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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DIRECTED ASSISTANCE MODULE (DAM) 7

Initial Demonstration of Capability Using EPA Method 334.0: 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 and Texas Optimization Program contractors. The TCEQ Water Supply Division (WSD) teaches instructors 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:

- Prepare chlorine calibration standards at multiple concentrations.
- Understand precision and accuracy requirements necessary to validate on-line instrument readings.
- Utilize the TCEQ-supplied Method 334 IDC Spreadsheet.
- Understand the continuing monitoring and comparison requirements between on-line and benchtop instruments.
- Document the use of the on-line instrument and Method 334 for compliance reporting purposes on an updated Drinking Water

Laboratory Approval Form (TCEQ Form 10450) that will be attached 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 the TCEQ Drinking Water Lab Approval Form (TCEQ-10450), and is comfortable working with Microsoft Excel workbooks and 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 can 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	Optimally, a 1.0 milliliter (mL) variable micropipette with 50 microliter (µL) or less increments and a bag/box of tips Alternately, a 1.0 mL graduated measuring Pipette (serological or Mohr) or a 1.0 mL TenSette pipette and a bag of tips *(for pipetting primary and working standards)*
1	10.0 mL graduated measuring Pipette ***OR*** a 10.0 mL TenSette pipette and a bag of tips *(for pipetting water)*
1	50 mL or 100 mL volumetric flasks or graduated cylinders
Several	Ampoules of a chlorine solution of known concentration (i.e., a primary chlorine standard or stock standard)
1	Optimally, at least 1 liter of organic-free dilution water Alternately, at least one gallon of deionized or distilled water (If deionized or distilled water is used, all of the dilutions should be accomplished from the same bottle.)
60+	Enough reagent to run at least 60 benchtop tests
1	Benchtop chlorine analyzer utilizing an EPA approved chlorine method
5+	Sample vials or cuvettes, Erlenmeyer flasks, or beakers (as applicable and as necessary) for each concentration range of calibration standard to be tested to be tested. *(typically, one or two very clean 250 or 500 mL flasks/beakers and a box of six 10 mL or 25 mL cuvettes)*
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. Either:
   a. An electronic copy of the Method 334 IDC Spreadsheet completed for Steps 1-4 and the initial Step 5 reading for at least one on-line instrument, ***OR***
   b. A printout of the **IDC Data** worksheet with the completed data for Steps 1-4 and the initial Step 5 reading for at least one on-line instrument.
3. Completed Recommended Action Plan Form.
4. Completed Plant Questionnaire from each participant.
5. Completed Project Completion Form (Instructor only).
6. 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 7.0 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	Review the DAM7 Course Manual and the IDC spreadsheet (30 minutes)
9:45 – 10:00	Break (15 minutes)
10:00 – 10:30	**Step 1 —** Prepare a working standard solution for the chlorine demand test (30 minutes)
10:30 – 11:30	**Step 2 —** Measure the chlorine residual in a reagent blank and the chlorine demand of the dilution water (60 minutes)
11:30 – 12:30	Lunch break (60 minutes)
12:30 – 1:00	**Step 3 —** Prepare a working standard solution for evaluating the accuracy and precision of the benchtop analyzer (30 minutes)
1:00 – 2:00	**Step 4 —** Measure the accuracy and precision of benchtop analyzer (60 minutes)
2:00 – 2:15	Break (15 minutes)
2:15 – 2:45	**Step 5 —** Compare online monitor readings to benchtop readings (30 minutes)
2:45 – 3:15	Drinking Water Lab Approval Form (30 minutes)
3:15 – 3:30	Recommended Action Plan (15 minutes)
3:30 – 4:00	Wrap up and Questionnaire (30 minutes)

Description of Agenda Activities

Introductions and overview (15 minutes)

The goal of this section of training is to allow the instructor to distribute the DAM7 Sign-Up Sheet and provide each participant with a copy of the DAM7 Course Manual. As the participants sign in, they and the instructor will introduce themselves and briefly summarize their operational and laboratory experience. The instructor will also briefly summarize the 5-step IDC procedure and describe what needs to be accomplished during and following the on-site training.

Plant tour (45 minutes)

IMPORTANT

If the plant staff have not already treated all the glassware that will be used during DAM7 to remove any chlorine demand, at least one of the participants will need to complete this task instead of accompanying the instructor on the plant tour.

The purpose of the plant tour is to allow the participants to show the instructor where the disinfectants are being applied at the plant and where the disinfectant concentration is being monitored. It is especially important for the operators to show the instructor where on-line chlorine or chloramine analyzers are or will be used for regulatory reporting.

The operator that is leading the tour will need to take a copy of the plant's Concentration/Time (CT) Study approval letter on the tour. This document will be especially important if the plant staff intend to use on-line instruments to determine the disinfectant residual at the end of one or more of the plant's designated 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.

Lab Tour (15 minutes)

Following the plant tour, the participants will take the instructor on a quick tour of the plant laboratory. While the group is in the lab, the operators will show the instructor the equipment used for manually measuring disinfectant residuals and briefly describe the sample collection and analytical procedures the plant staff uses.

Review the DAM7 Course Manual and IDC spreadsheet (30 minutes)

After returning from the tours, the instructor will spend a few minutes explaining how the DAM7 Course Manual is organized and to find information about how to complete each of the five IDC steps. The IDC spreadsheet is a Microsoft Excel file and the instructor's primary goal in this activity is to show the participants the IDC workbook and provide an overview of how it is organized and how it is used to collect and report the IDC results to the TCEQ.

More information about the IDC workbook and detailed instructions for entering the data for each IDC step are provided later in this document.

Step 1 — Prepare a working standard solution for the chlorine demand test (30 minutes)

The hands-on training begins with the preparation of a chlorine standard that the participants will use in Step 2. The instructor will help the plant staff record information about the reagents and standards that they will use to prepare the standard and provide technical assistance as the operators prepare the standard.

Instructions for preparing the working standard solution are found in the IDC Step 1 instructions, which begin on page 26, in Chapter 3.

Step 2 — Measure the chlorine residual in a reagent blank and the chlorine demand of the dilution water (60 minutes)

Important

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

Step 2 of the IDC involves determining if there are any interferences that could impact the data produced during subsequent IDC steps and to quantify the impact of those interferences if they exist. In this part of the DAM7 workshop, the instructor will provide technical assistance as the operators:

a) determine if the reagents, glassware, dilution water, or instrument are producing a false positive result in a sample of dilution water that contains no added chlorine;

b) prepare and analyze a series of samples; and

c) measure how much, if any, chlorine demand exists in the dilution water they are using for Steps 1 through 4 of the IDC.

Instructions for preparing the test solutions for the apparent residual and for the chlorine demand test are found in the IDC Step 2 instructions, which begin on page 31, in Chapter 3.

Step 3 — Prepare a working standard solution for evaluating the accuracy and precision of the benchtop analyzer (30 minutes)

Step 3 of the IDC is almost identical to Step 1. The instructor will again provide technical assistance as the operators prepare the standard.

Instructions for preparing the working standard solution are found in the IDC Step 3 instructions, which begin on page 37, in Chapter 3.

Step 4 — Measure the accuracy and precision of benchtop analyzer (60 minutes)

Important

Step 4 must be done **immediately** after Step 3 to avoid solution degradation.

Step 4 of the IDC involves using the benchtop (reference) method to measure the disinfectant residual at concentrations that will cover the entire range of values the plant expects the on-line analyzer to encounter. If the benchtop method uses a calibration curve, the data produced during Step 4 is also used to prepare a calibration curve for the reference method.

In this part of the DAM7 workshop, the instructor will provide technical assistance as the operators:

a) identify the maximum and minimum disinfectant residuals the plant has historically encountered at the proposed monitoring location and the upper and lower alarm settings that will be used for that on-line instrument;

b) prepare, characterize, and analyze a series of samples; and

c) determine if the reference method produced accurate and precise results over the entire range of expected values.

Instructions for identifying the instrument span and preparing the test solutions are in the IDC Step 4 instructions, which begin on page 37, in Chapter 3.

Step 5 — Compare online monitor readings to benchtop readings (30 minutes)

Once the participants have verified the accuracy and precision of the benchtop (reference) method, the operators can begin comparing the results obtained from the manual procedure with those produced by the on-line monitor and recorded by the plant's data logger.

In this part of the DAM7 workshop, the instructor will provide technical assistance as the operators:

a) identify and record the manufacturer and model number of the on-line analyzer(s) they will use to collect disinfection residual data reported to the TCEQ;

b) collect and analyze the disinfectant residual in a grab sample collected from the on-line monitor's sample line; and

c) record the disinfectant residual readings from the reference method, the on-line analyzer's display, and the plant's data recorder or SCADA system.

The instructor will also help the operators develop the procedures they will use to determine and record the minimum and maximum daily values recorded by the plant's data recorder or SCADA system.

Instructions for completed the Step 5 data and interpreting those results are in the IDC Step 5 instructions, which begin on page 45, in Chapter 3.

Drinking Water Lab Approval Form (30 minutes)

Once the plant staff successfully completes the data collection for Step 5 of the IDC, they must print and submit a copy of the **IDC Data** worksheet to the TCEQ for review. The plant staff must also submit an updated Drinking Water Lab Approval Form (DWLAF) with the IDC data so that the TCEQ will have a record of the new on-line instruments that will be used for collecting disinfection data that is reported to the agency. Although there is not enough time to help the operators completely update the plant's DWLAF, the instructor will provide technical assistance while the plant staff enters the data on the on-line instruments.

Instructions for preparing the packet of information that the operators must submit to the TCEQ begin on page 53 in Chapter 4.

Recommended Action Plan (15 minutes)

Since Step 5 requires the plant staff to report data for 14 days, it will be impossible to complete the IDC during the DAM7 workshop. Therefore, the instructor and participants will work together to produce an Action Plan for completing the IDC project. Although the Action Plan will contain at least three items (complete Step 5, submit the IDC packet to the TCEQ, and create an on-going instrument performance verification plant), it may include other items.

More information about how to develop and implement an Action Plan begins on page 59 of Chapter 5.

Wrap-up and Questionnaire (30 minutes)

The instructor will provide each of the participants with a copy of the DAM7 Plant Questionnaire. The TCEQ receives a copy of the completed questionnaires and would very much appreciate receiving feedback regarding the DAM7 training and training materials. The TCEQ relies heavily on this information when it reviews and updates its DAM materials.

Notes

Chapter 1. Introduction

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**; and
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 and a copy of an updated Drinking Water Lab Approval Form (TCEQ-10450) 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. The IDC spreadsheet is a Microsoft Excel workbook that provides a set of step-by-step data entry instructions, an **IDC Data** worksheet that automates many of the calculations the operators must perform, and an **IDC Data (Example)** worksheet that contains an example of the data from a properly-completed special study. Using this TCEQ tool can help operators eliminate the guesswork on calculations and QC checks and facilitates the TCEQ review process.

The instructor will provide the plant an electronic copy of each file during the DAM7 training event. However, the operators can also obtain copies by contacting the TCEQ at (512) 239-4691 and asking for one of the staff members assigned to the TOP.

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 shown in the Appendix A, which is located on page 63.

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, the TCEQ IDC spreadsheet does not address them. Consequently, the operators will need to create new form for recording the results of the weekly verifications or adapt one of the forms that they are currently using for other instruments.

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

Step 1: Prepare a working standard solution that will be used to determine the chlorine demand of the dilution water used throughout the first four steps of the IDC.

Step 2: Measure the apparent chlorine residual in a reagent blank and the chlorine demand of the dilution water.

Step 3: Prepare a working standard solution that will be used to evaluate the accuracy and precision of the benchtop (reference) method.

Step 4: Verify that the benchtop method is producing accurate results over the entire range of disinfectant concentrations that the on-line instrument will be encountering.

Step 5: Confirm that the results obtained from the manual benchtop method are consistent with those produced by the on-line instrument and recorded by the plant's data logger or SCADA system.

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 334.0 as published by the EPA is included as Appendix B, which begins page 65. Operators can also download an electronic copy (an Adobe pdf file) of Method 334.0 at the following Internet address:

https://www.nemi.gov/methods/method_summary/10617/

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) concerns.

Purpose of method

The purpose of EPA Method 334.0 is to give a water system a way to demonstrate that an online residual analyzer which uses an instrument-specific analytical method can accurately measure disinfectant levels. This is accomplished by showing that the on-line instrument produces the same results as a benchtop method that uses a more traditional EPA-approved method. To demonstrate this, the operators must conduct an initial demonstration of capability (IDC) before using the on-line analyzer for compliance monitoring. The IDC protocol is designed to show that:

- the operator's lab technique is correctly applied and precise enough to produce accurate results when using the EPA-approved benchtop method,
- the reagents used to measure the chlorine residual are of good quality,
- the laboratory's benchtop equipment and instrumentation are capable of producing accurate results over the entire range of disinfectant concentrations that will be measured by the on-line instrument, and
- the online analyzer and the benchtop method produce similar results.

General Methodology

As noted previously, conducting an IDC involves five steps.

- Steps 1 and 2 involve preparing a standard and then using that standard to verify that the benchtop method will produce accurate, precise readings at low disinfectant concentrations.
- Steps 3 and 4 involve preparing a standard and then using that standard to verify that the benchtop method will produce accurate, precise results over the entire range (or span) of readings that the operators anticipate measuring at the compliance monitoring point where the on-line instrument is installed.
- Step 5 involves verifying that the benchtop method and the on-line instrument produce the same readings and that the data logger accurately records the data produced by the on-line monitor.

Reagent quality and chlorine demand

The IDC procedure requires very precise measurements of chlorine residual at very low concentrations. Consequently, the operators or analysts must determine if the quality of the reagents, standards, and dilution water, or the condition of the glassware and benchtop instruments will have any impact on their ability to interpret the data produced during the IDC.

Reagents and standards

One potential source of error is the quality of the reagents and chlorine standards that are used to run the tests. If they are old or have not been properly stored, they may not be as reactive as fresh, properly-stored reagents and standards and produce results that are lower than expected. However, in some cases, reagents may also produce false positive readings (i.e., indicate the presence of chlorine in a sample that contains no chlorine). The impact of these conditions is evaluated during Step 2 of the IDC.

Dilution water

Another potential source of error is the quality of the (dilution) water that that the analyst or operator uses to prepare the standards and samples required during Steps 1 through 4 of the IDC. Although it is possible that the dilution water might contain a little chlorine, it is far more likely that the dilution water will contain materials that exert a chlorine demand. In order to minimize the chlorine demand of the dilution water, the operators should use commercially-prepared, organic-free water or, if that is not available, a high-quality deionized (DI) or distilled water.

It should be noted that each container of DI or distilled water may have a different chlorine demand, even if the water was produced by the same equipment. If this water is used for dilution, it might be beneficial to use a single, large container of water to complete the whole IDC procedure. If this is not possible, the analyst may want to consider mixing the containers before beginning the IDC. Even if the analyst uses commercially-prepared, organic-free water, it might be beneficial to make sure that each bottle has the same lot number. This precaution will help ensure the quality of the dilution water is as consistent as possible.

Glassware

Contaminated or damaged glassware is yet another potential source of error. It is very important to use clean glassware, pipettes, flasks, beakers, and sample cells when conducting the IDC. If there is any possibility that system's glassware has been contaminated as a result of previous use, it must be decontaminated or replaced. For example, if a sample cell was previously used to measure total chlorine, it must be thoroughly washed and rinsed to remove any trace of the total chlorine reagent . . . especially if the sample cell will be used to test for free chlorine. Dirty glassware may also contain materials that exert a chlorine demand on the sample being tested. 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.

Analytical technique

It is very important to use the same analytical methodology and technique throughout the entire IDC. If possible, the same analyst or operator should conduct Steps 1 through 4. At the very least, the individuals that complete Steps 2 and 4 should watch the person who prepares the standards used during these steps. These precautions might help the analysts identify any potential sources of error that might have contributed to unacceptable results if they occur.

Submitting the IDC results

After completing Steps 1 through 5, the water system must update its Drinking Water Lab Approval Form (TCEQ–10450) and submit a copy of both the IDC spreadsheet and the updated form to the TCEQ for review. The materials can also be submitted to the TCEQ electronically as an e-mail attachment. The system must also attach a copy of both documents to its Monitoring Plan.

An example of a completed IDC spreadsheet is shown in Appendix C, which is located on page 89 and an example of a blank DWLAF is included in Appendix D, located on page 95.

Periodic verification

After successfully completing the IDC, the plant must continue to monitor the accuracy of both the manual (benchtop) method and instruments, the on-line monitor, and the data recorder. Specifically, the operators must:

- Verify the accuracy of the EPA-approved manual method at least once every 90 days. This verification must be conducted using chlorine solutions with known concentrations.
- Verify the accuracy of the on-line monitor at least once every 7 days. The operators can conduct this verification using a chlorine solution of known concentration or by confirming that the result displayed on the

on-line monitor is within 15% or 0.1 mg/L (whichever is greater) of the result obtained using the manual method.

- Verify that the value recorded by the data recorder is within 0.1 mg/L of the value displayed on the on-line monitor. This verification must be conducted at the same time that the operator verifies the accuracy of the on-line monitor.

If routine maintenance is performed on the on-line analyzer, 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.

Notes

Chapter 2. Selecting and preparing the materials needed to conduct the IDC

It is difficult to overemphasize the importance of using appropriate glassware, pipettes, flasks, beakers, and sample cells when conducting the IDC. Table 1, located on page 3, provides a list of all the materials and laboratory equipment the plant staff will need to complete the IDC special study. Additional information about some of the items listed in Table 1 is shown below.

Pipettes

When conducting Steps 1 through 4 of the IDC, it is critically important for operators to be able to accurately and precisely measure sample volumes. To achieve this, the lab analysts will need two sizes of pipettes; a small pipette that can measure volumes of 1.0 mL or less and a larger pipette that can measure volumes as large as 10 ml. The analysts will use the smaller devices to pipette concentrated standards and the larger ones to pipette diluted standards and water.

These measurements can be made with adjustable mechanical pipettes (such as an adjustable micropipette or a Hach TenSette pipette) or manual measuring pipette (such as a serological pipette or a Mohr pipette).

One of the main advantages of using adjustable mechanical pipettes is that they use a disposable tip and an analyst can use a different pipette tip for each solution or sample concentration that needs to pipetted over the course of the IDC. Using adjustable mechanical pipettes can save lots of time.

If the analysts use manual measuring pipettes, it is critical that they have several pipettes of each size available or that they thoroughly rinse the pipettes each time they pipette a different solution to prevent cross-contamination of the samples. Additionally, it is critical for the analysts to know which type of manual measuring pipette they have.

- There are two types of serological pipettes; the "to deliver" (TD) pipette and the "to contain" (TC) pipette. Both types are graduated and calibrated to the tip. However, a TD pipette is designed to deliver the specified volume when it drains while the analyst must purge (or blow out) the TC pipette to deliver the full volume that the pipette contains.
- The Mohr pipette is also graduated but is not calibrated to the tip. Consequently, analysts should never allow a Mohr pipette to drain below the lowest graduation mark when they are pipetting the solutions.

Glassware

Analysts must also take care when selecting and preparing the glassware they will use to conduct the IDC special study. Inappropriate glassware can make it more difficult to successfully complete the IDC.

Volumetric versus measuring glassware

Volumetric glassware (such as volumetric flasks) are designed to contain a specific volume of solution (e.g. 50 ml, 100 mL, 250 mL, etc) but are not graduated to measure other volumes. Measuring glassware (such as graduate cylinders, Erlenmeyer flasks, and beakers) typically have graduated markings that allow them to measure a wider range of volumes.

Volumetric flasks typically allow an analyst to measure the volume of the solution with an accuracy of ±0.1 percent or so while graduated cylinders are generally considered to have an accuracy of ±1 percent or so. Beakers and Erlenmeyer flasks can only provide a very crude estimate of a sample volume because their accuracy for volume measurements is so poor. Flasks and beakers should only be used for mixing or storing a solution.

Optimally, an analyst will use volumetric glassware to prepare their working standards (i.e., the dosing solutions). However, many analysts can achieve an acceptable level of accuracy and precision using an appropriately-sized graduated cylinder. In general, to achieve a reasonable level of accuracy, the rated volume of the graduated cylinder should never be more than twice the volume of the volume being measured.

Preparing Glassware

It is difficult to overemphasize the importance of using use clean glassware when conducting the IDC. If there is any possibility that system's glassware has been contaminated as a result of previous use, it must be decontaminated or replaced. Dirty glassware can produce erroneously high results as well as erroneously low results. Either of these conditions make it more difficult for the analysts to successfully complete the IDC special study.

For example, a sample cell that was previously used to measure total chlorine must be thoroughly washed and rinsed to remove any trace of the total chlorine reagent . . . especially if the sample cell will be used to test for free chlorine. Even the slightest trace of iodide from the total chlorine reagent can contaminate the free chlorine test and cause a monochloramine interference that will produce an erroneously high free chlorine reading. Therefore, it is best to use separate, dedicated sample cells for free and total chlorine measurements. Stained sample cells can also produce erroneously high readings and should be discarded and replaced. Optimally, an analyst will use brand new sample cells when conducting the IDC study.

Used glassware may also contain materials that exert a chlorine demand on the sample being tested. If the glassware is thoroughly rinsed with deionized water and allowed to dry after each use, only occasional pretreatment is necessary. However, the glassware used in steps 1 through 4 of the IDC must be chlorine demand-free, so it may need to be pre-treated before starting the IDC. The pretreatment process requires the following steps.

- Prepare a dilute bleach solution by mixing 1 mL of commercial bleach in 1 L of deionized water.
- Soak the glassware in a dilute bleach solution for at least 1 to 3 hours.
- Rinse the glassware thoroughly with deionized water at least three times; be sure to rinse the entire inside, outside, and lip of glassware.
- Let the glassware air dry.

Standards and other reagents

All of the standards, standards, and dilution water used during the IDC must be fresh (i.e., have lot number that has not reached its expiration date) and properly stored (i.e., stored in accordance with the manufacturer's recommendations). If they are old or have been stored improperly, they may not be as reactive as fresh, properly-stored reagents and standards and may produce results that are lower than expected. However, in some cases, degraded reagents may also produce false positive readings (i.e., indicate the presence of chlorine in a sample that contains no chlorine).

Standards

During Steps 1 through 4 of the IDC, the analysts must use a chlorine solution of known concentration (i.e., a primary chlorine standard) to prepare samples that will be tested using an EPA-approved manual (benchtop) method. The samples tested during an IDC will typically contain chlorine concentrations that range from about 0.2 mg/L to about 4.5 mg/L.

The IDC spreadsheet requires the analyst to run 5 tests at each concentration to determine the analyst and analytical method can produce accurate and reproducible results. The total sample volume needed to run these five tests will depend on the method that the analyst will use as the reference method. For example, if the laboratory uses the DPD colorimetric method as its EPA-approved reference method, the analyst will need to prepare five 10 mL samples (which means a total sample volume of 50 to 60 mL). However, if the laboratory uses one of the titrimetric techniques as its EPA-approved reference method, the analyst may need to prepare as much as 500 to 550 mL of sample for each sample set.

If the laboratory uses the DPD colorimetric method, the analyst will usually need at least 20 to 40 mLs of primary standard if the primary standard contains between 50 and 75 mg/L of chlorine. If the primary standard

contains a lower concentration, more primary standard will be required and if it contains a higher concentration, less will be required.

Part of the IDC is to verify the chlorine concentration of the primary standard. Therefore, it is critically important that all of the primary standard used during Steps 1 through 4 of the IDC come from the same lot number.

Reagents

If everything goes well, the analysts and operators will use the EPA-approved reference method to measure the chlorine residual in at least 50 to 60 samples over the course of an entire IDC. It is critically important that all of the reagents used during Steps 1 through 5 of the IDC come from the same lot number.

Preparing Demand-Free Dilution Water

IMPORTANT

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

The analyst will be using large volumes of dilution water to prepare the prepare the standards and samples required during Steps 1 through 4 of the IDC.

While it is theoretically possible that the dilution water might contain a little chlorine, it is far more likely that the dilution water will contain materials that exert a chlorine demand. In order to minimize the chlorine demand of the dilution water, the operators should use commercially-prepared, organic-free water or, if that is not available, a high-quality deionized (DI) or distilled water.

It should be noted that each container of DI or distilled water may have a different chlorine demand, even if the water was produced by the same equipment. If this water is used for dilution, it might be beneficial to use a single, large container of water to complete the whole IDC procedure. If this is not possible, the analyst may want to consider mixing the containers before beginning the IDC. Even if the analyst uses commercially-prepared, organic-free water, it might be beneficial to make sure that each bottle has the same lot number. Both of these precautions will help the analysts ensure that the quality of the dilution water used during the IDC remains as consistent as possible.

It should also be noted that the analysts may need to make several gallons of chlorine-demand free water if the plant chooses not to purchase commercially-available organic-free water and is unable to locate a high-quality source of DI or distilled water. Procedures for the preparing the

chlorine demand-free water are included in ASTM-D 1253-06 and Standard Method 4500-Cl C. Although preparing chlorine-demand free water is a relatively simple process, it takes at least two days to complete. Therefore, if analysts want to make their own chlorine-demand free water, they need to complete the process before the DAM7 training event occurs.

The IDC workbook

The staff assigned to the TCEQ's TOP created the Method 334 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. The IDC spreadsheet is a Microsoft Excel workbook that contains the following three worksheets.

- The **Instructions** worksheet — contains a set of step-by-step data entry instructions and some additional information about how to use the spreadsheet,
- The **IDC Data** worksheet — provides space to record all of the essential information about the system, the analytical methods, reagents, standards, and test results.
- The **IDC Data (Example)** worksheet — 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.

The TCEQ's file did not contain any macros or viruses when it was created. However, the plant staff should scan the file for viruses before they open it. This precaution will make sure the file they uploaded to the plant computer has not been altered since it was originally obtained from the TCEQ.

Even though the file contains no macros, it does automate many of the calculations the operators must perform. It is password-protected to minimize that chance that a user will accidentally change one of the calculation formulas. However, the TCEQ did not password-protect any the data entry cells (the areas where analysts and operators might need to enter data). These unprotected cells are all located on the **IDC Data** worksheet and have a green color to help the users identify them. If you have any problems using the IDC spreadsheet, contact one of the TOP staff at (512) 239-4691 for help.

The spreadsheet tool is a required and integral part of the TCEQ's IDC approval process. Using this tool can help operators eliminate the guesswork on calculations and QC checks and facilitates the TCEQ review process.

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.

Notes

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Chapter 3. Step-By-Step Instructions for Completing the IDC

Before you begin the special study, you need to make sure you have all the equipment and reagents you will need to conduct Steps 1 through 4 of the IDC. These materials include:

- The laboratory (benchtop) instrument will be using to measure the chlorine residual in the samples you prepare;
- Any pipettes, pipette tips, sample cells, graduated cylinders, flasks, and beakers;
- The primary standards you will use to make the test samples;
- The dilution water you will use during the test;
- All of the reagents that you will use; and
- A computer and a copy of the **IDC Spreadsheet** file so you can enter the results of each test.

It might also be useful to have a printed copy of this chapter from the DAM7 Course Manual.

System-specific spreadsheet information

Open the **IDC Spreadsheet** workbook, select the **IDC Data** worksheet, and enter the following information about your water system and the equipment and reagents you will be using to conduct the IDC.

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 you will enter this information in other locations.

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 using a chlorine solution with a known concentration (the primary standard, or stock solution) to prepare a working standard (or dosing solution). This working standard will be used to create the test solutions you will use during Step 2 to determine the chlorine demand of the dilution water. The working standard may be undiluted aliquots of the primary standard or a diluted solution (a secondary standard) you prepare using your primary standard. Generally, you will need to prepare a diluted working standard unless you:

- have a micropipette that can accurately measure volumes of 50 microliters (µL), which is 0.05 mL, or less, or
- you are preparing 50 mL (or more) of test solution.

You will need to have enough working standard to make 100 to 200 mL of the test solution. If you think your dilution water has very little chlorine demand, the TCEQ recommends that chlorine concentration in test solution

be somewhere between 0.08 and 0.16 mg/L. However, if you think that your dilution water might have a higher chlorine demand, you might want to set an initial target concentration between 0.15 and 0.30 mg/L.

The concentration of a primary chlorine standard used for the IDC generally ranges from 25 mg/L up to 75 mg/L. However, the actual concentration varies from lot to lot. You need to know the actual concentration of the standard that you buy for the IDC special study. Manufacturer's typically put the lot number and its concentration of the primary standard on package (or box) rather than labelling the individual vials or ampoules it contains.

You can use the following equation to determine how much primary standard you will need to prepare your batch of test solution.

$$\text{Amount (Volume) of primary standard required} = \frac{\text{Desired concentration of test solution} \times \text{Total volume of test solution being prepared}}{\text{Concentration of the primary standard being used}} \quad \text{(Eqn 1)}$$

Where: Total volume = volume of dilution water + volume of primary standard

If your pipette can accurately measure the amount of primary standard required, you can use the primary standard as the working standard. If not, you will need to prepare a diluted working standard or make a larger batch of test solution.

It's important to notice that the total volume of the test solution depends on the amount of primary standard you add to the dilution water. Consequently, you won't really know the actual concentration of the test solution until after you use Equation 1 (Eqn 1) to determine how much standard is required. To determine the actual concentration of your test solution, you can use the following equation.

$$\text{Actual concentration of test solution} = \frac{\text{Volume of primary standard used} \times \text{Concentration of Primary Standard}}{\text{Volume of primary standard used} + \text{Volume of dilution water used}} \quad \text{(Eqn 2)}$$

It is also important to be aware that both Eqn 1 and Eqn 2 assume that:

- the stock standard has the exact concentration reported by the manufacturer,
- none of the chlorine in the stock standard volatized when the ampoule was opened and the standard was pipetted,
- the pipettes work perfectly so the amount of dilution water and standard you added was exactly what you reported it was, and
- the dilution water has absolutely no chlorine demand (unless the actual Step 2 test results show that it does).

The following examples illustrates how to use the two equations to determine how much primary standard an analyst will need to create the test solutions and whether or not the analyst can use undiluted primary standard as the working standard.

Example 1

1. Data
   a) desired (target) concentration of test solution = 0.20 mg/L
   b) desired volume of test solution (amount of dilution water used) = 100 mL
   c) concentration of primary standard = 62.8 mg/L
   d) pipette: 1 mL TenSette pipette with 0.1 mL increments
2. Calculations
   a) Required Volume of Primary Standard

$$\frac{0.20 \text{ mg/L} \times 100 \text{ mL}}{62.8 \text{ mg/L}} = 0.318 \text{ ml}$$

   b) Actual volume of primary standard required = 0.30 mL of primary standard (because the pipette can accurately measure in 0.1 mL increments)
   c) Actual Total Volume = 100 mL of dilution water + 0.3 mL of standard
      = 100.3 mL
   d) Actual concentration of test solution

$$\frac{0.30 \text{ mL (of standard)} \times 62.8 \text{ mg/L}}{100.3 \text{ mL (total volume of solution)}} = 0.188 \text{ mg/L}$$

3. Conclusions
   a) The analyst can use undiluted primary standard to make the test solution because the pipette can accurately pipette the amount of primary standard required.
   b) If a 0.188 mg/L test solution concentration is not acceptable alternative to the 0.20 mg/L test solution target, the analyst can reduce the amount of dilution water by 0.3 to compensate for the 0.3 mL of standard being added.

Example 2

1. Data
    a) desired (target) concentration of test solution = 0.20 mg/L
    b) desired volume of test solution (amount of dilution water used) = 10 mL
    c) concentration of primary standard = 62.8 mg/L
    d) pipette: 1 mL TenSette pipette with 0.1 mL increments
2. Calculations
    a) Required Volume of Primary Standard

$$\frac{0.20 \text{ mg/L} \times 10 \text{ mL}}{62.8 \text{ mg/L}} = 0.0318 \text{ ml}$$

    b) Actual volume of primary standard required = 0.10 mL of primary standard (because the pipette can only accurately measure in 0.1 mL increments)
    c) Actual Total Volume = 10 mL of dilution water + 0.1 mL of standard
    = 10.1 mL
    d) Actual concentration of test solution

$$\frac{0.10 \text{ mL (of standard)} \times 62.8 \text{ mg/L}}{10.1 \text{ mL (total volume of solution)}} = 0.628 \text{ mg/L}$$

3. Conclusions
    a) The analyst cannot use undiluted primary standard to make 10 mL of test solution because the pipette cannot accurately pipette the small amount of primary standard required.
    b) The analyst must either:
        i) use at least 3 times as much dilution water (because the actual concentration of the test solution is 3 times higher than desired), or
        ii) prepare a diluted working standard by adding 1 part of primary standard to 3 parts of water (e.g. 5 mL of standard and 15 mL of dilution water)

    so that 0.1 mL of working standard will produce a dose that is close to the 0.20 mg/L target.

Instructions for the Step 1 Section of the IDC Data Worksheet

Enter data in the fields below as required.

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

3. Lot No.:

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

4. Expiration Date:

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

5. Concentration:

Enter the manufacturer's reported concentration of the batch of primary 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 primary standard used to prepare the working standard. If the primary 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 primary standard. If the primary standard was not diluted, enter 0.

8. Assumed Working Standard Solution Concentration:

This is a calculated value based on the data you previously entered.

IDC Step 2

IMPORTANT

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

During Step 2 of the IDC, the analyst(s) accomplish two goals:

1. They determine if the analytical method detects an apparent chlorine residual even when the reagents are mixed with a sample of water that contains no chlorine. This result is referred to as a "false positive" and can occur:
    a. if the dilution water contains any compound that reacts with the reagents, or
    b. if the reagents produce an apparent chlorine residual even when they are mixed with a "contaminant-free" dilution water.
2. They determine if the dilution water contains any compounds that exert a chlorine demand when chlorine is added to the water.

This part of the special study is particularly important because the data obtained during Step 2 are used to correct for the impact of false positives and chlorine demand when primary standards are diluted and test samples are prepared for analysis. Basically, the **IDC Data** worksheet automatically adjusts the results you expect to obtain during Steps 3 and 4 of IDC special study based on the Step 2 results. For example, if the reagents produce a 0.15 mg/L false positive reading and you create a test sample that contains 0.2 mg/L of chlorine, you should expect to get a chlorine reading of 0.35 when the sample is tested (i.e., 0.15 + 0.20 = 0.35). Similarly, you should anticipate that the actual test result will be less than expected if the chlorine demand of the dilution water consumes some of the chlorine dose you apply.

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 "Dilution Water (Reagent Blank). The spreadsheet uses the data you enter on this row to determine the "apparent" residual present in a reagent blank (i.e., a sample that contains only dilution water and reagents but no working standard).

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. Reagent Blank Residual:

This is a calculated value that represents the "apparent" residual detected in the reagent blank. This value is based on the average of five readings you obtain when testing "reagent blank" samples. You may not enter data in these cells.

4. Assumed Chlorine Demand of the Dilution Water:

This is also a calculated value. 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. Volume of Dilution Water Used:

Enter the total amount of dilution water you are using to create your sample(s). In order to accurately determine the chlorine demand of the water, the analyst needs to test at least five samples. If you are using the DPD colorimetric method as your EPA-approved reference method, each sample will contain 10 mL of dosed dilution water. Therefore, you will need at least 50 mL of dilution water for each batch

of 5 samples you test. There are two ways to produce the 50 mL sample volume that you need to analyze and each has its advantages and disadvantages.

a. Method 1: Dose a 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 dosing a relatively large volume of water, you might be able to use your primary standard as your working standard/dosing solution.
        3. 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 you are measuring total chlorine, 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 sample in the sample set. This is less of an issue if you are using free chlorine reagents because you do not have to wait 3 minutes before taking the free chlorine reading. It is also less of an issue if the reagent is added to all five sample vials at the same time since the incubation periods run simultaneously instead of sequentially.
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 dosing small sample volumes, you may need to use a secondary standard as your working standard/dosing solution (i.e., dilute your primary standard and use the dilute solution to dose the five individual samples).
    2. Since you are using small volumes of water and working standard, 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 dose with your working standard. In these two examples, you would enter 60 mL if you are using Method 1 and 10 mL if you are using Method 2.

Note: You can use either of these methods to prepare your test samples regardless of which EPA-approved method you are using as your reference method. Examples 1 and 2, which are shown on pages 28 and 29, can help you decide which of the two methods you might want to consider using.

6. Volume of Working Standard Used:

Enter the amount of working standard you add to the dilution water.

The objective of Step 2 is to determine how much demand exists in the dilution water. Try to avoid using an "Applied Dose" that is significantly greater than the demand because it can change the value of the results you obtain. If you are pretty sure you are using a "demand free" dilution water, the TCEQ recommends that you use enough standard to produce an "Applied Dose" between 0.08 and 0.16 mg/L when you run the initial test. 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.

If the amount of working standard you are considering doesn't produce your target dose, adjust the amount of dilution water in the calibration standard (in 5 mL or larger increments) or the amount of working standard (in 0.1 mL or smaller increments) until you are within your target range. The minimum adjustment to the working standard volume will be based on the smallest change you can accurately measure with the pipette you are using to apply the standard.

7. Applied Concentration, Calculated:

This is a calculated value. You can use the spreadsheet to evaluate different combinations of dilution water and standard; just enter the proposed volume of each and see if it gives you the result you want. If it does not, make the adjustments described in items 5 and 6 above.

8. Expected Result:

This is a calculated value based on the calibration standard volume, the amount of working standard solution used, and the apparent residual detected in your reagent blank. It assumes the following:

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

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

c. The amount (volume) of working standard that you used 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 test 5 samples, 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.

This calculation is not necessary when evaluating the reagent blank samples (because, hopefully, a detectable residual will not be detected in the reagent blanks.) However, the value is calculated each time you run a test to determine the chlorine demand of the dilution water.

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 analyst 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. Once again, this calculation is not required for the dilution water.

If the actual average of the five "chlorine demand" samples 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. 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.

14. Chlorine Demand of Dilution Water:

This is a calculated value. If the analysts repeated the chlorine demand test, the value is based on the highest of the measured chlorine demands. This is the chlorine demand value used for the calculations in Steps 3 and 4.

15. Reagent Blank, Apparent Residual:

This is a calculated value and is based on the Dilution Water (Reagent Blank) results described in item 3 on page 32. TCEQ copied the result here just to make it easier for the analyst to find the data.

16. Actual Working Standard Concentration:

This is a calculated value. It is based on the Assumed Working Standard Concentration that was calculated in Step 1 and the results of the Step 2 tests.

Although this value is not used in the Step 3 and Step 4 calculations, it may give the analysts a general idea about what impact the chlorine demand of the dilution water when they complete Step 3.

IDC Step 3

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.

Step 3 of the IDC special study is essentially identical to Step 1 of the IDC because it involves preparing a working standard that will be used during Step 4 of the IDC. The primary difference between Steps 1 and 3 is that the working standard the analysts prepare in Step 3 will probably have a higher chlorine concentration than the one they prepared in Step 1.

The higher concentration is needed because, during Step 4, the analysts will be verifying the accuracy of the benchtop (reference) method over the full range of the concentrations that the operators will expect to see when they validate the performance of the on-line instrument. The chlorine doses needed to validate the upper end of this operational range are much higher than the one needed to measure the chlorine demand of the dilution water.

Still, we are not repeating the information presented during the discussion of Step 1 because the processes and principles for Steps 1 and 3 are so similar. Please refer to the Step 1 discussion which begins on page 26 and ends with Example 2 on page 29.

Instructions for the Step 3 Section of the IDC Data Worksheet

Since the data entry fields in this section of the worksheet are identical to those in Step 1, the instructions are not repeated. Please refer to the instructions and guidance for entering data for Step 1 section if you need help with understanding what you should enter in the Step 3 section. These instructions begin on page 30.

IDC Step 4

Step 4 of the IDC special study involves using an EPA–approved manual benchtop analytical method (the reference method) to measure the chlorine

concentration in a series of standardized samples that have been dosed with increasing amounts of working standard.

This part of the IDC study is where the accuracy of the benchtop (reference) method is evaluated over the entire range of values that the on-line instrument is likely to encounter. The range of concentrations that need to be evaluated should be consistent with the anticipated alarm settings that will be programmed into the on-line monitor or SCADA system. For example, if the operators will set the low-level alarm at 1.0 mg/L, the lower limit value should be no greater than 1.0 mg/L (since the operators should be notified of an operational problem before it reaches a critical level).

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 be conducting Step 4 of the IDC.

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 the system is installing a single monitor, the data will be based on the information for that single installation site. However, if the system is installing multiple monitors, the data 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 (LL):

Enter the lowest residual that you expect to ever detect at **any** of the sites 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. However, it may be different at your plant or these particular monitoring sites if you never expect the residual to drop this low.

4. Low Alarm (LA):

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 greater than or equal to the Lower Limit and lower than or equal to the High Alarm. 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. However, it may be different at your plant or these particular monitoring sites.

5. High Alarm (HA):

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 greater than or equal to than the Low Alarm and lower than or equal to the Upper Limit.

At many plants, this value is somewhere between 2.5 and 4.0 mg/L regardless of whether your system uses free chlorine or chloramines. However, it may be different at your plant or these particular monitoring sites.

6. Upper Limit (UL):

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 greater than or equal to 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 for up to six different sample concentrations. 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" (Mid) 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. Volume of Dilution Water Used:

Enter the total amount of dilution water you are using to create your performance verification (calibration) sample(s). As we discussed in Step 2, the volume of dilution water you need to use for each sample set depends on the analytical method the lab uses and you will need to prepare 5 samples for each sample set. However, regardless of the reference method you are using, there are two ways to prepare the samples you need to complete Step 4. The first way is to prepare enough test solution to run all 5 of the required tests and the other is to prepare 5 separate samples.

The primary difference between the Step 2 samples and the Step 4 samples is the concentrations of the test solutions. To save space, the information about the two sample prep methods is not repeated here. If you need some help deciding which of the two approaches you want to use, look back at the Step 2–item 5, which begins on page 32.

9. Volume of 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 Dose, Calculated:

This is a calculated value that is based on the volume and chlorine demand of dilution water used to create your calibration/verification sample, 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.

12. Actual Results:

There are spaces for you to record the results of each of the five samples 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, in most cases, 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.

To contact the TCEQ staff members that are reviewing EPA Method 334.0 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. (Note that this must be the same model used in Steps 2 and 4.) 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)

Note that this must be the same method used in Steps 2 and 4.

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. If they are not, you should consider repeating Step 4 so that you can verify that the reference method will accurately measure the enter range of values that you expect the on-line instrument to measure. The TCEQ may reject the results of the special study if you are trying to use a reference method that has not been validated over the entire range of concentrations the instrument is expected to encounter during Step 5.

a. Upper Limit:

Enter the highest residual that you expect to see at the site where the on-line monitor is 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 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 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 installed.

This value must be higher than the Minimum Residual 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. Minimum Residual:

Enter the lowest residual that you expect to see at the site where the on-line monitor is 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 same 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 0.1 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 0.1 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.

Step 5 Data: Analysis of Results

The three questions in this portion of the 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 spreadsheet will record “Yes” if the on-line reading was within 10% (or 0.1 mg/L, whichever is greater) of the value recorded by the SCADA system or data recorder. Otherwise, it will record “No” for that day. Please note that the spreadsheet may record a “Yes” value in both columns if the operating range was relatively narrow that day (i.e, the minimum and maximum readings that were recorded were pretty close to each other.)

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 exactly when you are collecting your grab sample. 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" at least 3 times during the study, 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 of the **IDC Data** worksheet and submit it to the TCEQ (or send them a copy of the whole spreadsheet).

Notes

Chapter 4. Lab Forms

After the plant successfully completes Step 5 of the IDC special study, the operators or lab analyst will need to update the plant's Drinking Water Lab Approval Form (TCEQ-10450). If the plant uses chloramines, they may also need to update the water system's List of Analytical Methods (LAM) form that is part of the system's Nitrification Action Plan (NAP). Both forms should be attached to a PWS's Monitoring Plan for review by TCEQ staff during periodic inspections. You can find more information about the required Drinking Water Monitoring Plan at:

www.tceq.texas.gov/drinkingwater/monitoring_plans

and you can find more information about the required NAP at:

https://www.tceq.texas.gov/drinkingwater/disinfection/nitrification.html

Downloading the Lab Approval Form

The DWLAF is an interactive Adobe Acrobat (.pdf) document that allows you to fill out the form on your computer . . . even if you only have the Adobe Reader. The DWLAF can be downloaded from the TCEQ website and, after you fill it out, you can save a copy of the completed form on your computer. You can find instructions for downloading the form in Appendix D.

The LAM form is one of the Microsoft Excel® worksheets that is part of the Nitrification Action Plan (NAP) template that the TCEQ developed to help a water system detect and control nitrification. You can download a copy of the NAP template from the TCEQ website or call the TCEQ's Water Supply Division at 512-239-4691 and request a copy.

As the plant staff updates the DWLAF and LAM, they need to be aware of a couple of things.

1) The forms only provide space to enter one laboratory method for each analyte. Consequently, the individual that updates the information will probably need to use fill out two forms; one for the benchtop methods and a separate one for the on-line instruments. When you save the two forms, each one needs to saved with a different name.
2) The completed forms only need to include the analytical methods and instruments that are used to report data to the TCEQ.

Entering Data on the Drinking Water Laboratory Approval Form

The DWLAF file includes notes and instructions that will help you fill out the form. Those notes and instructions are relatively complete and easy to understand. However, they are not provided for every piece of information you need to enter. Consequently, we are providing some supplemental guidance here. However, if you have any questions or need some help completing the DWLAF, you can call the TCEQ's Water Supply Division at (512) 239-4691 and ask to speak with the Laboratory Approval Coordinator.

Some of the information you enter on the DWLAF needs to be typed in and some of it is entered by selecting one of the answers provided in a drop-down box.

Lab and Contact Information

Figure 4-1 shows the portion of the DWLAF where the operator or analysts enters information about the plant lab and the contact information for the individual that completes the form. This section is located at the very top of the form.

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	☐ Yes
Zip		other Public Water Systems?	☐ No

Figure 4-1: Lab Approval Form – Laboratory and contact information

Laboratory or Plant Name

Enter the name of the laboratory that the DWLAF is describing. If the lab doesn't have a unique name, enter the name of the water treatment plant or public water system that operates the lab.

PWS ID

If the lab is owned or operated by a public water system, enter the 7-digit identification number that the TCEQ has assigned to that system. Otherwise, leave this space blank or enter "**Not Applicable**".

Lab ID No.

If the TCEQ has assigned the laboratory a unique lab identification number, enter that information on the form. If the lab is located at a surface water treatment plant, enter the unique ID number (UID) that the TCEQ has assigned to that plant. If the lab does not have a lab ID and the plant where

it is located does not have a UID, leave this space blank or enter "**Not Applicable**".

Address, City, State, and Zip Code

Enter the laboratory's mailing address.

Contact Name, E-mail, and Phone Number

Enter the contact information on the individual that can answer any questions that TCEQ might have when they review the completed form. Usually, this is the information about the person that has filled out and signed the completed form.

Date the form was completed

Enter the date that the individual who completed the form printed and signed it.

Does this lab perform analyses for other Public Water Systems?

If this lab runs tests for other water systems, click on the **Yes** box. Otherwise, click on the **No** box.

Analytes and Methods Information

Figure 4-2 shows the section of the form that information about the analytical methods, instruments, calibration, and accreditation. It is located immediately following the plant and contact information section. Although the section includes many of the analytes

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			±	NTU				
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				

Figure 4-2: Lab Approval Form – Analytes and Methods

Analyte

The analytes that are covered by the DWLAF are listed in the left side of the table. Note that the list only does not include monochloramine, free ammonia, or other tests that must be conducted at plants that use chloramines as a disinfectant. Consequently, the operator or analysts at these systems will also need to complete a LAM form to describe the laboratory methods that are used to meet mandatory Nitrification Action Plan (NAP) requirements.

Analytical Method

Select the analytical method that you use for each analyte listed from the drop-down box that TCEQ has provided. If the laboratory does not run one of the tests, select **Not Required** from the drop-down list for that test. If your plant sends some of your samples to another lab for analysis, select **Contract Lab** from the drop-down list for that test.

To open the drop-down box, click on the down arrow on the right side of the space where you want to enter the data. Once you see the drop-down list, use the cursor to highlight and then select the appropriate analytical method. If you don't see the method that the instrument uses for that specific analysis, you may need to scroll down a little to reveal the rest of the options.

Figure 5-3 illustrates how to select EPA Method 334 for the analytical method used to measure free chlorine. The red circle identifies the drop-down box arrow and the green oval identifies the scroll bar for additional methods.

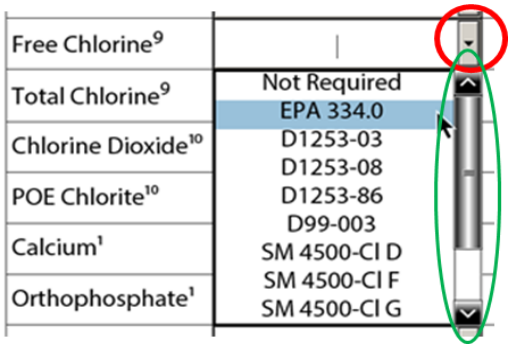


Figure 4-3: Drop-down list for Free Chlorine methods

Instrument Name

Enter the brand name and model number of the instrument used to run the test. If the method involves manual titration using a burette, enter **burette** in the space. Leave the instrument name space blank if the lab does not run that test.

Accuracy

Enter minimum change in concentration that can be displayed by the instrument or measured by the smallest measurable change in the amount of titrant used.

Calibration Frequency

Enter how often the laboratory verifies the accuracy of the analytical method and instrument. Some typical responses are: weekly, monthly, quarterly, every 7 days, every 30 days, and every 90 days.

Calibration Method

Record the method that the laboratory uses to verify the accuracy of the analytical method and instrument. Some typical responses are: primary standards, secondary standards, and proprietary device. The accuracy of some continuous on-line analyzers can be verified by comparing the results of the on-line instrument with those from an EPA-approved benchtop method; if this is the case for your instrument, enter **Comparison**.

NELAP Accredited? and PT Study

As the DWLAF form indicates, certain tests can only be run at a lab that has been accredited (approved) through the National Environmental Laboratory Accreditation Program (NELAP). The information you need to answer these questions are contained in the DWLAF and are not repeated in this course manual.

Notes

Chapter 5. Action Plan, Questionnaire, and Course Wrap-up

The final part of the training involves developing an Action Plan and completing a Participant Questionnaire. An effective Action Plan will help ensure that the plant staff complete the remaining steps needed to get the new on-line instrument approved and make sure that it continues to produce reliable data. The goal of completing the Participant Questionnaire is to provide feedback that will help the TCEQ and trainers identify any weakness in the training materials and make appropriate improvements.

Recommended IDC Action Plan

Because it takes at least a couple of weeks to collect all the data needed to complete Step 5 of the IDC, it is impossible to complete the special study during a one-day training event. Also, the plant staff will need to assemble and submit the IDC data and DWLAF once all the information has been compiled. To help make sure that all of the tasks get done in a timely manner, the TCEQ developed a Recommended Action Plan form that the instructor will help the participants complete. Once the plant staff has completed the form, which is shown in Appendix E, it will list the things that need to get done before the IDC packet is submitted to the TCEQ, identify who is responsible for completing each task, and state when the individual is expected to finish the job.

Some examples of items that are typically included in an IDC Action Plan

During the DAM7 training event, the participants will typically have enough time to complete Steps 1 – 4 for only one type of chlorine residual (i.e., either free chlorine or total chlorine) but not both. If you install on-line monitors for both types of residual, you will need to perform a second verification for the remaining type of residual. If this is the case at your plant, be sure you include this task in your action plan.

To complete IDC Step 5, the operators will need to verify the performance of each of the on-line monitors on a daily basis for at least 14 days. During this phase, an operator must compare the reading shown on the on-line instrument with the corresponding reading that has been recorded by the plant's data logger and with the results of a benchtop test on a sample that was collected at the same time the operator read the on-line meter. If the plant is manned only five days a week, TCEQ will allow three weeks of weekday samples to be performed (15 samples). Consequently, every IDC Action Plan will include this assignment and identify the individual who is

responsible for making sure the plant staff completes the task and records the data.

After the plant completes step 5 of the IDC and updates its DWLAF and LAM (if applicable), the water system must submit the materials to the TCEQ for review and approval. Consequently, every Action Plan needs to include this assignment.

While not part of the IDC, EPA method 334.0 requires an ongoing comparison of the on-line monitor, data recorder, and benchtop results at least every 7 days. Consequently, most IDC Action Plans will include one or more assignments to make sure these tasks get done on schedule, the results get recorded, and that appropriate corrective action is taken if the reading don't all match. For example, the plant may need to develop or update the log sheets the operators use to record calibration or other QA/QC data, update the workplans or duty schedules to include these tasks, and create SOPs to make sure the operators use identical procedures when verifying instrument performance.

Submitting the IDC Packet to TCEQ

As noted earlier, the water system must submit a copy of the completed IDC materials to the TCEQ for review and approval. A complete IDC packet will always include a copy of the completed IDC spreadsheet and the updated lab approval form(s). *(Please remember that the operators will need to include two copies of the DWLAF, one for the benchtop tests and one for the on-line monitors.)* Typically, it will also include a brief request for the TCEQ to approve the use of the new on-line instrument for compliance monitoring.

The packet can be submitted by using any of the methods shown under "Submitting the Form and related Documentation" on page 2 of the DWLAF.

You do not need to include copies of the Action Plan, any new or updated forms for future performance verification testing, SOPS, or other documents that were developed or updated following the IDC. If the TCEQ wants any supplemental information, they will let you know.

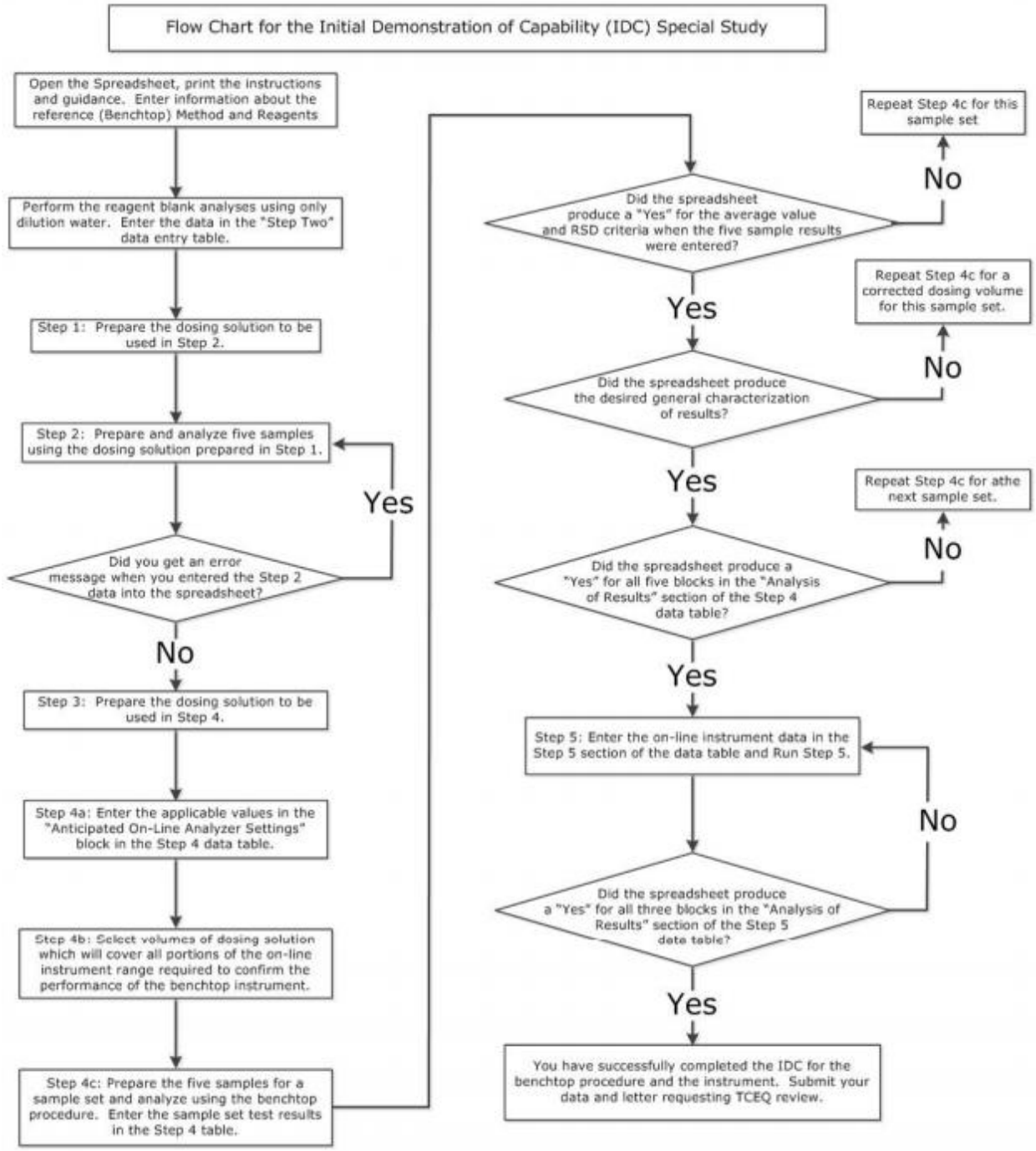
DAM7 Plant Questionnaire

One of the last things that the instructor will ask the participants to do at the end of the training is to complete a two-page DAM7 Plant Questionnaire. The TCEQ's TOP staff periodically updates its DAM training materials and any feedback you provide will help them improve the materials. When you complete the questionnaire, please be as specific as possible; the more information they get, the more improvements you will see. If you think of something later, you can call (512) 239-4691 and ask the receptionist to

speak to one of the TOP staff members. These folks are there to help you so you can also call them if you have other technical questions.

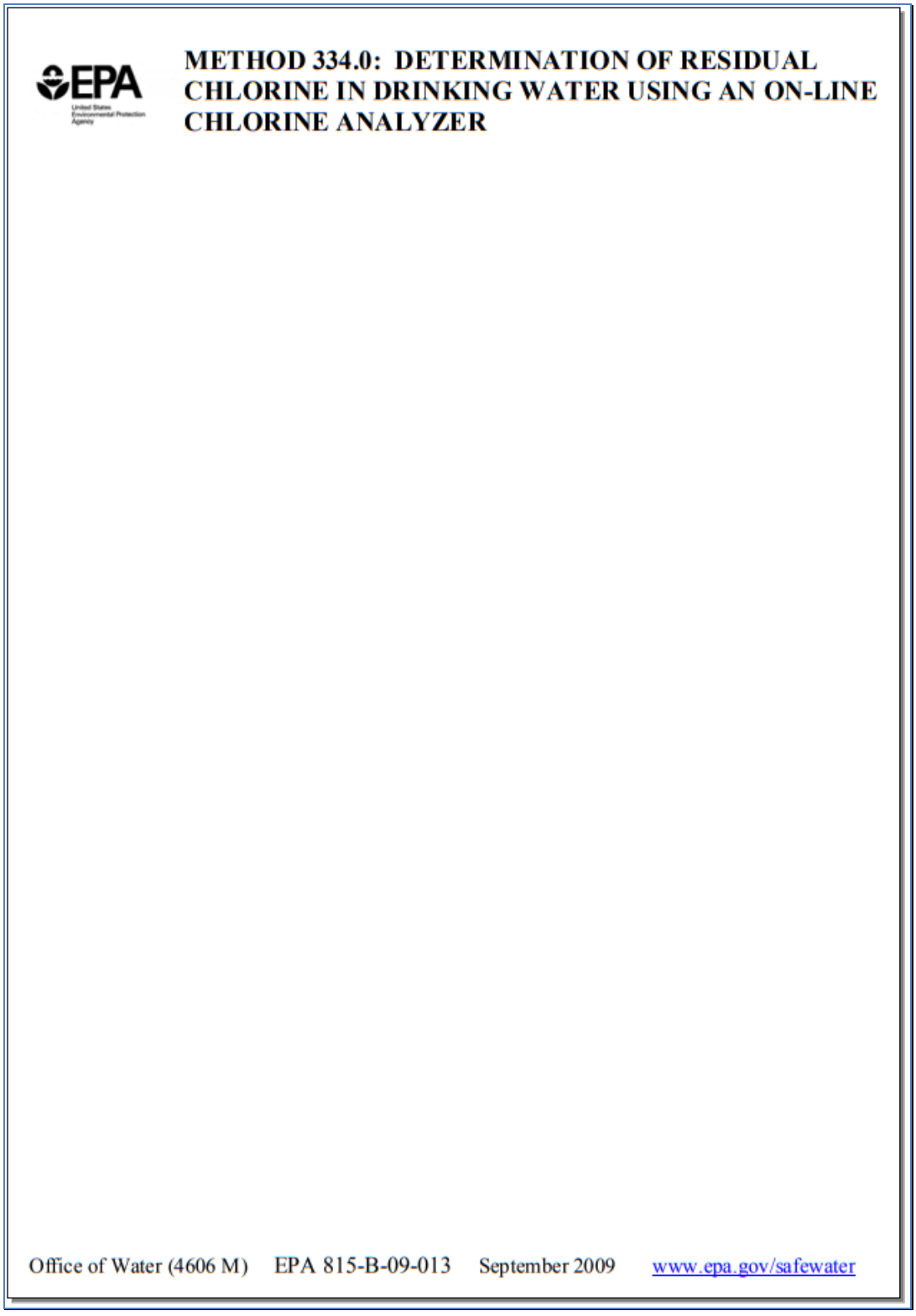
Notes

Appendix A. IDC Flow Chart



Notes

Appendix B. Adopted EPA Method 334



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

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Version 1.0

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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.

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

1. *Standard Methods for the Examination of Water and Wastewater*. 21st Edition. American Public Health Association. Washington DC. 2005.

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

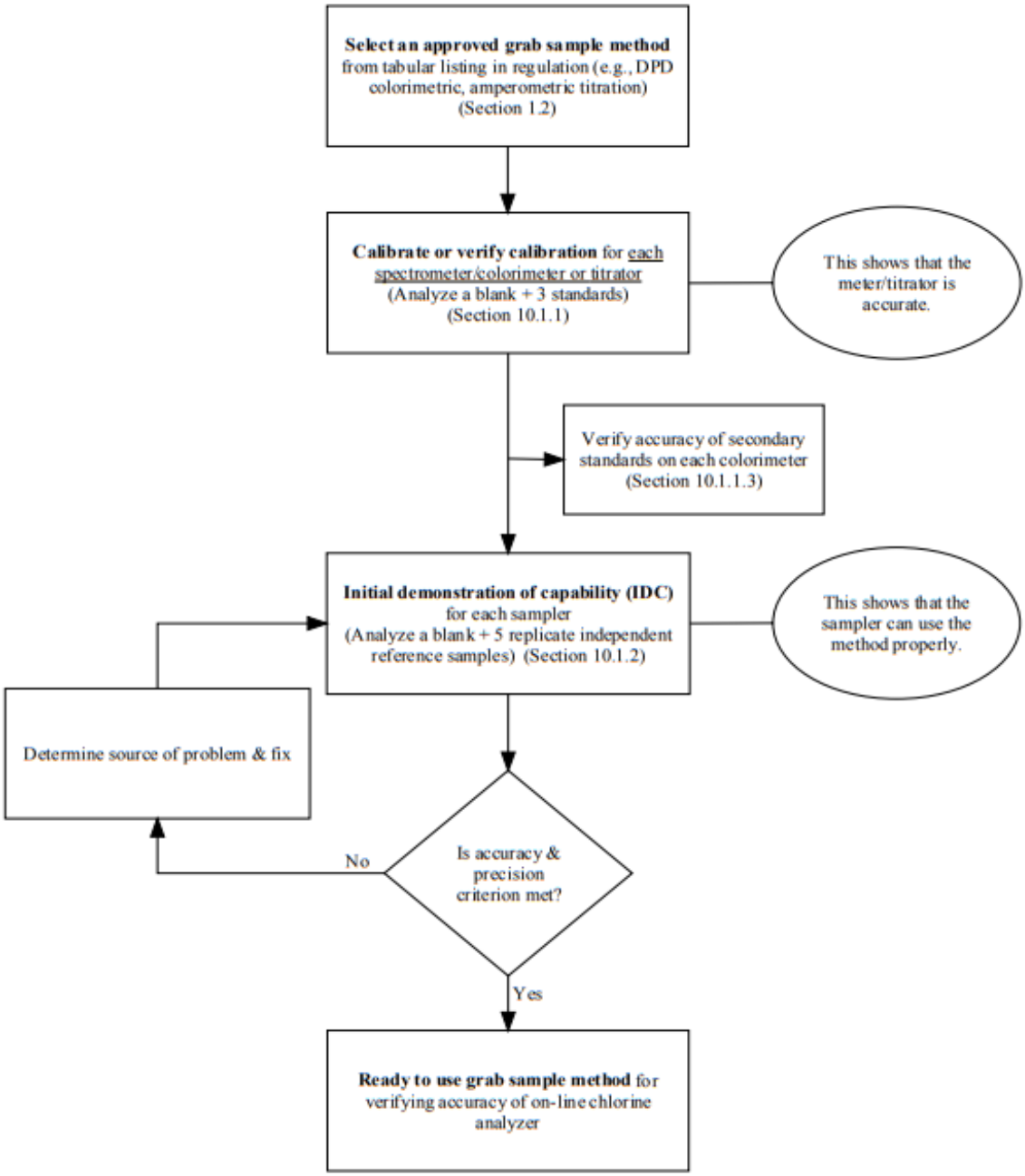
Table 3. Routine QC for Grab Sample Methodology

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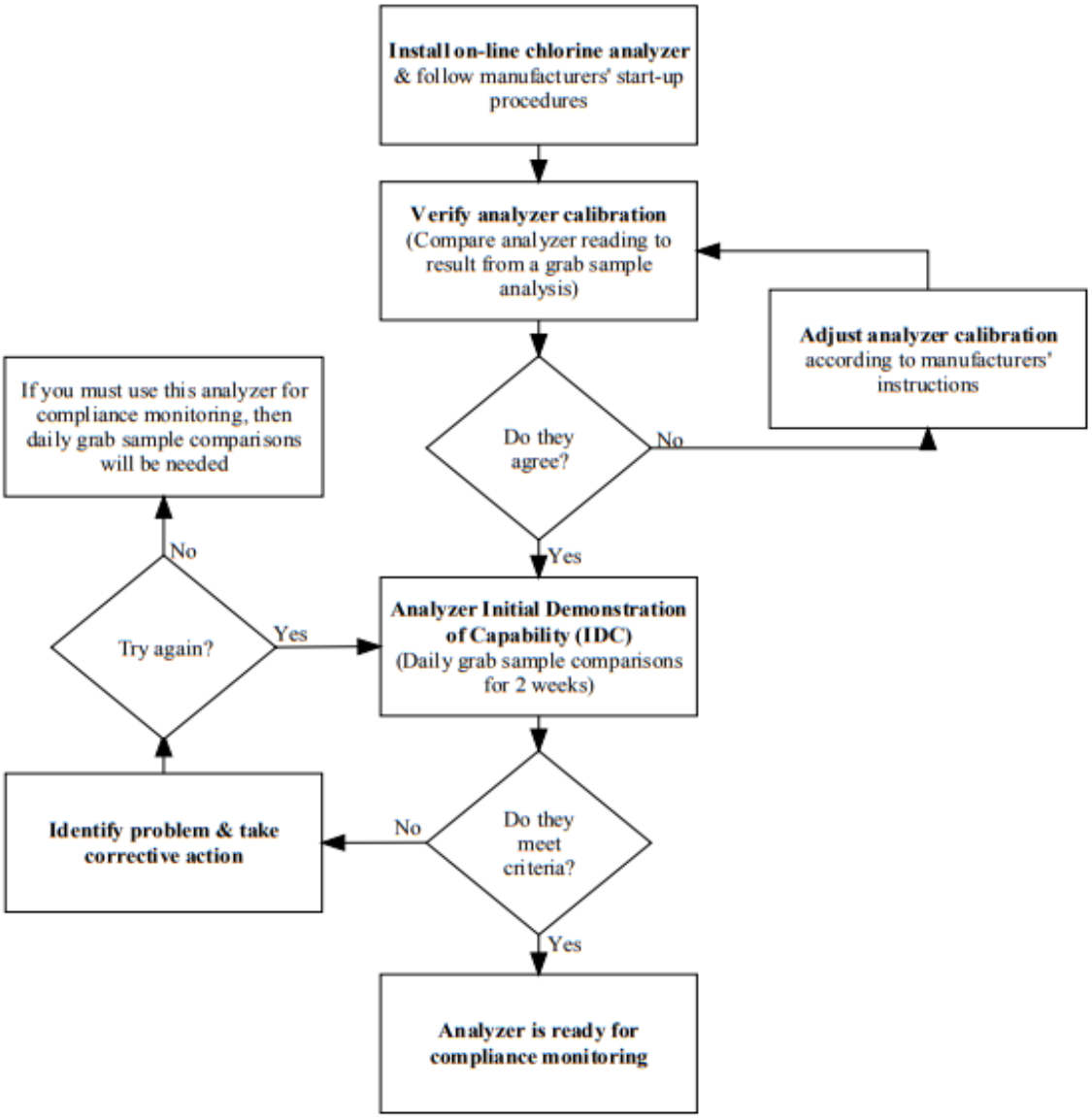
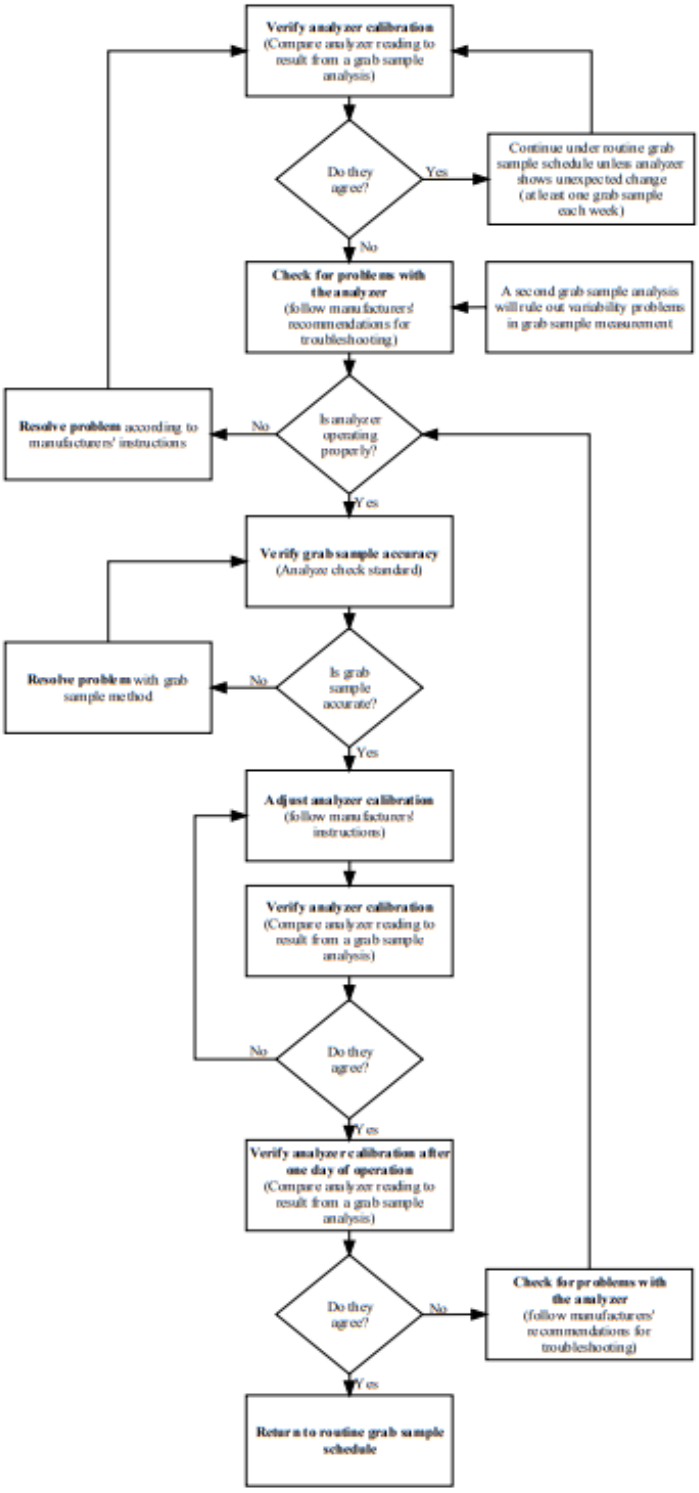
Flowchart 2. Start-up QC for On-line Chlorine Analyzer



20

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.

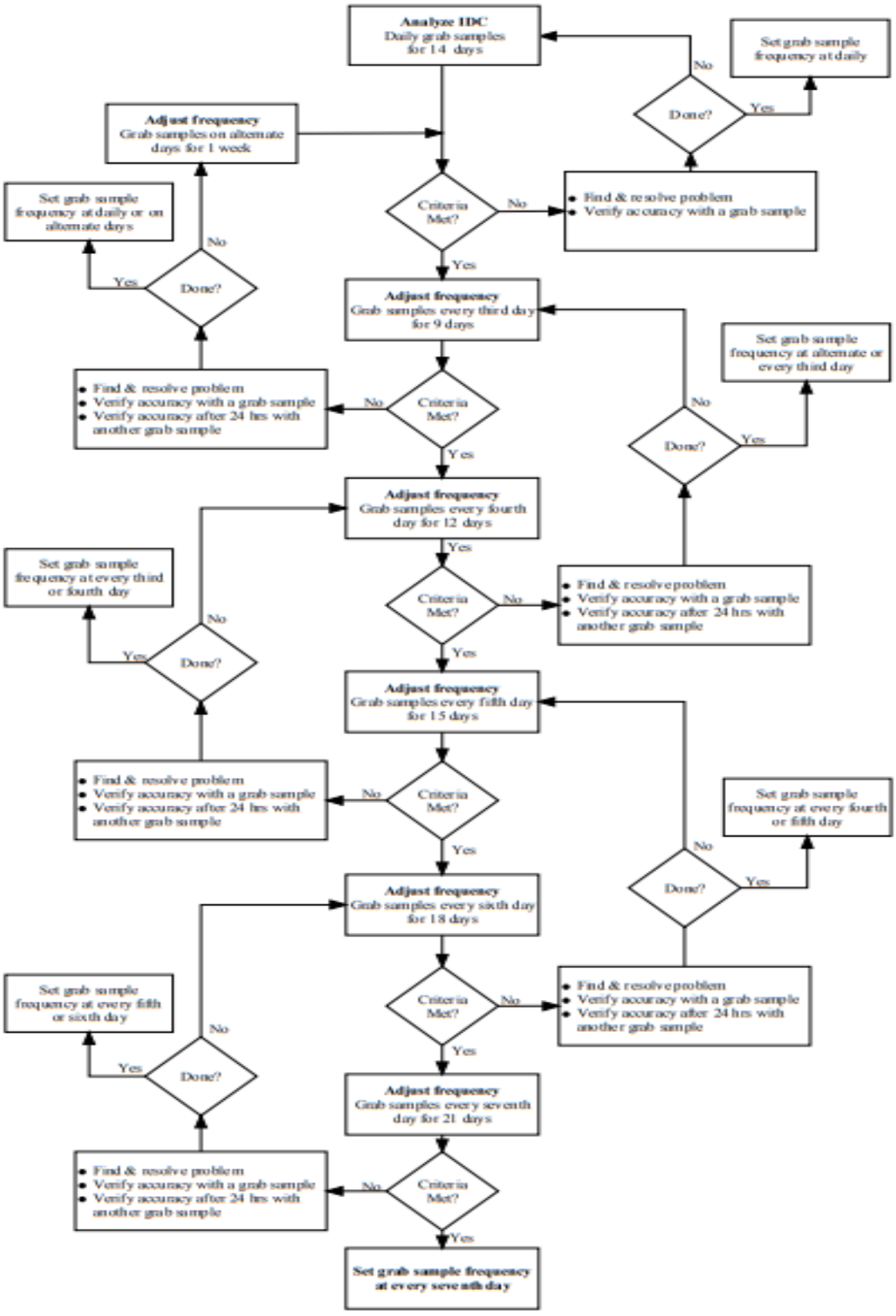
A.2 If the on-line chlorine analyzer continues to meet acceptance criteria over the above 9 day period, the grab sample interval can be extended to once every four days for 12 days.

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



Appendix C. Example IDC Worksheet

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 Test 1 (mg/L)	Test 2 (mg/L)	Test 3 (mg/L)	Test 4 (mg/L)	Test 5 (mg/L)	Average (mg/L)	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)
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.

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.

The Drinking Water Lab Approval Form (TCEQ-10450) is an interactive Adobe Acrobat (.pdf) document that allows you to fill out the form on your computer . . . even if you only have the Adobe Reader. The DWLAF can be downloaded from the TCEQ website.

As the plant staff updates the DWLAF, they need to be aware of a couple of things.

1) The form only provides space to enter one laboratory method for each analyte. Consequently, the individual that updates the information will probably need to use fill out two forms; one for the benchtop methods and a separate one for the on-line instruments. When you save the two forms, each one needs to saved with a different name.
2) The completed form only needs to include the analytical methods and instruments that are used to report data to the TCEQ.

Downloading the Lab Approval Form

To access the form, open your internet browser (e.g., Microsoft Edge, Google Chrome, Mozilla Firefox), and search for "TCEQ Forms". If you are using the Google search engine, it will open the following window.

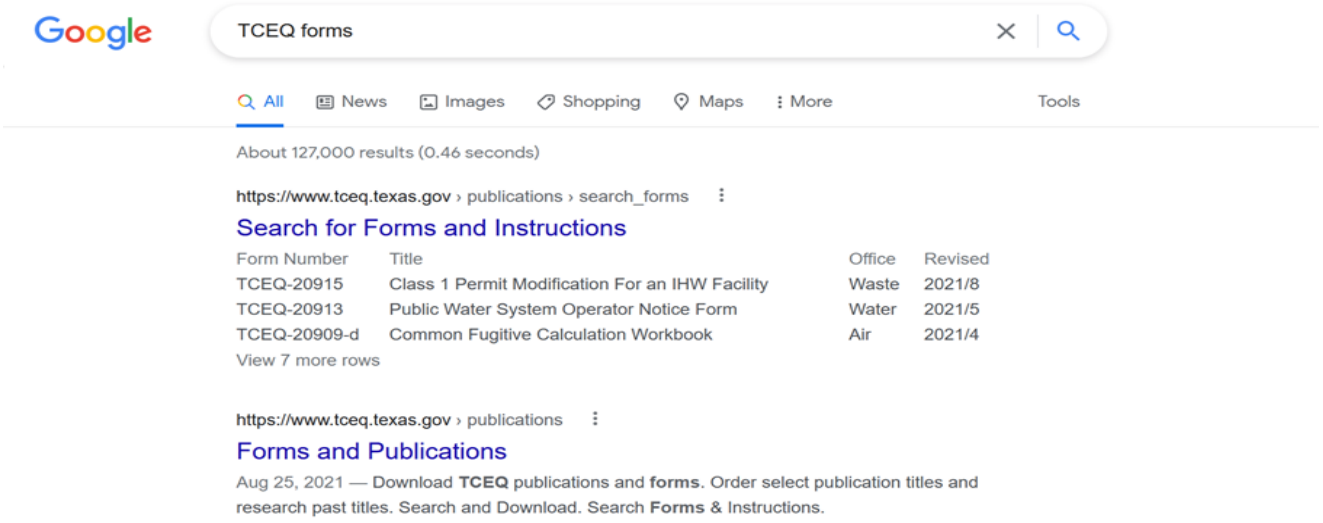


Figure 5-1: Searching for the TCEQ's Forms and Instructions webpage

Selecting the "Search for Forms and Instructions" link and entering "10450" in the "**Search:**" box will take you to the form you need to download.

Figure 5-2: Searching for the Drinking Water Lab Approval Form (TCEQ-10450)

Once you get to this window, putting your cursor on the "pdf" button and clicking the right mouse button will open a dialog box where you can select "Save Link As . . . " option.

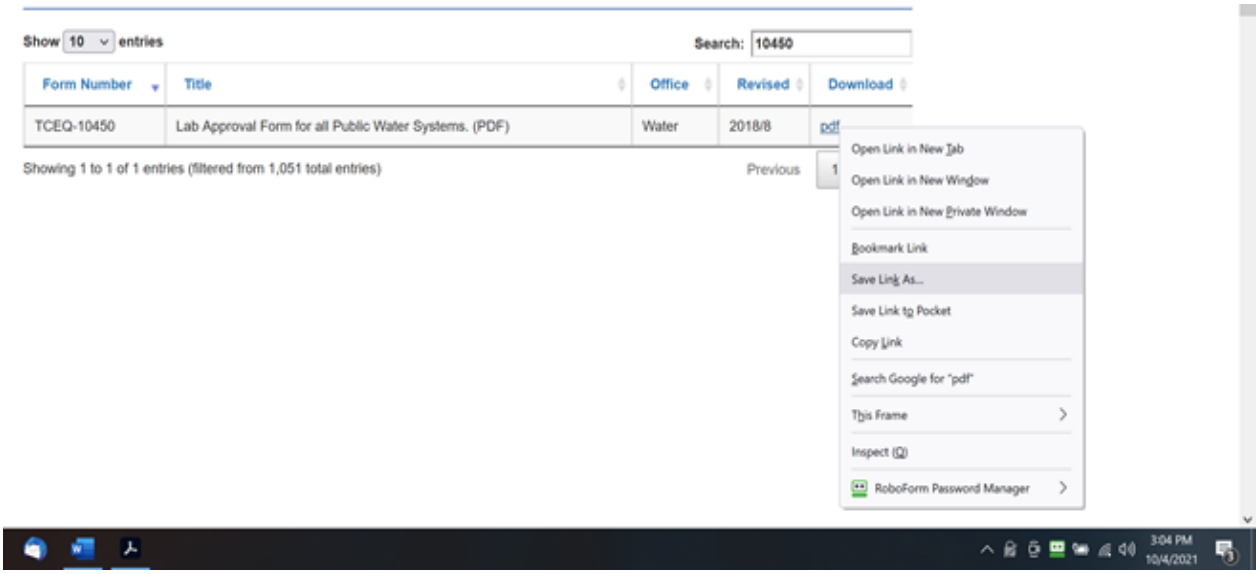


Figure 5-3: Downloading the DWLAF

Clicking "Save Link As . . . " will allow you to save a copy of the electronic form on your computer so you can use it.

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

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		

Appendix E. Recommended IDC Action Plan form

Description of Action Step	By Whom	By When

Typical Items in an IDC Action Plan

Additional benchtop verification if needed

1. Identify what type of residual needs additional benchtop verification procedures.
2. Place regent/equipment order. (any reagents or lab equipment needed to complete Steps 1 – 4 of the IDC)
3. Identify which on-line monitors need comparison with the additional benchtop residual measurements.
4. Review the historical data for sample point XXX. (to determine the range of values that we need to include when preparing the standards for Step 4)
5. Perform IDC Steps 1-4.

Daily on-line /benchtop comparisons

1. Complete the Anticipated Readings and Settings table for instrument XXX. (the min, max, and alarm settings for Step 5)
2. Perform daily benchtop analysis and record benchtop and on-line readings in IDC Step 5 spreadsheet.

Submitting IDC Packet

1. Complete the DWLAF (and LAM form, if applicable).
2. E-mail the completed lab forms and IDC spreadsheet to TCEQ (see instructions on page 60.

Ongoing weekly benchtop comparisons

1. Review the existing lab forms. (to determine if they need to be updated to include the required weekly and quarterly performance verification tests)
2. Create or update the quarterly lab verification form (used to document the results of quarterly performance verifications for the benchtop method)
3. Create or update the weekly lab verification form. (used to document the weekly performance verification results for the on-line chlorine residual analyzer)
4. Document the performance verification procedures in the plant's O&M manual or standard operating procedures.
5. Assign the performance verification tasks to one or more operators. (be specific, identify which operator is responsible for which instrument)
6. Incorporate verification duties into workplans or duty schedules.
7. Conduct performance verification tasks.

Appendix F. DAM7 – Plant Questionnaire

DAM7 – Determination of Residual Chlorine in Drinking Water Utilizing EPA Method 334.0: On-line Chlorine Analyzer Through an Initial Demonstration of Capability

(to be completed by plant staff who participated in training activities)

Training Location/Plant Name: _____

Date of Training: _____

Overall Evaluation:

① Strongly Agree ② Agree ③ No Opinion ④ Disagree ⑤ Strongly Disagree

The DAM agenda accurately described the materials and activities that were covered.	① ② ③ ④ ⑤
The technical aspects of the DAM activities were appropriate for the participants.	① ② ③ ④ ⑤
The DAM activities were reasonably timed and covered the right amount of information.	① ② ③ ④ ⑤
The participant handouts were understandable and helpful in completing DAM activities.	① ② ③ ④ ⑤
The DAM adequately covered working standard solution calculation.	① ② ③ ④ ⑤
The DAM adequately covered dilution water apparent residual.	① ② ③ ④ ⑤
The DAM adequately covered dilution water chlorine demand determination.	① ② ③ ④ ⑤
The DAM adequately covered chlorine calibration standard preparation.	① ② ③ ④ ⑤
The DAM adequately covered chlorine calibration standard benchtop verification.	① ② ③ ④ ⑤
The DAM adequately covered the data entry requirements for the IDC spreadsheet.	① ② ③ ④ ⑤
The IDC Spreadsheet is a useful tool in completing the IDC.	① ② ③ ④ ⑤
The on-site training approach enhanced the learning experience.	① ② ③ ④ ⑤
The DAM will help us complete the IDC.	① ② ③ ④ ⑤
We will complete the Recommended Action Plant that was developed during DAM7.	① ② ③ ④ ⑤
The DAM was <u>exactly</u> what we needed.	① ② ③ ④ ⑤

Specific Suggestions:

What could we change in the agenda to improve it?

(Questionnaire continues on the next page)

DAM7 – Plant Questionnaire (cont.)

DAM7 – Determination of Residual Chlorine in Drinking Water Utilizing
EPA Method 334: On-line Chlorine Analyzer Through an Initial Demonstration of Capability

Plant: _____

What did we not explain well enough for you to understand?

What areas did we spend too much time on?

What areas did we spend too little time on?

What are some other issues where you feel more training is needed?

What other comments or suggestions do you have?

Name (optional):_____

Inside back cover

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.
Revision	November 14, 2023	Add items to the agenda and reorganize the document

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