Course Manual

Directed Assistance Module (DAM) 7

Initial Demonstration of Capability Using EPA Method 334: Determination of Residual Chlorine in Drinking Water Using On-line Chlorine Analyzer

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Notes

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Notes

DIRECTED ASSISTANCE MODULE (DAM) 7

Initial Demonstration of Capability Using EPA Method 334: Determination of Residual Chlorine in Drinking Water Using On-line Chlorine Analyzer

Getting started

The TCEQ created this DAM to be delivered by the TCEQ's Financial, Managerial, and Technical (FMT) service providers. The TCEQ Water Supply Division (WSD) trains instructors in how to accomplish this training. Contact the TCEQ Water Supply Division at 512-239-4691 If you have any questions.

Course Objective

The purpose of this course is to provide a combination of classroom and hands-on training to the staff of any public water system (PWS) that wishes to report chlorine residuals (free or total) to the Texas Commission on Environmental Quality (TCEQ) from on-line analyzers using analytical methods other than those specifically approved by the United States Environmental Protection Agency (EPA).

To obtain approval to use these instruments, a system must demonstrate that the on-line monitors can reliably and accurately measure chlorine residuals by conducting an Initial Demonstration of Capability (IDC) and then periodically verifying the performance of the on-line instrument and benchtop reference method.

Learning goals:

After receiving the training, the water system's staff should be able to:

1. Prepare chlorine calibration standards at multiple concentrations.
2. Understand precision and accuracy requirements necessary to validate on-line instrument readings.
3. Utilize the TCEQ supplied Method 334 IDC Spreadsheet.
4. Understand the continuing monitoring and comparison requirements between on-line and benchtop instruments.

5. Document the use of Method 334 for validation of the on line instrument on the Drinking Water Laboratory Approval Form (TCEQ Form 10450) for attachment to the system's required Monitoring Plan.

Expertise Required

Instructor:

This Directed Assistance Module (DAM) must be given by an instructor who understands and can demonstrate the steps needed to properly prepare chlorine calibration standards, establish and record various chlorine calibration standard readings on a benchtop analyzer, compare on-line analyzer readings with benchtop analyzer readings, utilize the TCEQ Method 334 IDC spreadsheet, and is comfortable working with computers.

The instructor must be capable of completing all of the objectives of this DAM. This will require familiarity with the particular instruments in service at the plant and the analytical protocols for analyzing chlorine concentrations using that instrument.

The TCEQ would prefer that the instructor hold a Class C or higher Surface Water Operators license if compliance monitoring using the on-line instrument takes place in a surface water treatment plant.

Participant:

The public water system (PWS) staff attending this course should be familiar with the disinfection process and monitoring regimen used at their water treatment plant, familiar with the instruments used in their plant, and either already hold a Water Operators license or at least have a basic understanding of potable water chlorination and the laboratory processes for residual measurement.

Facilities and Materials Required at the Treatment Plant

Instructor:
The instructor must provide all of the materials described in the Course Description and Instructor Guide for Directed Assistance Module 7.

Training Site:
This training is to be conducted at a water treatment plant which is able to provide the materials and equipment shown in Table 1.

Table 1. Materials and equipment required at the treatment plant

Quantity	Item
1	Computer with Microsoft (MS) Excel
1	Copy of the Method 334 blank spreadsheet —Provided by the Instructor
1 mL	1.0 milliliter (mL) graduated measuring Pipette (serological or Mohr) or a 1.0 mL TenSette pipette
1 ea.	10.0 mL graduated measuring Pipette or a 10.0 mL TenSette pipette
1	50 mL or 100 mL graduated cylinders or volumetric flasks
Several	Ampoules of a chlorine solution of known concentration (i.e., a primary chlorine standard or stock standard)
1 L	1 liter of demand free dilution water (Deionized or distilled water may be used. If deionized or distilled water is used, all of the dilutions must be accomplished from the same bottle)
60	Enough reagent to run 60 benchtop tests
1	Benchtop chlorine analyzer utilizing an EPA approved chlorine method
5	Sample vials, cuvettes, Erlenmeyer flasks, or beakers (as applicable and as necessary) for each concentration range of calibration standard to be tested to be tested.
1	TCEQ approved Concentration Time (CT) Study
As Required	Installed "tee" on monitoring instrument supply line.

Deliverables

During this training event, the plant staff and Instructor will produce the following documentation:

1. Completed Participant Sign Up Sheet.
2. Method 334 IDC Spreadsheet completed for Steps 1-4 and the initial reading for Step 5.
3. A printout of at least one worksheet from Method 334 IDC spreadsheet with data entered for at least one on-line monitoring point.
4. Completed Recommended Action Plan Form.
5. Completed Plant Questionnaire from each participant.
6. Completed Project Completion Form (Instructor only).
7. Completed TCEQ Laboratory Approval Form (Form 10450) and List of Analytical Methods if the system uses chloramines.

Provisional Agenda

The completion of this DAM is expected to take approximately 4.5 hours. The provisional agenda for the DAM is shown in Table 2.

Table 2. Provisional agenda for DAM 7

Time	Activity
8:00-8:15	Introductions and overview (15 minutes)
8:15–9:00	Plant tour (45 minutes)
9:00-9:15	Lab tour (15 minutes)
9:15-9:45	**Step 1—**Working standard solution for chlorine demand test (30 minutes)
9:45-10:15	**Step 2—**Apparent chlorine residual of the dilution water and the chlorine demand of the dilution water (30 minutes)
10:15-10:30	**Step 3—**Working standard solution for preparing chlorine calibration standards (15 minutes)
10:30-11:00	**Step 4—**Determining accuracy and precision of benchtop analyzer from measurement of chlorine calibration standards (30 minutes)
11:00-11:30	**Step 5—**Comparison of online monitor readings to benchtop readings (30 minutes)
11:30-12:00	Recommended Action Plan (30 minutes)
12:00-12:30	Wrap up and Questionnaire (30 minutes)

Introduction

Quality Assurance/Quality Control (QA/QC)

Before getting started on the hands-on activities for this DAM, there are some things to think about for quality assurance/quality control (QA/QC) concern.

Purpose of method

The purpose of Method 334 is to give the system a way to demonstrate to the TCEQ that an online residual analyzer using an EPA-unapproved analysis can measure disinfectant level as accurately as an EPA-approved method. Before using the on-line analyzer for compliance monitoring, the IDC protocol can be used to show that:

- the operator's lab technique is correctly applied and precise enough,
- the laboratory equipment and instrumentation is sufficiently accurate and precise enough, and
- the reagents used for the IDC are of good quality and are reliable enough to accurately confirm the performance of the non-standard online analyzer by comparing the online instrument results against a benchtop test performed on an instrument that does use an EPA approved analytical technique.

Chlorine demand

In this method, chlorine demand is extremely important. If chlorine demand is not measured accurately, the results will not be useable.

The IDC procedure requires very precise measurements of chlorine residual at very low concentrations. That is why the chlorine demand of the dilution water must be known exactly before comparison with benchtop instruments.

One source of stray chlorine demand is glassware. A system's glassware may have been contaminated with a chlorine demand from previous uses. The glassware used in this test must be chlorine demand-free, so it may need to be pre-treated before starting the IDC.

The Hach-recommended procedure to remove chlorine demand in glassware is:

- Fill the glassware with a dilute solution of chlorine bleach prepared by adding 1 mL of commercial bleach to 1 liter of water.
- Soak in this solution at least one hour.

- After soaking, rinse thoroughly with deionized (distilled) water and allow it to dry before use.
- If the mixing cylinder is thoroughly rinsed with deionized water and allowed to dry after each use, only occasional pretreatment is necessary.

Don't switch from free to total

It is also recommended that the analyst not use the glassware for Free and Total Chlorine analysis without first thoroughly cleaning the glassware and applying the above procedure to remove chlorine demand.

Use a single aliquot of DI water

When using deionized (DI) or distilled water as dilution water to conduct the IDC, each container of DI (distilled) water may have a different chlorine demand, even if produced by the same equipment. Therefore, it is desirable to have a sufficient quantity of one-container DI water to complete the whole IDC procedure.

One analyst must complete the entire IDC

The entire IDC, Steps 1 through 5 must be completed by the same analyst. However, once the IDC has been completed and approved by the TCEQ, the weekly confirmation checks may be performed and documented by any operator trained to perform the analyses.

Periodic verification

The system may implement the Method 334 protocol to confirm the performance of an instrument that does use an EPA approved method using N, N-diethyl-p-phenylenediamine sulfate (DPD) without having to conduct primary calibrations of the instrument every 90 days.

If routine maintenance is performed on the instrument, the IDC does not have to be repeated in order to continue using that instrument at the approved location. However, the accuracy of the analyzer must be verified with a grab sample comparison after the analyzer is placed back in service and a second grab sample 24 hours after it is placed back in service.

If there is a major repair on an approved instrument, or if the instrument is replaced by another instrument of the same manufacturer and model, the Step 5 of the IDC must be repeated for seven calendar or business days, as applicable, based on the staffing of plant.

Description of Activities

1. Introductions and overview (15 minutes)

IMPORTANT

If the plant staff have not performed the dilute chlorine soak for all labware to satisfy any chlorine demand, this should be started during the introduction. In that case, the labware must be thoroughly rinsed with DI water after soaking during the plant tour.

The instructor will explain the purpose of the directed assistance and what needs to be accomplished before you leave.

If the option is available, participants who wish to receive Continuing Education Units (CEUs) must sign the Participant Sign Up Sheet which the instructor will provide.

2. Plant tour (45 minutes)

The instructor will accompany the plant staff on a limited plant tour. During the plant tour, the instructor will document:

a. General layout of the treatment units.

b. Location of all active and standby disinfectant (O_3, ClO_2, Cl_2, and ammonia) feed points.

c. Location of any existing on-line sampling taps that should be used to monitor the chlorine or chloramination process.

d. Instrument manufacturer, model number and analytical method for all on-line chlorine monitors installed.

The purpose of the plant tour is to identify locations where chlorine or chloramine on-line analyzers are or will be used for regulatory reporting. Therefore, if this training is conducted at a surface water treatment plant which intends to use an on-line instrument to determine the adequacy of inactivation, a copy of the plant's Concentration/Time (CT) Study approval letter will be needed for identifying the approved disinfection zones.

During the plant tour, the instructor and participants will begin completing the **Plant Information Form** provided by the instructor. Participants will accompany the Instructor and provide information on the various disinfection zones and location of on-line chlorine monitors.

If the PWS getting the training plans to use on-line monitoring for compliance with distribution system disinfectant residual levels, the plant tour will be shorter, and a CT Study will not be needed.

3. Lab Tour (15 minutes)

The instructor will accompany plant staff on a lab tour to gain an understanding of their lab equipment and general procedures used.

4. Step 1—Working standard solution for chlorine demand test (30 minutes)

In order to provide accurate chlorine concentration readings on the benchtop instrument, certain interferences must be determined and addressed.

The first step in doing this involves an analysis of the dilution water for any apparent chlorine residual and chlorine demand of the dilution water.

IMPORTANT

If chlorine demand free water is prepared for use in the directed assistance training, it must be prepared prior to the commencement of the training.

Commercially supplied organic-free water is acceptable dilution water for the preparation of chlorine calibration standards and eliminates the need to prepare chlorine-demand free water. Procedures for the preparation of chlorine demand-free water are included in ASTM-International's Standard D 1253-06 and Standard Method 4500-Cl C.

The Instructor will:

> Discuss the method for determining the makeup of the working standard solution based on the anticipated target concentration of the chlorine demand test. Instructions for preparing the working standard solution are found in the IDC Step 1 instruction found later in this document.

The Participants will:

> Calculate a target concentration based on the perceived quality of their dilution water and determine if the working standard solution needs to be diluted.

Instructions for preparing the working standard solution are found in the IDC Step 1 instruction found later in this document.

5. Step 2—Apparent chlorine residual of the dilution water and the chlorine demand of the dilution water (30 minutes)

Important

Step 2 must be done **immediately** after Step 1 to avoid solution degradation.

Using the working standard solution prepared in Step 1, Step 2 will analyze the dilution water for any apparent chlorine residual and will analyze a low concentration of the working standard solution to determine any chlorine demand in the dilution water. These steps are essential in improving the accuracy of the later chlorine calibration standard measurements. Precision in this step is extremely important.

Preparation of the calibration standard solutions must be done using the most precise measurement available. Measurement of the working standard solution must be done using pipettes. Measurement of the dilution water must be done with pipettes or volumetric flasks.

It is essential that the total volume of the prepared calibration standard be well in excess of the amount to be pipetted into the sample cells. Having a reserve amount of the calibration standard ensures that pipettes will have sufficient volume of calibration standard to draw without drawing air and jeopardizing the precision and accuracy of the tests.

The Instructor will:

a. Make sure that the labware and cells have been properly cleaned.

b. Discuss the analysis of the dilution water for apparent chlorine residual (This is the "**reagent blank**").

c. Discuss the preparation of the target low residual for the determination of chlorine demand in the dilution water.

d. Guide the participants through the preparation, analysis and recording of the results of the apparent residual tests and the dilution water chlorine demand tests.

The Participants will:

a. Prepare, analyze and record the results of the apparent chlorine residual of the dilution water in the IDC spreadsheet.

b. Prepare, analyze and record the results of the low concentration chlorine solution in the IDC spreadsheet to determine the chlorine demand of the dilution water.

Instructions for preparing the test solutions for the apparent residual and for the chlorine demand test are found in the IDC Step 2 instruction (found later in this document).

6. Step 3—Working standard solution for chlorine calibration standard tests (15 minutes)

Just like in Step 1, a working standard solution must be prepared which can be added to the dilution water in various volumes to hit the required target chlorine concentrations. The working standard solution may be undiluted aliquots of the supplied stock standard as long as the target chlorine residual concentrations can be achieved. The determination of whether a diluted working standard solution is necessary must be made before proceeding on to Step 4. The target chlorine calibration standard concentrations will generally be in the range of 0.2 milligrams per liter (mg/L) to 4.0 mg/L, but exact concentrations will need to be determined by the requirements of the IDC Step 4.

The Instructor will:

> Discuss the method for determining the concentration of the working standard solution based on the anticipated target concentration of the chlorine calibration standards in the required ranges.

The Participants will:

> Calculate the target concentration based on the range of on-line monitor settings and determine if the stock standard solution needs to be diluted (working standard).

Instructions for preparing the working standard solution are found in the IDC Step 1 instruction found later in this document.

7. Step 4—Determining the accuracy and precision of the benchtop analyzer from measurement of chlorine calibration standards (30 minutes)

Step 4 of the IDC protocol involves using an approved manual benchtop analytical method (reference method) to measure the chlorine concentration in a series of standardized samples that have been dosed with increasing amounts of stock standards (or working standard).

This part of the IDC study is where the accuracy of the benchtop (reference) method is evaluated. Procedures that will be used to test the on-line monitoring that is or will be installed will also be described. The data entered in the Step 4 section of the worksheet and the results of these tests are also

used to prepare a calibration curve if the benchtop method uses a calibration curve.

There is room to enter data for six sample sets on the IDC Step 4 Spreadsheet, but you only have to test the accuracy of the reference method using at least three different chlorine concentrations that span the entire range of values that you expect to see at any site where you plan to install an on-line monitor. In many instances, the low level and low alarm level tests may use the same chlorine concentration; the high level and high alarm tests may also use the same concentration as each other.

The Instructor will:

a. Discuss setting targets for chlorine calibration standard concentrations based on the on-line monitor alarm settings and expected low and high residual measurements.

b. Discuss the preparation of the target calibration standard concentration for the range of standards necessary to cover the on-line monitor alarm settings and expected low and high residual measurements.

c. Guide the participants through the preparation, analysis and recording of the results of at least three sets of chlorine calibration standard concentrations based on the on-line monitor alarm settings and expected low and high residual measurements.

The Participants will:

Prepare, analyze and record the results of the chlorine calibration standard tests in the IDC spreadsheet.

Instructions for preparing the test solutions for required chlorine concentrations are found in the IDC Step 4 instruction found later in this document.

8. Step 5—Comparison of online monitor readings to benchtop readings (30 minutes)

Step 5 of the IDC protocol involves comparing the results produced by the on-line monitor(s) to those produced by the benchtop reference method.

The grab samples for the reference method must be obtained from the same sample tap that supplies the online monitor so the operators must install a tee in the line that supplies at least one of the on-line instruments prior to the training.

The location, manufacturer, model number and analytical technique of all on line chlorine monitors should be identified as part of the plant and lab tour portions of the training.

For purposes of this training event, not all on-line monitors need to be compared to the benchtop reference method. However, the background information for the system, the benchtop analytical method, the benchtop instrumentation, and the anticipated/historical residuals and settings blocks should be completed for at least one instrument.

Further, at least one sample from the instrument selected should be collected and the benchtop reading should be compared to the reading displayed by the on-line monitor.

The Instructor will:

a. Choose one functioning on-line monitor location that has a tee installed to facilitate collecting grab samples.

b. Lead the participants in collecting grab samples from the tee connected to the on-line monitor.

c. Lead the participants in collecting on-line monitor reading at the time that the grab samples are collected.

(**Note:** *This reading should be taken when the chlorine residual is not in flux. The response of the on-line instrument will probably be averaged over a specific time particular to each model and/or manufacturer. The benchtop test will be based on the length of time it takes to collect the sample.)*

d. Discuss the 24-hour minimum and maximum residual grab sampling requirements.

e. Lead the participants in conducting a benchtop analysis of the grab samples and recording of the grab sample and on-line monitor results.

f. Enter the date, time, and analysts initials in to the Comparison No. 1 line in the On-Line Instrument No. 1 section of the spreadsheet.

g. Enter the on-line reading, and benchtop reading into the Comparison No. 1 line.

h. Discuss the fact that the General Characterization of On-line Result columns will not fill themselves in until the Maximum and Minimum values for the 24-hr On-line Record for Comparison No. 1 are filled in

i. Discuss the requirements for the 14 days of monitoring necessary to complete the actual Step 5 analysis.

j. Open the IDC Data (Example) page to the Step 5 portion and discuss the impact of having various values entered into the spreadsheet and the issue of getting all "**yes**es" in the Analysis of Results block.

The Participants will:

a. Collect grab samples from the selected on-line monitor location.

b. Record the on-line monitor reading at the time the grab samples are collected.

   (**Note:** *This reading should be taken when the chlorine residual is not in flux. The response of the on-line instrument will probably be averaged over a specific time particular to each model and/or manufacturer. The benchtop test will be based on the length of time it takes to collect the sample.)*

c. Analyze the grab samples using the benchtop analyzer used in Steps 1-4.

d. Record all results in the IDC spreadsheet.

9. Recommended Action Plan (30 minutes)

The Instructor and Participants will:

a. Identify specific steps that should be taken to complete the IDC process. This should include identification of all the on-line monitoring points and grab sample locations to be used for on-line and benchtop comparisons.

b. Identify locations where tees need to be installed to facilitate grab sampling.

c. Document the steps using the *Recommended Action Plan Form* provided by the instructor.

d. Complete the required *Drinking Water Laboratory Approval Form* (TCEQ 10450).

10. Wrap-up and Questionnaire (30 minutes)

a. Each Participant will complete the *Plant Questionnaire* provided by the instructor.

b. The Instructor will complete the *DAM Completion Form*.

Initial Demonstration of Capability (IDC)

Background Information

Some public water systems (PWSs) use on-line chlorine residual monitors to collect disinfectant residual data used for compliance reporting. Unless their on-line monitor uses an automated version of the DPD colorimetric method, a PWS must conduct a special study to verify that their instrument is capable of consistently producing accurate data.

This study is:

1. Called the **Initial Demonstration of Capability**, or IDC.
2. Conducted in accordance with the requirements of **EPA Method 334.0**.
3. Conducted (in most cases) on each "non-DPD" **on-line chlorine** monitoring instrument that the PWS uses to collect compliance data.

The results of an instrument's IDC study must be submitted to the TCEQ for review and approval before the device can be used for compliance monitoring.

The TCEQ created the IDC spreadsheet to help PWS operators, vendors, and consultants collect and report all the IDC data that the TCEQ needs to approve an on-line chlorine residual monitor. While EPA requires compliance with Method 334 including the IDC, the TCEQ IDC spreadsheet provides a step by step data entry process that eliminates the guesswork on calculations and QC checks.

The completed spreadsheet contains all of the information necessary for TCEQ’s review of the IDC and subsequent approval. A flowchart for the IDC process is included in Appendix A.

Once the IDC study is completed and approved, the PWS may use their on-line monitors for reporting purposes. However, the PWS must verify the continued accuracy of their on-line monitor at least once each week. Although Method 334.0 describes the follow-up performance verification process, this DAM and the TCEQ IDC spreadsheet does not address them.

To complete the IDC protocol, the PWS must complete the following five separate steps:

Step 1: Prepare the working standard solution that will be used to determine the chlorine demand of the dilution water used when evaluating the performance of the benchtop method.

Step 2: Determine the chlorine demand of the dilution water.

Step 3: Prepare the working standard solution that will be used to evaluate the performance of the benchtop method.

Step 4: Verify that the benchtop method is producing accurate results.

Step 5: Conduct the IDC test to show that the on-line monitor produces the same results as the benchtop (reference) method.

The data produced during each of these steps is recorded on the IDC Data worksheet and the instructions/guidance for each of these five steps are provided in separate text boxes in the spreadsheet.

References:

Method 334 as published by the EPA is included as Appendix B to this document. Operators can also download a copy of Method 334.0 at the following Internet address:

- water.epa.gov/scitech/drinkingwater/labcert/upload/met334_0.pdf

Preparing the IDC Data Worksheet

The IDC spreadsheet provides a stepwise process and data keeping tool to accomplish the five steps necessary to perform the IDC.

The spreadsheet tool is a required and integral part of the TCEQ's IDC approval process, so much of this DAM training is related to the proper use of the spreadsheet. The IDC Data worksheet contains space to record all of the essential information about the system, the analytical methods, reagents, standards, and test results that the operators and the TCEQ need to evaluate the performance of both the benchtop (reference) method and the on-line monitor.

Although the IDC worksheet is password-protected, the colored cells have been unlocked so that you (the operators, analysts, and consultants) can enter the necessary information in them.

The TCEQ prepared an example of a completed IDC Data worksheet to help you complete the form for the plant instruments and procedures. This worksheet is completely password protected to prevent anyone from accidentally changing it. A printed copy of the example IDC worksheet is included in Appendix C.

System-specific spreadsheet information

The information to be entered on the spreadsheet is:

1. **System Information.**
    a. PWS Name:

       Enter the name of the water system where the IDC test is being conducted.

    b. PWSID:

       Enter the Public Water System's 7-digit Identification Number.

2. **Benchtop Method Information.**
    a. Benchtop Analytical Method:

       Enter the analytical method used during benchtop testing, for example:

       i. DPD Colorimetric (SM 4500-CL G)
       ii. DPD-FAS Titration (SM 4500-CL F)
       iii. Amperometric Titration (SM 4500-CL D)

b. Instrument Manufacturer and Model:

Enter the manufacturer's name and model number of the colorimeter or amperometric titrator used for the benchtop analysis (if applicable). For example:

- Hach Colorimeter II
- Hach Amperometric Titrator
- Hach DR/890
- W&T A-790 Amperometric Titrator
- LaMotte Smart 3
- Capital Controls 17T2000 Amperometric Titrator

You do not need to enter information on titration burettes, pipettes, or other glassware.

c. **Reagents**: Identify manufacturers, expiration dates, and (if known) the lot numbers of all reagents, reagent kits, titrants, buffers, dilution waters, etc. used during the IDC study.

You do not need to list the stock standards used to prepare the working standards in this area because the information will be provided in other locations.

IMPORTANT

If chlorine demand free water is used in this training, it must be prepared well before starting the training.

Preparing Glassware and Demand Free Water

1. Treatment of labware for chlorine demand.

Pretreat sample containers, pipettes, beakers, volumetric flasks, graduated cylinders, etc. to remove any chlorine demand by:

- Soak the container in a dilute bleach solution (1 mL commercial bleach in 1 L of deionized water) for at least 1 to 3 hours.
- Rinse thoroughly with deionized water.
- Rinse the entire inside, outside, and lip of glassware at least three times.
- Air dry.

If the sample containers are rinsed thoroughly with deionized water after use, only occasional pretreatment is necessary.

2. Sample cells.

Do not use the same sample cells for free and total chlorine testing.

Even the slightest trace of iodide from the total chlorine reagent can contaminate the free chlorine test and cause a monochloramine interference. Therefore, it is best to use separate, dedicated sample cells for free and total chlorine measurements.

3. Chlorine demand-free water

If water that has chlorine demand is used in Method 334.0, the results will not be accurate.

Chlorine-demand free water can be made in the lab or it can be purchased. Commercially supplied organic-free water is acceptable for the preparation of chlorine standards and eliminates the need to prepare chlorine-demand-free water.

Procedures for the preparation of chlorine demand-free water are included in ASTM-D 1253-06 and Standard Method 4500-Cl C. If chlorine demand free water is prepared for use in the directed assistance module training, it must be prepared before starting the training.

IDC Step 1

IMPORTANT

You must complete Steps 1 and 2 at the same time. The stock standard/working standard you create in Step 1 and use in Step 2 begins to lose its strength as soon as you open the ampoule of stock standard.

Step 1 of the IDC protocol involves preparing the working standard solution that will be used to determine the chlorine demand of the dilution water (which is Step 2 in the IDC protocol).

The data you enter in the Step 1 section of the worksheet is used to calculate the concentration of this working standard solution. The working standard solution is applied to each of the calibration standards used in subsequent benchtop tests to approach the target chlorine concentration. The working standard solution may be undiluted aliquots of the stock standard as long as the target chlorine residual concentration can be achieved.

The lowest chlorine concentration needed will be used for the second test(s) in Step 2 which determines the chlorine demand of the dilution water.

TCEQ recommends that you use enough stock or working standard to produce an "Applied Concentration" between 0.08 and 0.16 mg/L. If you think your dilution water might have a chlorine demand, you might want to set a target concentration between 0.15 and 0.30 mg/L.

You must determine whether a diluted working standard solution is necessary before proceeding to Step 2.

To approximate the volume of working standard solution needed to hit the target, use the following procedure.

Chlorine calibration standard solutions are prepared by dilution of a concentrated (50 to 75 mg/L Cl_2) primary chlorine stock standard contained in ampoules. The actual concentration changes for each lot of stock standard and is printed on the package label.

1. Calculate the estimated volume of stock standard to be pipetted from the ampoule using the following formula:

$$\frac{\text{Desired final chlorine calibration standard concentration} \times \text{calibration standard volume}}{\text{stock standard concentration (from label)}} = \text{Estimated pipetted volume}$$

2. Round the estimated volume to the nearest 0.05 mL (most pipettors read to 0.05 mL only).
3. The spreadsheet will calculate the actual concentration of the applied concentration and the expected concentration.

Example

As an example, consider a system with the following data:

1. Assumptions

   a. Chlorine stock standard concentration = 65 mg/L

   b. Calibration standard volume = 60 mL

   c. Desired final chlorine concentration= 0.20 mg/L

2. Calculations

   d. 0.20 mg/L x 60 mL = 0.185 mL

   65 mg/L

   e. Round to nearest 0.05 mL

   = 0.20 mL of stock standard to be pipetted

   f. Applied concentration
   (example only –will be calculated by spreadsheet)

$$\frac{\text{0.2 mL pipette x 0.65 mg/L stock standard concentration}}{\text{60.2 mL calibration standard volume}} = 0.216(0.22)\ \text{mg/L}$$

Instructions for the Step 1 Section of the IDC Data Worksheet

Enter data in the fields below as required. Note: a number of the fields are calculated by the spreadsheet. These calculated values or Quality Control (QC) indicator fields are provided as a tool in assisting the analyst in complying with the IDC requirements.

1. Analyst:

Enter the name of the analyst(s) who will prepare the stock solution used to measure the chlorine demand of the dilution water.

2. **Chlorine Standard, Source and Product No.:**

   Enter the product information about the chlorine stock standard that will be used to prepare the working standard solution. Include the name of the stock standard's manufacturer (or vendor) and the associated product or stock number.

3. **Lot No.:**

   Enter the manufacturer's lot number of the batch of stock standard you will be using.

4. **Expiration Date:**

   Enter the date (month and year) that the stock standard expires.

5. **Concentration:**

   Enter the manufacturer's reported concentration of the batch of stock standard you are using. If the manufacturer also provided an error range for the batch, also enter it. Even though this data is not used for any of the calculations, including it may help you or the TCEQ reviewer explain any unexpected results in Step 2.

6. **Volume of Stock Std Used:**

   Enter the volume of stock standard used to prepare the working standard. If the stock standard was not diluted, enter the nominal volume of the standard ampoule; for example, enter 2.0 if the standard is not diluted and the ampoule contains 2 mL of stock standard.

7. **Volume of Dilution Water Used to Prepare the Working standard Solution:**

   Enter the volume of water used to dilute the stock standard. If the stock standard was not diluted, enter 0.

8. **Assumed Working standard Solution Concentration:**

   These are calculated values based on the data you have previously entered.

9. **Chlorine Demand of Dilution Water:**

   This is a calculated value. If the working standard solution you use for Step 2 is undiluted stock standard, the spreadsheet will enter "NA" in this cell. However, if you prepare your working standard solution using a diluted stock standard, the actual concentration of the working standard solution will be affected by the chlorine demand of the

dilution water. In this case, the spreadsheet determines the value based on the results of the Step 2 tests.

10. Actual Working Standard Solution Concentration:

Again, this is a calculated value based on the data you entered and, if you diluted the stock standard, the results of the Step 2 tests.

IDC Step 2

IMPORTANT

You must conduct the Step 2 tests as soon as you finish preparing the working standard solution in Step 1.

Step 2 of the IDC special study involves determining the chlorine demand of the dilution water used throughout the IDC study. The data you enter in the Step 2 section of the worksheet and the results of these tests are used to correct for the impact of chlorine demand when standards are diluted and calibration standards are prepared for analysis.

IMPORTANT

Read before doing!

It is best to *read the test procedure* used for performing the benchtop test to ensure that:

- the correct sample vials are used,
- the correct reagent is used, and
- the correct reaction times are allowed for, as applicable.

Instructions for the Step 2 Section of the IDC Data Worksheet

Enter data in the fields below as required.

Note: *A number of the fields are calculated by the spreadsheet. These calculated values or QC indicator fields are provided as a tool in assisting the analyst in complying with the IDC requirements.*

1. **Analyst:**

   Enter the name of the analyst(s) who will determine the chlorine demand of the dilution water.

2. **Sample ID:**

   There are four rows available to enter data. You must enter data in the first row, which is labeled as "Dilution Water (Reagent Blank). The spreadsheet uses these results to determine the "apparent" residual present when you add reagents but no chlorine stock standards or working standard (i.e., the "apparent residual" in the "reagent blank"). You must also enter data in the row, identified as "Initial Test". You will only need to enter data in one or both of the "Repeat Test" rows if

the initial tests do not produce acceptable results. Once the spreadsheet is able to calculate the chlorine demand of the dilution water, you do not have to repeat the test.

3. Measured Residual:

This is a calculated value that represents the "apparent" residual in the dilution water when you add your reagents but no stock standard or working standard (i.e., the reagent blank). You may not enter data in these cells.

4. Assumed Chlorine Demand of the Dilution Water:

Most of the time dilution water has a very low chlorine demand. This is especially true for organic-free water and for fresh deionized water that has been stored in glass bottles. Therefore, the worksheet initially assumes that the dilution water has no appreciable chlorine demand. You may not enter data in these cells.

5. Calibration Standard Volume:

In order to accurately determine the chlorine demand of the water, the analyst needs to test at least five samples. Since each sample will contain 10 mL of dosed dilution water, you will need to prepare at least 50 mL of dilution water for each batch of 5 samples you test. There are two ways to produce the 50 mL of calibration standard that you need to analyze and each has its advantages and disadvantages.

a. Method 1: Dose 60 mL volume of dilution water and then analyze five 10 mL portions of the 60 mL batch.
    i. Advantages:
        1. Since you are only pipetting the working standard solution once, you only have one chance to make a pipetting error.
        2. Since you are using a large volume of water and a large amount of working standard solution, small measurement or pipetting errors have minimal impact on the results.
    ii. Disadvantages:
        1. If you make a mistake, it affects all of the five samples.
        2. If measuring total chlorine, it takes up to 3 minutes to run each test (unless the reagent is added to multiple sample vials at the same time) and you may not get consistent results if the dilution water has a chlorine demand because it may be 15 minutes or so before

the analyst can run the test on the last aliquot in the sample set.

b. Method 2: Dose and analyze five separate 10 mL samples of dilution water.
    i. Advantages:
        1. A measuring or pipetting error only affects a single sample.
        2. The samples can be analyzed as soon as they are dosed.
    ii. Disadvantages:
        1. Since you are using small volumes of water and working standard solution, the impact of small dilution errors are increased.

Once you have decided which method you are going to use, enter the volume of dilution water you are going to treat with working standard solution.

6. Working Standard Solution Used:

Determine the amount of stock standard (or working standard solution) that you need to add to the sample of dilution water you are using. If you are pretty sure you are using a "demand free" dilution water, the TCEQ recommends that you use enough stock or working standard to produce an "Applied Concentration" between 0.08 and 0.16 mg/L. If you think your dilution water might have a chlorine demand, you might want to set a target concentration between 0.15 and 0.30 mg/L. The objective of Step 2 is to determine how much demand exists in the dilution water and testing "Applied Concentrations" that produced residuals significantly greater than the demand can change the value of the results you obtain. If the amount of stock or working standard you are considering doesn't produce your target "Calculated Applied Concentration" adjust the amount of dilution water in the calibration standard (in 5 mL increments) or the amount of stock or working standard (in 0.1 mL increments) until you are within your target range.

7. Applied Concentration, Calculated:

This is a calculated value. See the discussion above for information on how to use this data point.

8. Expected Result:

This is a calculated value based on the calibration standard volume, the amount of working standard solution used, and the results of Step 2. It assumes the following:

a. Stock standard has the exact concentration reported by the manufacturer,

b. None of the chlorine in the stock standard volatized when the ampoule was opened and the stock standard was pipetted,

c. Calibration standard volume was exactly what you reported it was and that the pipettes work perfectly,

d. Dilution water has absolutely no chlorine demand,

e. Analyst has perfect laboratory technique, and

f. Labware, sample cuvettes, and instruments are perfectly clean and introduce no error.

Basically, this a theoretical result that can be achieved if absolutely nothing goes wrong.

9. Actual Results:

There are spaces to record the results of five tests that must be run by the analyst as well as a space for the average value (which is calculated by the spreadsheet).

Since EPA Method 334.0 requires you to run 5 samples at each set of blanks, the IDC spreadsheet will not display the average until you have entered **all five** of the test results.

10. Was a Residual Detected in at Least Four Samples?

This is a calculated value.

The chlorine demand result (which is calculated later) may not be accurate unless a measurable residual is obtained in at least 4 of the 5 tests. If the spreadsheet answers this question "No", the analysts needs to repeat the test using a slightly higher "applied concentration".

11. Was the Average Within 0.020 mg/L or 15% of Expected?

This is a calculated value.

If the actual average of the five tests is close enough to the "Expected Result", the spreadsheet will assume that the difference between the two values is the result of one or more of the variables described

above (as opposed to an actual demand in the dilution water). If this is the case, the spreadsheet will report that the dilution water has a 0.00 mg/L chlorine demand.

If this is not the case, the spreadsheet will either calculate the chlorine demand of the dilution water or report that there appears to be a problem with the results and the test needs to be repeated.

12. What is the Calculated Chlorine Demand of the Dilution Water?

This is a calculated value. This result is used for the calculations if needed in Steps 3 and 4.

If the actual average of the five tests is close enough to the "Expected Result", the spreadsheet will assume that the slight difference between the two values is not large enough to interfere with the results of later tests. However, if the expected result is more than 0.02 mg/L (or 15%, whichever is greater) higher than the average, the spreadsheet will calculate how much chlorine demand exists.

On the other hand, if the test results don't make sense for one reason or another, the spreadsheet will detect and identify the nature of the problem and refer you to one of the notes located just below the Step 2 data table.

13. Comments:

There is a comment box that you can use to add a few notes/comments about the analytical procedures and equipment used to complete Step 2.

IDC Step 3

Step 3 of the IDC special study involves preparing the working standard solution that will be used to verify the performance of the benchtop (reference) method (the next step in the IDC special study).

The data you enter in the Step 3 section of the worksheet is used to calculate the concentration of this working standard solution used in Step 4.

Once again, the working standard solution is applied to each of the subsequent benchtop tests, this time in various volumes to approach target chlorine concentrations in the calibration standard.

The working standard solution may be undiluted aliquots of the supplied stock standard as long as the target chlorine residual concentrations can be achieved. The determination of whether a diluted working standard solution is necessary must be made before proceeding on to Step 4.

Instructions for the Step 3 Section of the IDC Data Worksheet

Since the data entry fields in this section of the IDC Data worksheet are identical to those in Step 1, the instructions are not repeated.

Refer to the Step 1 instructions for help on completing this portion of the worksheet.

IMPORTANT:

You must complete Steps 3 and 4 at the same time.

The stock standard/working standard you create in this step (and use in next) begins to lose its strength as soon as you open the ampoule of stock standard.

IDC Step 4

Step 4 of the IDC special study involves using an EPA approved manual benchtop analytical method (reference method) to measure the chlorine concentration in a series of standardized samples that have been dosed with increasing amounts of stock standard or working standard.

This part of the IDC study is where the accuracy of the benchtop (reference) method is evaluated. The procedures that will be used to test the on-line monitoring that is or will be installed are also evaluated.

The data entered in the Step 4 section of the worksheet and the results of these tests are also used to prepare a calibration curve if the benchtop method uses a calibration curve.

IMPORTANT

Remember! Step 4 must begin as soon as Step 3 is completed.

The stock standard/working standard created in Step 3 begins to lose its strength as soon as the ampoule of stock standard is opened.

Instructions for the Step 4 Section of the IDC Data Worksheet

1. **Analyst:**

   Enter the name of the analyst(s) who will determine the chlorine demand of the dilution water.

2. **Anticipated On-line Analyzer Settings:**

   The data for the On-line Analyzer Setting table needs to be provided by the operators who will be setting up the on-line monitor(s).

   If your system is installing a single monitor, the data you enter will be based on the information for that single installation site. However, if your system is installing multiple monitors, the data you enter will be a composite of the lowest and highest readings you expect at any of the sites because the benchtop method verification procedure must span the entire range of all the instruments being installed.

   Please note that the data you enter in this block must be consistent with the information you enter when you conduct Step 5 of the IDC study.

3. **Lower Limit:**

Enter the lowest residual that you expect to see at any site where you propose to install the on-line monitor(s).

If you are measuring free chlorine, this value should be somewhere between 0.0 and 0.2 mg/L. If you are measuring total chlorine, this value should probably be between 0.0 and 0.5 mg/L.

4. **Low Alarm:**

Enter the lowest residual you want to see at any of the sites where you propose to install the on-line monitor(s).

This is usually the monitor's low alarm setting or the residual that would prompt you to take some corrective action because it is too low. The value entered here must be higher than the Lower Limit, above. Usually this value is somewhere between 0.2 and 0.5 mg/L for free chlorine systems and between 0.5 and 1.0 mg/L for systems using chloramines.

5. **High Alarm:**

Enter the maximum residual you want to see at any of the sites where you propose to install the on-line monitor(s).

This is usually the monitor's high alarm setting or the residual that would prompt you to take some corrective action because the residual is too high. The value entered here must be higher than the Low Alarm, above.

Usually, this value is somewhere between 2.5 and 4.0 mg/L regardless of whether your system uses free chlorine or chloramines.

6. **Upper Limit:**

Enter the highest residual that you expect to see at any site where you propose to install an on-line monitor.

The value entered here must be higher than the High Alarm, above. Usually, this value is somewhere between 2.5 and 4.0 mg/L and will be slightly higher than the high alarm or upper action level.

7. **Sample ID:**

There are six rows available to enter data so the analyst(s) can test up to six sample sets. Although there is room to enter data for six sample sets, you must test the accuracy of the reference method using at least three different chlorine concentrations that span the entire range of values that you expect to see at any site where you plan to install

an on-line monitor. Specifically, the testing must meet the following requirements.

a. At least one of the calibration standard sets (the Low Limit sample set) must be conducted at a concentration that is no greater than 0.5 mg/L higher than the Low Limit level that was entered in the On-line Analyzer Settings block above.

b. At least one of the calibration standard sets (the Low Alarm set) must have a concentration that is between the Lower Limit and Low Alarm settings entered in the On-line Analyzer Settings block above.

c. At least one "mid range" calibration standard set must be tested. These calibration standards must have a chlorine residual between the Lower Alarm and the Upper Alarm settings entered in the On-line Analyzer Settings block above.

d. At least one "High Alarm" calibration standard set must be tested. These calibration standards must contain a chlorine residual between the High Alarm and the Upper Limit settings entered in the On-line Analyzer Settings block above.

e. At least one "Upper Limit" calibration standard set must be tested. These calibration standards must contain a chlorine residual that is no more than 1.0 mg/L lower than the Upper Limit settings entered in the On-line Analyzer Settings block above.

Depending on the values entered in the On-Line Analyzer Settings block and the Applied Concentration you select, a single calibration standard set can fulfill more than one of the requirements.

For example, one calibration standard set concentration may meet the requirements for both the Low Limit and Low Alarm calibration standard sets. The TCEQ included a block of cells on the far right of the Step 4 table that will tell you where the calibration standard set is expected to lie once you have entered the information needed into the Calibration Standard Volume and Working Standard Used cells as well as where the measured residual actually lies after you enter the five readings.

8. Calibration Standard Volume:

In order to accurately determine the chlorine residual at a given concentration, you need to test at least five samples since each sample will contain at least 10 mL of dosed dilution water. So you will

need to prepare at least 50 mL (maybe more, depending on your lab method) of dilution water for each batch of 5 calibration standards that you will test. As noted in the Step 3 instructions, there are two ways to produce the required 50 mL of calibration standard and each has its advantages and disadvantages.

a. **Method 1:**
   Dose 60 mL volume of dilution water and then analyze five 10 mL portions of the 60 mL batch.

   i. Advantages:

      1. Since you are only pipetting the working standard solution once, you only have one chance to make a pipetting error.
      2. Since you are using a large volume of water and a large amount of working standard solution, small measurement or pipetting errors have minimal impact on the results.

   ii. Disadvantages:

      1. If you make a mistake, it affects all of the five samples.
      2. It takes up to 3 minutes to run each test and you may not get consistent results if the dilution water has a chlorine demand because it may be 15 minutes or so before the analyst can run the test on the last aliquot in the sample set.

b. **Method 2:**
   Dose and analyze five separate 10 mL samples of dilution water.

   i. Advantages:

      1. A measuring or pipetting error only affects a single sample.
      2. The samples can be analyzed as soon as they are dosed.

   ii. Disadvantages:

      1. Since you are using small volumes of water and working standard solution, the impact of small dilution errors are increased.

Once you have decided which method you are going to use, enter the volume of dilution water you are going to treat with working standard solution.

9. Working Standard Used:

Determine the amount of stock standard or working standard that you need to add to each sample of dilution water. This is sort of a trial and error process; pick a working standard solution amount and see if the amount of standard you are considering produces your target "Applied Concentration". If it doesn't, you can adjust the amount of stock or working standard you will add until you are within your target range. Again, the TCEQ added a block of cells, titled "General Characterization of Results", that can help you select the amount of stock or working standard you want to add to each batch of calibration standards and which will assess the actual test results once you have measured the residual in each of the five test samples.

10. Applied Concentration, Calculated:

This is a calculated value that is based on the calibration standard dilution water volume and the amount of working standard you added to it.

11. Expected Result:

This is a calculated value based on the calibration standard volume, the amount of working standard solution used, and the results of Step 2. As noted in the discussion of Step 2, the calculation assumes that:

a. Stock standard has the exact concentration reported by the manufacturer,

b. None of the chlorine in the stock standard volatized when the ampoule was opened and the stock standard was pipetted,

c. Calibration standard volume was exactly what you reported it was and that the pipettes work perfectly,

d. Analyst has perfect laboratory technique, and

e. Labware, sample cuvettes, and instruments are perfectly clean and introduce no error.

Basically, this a theoretical result that can be achieved if absolutely nothing goes wrong goes wrong.

12. Actual Results:

There are spaces for you to record the results of each of the five tests that you must run at each concentration of calibration standard you have prepared as well as a space for the average value (which is calculated by the spreadsheet). EPA Method 334.0 requires you to run five samples at each calibration standard concentration, so the IDC

spreadsheet will not display the average until you have entered all five of the test results.

13. Was the Average Within 15% of Expected?

This is a calculated value and is the first performance criteria that each group of results must meet. EPA Method 334.0 requires that the average of the 5 samples must be within 15% of the expected value. If the average is not within 15% of the expected value, the data suggests that the benchtop method is not accurate enough to serve as a reference method. If the answer to the question is "No", you will need to repeat the sample set. If the repeat test again produces unacceptable results, you need to determine what is causing the problem, make appropriate changes, and restart the IDC study from the very beginning.

14. Relative Standard Deviation (RSD):

This is a calculated value. Again, the spreadsheet will not display the results of the RSD calculation until you have entered all 5 of the test results.

15. Was the Relative Standard Deviation (RSD) less than or equal to 15%?

This is another calculated value and is the second performance criteria that each group of results must meet. EPA Method 334.0 requires that the RSD for the sample set be no greater than 15%. Higher RSD's indicate the benchtop method is not producing repeatable results. Therefore, you will have to repeat the sample set if the answer to the question is "No". If the repeat test again produces inconsistent readings, you will need to determine what is causing the problem, make appropriate changes, and restart the IDC study from the very beginning.

16. General Characterization of the Results:

These are calculated values. If the average reading was not within 15% of the expected results or the RSD for the sample set was greater than 15%, the spreadsheet will report that the data set contains "Bad Data". If the two performance criteria (discussed previously) are both met, the spreadsheet will automatically determine what general category the calibration standard concentration falls within. The legend for the displayed codes is shown below.

a. **LL—**the calibration standard set represents the anticipated Lower Limit of the on-line monitor. This type of reading is

typically associated with some sort of regulatory violation or short-term public health threat.

b. **LA—**the calibration standard set represents a reading that is between the Lower Limit and the Lower Alarm setting of the on-line monitor. This is a reading that would normally prompt the operator to take corrective action to raise the residual back to within the desired operating range.

c. **mid—**the calibration standard set represents a reading between the on-line monitor's Lower Alarm and Upper Alarm settings. This type of reading is typically associated with acceptable operating conditions.

d. **UA—**the calibration standard set represents a reading between the on-line monitor's Upper Alarm setting and the Upper Limit of the expected results. This kind of reading would normally prompt the operator to take corrective action to decrease the chlorine residual so that it would be within the desired operating range.

e. **UL—**the calibration standard set represents a reading that is close to the Upper Limit that the operators expect to see at the on-line monitoring site(s). This is a reading that would typically cause taste and odor complaints but is unlikely to pose any kind of public health threat.

As noted previously, a single calibration standard set can produce results that fall in up to two given categories. Consequently, the TCEQ designed the spreadsheet so that it would report all the general categories that would describe the calibration standard set.

It should also be noted that the spreadsheet will predict the expected category that a calibration standard set will fall into based on the set's Expected Result. When the categorization is based on the Expected Result (rather than the actual test results), the cells for this sample set will automatically format with a light-yellow background. This shaded background will disappear as soon as you have finished testing all five test samples in the calibration standard set.

Note: The next five questions (17, 18, 19, 20, & 21) are grouped together.

17. Was at least one calibration standard set within 0.5 mg/L of the anticipated Lower Limit of the instrument's span?

18. Was at least one calibration standard set between the anticipated Lower Limit and Low Alarm settings?

19. Was at least one calibration standard set within the normal operating range you expect to see on the instrument?

20. Was at least one calibration standard set between the anticipated High Alarm and Upper Limit settings?

21. Was at least one calibration standard set within 1.0 mg/L of the anticipated Upper Limit of the instrument's span?

These are calculated values.

The spreadsheet automatically determines the answer to each of these five questions. EPA Method 334.0 requires that the calibration standard sets cover the entire range of values that you may obtain from your on-line monitor. Therefore, you may have some difficulty getting the TCEQ to approve your IDC special study if the answer to any of these questions is "No."

22. Comments:

There is a comment box that you can use to add a few notes/comments about the analytical procedures and equipment used to complete Step 4.

IDC Step 5

Step 5 of the IDC special study involves comparing the results of the on-line monitor to those of the benchtop reference method.

Important

The grab samples for the reference method must be obtained from the same sample tap that supplies the online monitor so the operators must install a tee in the line that supplies the on-line instrument.

The IDC Data worksheet provides space to enter data for up to six on-line instruments because EPA Method 334.0 requires you to conduct and IDC study on each online monitor you use. If your system uses more than six on-line monitors to collect compliance data, you will need to contact the TCEQ's Water Supply Division to obtain a modified IDC spreadsheet or copy the results of Steps 1 through 4 into a second IDC spreadsheet.

You may also contact the Water Supply Division staff if you want to request permission to test a subset of the monitors you use for compliance reporting or to reduce the duration of the test for one or more of the additional instruments.

To contact the TCEQ staff members that are reviewing IDC studies, call the Water Supply Division at 512/239-4691.

Instructions for the Step 5 Section of the IDC Data Worksheet

Description of Benchtop Instrument

1. **Benchtop Instrument Manufacturer and Model No.**

   Enter the manufacturer's name and model number of the colorimeter or amperometric titrator used for the benchtop analysis. For example:

   a. Hach Colorimeter II

   b. Hach Amperometric Titrator

   c. Hach DR/890

   d. W&T A-790 Amperometric Titrator

   e. LaMotte Smart 3 Capital Controls

   f. 17T2000 Amperometric Titrator

   You do not need to enter information on titration burettes, pipettes, or other glassware.

2. Benchtop Analytical Method:

Enter the analytical method used during benchtop testing, for example:

a. DPD Colorimetric (SM 4500-CL G)

b. DPD-FAS Titration (SM 4500-CL F)

c. Amperometric Titration (SM 4500-CL D)

Description of On-line Instrument(s):

For each of the on-line instruments, enter the following information in the appropriate spreadsheet cells.

1. Instrument Manufacturer and Model No.:

Enter the manufacturer's name and model number of the on-line instrument.

2. Analytical Method:

Briefly identify the analytical method used by the on-line monitor.

For example: Proprietary direct read amperometric sensor

3. Installation Site and Monitoring Point:

Identify the treatment plant, pump station, or distribution system address where the on-line monitor is installed. For example:

Tharp SWTP, Combined Filter Effluent (CFE)

Schwarz Pump Station, Entry Point, EP006

Distribution monitoring point DBP2-02,
1234 Gammage Memorial Parkway

4. Date Installed:

Enter the date that the on-line monitor was placed into service.

5. Intended Use:

Select one of the options contained in the drop-down list. To see the list, select the cell and then click on the down arrow to display the list. Once the spreadsheet shows the list, click on the option that applies to the monitor. The options contained in the list are:

a. Compliance Monitoring and Reporting only:

select this option if you are going to use the data produced by the on-line monitor to complete any report or document submitted to the TCEQ.

b. Process Control only:

Select this option if the data produced by the on-line monitor is not going to be reported to the TCEQ. Please be aware that you do not have to conduct an IDC study on an instrument that is only used to produce process control data.

c. Both Compliance Monitoring/Reporting and Process Control:

Select the option if you are going to report the data but will also routinely use the information to adjust the treatment process or make other operational decisions.

6. Anticipated or Historical Residual Trends and Monitor Settings:

Enter the maximum and minimum chlorine levels you expect to see at this monitoring site and the High and Low Alarm settings or action levels.

Please note that the data you enter in this block must be consistent with the information you entered when you conducted Step 4 of the IDC study. Basically, this means that the Lower Limit and Low Alarm settings should be no lower than the corresponding values you used when you conducted Step 4 of the IDC study. Similarly, the High Alarm and Upper Limit values should be no greater than the corresponding values you used when you entered the Step 4 data.

a. Upper Limit:

Enter the highest residual that you expect to see at the site where the on-line monitor is or will be installed. This value must be higher than the High Alarm or Action Level discussed below. If you have historical information on this monitoring site, the value you enter here should be consistent with those historical levels. If you have no historical record, you should probably select a value between 2.5 and 4.0 mg/L and that will be will be slightly higher than the high alarm or upper action level.

b. High Alarm or Action Level:

Enter the maximum residual you want to see at the site where on-line monitor is or will be installed.

This value must be higher than the Low Alarm or Action Level discussed below. This is usually the monitor's high alarm setting or the residual that would prompt you to take some corrective action because the residual is too high.

If you have historical information on this monitoring site, the value you enter here should be consistent with those historical operating practices. If you have no historical practice, the value will likely be somewhere between 2.5 and 4.0 mg/L regardless of whether your system uses free chlorine or chloramines.

c. Low Alarm or Action Level:

Enter the lowest residual you want to see at the site where the on-line monitor is or will be installed.

This value must be higher than the Lower Limit discussed below. This is usually the monitor's low alarm setting or the residual that would prompt you to take some corrective action because it is too low.

If you have historical information on this monitoring site, the value you enter here should be consistent with those historical operating practices. If you have no historical practice, the value should probably be somewhere between 0.2 and 0.5 mg/L if the monitor is measuring free chlorine and between 0.5 and 1.0 mg/L for systems using chloramines.

d. Lower Limit:

Enter the lowest residual that you expect to see at the site where the on-line monitor is or will be installed.

If you have historical information on this monitoring site, the value you enter here should be consistent with that historical record. If you have no historical information for this site, the value should probably be somewhere between 0.0 and 0.4 mg/L if you are measuring free chlorine or between 0.4 and 0.8 mg/L if you are measuring total chlorine.

Data Table:

The EPA Method 334.0 requires that the on-line reading be compared to the reference grab sample results for 14 consecutive days. However, if your water plant is not staffed throughout the weekends, the TCEQ will allow you to run the comparison study on Monday through Friday for three consecutive weeks. Therefore, the data table for each instrument contains enough space to enter the results of 15 comparisons.

1. Date and Time:

Enter the date and time that the grab sample was collected and the on-line monitor reading was obtained.

2. **Analyst's Initials:**

   Enter the initials of the analyst that runs the benchtop test. If possible, this individual should also be the person that records the reading from the on-line instrument.

3. **On-line Reading:**

   Enter the reading from the on-line instrument at the time that the grab sample was collected. (Note: This reading should be taken when the chlorine residual is not in flux. The response of the on-line instrument will probably be averaged over a specific time particular to each model and/or manufacturer. The benchtop test will be based on the length of time it takes to collect the sample.)

4. **Grab Sample Result:**

   Enter the result you obtain when you use the benchtop reference method to measure the chlorine residual in the grab sample.

5. **Difference:**

   This is a calculated value obtained by subtracting the on-line reading from the grab sample result.

6. **Is the on-line reading within 15% of the grab sample result?**

   EPA Method 334.0 considers that the data produced by on-line and benchtop methods agree if the two values are within 15% (or 0.10 mg/L, whichever is greater) of one another.

7. **Minimum and Maximum Daily Readings:**

   Enter the minimum and maximum reading that was captured by the on-line monitor's data recorder or the laboratory bench sheet during the 24-hours before you collected the grab sample.

8. **General Characterization of the On-line Reading:**

   There are three questions beneath this header cell and the spreadsheet automatically answers each of them based on the daily data you enter in the table.

   a. Was the on-line reading close to the maximum daily reading captured by the recorder?

      The spreadsheet will answer this question "Yes" if the on-line reading is within 10% or 0.2 mg/L (whichever is greater) of the highest residual recorded during the last 24 hours.

   b. Was the on-line reading a mid-range reading?

The spreadsheet will answer this question "Yes" if the on-line reading is not close to either the highest or lowest residuals recorded during the last 24 hours. Basically, the only time this answer will be "Yes" is when the questions on both sides of it are "No".

c. Was the on-line reading close to the minimum daily reading captured by the recorder?

The spreadsheet will answer this question "Yes" if the on-line reading is within 10% or 0.2 mg/L (whichever is greater) of the lowest residual recorded during the last 24 hours.

Please be aware that the on-line reading can be close to both the maximum and minimum recorded residuals if these two recorded values were pretty close together during the last 24 hours, Basically, the on-line reading can be both a high and low reading if the daily operating range is narrow enough.

Analysis of the Step 5 Data:

The three questions in this portion of the IDC worksheet are used summarize the Step 5 results. They are all answered by the spreadsheet but the answers will not be accurate until you have finished the study and entered all the data you collected.

1. Were all the required data collected and were all of the on-line readings within 15% or 0.10 mg/L of the corresponding grab sample reading?

This is a calculated value based on the information you entered in the data table.

Please be aware that the TCEQ cannot approve the IDC special study unless you collect all of the data required by EPA Method 334.0. Similarly, the TCEQ cannot approve the IDC study if the results reveal that the on-line monitor does not consistently produce readings that agree with the grab sample results.

Therefore, the TCEQ cannot approve your IDC study results if the answer to this question is "No". If the spreadsheet determines that the performance criteria are not met, you must determine and correct the cause of the inconsistency and repeat Step 5 of the IDC.

Note: The next two steps (2 & 3) go together.

2. Were at least 3 of the on-line readings near the maximum recorded daily reading?

3. **Were at least 3 of the on-line readings near the minimum recorded daily reading?**

Both item 2 and 3 answers are calculated values that are based on the data you entered in the data table.

The on-line monitor must be programmed and calibrated so that it will accurately record data under the "worst-case" residual levels the operators expect to see at any given time. However, it is unlikely that these "absolute minimum" and "absolute maximum" residuals will occur during the IDC study. Therefore, the spreadsheet compares the daily on-line reading with the corresponding minimum and maximum values recorded during the 24 hour period before grab sample was collected.

It is important that at least three of your comparisons were conducted when the residual was near the maximum daily recorded value and that at least three of your comparisons were conducted when the on-line reading was near the minimum daily recorded value. If the spreadsheet doesn't answer both of these two questions "Yes", you will need to repeat Step 5 of the IDC.

4. **Comments:**

There is a comment box that you can use to add a few notes/comments about the analytical procedures and equipment used to complete Step 5 and to describe any operational or maintenance issues that you had to address during Step 5 testing.

If the on-line monitor has already been installed, you should also discuss any unusual operational or maintenance problems you have experienced since its installation. If you need more room than the comment box provides, you can insert a Text Box on Sheet 3 of the spreadsheet and the additional information there.

Congratulations! Save your work.

At this point, you have completed the spreadsheet. Save the file in a location that you can find in the future. Print a copy to submit to the TCEQ.

Notes

Course Wrap-up

Submitting the IDC to TCEQ

After the IDC has been completed (14 or 15 days of daily chlorine residual comparisons as applicable), a printout of the final spreadsheet must be submitted to TCEQ Water Supply Division (WSD) Technical Review and Oversight Team (TROT) for approval.

The spreadsheet, with Step 5 completed for each IDC applicable on-line analyzer, must be submitted along with a cover letter that identifies each instrument for which approval is requested.

The request for approval letter and the spreadsheet must be submitted to:

Texas Commission on Environmental Quality
Attn: WSD/TROT Mail Code 154
PO Box 13087
Austin, Texas 78711-3087

It is highly recommended that before submitting the request, you call and talk to one of the TROT staff to get guidance on details of how to submit your request. You may call the main number—**512-239-4691**—and ask to speak to a representative on TROT.

Ongoing Requirement for Monitoring under Method 334

While not part of this training, approval of the IDC by TCEQ requires the water system to regularly make comparisons of the on-line monitors to the bench-scale analyzer. As this is comparison monitoring is a regulatory requirement, it must be accounted for in the water system's Monitoring Plan.

Monitoring Plan

TCEQ has developed guidance on how to develop a monitoring plan for a PWS which can be downloaded from the TCEQ website at:

www.tceq.texas.gov/drinkingwater/monitoring_plans

Laboratory Approval Form & List of Analytical Methods

As part of the Monitoring Plan requirements, the PWS must also complete and submit the required Drinking Water Laboratory Approval Form (TCEQ 10450).

Additionally, systems that use chloramines must complete a List of Analytical Methods (LAM) as part of their Nitrification Action Plan (NAP).

The Laboratory Approval Form is included as Appendix D and is available on the TCEQ website at:

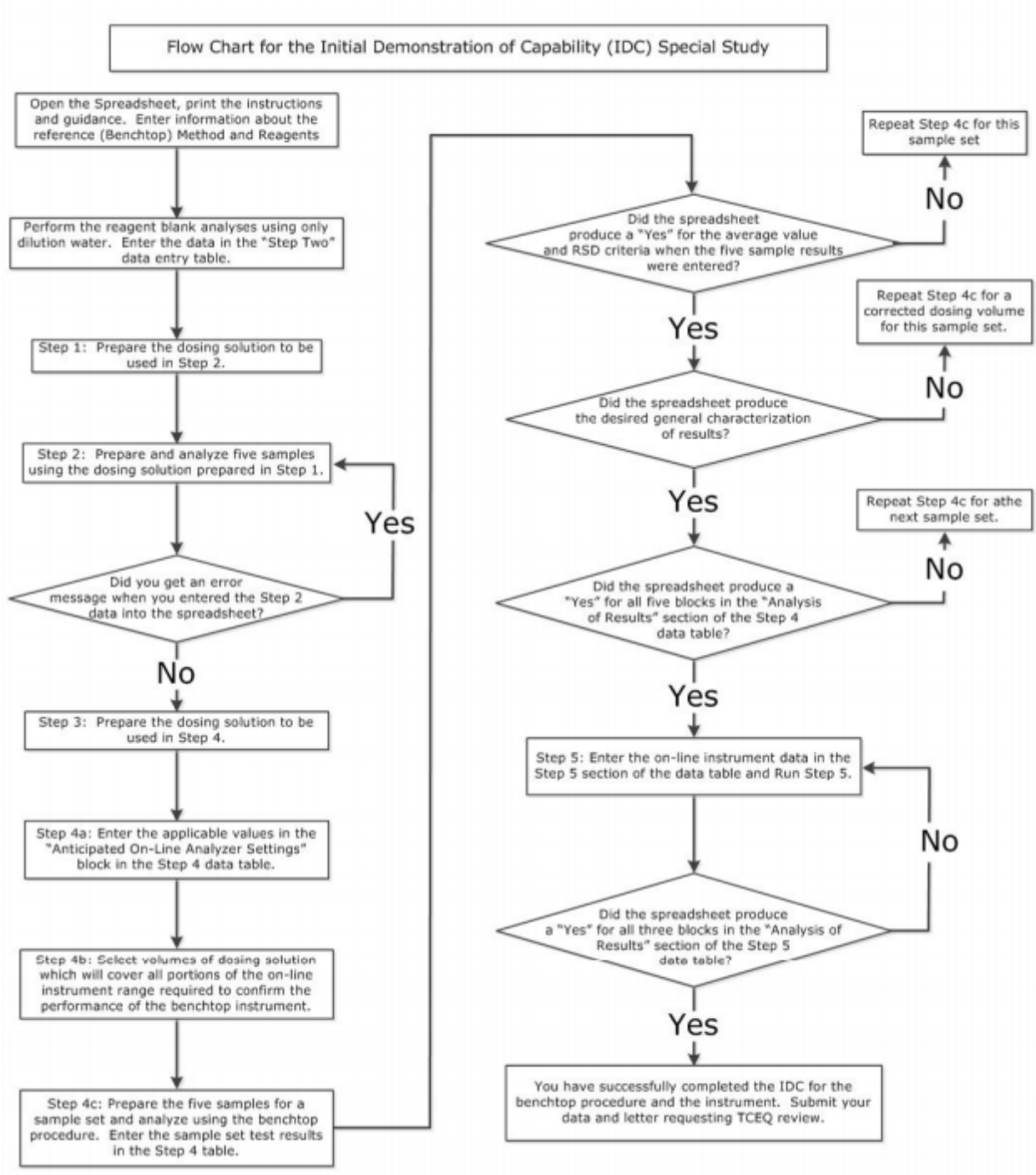
> www.tceq.texas.gov/assets/public/permitting/watersupply/pdw/DrinkingWaterLaboratoryApprovalForm.pdf

The List of Analytical Methods is also in Appendix D. It is available by calling the TCEQ at **512-239-4691** or on the TCEQ website at:

> www.tceq.texas.gov/drinkingwater/disinfection/nitrification.html

Appendix A. IDC Flow Chart

Notes


Flow Chart for the Initial Demonstration of Capability (IDC) Special Study
Open the Spreadsheet, print the instructions and guidance. Enter information about the reference (Benchtop) Method and Reagents
Perform the reagent blank analyses using only dilution water. Enter the data in the "Step Two" data entry table.
Step 1: Prepare the dosing solution to be used in Step 2.
Step 2: Prepare and analyze five samples using the dosing solution prepared in Step 1.
Did you get an error message when you entered the Step 2 data into the spreadsheet?
Yes
No
Step 3: Prepare the dosing solution to be used in Step 4.
Step 4a: Enter the applicable values in the "Anticipated On-Line Analyzer Settings" block in the Step 4 data table.
Step 4b: Select volumes of dosing solution which will cover all portions of the on-line instrument range required to confirm the performance of the benchtop instrument.
Step 4c: Prepare the five samples for a sample set and analyze using the benchtop procedure. Enter the sample set test results in the Step 4 table.
Did the spreadsheet produce a "Yes" for the average value and RSD criteria when the five sample results were entered?
No
Repeat Step 4c for this sample set
Yes
Did the spreadsheet produce the desired general characterization of results?
No
Repeat Step 4c for a corrected dosing volume for this sample set.
Yes
Did the spreadsheet produce a "Yes" for all five blocks in the "Analysis of Results" section of the Step 4 data table?
No
Repeat Step 4c for athe next sample set.
Yes
Step 5: Enter the on-line instrument data in the Step 5 section of the data table and Run Step 5.
Did the spreadsheet produce a "Yes" for all three blocks in the "Analysis of Results" section of the Step 5 data table?
No
Yes
You have successfully completed the IDC for the benchtop procedure and the instrument. Submit your data and letter requesting TCEQ review.

Notes

Appendix B. Adopted EPA Method 334

Notes

METHOD 334.0: DETERMINATION OF RESIDUAL CHLORINE IN DRINKING WATER USING AN ON-LINE CHLORINE ANALYZER

Office of Water (4606 M) EPA 815-B-09-013 September 2009 www.epa.gov/safewater

METHOD 334.0: DETERMINATION OF RESIDUAL CHLORINE IN DRINKING WATER USING AN ON-LINE CHLORINE ANALYZER

Version 1.0

September 2009

Steven C. Wendelken, Derek E. Losh, and Patricia S. Fair
Office of Ground Water and Drinking Water

TECHNICAL SUPPORT CENTER
OFFICE OF GROUND WATER AND DRINKING WATER
U. S. ENVIRONMENTAL PROTECTION AGENCY
CINCINNATI, OHIO 45268

METHOD 334.0

DETERMINATION OF RESIDUAL CHLORINE IN DRINKING WATER USING AN ON-LINE CHLORINE ANALYZER

SCOPE AND APPLICATION

1.1 This method is for the analysis of residual chlorine (free or total) in drinking water. It is primarily intended to be used by drinking water utilities for compliance with daily monitoring requirements. This method allows the use of any type of on-line chlorine analyzer (e.g., amperometric, DPD, etc.) for compliance monitoring when used in conjunction with a grab sample reference method that is approved for drinking water compliance monitoring. This method is intended to be used when chlorine residuals (free or total) are in the range of 0.2 mg/L to 4 mg/L.

1.2 The grab sample reference method must be listed in the methods table of the regulation under which the monitoring is being conducted. (A method in Appendix A may be used if it is listed as approved for the regulation.) Color wheels or optical comparison scales are not allowed for methods which specify the use of a spectrophotometer.

SUMMARY OF METHOD

2.1 An on-line chlorine analyzer is used to continuously monitor the chlorine concentration at a drinking water sample point. The instrument is calibrated using aqueous standards or the results from paired grab samples that are collected at the same sample point and time. The grab samples are analyzed for chlorine (free or total) using a method that is approved for drinking water compliance monitoring. The on-line analyzer accuracy is periodically verified/adjusted based on results from grab sample analyses.

INTERFERENCES

3.1 A general discussion of potential interferences to the grab sample measurements is included in Standard Method 4500-Cl A.[1] More specific information is included with each reference method and should guide the user when selecting a method. Amperometric titration methods are less subject to interferences from common oxidizing agents, turbidity and color. Organic contaminants and high concentrations of monochloramine may produce false free chlorine readings in colorimetric methods. Colorimetric methods specify procedures to reduce interferences from copper, chromate, and reduced manganese. Strong oxidizing agents (e.g., permanganate, ozone) interfere with free chlorine measurements in all methods.

3.2 Consult the manufacturer's literature regarding potential interferences to the measurements by on-line chlorine analyzers. Amperometric analyzers are sensitive to pH, flow and temperature changes, but compensation for these variables is usually incorporated into the design of the analyzer. DPD analyzers are subject to the same interferences as the DPD grab sample methods.

4. SAFETY

4.1 The toxicity or carcinogenicity of each reagent used in this method has not been precisely identified; each chemical compound should be treated as a potential health hazard, and exposure to these chemicals should be minimized. The laboratory/water system is responsible for maintaining documentation of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) should also be made available to all personnel involved in the chemical analysis. Additional references to laboratory safety are available.[2-5]

5. EQUIPMENT AND SUPPLIES

5.1 ON-LINE CHLORINE ANALYZER – The selection of an analyzer must consider the water quality characteristics of the drinking water, the treatment process, and the physical location of the analyzer installation. Some of the water quality parameters to consider include variability in the water pH, temperature, ionic strength and the presence of potential interferences such as iron, manganese, and copper. The treatment process dictates whether the on-line analyzer must measure free or total chlorine residuals. The concentration of residual chlorine being measured establishes the required instrument range. The range should be as small as possible, while still bracketing expected concentrations (e.g., Residual concentrations in the range of 0.5 to 1.5 mg/L should be monitored using an analyzer with a linear dynamic range of 0 to 2 mg/L rather than 0 to 10 mg/L.) The analyzer must be installed according to the manufacturer's instructions so that changes in pressure or flow will not influence the analyzer measurements. Install the analyzer as close to the sampling point as feasible and in a location that is easily accessible for maintenance. Install a sample tap as close as feasible to the location where the sample enters the analyzer to allow for collection of discrete grab samples for calibration and accuracy verification.

5.1.1. The analyzer must have a readout at its installation location and the readings must be continually recorded (hard copy chart or electronic data). For remote installations, the analyzer should also have the capability for transmission of the output to a centralized location.

5.1.2. The on-line monitoring system should have the capability to activate an alarm when the chlorine concentration is outside the normal operating range.

5.1.3. The analyzer must allow manual adjustment for calibration.

5.2 GRAB SAMPLE REFERENCE METHOD – Amperometric titration or N,N-Diethyl-p-phenylenediamine (DPD) colorimetric methods are the most commonly used approved grab sample methods. Additional choices are included in the methods table of the regulation under which monitoring is being conducted. Consult the method for a listing of equipment and supplies.

5.3 GLASSWARE – Free of chlorine demand. See ASTM D 1253-03 [6] or Standard Method 4500-Cl D [1], if glassware needs to be treated to remove chlorine demand.

5.3.1. BEAKERS – Varying sizes.

5.3.2. VOLUMETRIC FLASKS – Class A, of varying sizes.

5.3.3. PIPETTES – Class A, varying sizes or a variable volume single channel pipette with disposable plastic tips. (e.g., Eppendorf Series 2000 pipetter, No. 022470302; or Hach Tensette® pipette, No 1970001)

6. REAGENTS AND STANDARDS

6.1 REFER TO THE ON-LINE CHLORINE ANALYZER OPERATING MANUAL FOR A LIST OF REAGENTS SPECIFIC TO THE INSTRUMENT– Reagent grade or better chemicals should be used. Unless otherwise indicated, all reagents should conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first determined that the reagent is of sufficiently high purity to permit its use without lessening the quality of the determination. Reagents must be stored according to the manufacturer's recommendations and only used within the manufacturer's designated lifespan (prior to expiration date).

6.2 REFER TO THE SELECTED GRAB SAMPLE METHOD FOR A LIST OF REAGENTS SPECIFIC TO THE METHOD – Reagent grade or better chemicals should be used. Unless otherwise indicated, all reagents should conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first determined that the reagent is of sufficiently high purity to permit its use without lessening the quality of the determination. Titrants that are purchased in their diluted form, ready to use in the grab sample method, should be NIST traceable or certified in an equivalent manner. Reagents must be stored according to the manufacturer's recommendations and only used within the manufacturer's designated lifespan (prior to expiration date).

6.3 REAGENT WATER – Purified water (typically either deionized or distilled) is usually acceptable. Reagent water can be purchased from a scientific supply company, if it is not available on site. If a chlorine demand is present, suggested

procedures for preparing chlorine demand-free water are included in ASTM D 1253-03 [6] and Standard Method 4500-Cl C [1].

6.4 CALIBRATION STANDARD SOLUTIONS – Use the type of aqueous standard (e.g., chlorine or potassium permanganate) specified in the selected grab sample method. A concentrated stock standard solution can be purchased from a commercial source (e.g., Environmental Resource Associates, Catalog # 696; Hach, Product # 1426820, or equivalent). A purchased stock standard must be NIST traceable or certified in an equivalent manner. The stock standard must be stored according to the manufacturer's recommendations and only used within the manufacturer's designated lifespan (prior to expiration date). The stock solution is diluted using reagent water to obtain calibration standard solutions in the range of 0.2 mg/L to 4.0 mg/L. Calibration standards should be prepared fresh for each use unless manufacturer's instructions specify otherwise.

6.5 ROUTINE GRAB SAMPLE CALIBRATION CHECK STANDARD – Calibration standards prepared above may also be used as calibration check standards. Calibration check standards must be freshly prepared.

6.6 SECONDARY STANDARD – Colorimetric standards may be purchased for use with DPD spectrophotometers/colorimeters. The accuracy of secondary standards must be verified on each recently-calibrated spectrophotometer/colorimeter for which they will be used. Secondary standards may not be used to calibrate the spectrophotometer.

6.7 INDEPENDENT REFERENCE SAMPLE – Purchase a chlorine standard solution that is NIST traceable or certified in an equivalent manner from a different source than the source of the calibration standards. Calibration standards and the independent reference samples that are purchased from the same supplier must be from different lots. The independent reference sample must be stored according to the manufacturer's recommendations and only used within the manufacturer's designated lifespan (prior to expiration date).

7. SAMPLE COLLECTION, PRESERVATION, AND STORAGE

7.1 SAMPLE COLLECTION – The grab sample collection point should be as close as possible to the location where the sample enters the on-line chlorine analyzer, so that the grab sample reflects the same water as the on-line analyzer is measuring. A sample line may be equipped with a valve (e.g., T or Y configuration) that allows for intermittent grab sampling with minimal disruption of flow to the analyzer. Follow the sample collection instructions specified in the grab sample method. Collect the grab sample with minimal agitation. Exposure to sunlight or strong light will cause loss of chlorine. Begin analysis immediately after sample collection. Do not store samples.

8. QUALITY CONTROL

8.1 Quality control (QC) procedures are incorporated into analytical methods in order to demonstrate that the results are valid and within the accuracy and precision ranges needed for protection of public health. Grab sample methods for measuring chlorine residuals are designed to be independent of other chlorine measurement methods. As a result, some of the normal QC requirements may not be necessary when the grab sample method is used in conjunction with an on-line chlorine analyzer. For example, Part 4020 in Standard Methods [1] indicates daily analysis of method blanks, calibration check standards, fortified blanks, and duplicates (with each batch of samples). Although these QC samples are useful and may be included as part of the standard operating procedure (SOP), they are not necessary when the grab sample measurement is being compared to an analyzer measurement because the comparison of the two measurements serves as a QC check. If grab sample analyses are only being performed in conjunction with on-line chlorine analyzers, the analyst is only required to follow the minimum requirements set forth in this method. However, this method is not intended to supersede the QC requirements that are requisite when the data are used for other purposes.

8.2 The requirements of the QC program for the grab sample method that is used as the reference for the on-line chlorine analyzer consist of an Initial Demonstration of Capability (IDC) and periodic analyses of calibration check standards and independent reference samples. The QC program for the on-line chlorine analyzer consists of an IDC and periodic comparisons of the instrument reading to results of a sample analyzed using the grab sample reference method. These QC procedures and the acceptance criteria are described in Sections 10 and 11 of this method. It is desirable to maintain consistency with regard to personnel responsible for instrument QA/QC checks and related field sampling.

8.3 OPTIONAL QC – Laboratories/water systems are encouraged to institute additional QC practices to meet their specific needs. The remainder of this section describes various optional QC procedures that may be incorporated into a QC program for grab sample verification of on-line chlorine analyzer performance.

8.3.1. GRAB SAMPLE DUPLICATE – Analysis of duplicate grab samples (two samples collected at the same time) provides an estimate of the precision of the grab sample analyses that are used to verify/adjust the accuracy of the on-line chlorine analyzer. Poor grab sample precision can cause problems in the analyzer adjustment. Analysis of grab sample duplicates is suggested when there are difficulties in adjusting the analyzer calibration to agree with the grab sample measurement. Calculate the relative percent difference (RPD) between the Sample (FD1) and the Sample Duplicate (FD2) as shown below. The RPD for samples with concentrations greater than the lowest calibration standard should not exceed 15%. The RPD at concentrations at or near the lowest calibration standard should not exceed 50%.

$$RPD = \frac{|FD1 - FD2|}{(FD1 + FD2)/2} \times 100\%$$

If the *RPD* for the Sample and the Sample Duplicate falls outside the designated range, perform duplicate analyses of a calibration check standard to verify that the grab sample method is in control.

8.3.2. INDEPENDENT REFERENCE SAMPLE – Analysis of a sample from an external source (different from the calibration standards) provides an independent check of the calibration of the grab sample method. It is recommended semiannually or any time a new calibration curve is generated.

8.3.3. PROFICIENCY TESTING (PT) or PERFORMANCE EVALUATION (PE) SAMPLE – Successful participation in a PT or PE Study is a good QC tool for demonstrating proficiency with the grab sample method. A certified solution of chlorine whose concentration is unknown to the analyst can be purchased by the laboratory/water system. An aliquot of the certified solution is added to a known volume of reagent water and analyzed as a grab sample. The analytical results are reported to the PT/PE Study Provider where they are compared to data from all analyses of the sample. Acceptance criteria are established for each study. Generally, a different analyst should participate in each study, so that over time each analyst has an opportunity to demonstrate proficiency. If the analyst is a field sampler, the sample can be prepared by laboratory personnel for the analyst.

9. CALIBRATION

9.1 An acceptable initial calibration for the grab sample method must be established before the results from the grab sample method can be used to verify the accuracy of an on-line chlorine analyzer. After initial calibration is successful, a calibration check standard or independent reference sample is periodically analyzed to verify that the grab sample method calibration is still valid.

9.2 The calibration of the on-line chlorine analyzer is verified against a grab sample measurement. (On-line chlorine analyzers that use the same chemistry as an approved grab sample method may use aqueous standards for initial calibration verification instead of comparison to grab sample measurements. Routine calibration checks are made by comparison with grab sample measurements.)

9.3 The calibration procedures and acceptance criteria are described in Sections 10 and 11 of this method.

10. START-UP PROCEDURES

10.1 GRAB SAMPLE METHOD – Refer to the selected grab sample method for a complete description of the procedure. (Each drinking water regulation includes a tabular listing of methods that are approved for analyses of compliance samples. The regulation also identifies how to obtain a copy of each method.) Section 15 – Table 1 and Flowchart 1 summarize the start up QC for the grab sample method.

10.1.1. **Prepare or verify the initial calibration curve**. This must be done for each meter or titrator according to the procedure described below. The accuracy of secondary standards must also be verified. These steps can be performed by laboratory personnel or field samplers. A record of the calibration results must be maintained for each meter/titrator.

10.1.1.1. Prepare a method blank (reagent water) and a set of at least three aqueous calibration standards. The lowest concentration calibration standard must be at or below 0.2 mg/L or the minimum chlorine residual required by the state. The standards must span the concentration range that is expected to be observed in the grab samples. (Note: If the range extends above the maximum concentration specified for the DPD reagents and colorimeter, prepare three standards within the range specified by the manufacturer and a fourth standard at the highest concentration expected for the grab samples.)

10.1.1.2. Analyze the calibration standards and method blank according to the grab sample procedure. (Note: If the highest concentration standard is above the maximum concentration specified for the DPD reagents and colorimeter, dilute and analyze it according to manufacturer's instructions. Use the data from this analysis to check the accuracy of the dilution process, not the calibration curve.)

10.1.1.2.1. For methods that do not require the preparation of a curve or that use an internal, factory set calibration curve, compare the measured concentration of each standard to the expected value. Each calibration point must be within ± 15% of its expected value. If the internal curve does not meet these criteria, the internal curve must be updated by following the manufacturers' instructions for generating/inputting a curve. Otherwise, send the meter to the vendor for repair/updating.

10.1.1.2.2. For methods that require the preparation of a curve, use the concentration of each standard versus the instrument response to calculate the best fit curve according to the procedure described in the grab

sample method. Validate the curve by calculating the concentration of each standard using the curve. Each calibration point must be within ± 15% of its expected value.

10.1.1.3. If secondary standards are available for the grab sample method, they must be verified prior to use by analyzing them immediately after initial calibration is verified. The secondary standards must be within ± 10% of their expected concentrations when compared to the initial calibration curve. New secondary standards must be purchased if this criterion cannot be met. The secondary standards must meet the criterion on every meter for which they will be used. Secondary standards must be verified each time the initial calibration procedure is repeated. Secondary standards must not be used beyond the manufacturer's expiration date.

10.1.2. Each field sampler must perform an **initial demonstration of capability (IDC)** prior to using the grab sample method to verify the accuracy of on-line chlorine analyzers. If the accuracy and precision criteria described below are not met, determine the source of the problem, take corrective action and repeat the IDC. The IDC consists of a demonstration of accuracy and a demonstration of precision using the procedure described below.

10.1.2.1. INITIAL DEMONSTRATION OF ACCURACY – Prepare and analyze a method blank (reagent water) and five independent reference samples at the same concentration. The concentration of the samples should be in the mid range of the calibration curve or near the expected concentration of the water samples. Calculate the average chlorine concentration for the five analyses. The average concentration for the five replicates must be within ± 15% of the expected value. The method blank concentration must be ≤ ⅓ the concentration of the lowest standard used to prepare/verify the calibration curve (Section 10.1.1.1).

10.1.2.2. INITIAL DEMONSTRATION OF PRECISION – Using the same set of replicate data generated for Section 10.1.2.1, calculate the standard deviation and relative standard deviation (*RSD*) of the replicate values. The *RSD* is calculated using the equation

$$RSD = \frac{S}{\overline{X}} \times 100\%$$

where
S is the standard deviation for the replicate values,
and $\overline{X}$ is the average value for the replicates.

9

The RSD of the results of the replicate analyses must be ≤15%.

10.1.3. Each field sampler must successfully complete the IDC procedure described above (Section 10.1.2) prior to using the grab sample method in conjunction with an on-line chlorine analyzer. Laboratory personnel may prepare the independent reference samples for analyses by field samplers. A record of the IDC results must be maintained for each field sampler.

10.2 ON-LINE CHLORINE ANALYZER – Install the analyzer according to the manufacturer's specifications. Follow all start-up procedures outlined in the operator's manual including specific instructions regarding calibration of the analyzer. The following procedure must be followed for each analyzer. (Section 15 – Table 2 and Flowchart 2 summarize the start-up QC for on-line chlorine analyzers.)

10.2.1. After the analyzer is providing stable readings, proceed with verifying/adjusting the **initial calibration**. If the analyzer uses the same chemistry as an approved grab sample method, the calibration curve can be established/verified using aqueous chlorine standards in a manner similar to the grab sample procedure described above in Section 10.1.1. Alternately, calibration of the analyzer may be verified/adjusted based on the results of grab sample measurements as described below. All other types of analyzers must use the following procedure:

10.2.1.1. Collect and analyze a grab sample collected as close as feasible to the location where the sample enters the on-line chlorine analyzer. Compare the results from the grab sample analysis to the measurement made by the on-line chlorine analyzer.

10.2.1.2. Follow the manufacturer's instructions to adjust the calibration of the analyzer so it gives the same value as the grab sample analysis.

10.2.1.3. Repeat steps 10.2.1.1 and 10.2.1.2 until the on-line chlorine analyzer measurement agrees with the grab sample measurement. (Ideally, the two measurements will be the same, but realistically this won't always be possible. Note that during routine operation of the analyzer, the readings must be within ± 0.1 mg/L or ± 15% of the grab sample measurement. Use that criterion as a guide for deciding when the analyzer calibration is properly adjusted during this start-up procedure.)

10.2.2. Conduct the **initial demonstration of capability (IDC)** after the calibration of the on-line chlorine analyzer has been verified. Requirements for the IDC are described in 10.2.2.3. The full IDC must be conducted prior to using the analyzer for compliance monitoring

measurements. This will take a minimum of 14 days. The data collected during the IDC must be recorded and maintained.

10.2.2.1. The IDC for the on-line chlorine analyzer is not required if historical operating data for the on-line chlorine analyzer demonstrate the criterion are being met on an on-going basis. Historical data must show that the analyzer remains in agreement with the grab sample method over a period of two consecutive weeks without analyzer maintenance or calibration adjustment. Agreement is defined as being within ± 0.1 mg/L or ± 15% (whichever is larger) of the grab sample measurement. The following procedures must be completed prior to using the analyzer for compliance monitoring.

10.2.2.1.1. Verify the calibration of the grab sample measurement according to 10.1.1.

10.2.2.1.2. Each field sampler must complete the IDC requirements for the grab sample measurement according to 10.1.2.

10.2.2.1.3. Calibration of the on-line chlorine analyzer must be verified according to 10.2.1 after the grab sample IDC is completed.

10.2.2.1.4. Proceed to 10.2.3.

10.2.2.2. When multiple on-line chlorine analyzers are being installed, the primacy agency may allow the IDC to be shortened under the following conditions.

10.2.2.2.1. The same model analyzer is installed at each location.

10.2.2.2.2. The water quality characteristics and treatment processes are equivalent at each location.

10.2.2.2.3. A successful IDC (Section 10.2.2.3) is completed for the first analyzer that is placed in service.

10.2.2.2.4. The IDC for subsequent analyzers can be shortened to 7 consecutive days (or 7 consecutive business days) of daily grab sample comparisons. The analyzer reading must be within ± 0.1 mg/L or ± 15% (whichever is larger) of the grab sample measurement for each data pair. When you obtain 7 consecutive days (or business days) of data pairs

that meet the acceptance criterion, proceed to 10.2.3.

10.2.2.3. Compare the concentration determined by the on-line chlorine analyzer with grab sample analyses collected at least daily for 14 days. (If samples cannot be collected during the weekend, 14 consecutive business days is acceptable.) During the 14 days, grab samples should be collected at concentrations that represent highs and lows, as indicated by the analyzer. (e.g., if the analyzer indicates the chlorine concentration varies between 0.5 mg/L and 1.0 mg/L, grab samples should be collected to verify accuracy at both of these concentrations.) The analyzer reading must be within ± 0.1 mg/L or ± 15% (whichever is larger) of the grab sample measurement for each data pair. If this criterion is not met, determine the source of the problem, take corrective action and continue collecting daily grab samples. When you obtain 14 consecutive days (or business days) of data pairs that meet the acceptance criterion, proceed to 10.2.3.

10.2.2.4. If you are unable to meet the criterion in 10.2.2.3, verify you have chosen an appropriate analyzer for your water quality and operating conditions. An on-line chlorine analyzer that cannot meet the criterion in 10.2.2.3 may be used for compliance monitoring only if grab sample comparisons are conducted daily or at a frequency approved by the primacy agency.

10.2.3. Upon successful completion of the IDC, the analyzer can be put into service for compliance monitoring. Control or warning limits should be established for the analyzer readings, so that operators are immediately alerted to unexpected changes in the chlorine measurements. For remote installations, interfacing the analyzer with a SCADA system, automated phone dialer, or a similar notification system is a critical consideration.

10.2.4. A routine schedule for grab sample comparisons can be established based on the results from intense monitoring over the course of the first few months of operation. **The maximum time between grab samples must not exceed once every seven days.** (Appendix A provides an optional systematic approach for establishing a routine schedule for grab sample comparisons. Alternative approaches may be used to determine the optimum frequency of grab sample comparisons.)

10.2.5. All manufacturers' recommendations for routine maintenance should be followed. When maintenance is performed, the accuracy of the analyzer must be verified with a grab sample comparison after the analyzer is placed back in service. The accuracy must be verified again after one day of operation (Section 11.2). If the accuracy criteria are not met and

the analyzer is operating properly, adjust the analyzer calibration according to the procedure in Sections 11.2.3 – 11.2.7.

11. ROUTINE PROCEDURES

11.1 ROUTINE CALIBRATION CHECK FOR THE GRAB SAMPLE METHOD – Prepare an aqueous calibration check standard at a concentration near the expected concentration of the water samples. (Over time, vary the grab sample calibration check standard concentration when multiple analyzers are being verified and the drinking water chlorine concentration at each analyzer is different.) The grab sample measured concentration of the calibration check standard must be within ± 15% of the expected value. If this criterion is not met, the analyst must identify and resolve the problem with the grab sample method prior to proceeding with analyses of grab samples to verify the on-line chlorine analyzer accuracy. The results from analyses of calibration check standards must be recorded and maintained according to the requirements of the primacy agency.

11.1.1. A check standard must be analyzed:

11.1.1.1. when the grab sample measurement is used to adjust the calibration of the on-line chlorine analyzer

11.1.1.2. a minimum of once quarterly.

11.1.2. Analysis of secondary standards is an easy way to verify the spectrophotometer is operating properly for colorimetric methods. Analysis of secondary standards does not replace the analysis of aqueous check standards. Each secondary standard must be within ± 10% of its expected concentration.

11.2 ROUTINE CALIBRATION CHECK FOR ON-LINE CHLORINE ANALYZER – The accuracy of the on-line chlorine analyzer is monitored during routine use by periodic comparisons of the analyzer readings to grab sample measurements. The maximum time between grab samples must not exceed once every 7 days (i.e., a weekly grab sample). The analyzer concentration must be within ± 0.1 mg/L or ± 15% (whichever is larger) of the grab sample measurement. (Section 15 – Table 4 and Flowchart 3 summarize the routine QC for on-line chlorine analyzers.) All data from these comparisons must be recorded and maintained according to the requirements of the primacy agency.

11.2.1. Disagreement between the grab sample and analyzer measurements may indicate a need for maintenance on the analyzer (e.g., flow adjustment, pH adjustment, cleaning, new membrane, fresh reagents, etc.) The operator must conduct trouble-shooting activities and rule out problems with the analyzer prior to making calibration adjustments.

11.2.1.1. The operator may perform a second comparison between the analyzer and a grab sample to rule out variability in the grab sample as the cause for disagreement.

11.2.1.2. Follow the manufacturer's instructions for troubleshooting problems with the analyzer.

11.2.2. If the analyzer is operating properly, verify that the grab sample measurement is accurate by analyzing a grab sample calibration check standard (Section 11.1).

11.2.2.1. For remote sites, the accuracy of the grab sample measurement can initially be verified using secondary standards that have been tested for accuracy according to Section 10.1.1.3. The secondary standards must be within ± 10% of their expected concentration.

11.2.2.2. If secondary standards are used in the field, a grab sample calibration check standard should be analyzed using the same lot of reagents within 24 hours unless an alternative time frame is approved by the primacy agency.

11.2.3. After the accuracy of the grab sample measurement is verified, follow the manufacturer's instructions to adjust the calibration of the analyzer so it gives the same value as the grab sample analysis.

11.2.4. Confirm that the calibration adjustment is accurate by analyzing another grab sample and comparing the result to the reading from the analyzer.

11.2.5. Repeat steps 11.2.3 and 11.2.4 until the on-line chlorine analyzer measurement agrees with the grab sample measurement. (The two measurements should be as close as possible. Note that during routine operation of the analyzer, the readings must be within ± 0.1 mg/L or ± 15% of the grab sample measurement. Use that criterion as a guide for deciding when the analyzer calibration is properly adjusted.)

11.2.6. An additional grab sample must be collected and analyzed after one day of operation in order to verify that the calibration adjustment was performed accurately. If the criterion is not met, follow 11.2.3 -11.2.6 to adjust the calibration of the analyzer or take other corrective steps consistent with manufacturer instructions.

11.2.7. Return to the routine schedule for grab sample comparisons. **A grab sample must be analyzed at least once each week**.

11.3 NON-ROUTINE CALIBRATION CHECK FOR ON-LINE CHLORINE ANALYZER – Certain conditions may trigger the need to compare the analyzer reading to a grab sample measurement outside the routine schedule. When a non-

routine comparison is made, the analyzer concentration must be within ± 0.1 mg/L or ± 15% (whichever is larger) of the grab sample measurement. If this criterion is not met, the operator must take corrective action to bring the analyzer back into agreement with the grab sample measurement. The steps in Section 11.2 must be followed. Problems with the analyzer must be ruled out or fixed prior to any calibration adjustment to the on-line chlorine analyzer.

11.3.1. The on-line chlorine analyzer measurement must be compared to a grab sample measurement when routine maintenance (such as cleaning, replenishment of reagents, membrane replacement, adjustment of flow rate, pH calibration, etc.) is performed on the analyzer.

11.3.2. If the analyzer measurements indicate a gradual drift upward or downward when no changes in chlorine concentration are expected, a grab sample measurement should be performed.

11.4 EMERGENCY CALIBRATION CHECK FOR ON-LINE CHLORINE ANALYZER – If the on-line chlorine analyzer indicates a large (≥ 50%) unexpected change in chlorine residual concentration (based on process control and water quality conditions), a grab sample should be collected and analyzed as soon as possible. When an emergency comparison is made, the analyzer concentration must be within ± 0.1 mg/L or ± 15% (whichever is larger) of the grab sample measurement. If this criterion is not met, the operator must take corrective action to bring the analyzer back into agreement with the grab sample measurement. The steps in Section 11.2 must be followed. Problems with the analyzer must be ruled out or fixed prior to any calibration adjustment to the on-line chlorine analyzer.

11.5 RETURNING AN ON-LINE CHLORINE ANALYZER TO SERVICE – After a major repair or after replacement of the on-line chlorine analyzer with an equivalent model, follow all start-up procedures outlined in the operator's manual. Calibrate according to the procedure in Section 10.2.1. Return to the routine schedule for grab sample comparisons (Section 11.2) after verifying the accuracy of the analyzer on a daily basis for 7 consecutive days (or business days) or for a period specified by the primacy agency.

12. POLLUTION PREVENTION

12.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

12.2 Quantity of a chemical purchased should be based on expected usage during its shelf-life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

12.3 For information about pollution prevention that may be applicable to laboratory operations, consult "Less is Better: Guide to Minimizing Waste in Laboratories."[7]

13. WASTE MANAGEMENT

13.1 The analytical procedures described in this method generate relatively small amounts of waste since only small amounts of reagents are used. The matrices of concern are drinking water. However, the Agency requires that waste management practices be conducted consistent with all applicable rules and regulations, and that the air, water, and land is protected by minimizing and controlling all releases from bench operations. Also, compliance is required with any sewage discharge permits and regulations, particularly the hazardous waste identification rules and land disposal restrictions.

14. REFERENCES

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2. *Safety in Academic Chemistry Laboratories*. Vol 1. 7th Edition. American Chemical Society Publication; Committee on Chemical Safety, Washington DC, 2003. (available for download at http://membership.acs.org/C/CCS/pub_3.htm).

3. *Chemical Safety Manual for Small Businesses*. 3rd Edition. American Chemical Society, Committee on Chemical Safety, Washington DC, 2009. (available for download at http://membership.acs.org/C/CCS/pub_5.htm).

4. Occupational Safety and Health Administration (OSHA), Hazard Communication. 29 CFR 1910.1200.

5. Occupational Safety and Health Administration (OSHA), Occupational Exposure to Hazardous Chemicals in Laboratories. 29 CFR 1910.1450.

6. *Standard Test Method for Residual Chlorine in Water*. ASTM D 1253-03. ASTM International, West Conshohocken, PA. 2003.

7. *Less is Better: Guide to Minimizing Waste in Laboratories.* American Chemical Society, Task Force on Laboratory Environment, Health, & Safety, Washington DC, 2002. (available for download at http://membership.acs.org/C/CCS/pub_9.htm).

15. TABLES AND FLOWCHARTS

Table 1. Summary of Start-up QC for Grab Sample Methodology

Method Reference	Requirement	Specification	Acceptance Criteria
10.1.1.2	Generate or validate calibration curve	Analyze method blank & 3 calibration standards that span concentration range (Lowest standard ≤ 0.2 mg/L or the minimum required by primacy agency.)	Each standard is within ±15% of its expected concentration when compared to curve
10.1.1.3	Verify accuracy of secondary standards	Analyze secondary standards on each meter for which they will be used.	Each secondary standard is within ±10% of its expected concentration
10.1.2.1	Initial Demonstration of Capability (IDC) - Accuracy	Analyze method blank & 5 replicate independent reference samples fortified at a concentration near the drinking water concentration	Method blank ≤ ⅓ concentration of lowest calibration standard; Average of 5 replicates is within ±15% of expected concentration
10.1.2.2	Initial Demonstration of Capability (IDC) - Precision	Calculate relative standard deviation (RSD) for 5 independent reference sample replicate analyses	RSD ≤ 15%
10.1.3	Field Sampler IDC	Each sampler must successfully complete 10.1.2.1 and 10.1.2.2 (IDC samples may be prepared by laboratory personnel for analyses by field samplers.)	

Table 2. Summary of Start-up QC for On-line Chlorine Analyzer

Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
10.2.1	Verify or adjust analyzer calibration	Analyze grab sample & compare to analyzer reading; Adjust analyzer to agree with grab sample measurement; Iterative process until agreement is reached	Analyzer reading is within ± 0.1 mg/L or ± 15% (whichever is larger) of grab sample measurement
10.2.2	Initial Demonstration of Capability (IDC)	Compare analyzer measurement to a grab sample analysis on a daily basis for 14 consecutive days (or business days)	Analyzer reading must be within ± 0.1 mg/L or ± 15% (whichever is larger) of the grab sample measurement for each data pair

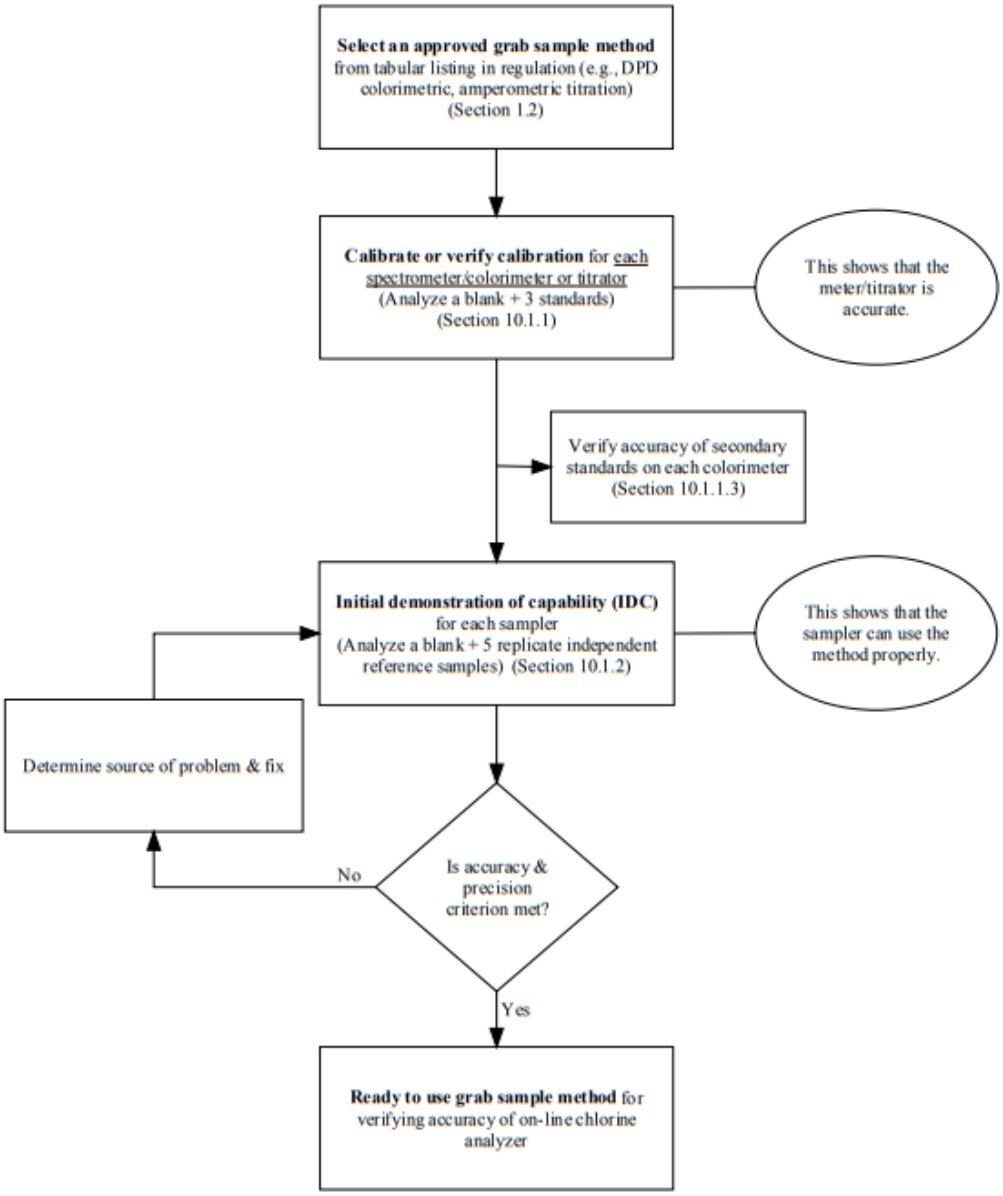
Table 3. Routine QC for Grab Sample Methodology

Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
11.1.1	Routine calibration check	Analyze a check standard: • When calibration of the on-line chlorine analyzer is adjusted • At least quarterly	Standard is within ±15% of its expected concentration
11.1.2	Secondary standards	Recommended: analyze each day grab sample method is used (This is only applicable to methods that use a spectrophotometer/colorimeter.)	Each secondary standard is within ±10% of its expected concentration

Table 4. QC for On-line Chlorine Analyzer

Method Reference	Requirement	Specification and Frequency	Acceptance Criteria
11.2	Routine calibration check	Compare analyzer measurement to a grab sample analysis: • on a routine basis (at least once each week) • immediately after analyzer calibration is adjusted • one day after analyzer calibration is adjusted	Analyzer reading must be within ± 0.1 mg/L or ± 15% (whichever is larger) of the grab sample measurement
11.3	Non-routine calibration check	Compare analyzer measurement to a grab sample analysis: • after routine maintenance • when analyzer drifts upward or downward without explanation (recommended)	Analyzer reading must be within ± 0.1 mg/L or ± 15% (whichever is larger) of the grab sample measurement
11.4	Emergency calibration check	If the analyzer indicates a large (≥ 50%) unexpected change in chlorine residual, compare analyzer measurement to a grab sample analysis as soon as possible	Analyzer reading must be within ± 0.1 mg/L or ± 15% (whichever is larger) of the grab sample measurement

Flowchart 1. Start-up Procedure for Grab Sample Method



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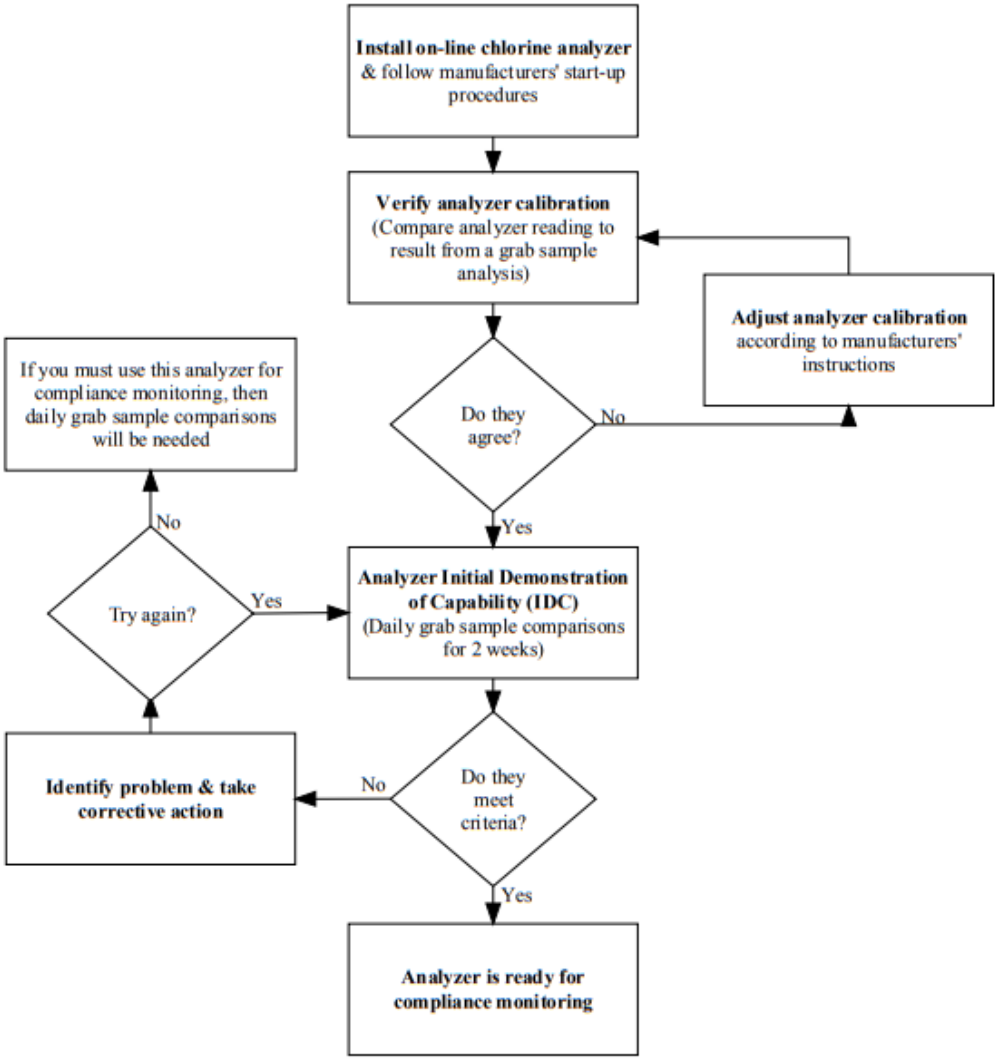
Flowchart 2. Start-up QC for On-line Chlorine Analyzer



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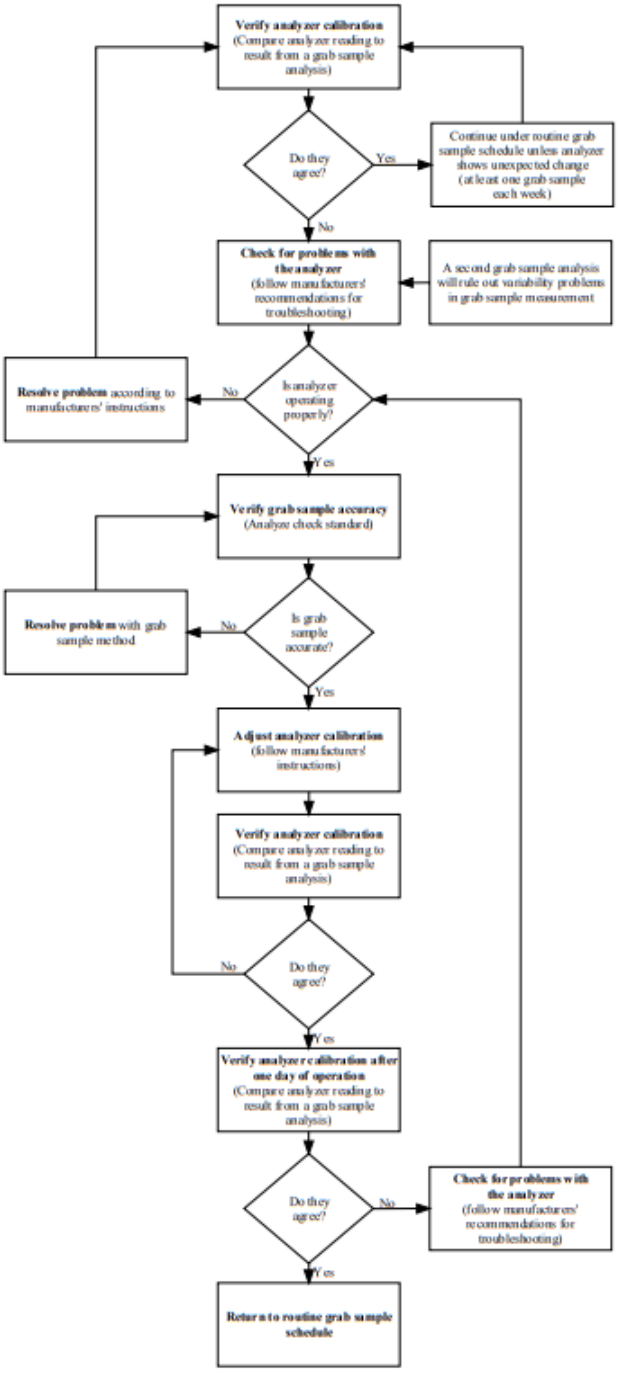
Flowchart 3. Routine QC for On-line Chlorine Analyzer



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METHOD 334.0 APPENDIX A

OPTIONAL PROCESS FOR ESTABLISHING A SCHEDULE FOR ROUTINE GRAB SAMPLE COMPARISONS TO ON-LINE CHLORINE ANALYZER READINGS

A. Historical data can be used to establish a routine schedule for comparing grab sample measurements to the results from the on-line chlorine analyzer. The data must demonstrate that the grab sample measurements are frequent enough to detect problems with the analyzer within a reasonable period of time after the problems occur. The following protocol is presented as a conservative approach to developing a routine schedule when historical data are not available. The acceptance criterion that must be met in each step is that the on-line chlorine analyzer reading is within ± 0.1 mg/L or ± 15% (whichever is larger) of the grab sample measurement. (Section B provides a flowchart of this process.)

A.1 The data from the on-line analyzer IDC (See Section 10.2.2) can be used as the initial data set. If the on-line chlorine analyzer and grab sample results meet the acceptance criteria over the 14 day period of the IDC, compare the concentration determined by the on-line chlorine analyzer with grab sample analyses collected every three days for 9 days.

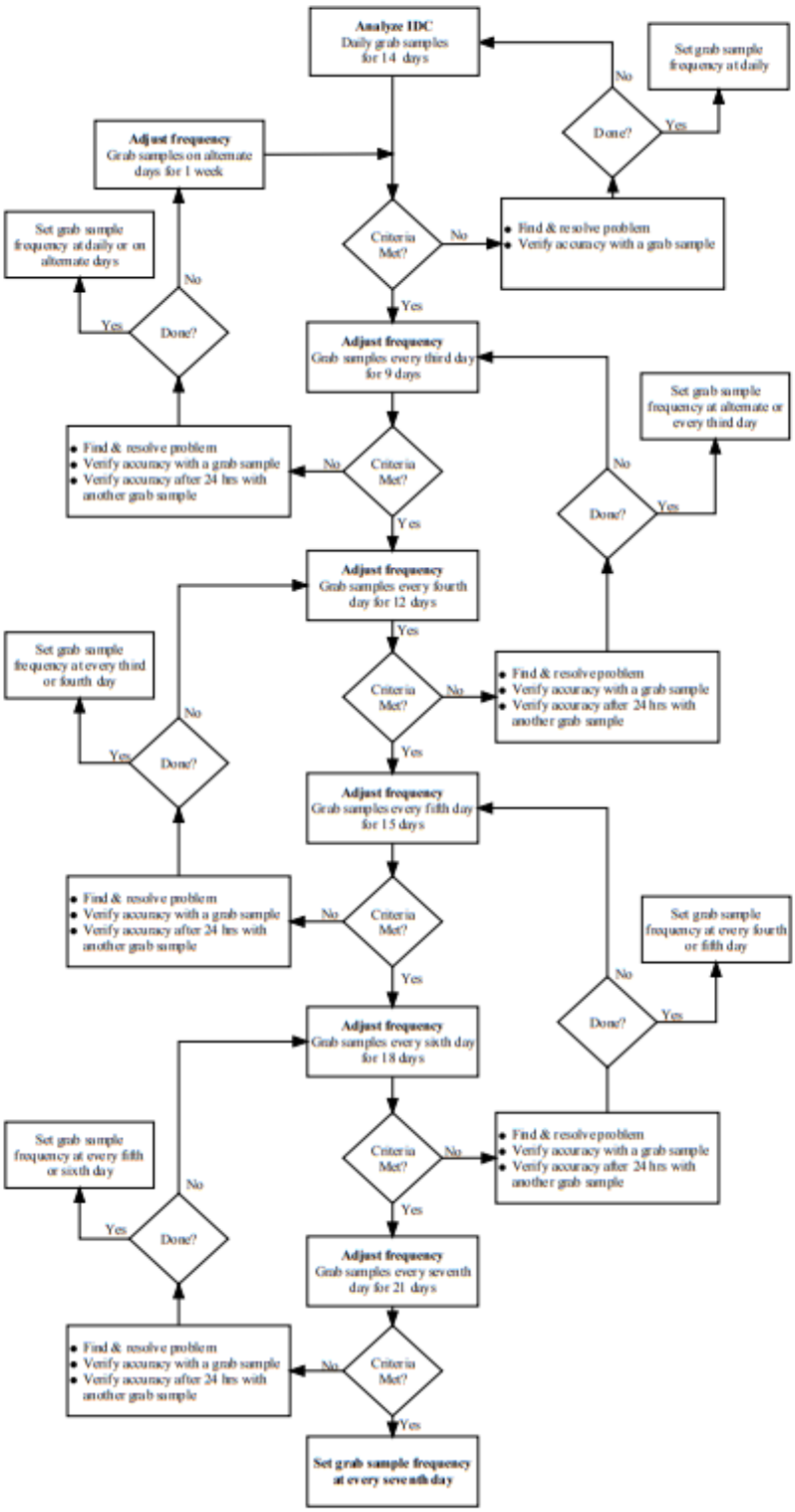
A.2 If the on-line chlorine analyzer continues to meet acceptance criteria over the above 9 day period, the grab sample interval can be extended to once every four days for 12 days.

A.3 As long as the acceptance criterion is met, continue extending the interval between grab samples using the same pattern as established in A.2 (i.e., once every 5 days for 15 days, once every 6 days for 18 days, etc). Collect a minimum of three grab samples each time the interval is extended by one day. **The maximum time between grab samples must not exceed once every 7 days (i.e., a weekly grab sample)**.

A.4 When the on-line analyzer fails to meet the acceptance criteria, resolve the problem following the protocol in Section 11.2. After the analyzer/grab sample agreement has been reestablished, examine the data collected in steps A.2 to A.3 to decide whether to continue extending the time between grab samples or to establish a schedule based on the existing data. Continue extending the time intervals between grab samples beginning with the interval that was being used prior to when the on-line analyzer failed to meet the acceptance criteria.

A.5 Establish the routine grab sample frequency at an interval which is no greater than one seventh of the average length of time between observed failures. **The maximum time between grab samples must not exceed once every seven days**.

B. Process for Establishing Frequency of Routine Grab Sample Comparisons to Analyzer Readings



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Appendix C. Example IDC Worksheet

Eight pages:

1 of 8: Steps 1 & 2—System information and dilution water chlorine demand

2 of 8: Steps 3 & 4—Prepare standard and verify benchtop

3 of 8: Step 5 for online instrument # 1

4 of 8: Step 5 for online instrument # 2

5 of 8: Step 5 for online instrument # 3

6 of 8: Step 5 for online instrument # 4

7 of 8: Step 5 for online instrument # 5

8 of 8: Step 5 for online instrument # 6

Notes

Method 334.0 IDC Spreadsheet

(for use by systems when submitting a request to use an on-line chlorine residual analyzer)

System Information

PWS Name: PWS WSC

PWS ID No. 1234567

Description of Benchtop Method

Benchtop Analytical Method:	DPD Colorimetric
Manufacturer Procedure No.: (if applicable)	Hach Methods 8167 and 10070
Instrument Manufacturer & Model: (if applicable)	Hach DR/2800

Reagent(s) Used During this Study	Manufacturer	Lot No. (if applicable)	Expiration Date
DPD Total Chlorine Reagent Powder Pillows, 10-mL	Hach	A8291	October-2013
DPD Total Chlorine Reagent Powder Pillows, 25-mL	Hach	A8243	October-2013
Distilled Water	Hill Country Springs	unknown	unknown

Step 1: Prepare the Dosing Solution for the Chlorine Demand Test

Analyst:	Ima deBoss			
Cl_2 Stock Standard, Source and Product No.:	Hach Chlorine Solution Ampoule (50-75 mg/L, 10 mL) Product #: 14268-10			
Lot No. :	A9653			
Expiration Date:	August-2011			
Concentration:	62.32	mg/L ±	0.18	mg/L
Volume of Stock Std Used:	2.0	mL		
Volume of Dilution Water Used to Prepare the Working Standard :	2.0	mL		
Assumed Working Standard Conc.:	31.16	mg/L ±	0.18	mg/L
Chlorine Demand of Dilution Water:	0.05	mg/L	(if the standard is being diluted, this value is based on the chlorine demand results from Step 2 below)	
Actual Working Standard Conc.:	31.11	mg/L		

Step 2: Determine Chlorine Demand of the Dilution Water

Analyst: Hardy Worker

Sample ID	Measured Residual (mg/L)	Assumed Chlorine Demand of Dilution Water (mg/L)	Calibration Standard Volume (mL)	Working Standard Used (mL)	Applied Concentration (calculated) (mg/L)	Expected Result (mg/L)	Actual Results						Was a Detectable Residual in at Least Four Samples? (Yes/No)	Was the Average Within 0.020 mg/L or 15% of Expected? (Yes/No)	Calculated Chlorine Demand of Dilution Water (mg/L)
							Test 1 (mg/L)	Test 2 (mg/L)	Test 3 (mg/L)	Test 4 (mg/L)	Test 5 (mg/L)	Average (mg/L)			
Dilution Water (Reagent Blank)	NA	NA	NA	0.0	0.00	0.000	0.00	0.01	0.02	0.00	0.01	0.008	See Note 1 Below		
Initial Test	0.01	0.00	60	0.3	0.15	0.163	0.00	0.02	0.02	0.04	0.00	0.016	No	No	See Note 2 Below
Repeat Test (if necessary)	0.01	0.00	60	0.5	0.26	0.265	0.24	0.22	0.21	0.18	0.21	0.212	Yes	No	0.053
Repeat Test (if necessary)	0.01	0.00													

Note 1: This step determines the apparent "measure residual" value for a reagent blank, i.e., dilution water that contains only the reagents but no working standard solution.

Note 2: A detectable residual was not achieved in at least 4 of the tests so the demand cannot be determined. Repeat the test with slightly more working standard solution.

Note 3: The test results appear to be invalid because the average measured residual significantly higher than the expected result. Repeat the test with the same applied concentration.

Comments: The dilution water sample was measured using a 100 mL graduated cylinder, the water was placed in a 250 mL beaker, and the working standard solution was added using a 1.0 mL TenSettte® pipette. These tests were run using the Hach Low Range Cl2 method (Hach Method 8167, DR/2800 Program Code 80) and total chlorine DPD pillows. A single sample cell was used for all tests and was rinsed twice with distilled water before the next 10 mL aliquot was tested. Readings were taken 3 minutes after reagent was introduced and all the tests were run within 18 minutes of preparing the first working standard.

Method 334.0 IDC Spreadsheet

(for use by systems when submitting a request to use an on-line chlorine residual analyzer)

System Information

PWS Name: PWS WSC

PWS ID No. 1234567

Step 3: Prepare the Working Standard Solution for the Benchtop Method Evaluation

Analyst:	Ima deBoss			
Cl_2 Stock Standard, Source and Product No.:	Hach Chlorine Solution Ampoule (50-75 mg/L, 10 mL) Product #: 14268-10			
Lot No. :	A9653			
Expiration Date:	March-2012			
Concentration:	62.32	mg/L ±	0.18	mg/L
Volume of Stock Std Used:	10.0	mL		
Volume of Dilution Water Used to Prepare the Working Standard :	0.0	mL		
Assumed Working Standard Conc.:	62.32	mg/L ±	0.18	mg/L
Chlorine Demand of Dilution Water:	NA	mg/L	(if the standard is being diluted, this value is based on the chlorine demand results from Step 2 above)	
Actual Working Standard Conc.:	62.32	mg/L		

Step 4: Verify the Performance of the Benchtop Method

Analyst: Hardy Worker

Anticipated On-line Analyzer Settings			
Lower Limit (mg/L)	Low Alarm (mg/L)	High Alarm (mg/L)	Upper Limit (mg/L)
0.20	0.50	3.00	5.00

Sample	Chlorine Demand of Dilution Water (mg/L)	Calibration Standard Volume (mL)	Working Standard Used (mL)	Applied Concentration (calculated) (mg/L)	Expected Result (mg/L)	Actual Results Test 1 (mg/L)	Test 2 (mg/L)	Test 3 (mg/L)	Test 4 (mg/L)	Test 5 (mg/L)	Average (mg/L)	Was the Average Within 15% of Expected? (Yes/No)	Relative Standard Deviation (%)	Was the RSD Value <= 15%? (Yes/No)	General Characterization of Results (LL,LA,Mid,HA,UL)	
Calibr.Std Set 1	0.05	60	0.4	0.41	0.36	0.29	0.32	0.33	0.35	0.33	0.324	Yes	7%	Yes	LL	LA
Calibr.Std Set 2	0.05	60	1.0	1.02	0.97	0.95	1.10	1.18	0.98	1.24	1.090	Yes	11%	Yes	Mid	
Calibr.Std Set 3	0.05	60	3.0	2.97	2.91	2.80	2.70	2.75	2.78	2.80	2.766	Yes	2%	Yes	Mid	
Calibr.Std Set 4	0.05	60	5.0	4.79	4.74	4.50	4.40	4.60	4.80	4.60	4.580	Yes	3%	Yes	HA	UL
Calibr.Std Set 5																
Calibr.Std Set 6																

Analysis of Results		
	Was at least one sample set within 0.5 mg/L of the anticipated Lower Limit of the instrument's span?	Yes
	Was at least one sample set between the anticipated Lower Limit and the Low Alarm settings?	Yes
	Was at least one sample set in the normal operating range you expect to see on the instrument?	Yes
	Was at least one of the standards between the anticipated High Alarm and Upper Limit settings?	Yes
	Was at least one of the standards within 1.0 mg/L of the anticipated Upper Limit of the instrument's span?	Yes

Comments:

The dilution water sample was measured using a 100 mL graduated cylinder, the water was placed in a 250 mL beaker. The working standard for Calibration Standard Sets 1 and 2 was added using a 1.0 mL TenSette® pipette and the working standards for Calibration Standard Sets 3 and 4 were added using a 10 mL Tensette® pipette. All of the working standard solutions were prepared immediately after opening the ampoule of stock standard. All of these tests were run using the Hach High Range Cl2 method (Hach Method 10070, DR/2800 Program Code 88) and total chlorine DPD pillows. A single sample cell was used for all tests in a given calibration standard set and the four cells were rinsed twice with distilled water before the next 10 mL aliquot was tested. Readings were taken 3 minutes after reagent was introduced and all the tests were run within 25 minutes of preparing the working standard solutions.

Method 334.0 IDC Spreadsheet

(for use by systems when submitting a request to use an on-line chlorine residual analyzer)

System Information

PWS Name: PWS WSC

PWS ID No. 1234567

Step 5: Conduct the 14-Day Initial Demonstration of Capability (IDC)

Benchtop Instrument Manufacturer & Model (if applicable): Hach DR/2800

Benchtop Analytical Method: DPD Colorimetric (Hach Methods 8167 and 10070)

On-line Instrument No. 1

Instrument Manufacturer & Model: Prominent Dulcometer and total chlorine probe

On-line Analytical Method: Proprietary amperometric membrane-style sensor

Installation Site/Monitoring Point: Chuckiepoo WTP, clearwell effluent

Date Installed: November-2008

Intended Use: Compliance Monitoring/Reporting and Process Control

Anticipated/Historical Residuals and Settings		
Maximum Residual	5.0	mg/L
High Alarm Setting	4.0	mg/L
Low Alarm Setting	2.5	mg/L
Minimum Residual	1.0	mg/L

Comparison No.	Date	Time	Analyst's Initials	Data Comparison			On-Line Within 15% of Grab? (Yes/No)	24-hr On-line Record		General Characterization of On-line Result Was the on-line reading . . .			Analysis of Results
				On-line (mg/L)	Grab (mg/L)	Difference (mg/L)		Max (mg/L)	Min (mg/L)	within 10% of the Max Reading?	between the Max and Min ranges	within 10% of the Min Reading?	
1	12/27/10	8:00 AM	HW	2.90	2.86	0.04	Yes	3.6	2.9	No	No	Yes	Was all the required data collected and were all of the on-line readings within 15% of the corresponding grab sample reading?
2	12/28/10	8:15 AM	HW	2.90	2.94	-0.04	Yes	3.0	2.8	Yes	No	Yes	
3	12/29/10	11:15 AM	IB	2.80	2.86	-0.06	Yes	2.8	2.3	Yes	No	No	
4	12/30/10	8:00 AM	HW	2.80	2.74	0.06	Yes	3.0	2.8	Yes	No	Yes	
5	12/31/10	8:30 AM	HW	3.60	3.24	0.36	Yes	3.8	3.4	Yes	No	Yes	Yes
6	01/03/11	8:15 AM	HW	3.00	2.86	0.14	Yes	3.1	3.0	Yes	No	Yes	Were at least 3 of the results near the max daily reading?
7	01/04/11	8:15 AM	HW	3.20	3.32	-0.12	Yes	3.2	2.8	Yes	No	No	
8	01/05/11	8:00 AM	IB	3.00	3.02	-0.02	Yes	3.3	3.0	Yes	No	Yes	Yes
9	01/06/11	8:30 AM	HW	2.90	3.10	-0.20	Yes	3.9	2.9	No	No	Yes	Were at least 3 of the results near the low daily reading?
10	01/07/11	7:30 AM	HW	3.30	3.20	0.10	Yes	3.5	2.9	Yes	No	No	
11	01/10/11	7:45 AM	HW	3.10	3.18	-0.08	Yes	3.3	3.0	Yes	No	Yes	Yes
12	01/11/11	7:30 AM	HW	3.00	3.22	-0.22	Yes	3.6	3.0	No	No	Yes	
13	01/12/11	8:00 AM	HW	3.20	3.06	0.14	Yes	3.5	2.9	Yes	No	No	
14	01/13/11	8:15 AM	HW	3.30	3.28	0.02	Yes	3.8	2.9	No	Yes	No	
15	01/14/11	7:45 AM	HW	3.10	3.10	0.00	Yes	3.3	3.0	Yes	No	Yes	

Comments: All of the grab sample tests were run using the Hach High Range Cl2 method (Hach Method 10070, DR/2800 Program Code 88) and total chlorine DPD pillows. Chlorine cylinder replaced on 12/29/10.

Routine maintenance of the Prominent sensor was performed prior to beginning Step 5 testing.

Method 334.0 IDC Spreadsheet

(for use by systems when submitting a request to use an on-line chlorine residual analyzer)

System Information

PWS Name: PWS WSC

PWS ID No. 1234567

On-line Instrument No. 2

Instrument Manufacturer & Model:

On-line Analytical Method:

Installation Site/Monitoring Point:

Date Installed:

Intended Use:

Anticipated/Historical Residuals and Settings		
Maximum Residual		mg/L
High Alarm Setting		mg/L
Low Alarm Setting		mg/L
Minimum Residual		mg/L

Comparison No.	Date	Time	Analyst's Initials	Data Comparison			On-Line Within 15% of Grab? (Yes/No)	24-hr On-line Record		General Characterization of On-line Result Was the on-line reading . . .			Analysis of Results
				On-line (mg/L)	Grab (mg/L)	Difference (mg/L)		Max (mg/L)	Min (mg/L)	within 10% of the Max Reading?	between the Max and Min ranges	within 10% of the Min Reading?	
1													Was all the required data collected and were all of the on-line readings within 15% of the corresponding grab sample reading?
2													
3													
4													
5													
6													Were at least 3 of the results near the max daily reading?
7													
8													
9													Were at least 3 of the results near the low daily reading?
10													
11													
12													
13													
14													
15													

Comments:

Method 334.0 IDC Spreadsheet

(for use by systems when submitting a request to use an on-line chlorine residual analyzer)

System Information

PWS Name: PWS WSC

PWS ID No. 1234567

On-line Instrument No. 3

Instrument Manufacturer & Model:

On-line Analytical Method:

Installation Site/Monitoring Point:

Date Installed:

Intended Use:

Anticipated/Historical Residuals and Settings		
Maximum Residual		mg/L
High Alarm Setting		mg/L
Low Alarm Setting		mg/L
Minimum Residual		mg/L

Comparison No.	Date	Time	Analyst's Initials	Data Comparison			On-Line Within 15% of Grab? (Yes/No)	24-hr On-line Record		General Characterization of On-line Result Was the on-line reading . . .		
				On-line (mg/L)	Grab (mg/L)	Difference (mg/L)		Max (mg/L)	Min (mg/L)	within 10% of the Max Reading?	between the Max and Min ranges	within 10% of the Min Reading?
1												
2												
3												
4												
5												
6												
7												
8												
9												
10												
11												
12												
13												
14												
15												

Analysis of Results
Was all the required data collected and were all of the on-line readings within 15% of the corresponding grab sample reading?
Were at least 3 of the results near the max daily reading?
Were at least 3 of the results near the low daily reading?

Comments:

Method 334.0 IDC Spreadsheet

(for use by systems when submitting a request to use an on-line chlorine residual analyzer)

System Information

PWS Name: PWS WSC

PWS ID No. 1234567

On-line Instrument No. 4

Instrument Manufacturer & Model:

On-line Analytical Method:

Installation Site/Monitoring Point:

Date Installed:

Intended Use:

Anticipated/Historical Residuals and Settings		
Maximum Residual		mg/L
High Alarm Setting		mg/L
Low Alarm Setting		mg/L
Minimum Residual		mg/L

Comparison No.	Date	Time	Analyst's Initials	Data Comparison			On-Line Within 15% of Grab? (Yes/No)	24-hr On-line Record		General Characterization of On-line Result Was the on-line reading . . .			Analysis of Results
				On-line (mg/L)	Grab (mg/L)	Difference (mg/L)		Max (mg/L)	Min (mg/L)	within 10% of the Max Reading?	between the Max and Min ranges	within 10% of the Min Reading?	
1													Was all the required data collected and were all of the on-line readings within 15% of the corresponding grab sample reading?
2													
3													
4													
5													
6													Were at least 3 of the results near the max daily reading?
7													
8													
9													Were at least 3 of the results near the low daily reading?
10													
11													
12													
13													
14													
15													

Comments:

Method 334.0 IDC Spreadsheet

(for use by systems when submitting a request to use an on-line chlorine residual analyzer)

System Information

PWS Name: PWS WSC

PWS ID No. 1234567

On-line Instrument No. 5

Instrument Manufacturer & Model:

On-line Analytical Method:

Installation Site/Monitoring Point:

Date Installed:

Intended Use:

Anticipated/Historical Residuals and Settings		
Maximum Residual		mg/L
High Alarm Setting		mg/L
Low Alarm Setting		mg/L
Minimum Residual		mg/L

Comparison No.	Date	Time	Analyst's Initials	Data Comparison			On-Line Within 15% of Grab? (Yes/No)	24-hr On-line Record		General Characterization of On-line Result Was the on-line reading . . .			Analysis of Results
				On-line (mg/L)	Grab (mg/L)	Difference (mg/L)		Max (mg/L)	Min (mg/L)	within 10% of the Max Reading?	between the Max and Min ranges	within 10% of the Min Reading?	
1													Was all the required data collected and were all of the on-line readings within 15% of the corresponding grab sample reading?
2													
3													
4													
5													
6													Were at least 3 of the results near the max daily reading?
7													
8													
9													Were at least 3 of the results near the low daily reading?
10													
11													
12													
13													
14													
15													

Comments:

Method 334.0 IDC Spreadsheet

(for use by systems when submitting a request to use an on-line chlorine residual analyzer)

System Information

PWS Name: PWS WSC

PWS ID No. 1234567

On-line Instrument No. 6

Instrument Manufacturer & Model:

On-line Analytical Method:

Installation Site/Monitoring Point:

Date Installed:

Intended Use:

Anticipated/Historical Residuals and Settings		
Maximum Residual		mg/L
High Alarm Setting		mg/L
Low Alarm Setting		mg/L
Minimum Residual		mg/L

Comparison No.	Date	Time	Analyst's Initials	Data Comparison			On-Line Within 15% of Grab? (Yes/No)	24-hr On-line Record		General Characterization of On-line Result Was the on-line reading . . .			Analysis of Results
				On-line (mg/L)	Grab (mg/L)	Difference (mg/L)		Max (mg/L)	Min (mg/L)	within 10% of the Max Reading?	between the Max and Min ranges	within 10% of the Min Reading?	
1													Was all the required data collected and were all of the on-line readings within 15% of the corresponding grab sample reading?
2													
3													
4													
5													
6													Were at least 3 of the results near the max daily reading?
7													
8													
9													Were at least 3 of the results near the low daily reading?
10													
11													
12													
13													
14													
15													

Comments:

Notes

Appendix D. Lab forms

Laboratory Approval Form and List of Analytical Methods

Laboratory Approval Form is required for all PWSs. Available at

www.tceq.texas.gov/drinkingwater/monitoring_plans

List of Analytical Methods is required for PWSs that have chloramines. Available upon request from the TCEQ Water Supply Division at 512-239-4691.

Both forms should be attached to a PWS's Monitoring Plan for review by TCEQ staff during periodic inspections.

Notes

Laboratory Approval Form (LAF)

This must be attached to the Laboratory Approval Form

To remove this form click here

Drinking Water Lab Approval Form

Laboratory or Plant Name		Contact Name	
PWS ID (TCEQ issued)		E-mail	
Lab ID No		Phone	
Address		Date form completed	
City/State		Does this lab perform analyses for other Public Water Systems?	☐ Yes ☐ No
Zip			

Analytes and Methods

Analyte	Analytical Method [2]	Instrument Name [3]		Accuracy [4]	Calibration Frequency [5]	Calibration Method [6]	NELAP Accredited[7]	PT Study [8]
Turbidity	EPA 180.1	hjghjhgjhj	±	ghjghj NTU	ghj	ghj		
pH			±	pH unit				
Temperature			±	°C				
TOC			±	mg/L				
UV_{254}			±	cm^{-1}				
Alkalinity			±	mg/L				
Free Chlorine[9]			±	mg/L				
Total Chlorine[9]			±	mg/L				
Chlorine Dioxide[10]			±	mg/L				
POE Chlorite[10]			±	mg/L				
Calcium [1]			±	mg/L				
Phosphate [1]			±	mg/L				
Conductivity [1]			±	µmho/cm				
Silica [1]			±	mg/L				

Lab Analyst or Operator Validation

I certify that I am familiar with the information contained in this report and that, to the best of my knowledge, this information is true, complete and accurate.

Lab Analyst or Operator's Name and Title

Lab Analyst or Operator's Signature

Notes

List of Analytical Methods (LAM) (for PWSs using chloramines)

This must be attached to the Laboratory Approval Form

Analyte	**Method (& Analyzer Type)**	**Accuracy[5]**	**Calibration Frequency[6]**	**Calibration Method**
pH		± pH unit		
Temperature		± C		
Disinfectant				
Total Chlorine		± mg/L		
Free Chlorine		± mg/L		
Monochloramine		± mg/L		
Free Ammonia (as nitrogen)		± mg/L		
Chlorine Dioxide		± mg/L		
Chlorite		± mg/L		
Ozone		± mg/L		
Nitrification				
Nitrite		± mg/L		
Nitrate		± mg/L		
Other-Microbial				
HPC (Heterotrophic plate count bacteria)		± CFU/100 mL		
DNA (Microbial DNA)		± mg/L		
Other		±		
Hardness		± mg/L		
Alkalinity		± mg/L		
Total dissolved solids		± mg/L		
Dissolved oxygen (DO)		± mg/L		

Notes

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Revision history:

Revision table

Action	Date	Comment
Create DAM	January 28, 2013	
Minor Revision	Ca. January 2015	Reformat
Revision	April 27, 2019	Incorporate QC findings. Make accessible.

Thanks for participating in DAM 7.
Please, remember to submit your evaluation form to the instructor.