlorine-free water and dilute to 1.00 L. Dilute 10.00 mL of that solution to 100.0 mL with chlorine-free water. That solution is used for the standardization of the PAO and should be freshly prepared.

e. *Acetate buffer solution*, pH 4. See Standard Methods¹ Section 409B, paragraph 3e.

f. *Potassium iodide*, (KI), reagent grade crystals.

Procedure

a. *Titrant selection*. Normally a 200-mL sample is used in titration. Each 0.1 mL of 0.000564 N PAO corresponds to 0.01 mg/L in a 200-mL sample. The titrant normality should be selected such that no more than about 4 mL of titrant will be required to reach the equivalence point. Thus, if the chlorine concentration in the majority of the samples to be titrated is less than about 0.4 mg/L, use 0.000564 N PAO as the titrant. If only samples containing chlorine concentrations in excess of 0.4 mg/L are to be analyzed, use 0.00564 N PAO as the titrant. If samples containing concentrations of chlorine in excess of about 0.4 mg/L are to be titrated only occasionally and the volume of 0.000564 N PAO required for titration is found to be excessive, a suitable subsample may be used and diluted to 200 mL with chlorine-free water.

b. *Titration procedure* (total residual chlorine). Prior to beginning the titration, rinse the buret with PAO titrant by filling it completely and allowing the titrant to run into an empty sample cup. Repeating this operation three or four times will ensure that the correct titrant concentration reaches the sample cup. Remove the sample cup and rinse with distilled water and with the sample to be titrated. Add 200 mL of the sample to the sample cup. Add approximately 1.5 g (± 0.2 g) crystalline KI and allow to dissolve, using the agitator on the titrator for mixing. The exact amount of KI added is not critical, but the analyst should weigh 1.5 g of this reagent periodically to become familiar with the approximate amount required. Add 1 mL of acetate buffer and allow the microammeter on the titrator to reach a stable reading; the titration should be started within about 30 seconds following the addition of the KI to the sample.

Full-scale deflection on the microammeter is 100 units. The meter should be initially adjusted to read between 90 and 100 units. Record the initial reading prior to the addition of titrant. Titrate by adding suitable volumes of titrant and recording the titrant volume added and the resultant current reading. At least three (and preferably five to ten) readings of current and titrant volume added should be obtained prior to passing the equivalence point; then add excess titrant to ensure that there is no further meter deflection. Record the final meter reading. If, during the titration, the meter reading falls to near or below 10 units, record the low reading, re-adjust the meter to read between 90 and 100 units, record the high reading, and continue the titration. This approach allows calculation of the total meter deflection, which is used in determining the equivalence point.

The equivalence point is determined by plotting the total meter deflection as a function of titrant volume added. It is important that the total meter deflection be used in preparing this plot. A straight line is drawn through the first few points in the plot and a second straight line is drawn parallel to the abscissa and corresponding to the final total deflection in the meter reading. The equivalence point is determined by the intersection of those two lines. When 0.000564 N PAO is used as the titrant, the chlorine concentration is 0.1-times the titrant volume at the equivalence point. This plotting procedure is also outlined in the ASTM Water Manual⁸ under procedures ASTM D1253 (Tests for Residual Chlorine in Water) and ASTM D1427 (Tests for Residual Chlorine in Waste Water).

c. *Sample storage and handling*. Chlorine measurements should be made as soon after sample collection as possible. Samples to be analyzed for chlorine should be stored in the dark and packed on ice if they must be held for more than a few minutes before analysis. Chlorine compounds are highly reactive and may be rapidly lost from samples due to the effects of volatilization, phototransformation, and chlorine demand. Storage of samples on ice and in the dark between sampling and analysis will help minimize the rate of dissipation.

It is important to estimate the changes that occur in chlorine content in the subject water between sample collection and analysis. This can be accomplished by performing a "time-lag" test. To perform a time-lag test, a single large (approximately 2-L) sample of the water being analyzed is collected. The chlorine concentration in that sample is determined six to ten times over a period of one to three hours, depending on the normal sample holding time. The measured concentrations are then plotted as a function of time, normally on semilog paper. In most cases,

the decrease in chlorine concentration over time can be described by first-order reaction kinetics. The original chlorine content in any sample can be computed given the measured concentration and the holding time. A time-lag study should be performed on a regular basis for each type of water being analyzed because of variability in water compositions. The sample set used for the study should be handled in the same way as other samples (i.e., the samples should be kept cold and in the dark). Even when time-lag studies are made a part of the routine analytical procedure, it is important that the delay between sample collection and chlorine analysis be held to a minimum.

Procedure Evaluation

Previous studies on the accuracy of various analytical techniques for determining chlorine have generally compared the results of different procedures and arbitrarily assigned the results of one procedure as the “true” concentration^{5,6}. That approach is of limited value in determining the true accuracy of an analytical procedure. Further, it is difficult, if not impossible, to prepare a chlorine standard suitable for use in determining the accuracy of an analytical procedure due to the inherent instability and reactivity of chlorine-containing compounds. To date, no viable method for determining the true accuracy of a procedure intended for the analytical measurement of chlorine concentrations in aqueous solutions has been presented in the literature.

In spite of these limitations in methods available for evaluating the acceptability of analytical procedures for chlorine, it is essential that such evaluations be made. To determine the suitability of the amperometric titration procedure described here for total chlorine analysis, in-depth studies were made of the precision and relative accuracy of the procedure. Precision was determined by replicate analyses of samples at selected nominal concentrations. Relative accuracy was measured by analyses of serial dilutions of chlorine-containing samples.

To estimate the precision of the procedure, a number of samples having sufficient volume for repeated analysis were obtained. Two types of samples were used for these precision determinations. The first type included samples collected from a WWTP outfall and from the river downstream from the outfall. The second type consisted of samples prepared using chlorine-free water, an HOCl-OCl⁻ solution, and NH₄Cl. These samples, termed “synthetic chloramines,” were prepared by combining Cl₂ and NH₃-N approximately 1:10 by weight. The NH₃-N was maintained in excess and the appropriate amount of chlorine solution was added slowly with rapid mixing to avoid localized break-point chlorination.

The analytical results of the precision analyses are presented in Table 1. It can be seen from these data that the relative standard deviations increased somewhat with decreasing chlorine concentrations, as would be expected. In the lowest range tested (0.005 to 0.009 mg/L) the relative standard deviation averaged 23%, or about three times that obtained by Brooks and Seegert⁶ (9%) using their more elaborate recording polarographic technique. Andrew and Glass⁹ reported relative standard deviations of 10% at 0.01 mg/L of Cl and 100% at 0.001 mg/L of Cl, also using a recording polarograph. Larson et al.¹⁰ indicated that they were able to obtain suitable precision at 0.001 mg/L of Cl using an amperometric titrator, although details of their procedure were not presented.

Table 1. Precision Test Data for the Amperometric Titration Procedure

Measured Mean Chlorine Concentration (mg/L as Cl)	Standard Deviation (mg/L as Cl)	Relative Standard Deviation (%)	Number of Determinations
Chlorinated WWTP Effluent and River Water Samples			
0.268	0.018	7.1	9
0.158	0.012	7.6	9
0.028	0.004	14.3	9
0.025	0.003	12.0	8
0.009	0.003	33.3	8
Synthetic Chloramines			
0.006	0.001	16.7	5
0.005	0.001	20.0	6

The relative accuracy of the amperometric titration procedure described herein was determined by preparing and analyzing serial dilutions of a chloramine solution, a hypochlorite solution, and a municipal WWTP effluent. The results are presented in Tables 2A and 2B. Those data indicate that the relative error of the procedure is less than 20% at chlorine concentrations as low as 0.006 mg/L. The difference between the predicted and measured chlorine concentrations was less than or equal to 0.002 mg/L in all samples having a predicted chlorine concentration of 0.020 mg/L or less.

The lower limit of measurement for the method is 0.003 mg/L. This corresponds to the minimum volume of titrant (0.003 mL) that can be added incrementally such that data for preparing a titrant volume-meter deflection plot of the type described earlier can be collected. The detection limit of the procedure is 0.001 mg/L. It was concluded that the procedure can accurately and precisely measure chlorine concentrations as low as 0.006 mg/L or below.

Experience in Procedure Application

The amperometric titration procedure described herein has been used successfully by the authors for the measurement of chlorine in the range of 0.003 to 1.0 mg/L in toxicological studies conducted in several Colorado Front Range rivers. The primary source of chlorine in the waters analyzed in these studies was municipal WWTP effluent to which free chlorine had been added for partial disinfection.

The authors found that the rate of dissipation of chlorine from chlorinated municipal wastewater effluent samples, and samples of river water – effluent mixtures collected downstream from

Table 2A. Relative Accuracy Test Data for the Amperometric Titration Procedure – Synthetic Chloramines

Dilution (% of Original Concentration)	Measured Chlorine Concentration (mg/L as Cl)	Mean Chlorine Concentration (mg/L as Cl)	Relative Error (%) *
100	0.325	0.321	–
	0.317		
10	0.032	0.033	3.1
	0.034		
2	0.007	0.006	0
	0.005		
	0.006		
	0.007		
	0.006		
1	0.006	0.005	66.7
	0.003		
	0.005		
	0.005		
	0.005		
	0.004		

* Ratio of the difference between the measured and predicted means to the measured mean. The predicted mean was based on the measured mean concentration of the 100% solution.

municipal WWTP outfalls – is dependent on the nature of the effluent, as well as how the samples were held prior to analysis. The rate of dissipation of chlorine from samples of high-quality effluent (based on BOD and suspended solids criteria) held in the dark at constant temperatures was found to be approximately 20% per hour at temperatures between 15 and 25 C. Rates of dissipation of chlorine from lower quality effluent samples have been observed to be as high as 50% per hour when the samples were held in the dark but not cooled. When samples were held on ice and in the dark, the rates of dissipation were decreased substantially, with the observed concentration decrease being less than 10% per hour. It also appears that chlorine dissipation is a function of pH; the extent of the effect of pH on the rate of dissipation is unclear at this time.

Although the packing of samples on ice substantially reduces chlorine dissipation, it is equally important to keep them in the dark. The major mechanism of chlorine dissipation in a sealed

Table 2B. Low-Level Recovery Data for the Amperometric Titration Procedure

% of Original Concentration	Measured Chlorine Concentration (mg/L as Cl)	Mean Measured Chlorine Concentration (mg/L as Cl)	Relative Error (%) *
Sodium Hypochlorite Solution (in chlorine-free water)			
100	0.410	0.405	-
	0.420		
10	0.045	0.046	+ 15.0
	0.047		
5	0.021	0.022	+ 10.0
	0.023		
1	0.004	0.004	0.0
	0.004		
Pueblo, Colorado WWTP Effluent			
100	0.065	-	-
10	0.007	-	+ 16.7
5	0.003	-	0

* Ratio of the difference between the measured and predicted means to the measured mean. The predicted mean was based on the measured mean concentration of the 100% solution.

Dash (-) indicates not applicable

sample container that is protected from the light is the exertion of “demand” or oxidation–reduction reactions between reduced organic compounds and chlorine. By lowering the temperature of the sample, this process is slowed. However, if light reaches the sample, the oxidation reactions appear to be catalyzed, even at low temperatures. For example, as indicated above, dissipation rates on the order of 20 and 50% per hour have been observed for high- and low-quality effluents, respectively, when the samples were held in the dark. Exposure of the same samples to direct sunlight increased the dissipation rates to 30 and 65% per hour, respectively.

Qualitative observations have been made about the rates of chlorine dissipation in “high”- and “low”-quality effluents. It is possible that the dissipation rate in water samples could be correlated with a characteristic such as the total organic carbon concentration; however, at present, a correlation of this type is not available.

The basis for the amperometric titration procedure is oxidation of iodide to iodine by chlorine in the sample. Iodine is an oxidizing agent and may be reduced by organics and other reduced

materials in the sample. Such reactions would result in iodine demand, analogous to chlorine demand. It is reasonable to expect, therefore, that there will be a decrease in titrable iodine in the sample as the time delay between KI addition and sample titration increases. A range-finding test was performed to determine the magnitude of this effect in high-quality WWTP effluent; the results are presented in Table 3. It appears from those data that there is an initial rapid iodine demand that is virtually complete within one minute. The concentrations measured from one to five minutes after KI addition were virtually the same, and were about 10% less than the concentration measured at 0.5 minutes. It is difficult to begin the titration within less than 0.5 minutes after KI addition, since that is approximately the length of time that is normally required for the reading on the microammeter to stabilize. While it appears that the time delay between KI addition and sample titration is not critical, it is good practice to commence the titrant addition as soon as the microammeter needle has stabilized.

Table 3. Effects of Varying Time-Delays between KI Addition & Sample Titration on Residual Chlorine Determinations for Chlorinated Municipal WWTP Effluent

Time Delay (min)	Measured Chlorine Residual (mg/L as Cl)	
	Measured	Mean
0.5	0.437	0.423
	0.409	
1	0.387	0.385
	0.383	
2	0.402	0.390
	0.377	
5	0.369	0.381
	0.393	

It is important that sufficient KI be added to the sample before titration. The procedure presented in Standard Methods¹ calls for the addition of the equivalent of 0.05 g KI to a 200-mL sample. Chlorinated WWTP effluent samples were titrated using varying amounts of KI; the results are presented in Table 4. Those data indicate that the measured chlorine concentration is a function of the amount of KI added for additions of less than about 1 g to 200-mL samples. The recommended KI addition in the procedure outlined herein is 1.5 g.

If it is necessary to perform the titrations in the field, care should be taken to avoid exposing the titrator cup containing sample and KI to direct sunlight. Sunlight tends to catalyze the reduction of liberated iodine by organic compounds in the sample. Exposure to sunlight could thus produce an erroneously low concentration measurement.

A limited number of studies conducted to evaluate analytical procedures for total residual chlorine determination have been reported by others. Studies on the accuracy and precision of

Table 4. Effects of Varying KI Additions on Chlorine Residual Determinations for Chlorinated Municipal WWTP Effluent

KI Added (g)	Measured Chlorine Residual (mg/L as Cl)
Sample A	
0.05	0.134
	0.140
0.1	0.157
	0.154
0.3	0.173
	0.181
0.6	0.191
Sample B	
0.3	0.093
	0.100
0.6	0.121
	0.119
1.5	0.154
	0.136
3.0	0.150
	0.142

the Standard Methods¹ amperometric titration procedure and certain modifications of it were mentioned earlier. As indicated, essentially all reported studies on the accuracy of the procedures have entailed arbitrarily assigning the results of one procedure as the “true” value, which does not result in actual accuracy determinations. The two most common routine analytical methods for chlorine measurement are amperometric titration and the DPD colorimetric procedure. Of these two procedures, the DPD procedure typically results in higher values^{5, 11}. It has been recommended⁵ that amperometric back-titration, in which excess PAO is titrated with standard iodine, be used in place of the forward-titration, of which the procedure presented here is a modification. However, a recent report suggests that back-titration is unsuitable for a variety of samples¹². Until research is conducted to evaluate the true accuracy of each of those various procedures, questions remaining about the comparative merits of the various procedures are unlikely to be resolved. The relative accuracy, precision, and simplicity of the amperometric titration procedure described in this paper appear to make it ideally suited for both routine analyses and research work.

Recently, the senior author (Lee) had the opportunity to evaluate the Fischer-Porter amperometric titrator for residual chlorine determination. He found that that apparatus did not

have adequate sensitivity for use in this procedure for determination of chlorine at less than about 20 ug/L Cl. It is therefore not suitable for determination of residual chlorine at or near US EPA criteria or many states' water quality standards.

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