7. ANALYTICAL METHODS

Introduction

To ensure that the water you produce is safe for drinking, your plant must be able to accurately measure several important performance parameters. The parameters include:

- the flow rate of the raw and treated water
- the turbidity level of the raw, settled, IFE, and CFE waters
- the total organic carbon level of the raw and CFE waters
- the temperature in each disinfection zone
- the pH in each disinfection zone
- the disinfectant residual at the end of each disinfection zone
- the disinfectant residual leaving the plant
- the disinfectant residual in the distribution system

If you are using innovative treatment like membranes or ultraviolet light disinfection, you may be required to analyze additional parameters.

Because performance monitoring is so important to public health protection, we require you to develop a monitoring plan for your plant and its distribution system. We also require that you submit a copy of this plan for our review and approval, and send us a copy of any revisions that you make to the plan. Since every public water system in Texas is required to develop this plan, we have published a separate guidance document entitled *How to Develop a Monitoring Plan for a Public Water System* (TCEQ publication RG-384). Please call 512-239-4691 or e-mail <PWSCHEM@tceq.gov> to obtain copies of this and other TCEQ publications.

All testing to meet our minimum monitoring and reporting requirements must be performed at a laboratory that we approve. In order to get your laboratory approved, you must use one of our approved methods to run each test, your equipment must be properly calibrated and maintained, and you must use proper laboratory techniques and maintain acceptable records.

7.1 ACCEPTABLE ANALYTICAL METHODS

In order to maintain consistency throughout the state, we are requiring that you use certain methods to conduct your turbidity, temperature, pH, and disinfectant residual tests. The approved methods are shown in Table 7.1 and 7.2.

Tables 7.1 and 7.2 also list examples of commercially available test kits or lab equipment. These lists are not all-inclusive. If you find that a commercial product we have listed here is no longer available, ask the manufacturer which products would offer the same sensitivity.

Table 7.1. Acceptable laboratory methods for measuring turbidity, temperature, and pH.

Parameter	Minimum Accuracy[a]	Acceptable Methods[b]	Examples of Commercial Test Kits or Equipment[c]
Turbidity	± 0.05 NTU	Nephelometric (SM 2130 B) Nephelometric (EPA 180.1)	Hach 2100N and 2100AN HF Scientific Micro 100 and Micro 1000 Hanna HI88703 Orion AQ4500 Hach 1720D or E (online monitors) HF Scientific MicroTol (online monitor) LaMotte 2020 ClearTrace (online monitor)
		Great Lakes Instruments Method 2	Great Lakes Accu4 (online monitor) Orion AQ4500
		AMI Turbiwell	Swan AMI Turbiwell with LED (online monitor)
		Mitchell M5331	
		Orion AQ4500	Orion AQ4500
	± 50 mNTU	Hach FilterTrak Method 10133	Hach FilterTrak 660 (online monitor)
		Mitchell M5271	(online monitor)
Temperature	± 0.5°C	Thermometric (SM 2550)	Any good mercury-filled thermometer, but thermocouples are acceptable
pH	± 0.01 pH unit	Electrometric (SM 4500-H+) Electrometric (EPA 150.1&2)	Hach H series, HQ series, & sensION series Orion A series, 300 series, & "Star" series Hanna HI220, 2200, 3200, and 4200 series LaMotte pHPlus Oakton 310 series, 510 series, & 700 series

[a] This value is the minimum accuracy needed to comply with TCEQ requirements. The value shown may differ from the value in the EPA's *Standard Methods* (see following note) or EPA procedures.

[b] SM—*Standard Methods*, 22nd Edition; EPA—EPA methods.

[c] This is neither a complete list of all commercially available test kits nor an endorsement of any specific product.

Table 7.2. Acceptable laboratory methods for measuring residual disinfectant.

Parameter	Minimum Accuracy[a]	Acceptable Methods[b]	Examples of Commercial Test Kits or Equipment[c]
Free chlorine (Cl_2)	± 0.1 mg/L	Amperometric titration[d] (SM 4500-Cl D)	Hach Amperometric Titrator and AutoCAT 9000 Fischer-Porter 17T200 Wallace and Tiernan Series A790
		DPD-ferrous titration (SM 4500-Cl F)	LaMotte 6806/DT LaMotte 3176-01DT-DR
		DPD, colorimetric[e] (SM 4500-Cl G)	Hach DR100, DR800, and DR/2000 series Hach Pocket Colorimeter LaMotte DC-1100CL LaMotte SMART Colorimeter Hach CL17 (online monitor)
		Syringaldizine (FACTS) (SM 4500-Cl H)	
Chloramine (NH_2Cl)	± 0.1 mg/L	Amperometric titration[d] (SM 4500-Cl D)	Hach Amperometric Titrator Fischer-Porter 17T200 Wallace & Tiernan Series A790
		DPD-ferrous titration (SM 4500-Cl F)	LaMotte 6806/DT LaMotte 3176-01DT-DR
		DPD, colorimetric[e] (SM 4500-Cl G)	Hach DR100, DR700, and DR/2000 Hach Pocket Colorimeter LaMotte DC-1100CL LaMotte SMART Colorimeter Hach CL17 (online monitor)
Chlorine dioxide (ClO_2)	± 0.05 mg/L	Amperometric titration[f] (SM 4500-ClO2 C)	Hach Amperometric Titrator Fischer-Porter 17T200 Wallace & Tiernan Series A790
		Amperometric titration[f] (SM 4500-ClO2 E)	
		Colorimetric (EPA Method 327.0)	
Ozone (O_3)	± 0.02 mg/L	Indigo method[g] (SM 4500-O3 B)	Hach DR/2000 and DR/4000
MIOX	± 0.1 mg/L	Absent EPA recommendations, any acceptable method for free chlorine	

[a] This value is the minimum accuracy needed to comply with TCEQ requirements. The value shown may differ from the value in the EPA's *Standard Methods* or EPA procedures.
[b] SM—Standard Methods, 22nd Edition; EPA—EPA Methods.
[c] This is neither a complete list of all commercially available test kits nor an endorsement of any specific product.
[d] On the date of publication, there were no online instruments using the EPA-approved amperometric titration method. Although there are online amperometric instruments, all of them use proprietary direct amperometric measurement methods rather than the titrimetric method specified by the EPA. However, the EPA is working with instrument manufacturers to approve individual instruments case by case. Contact us for the latest information if you are interested in using one of the online amperometric monitors that are currently available.
[e] Color comparator test kits, such as Hach's color wheels and LaMotte's Octet comparator, are not acceptable for in-plant testing. These test kits may be used for distribution testing, although more sophisticated colorimetric meters are recommended.
[f] Platinum-platinum electrodes are required.
[g] A spectrophotometric procedure is required.

7.2 Calibrating Instruments and Other Equipment

Before you can effectively use your performance data, it must be accurate. One of the most important ways to ensure this accuracy is to keep your instruments and equipment properly calibrated and maintained. Consequently, we have established some minimum calibration requirements for lab equipment and flowmeters.

Turbidity Meters

Once every three months, you must calibrate your turbidimeter in accordance with the manufacturer's directions. This quarterly calibration must be conducted using primary turbidity standards. If you are using a benchtop turbidimeter, you must restandardize your secondary standards each time that you calibrate the unit with primary standards.

If you are using a benchtop turbidimeter to collect data that you report to us, you must check its calibration with a primary or secondary standard each time that you run a series of samples. If the unit is not giving an accurate reading, you must recalibrate it with primary standards.

If you are using online turbidimeters to collect data that you report to us, you must also check the calibration of your turbidimeter once per week using a primary or a secondary standard, the manufacturer's proprietary calibration device, or by using the following procedure:

1. Check the calibration of the bench-scale turbidity meter with a primary or secondary standard.
2. Record the turbidity reading shown on the online monitor.
3. Collect a sample from the inlet or outlet of the online monitor.
4. Measure and record the turbidity of the sample from the online monitor.
5. Compare the turbidity readings from the two instruments.
    a. If the values differ by more than 0.10 NTU:*
        i. Follow the manufacturer's instructions and recalibrate both the online and bench turbidimeters using primary turbidity standards.
        ii. Repeat Steps 1–6. If the values still differ by more than 0.10 NTU,* contact the instrument's manufacturer for further instructions.
    b. If the values differ by no more than 0.10 NTU,* complete calibration of the units is not required.
6. If a continuous recorder is used, compare the value reported by the recorder with the value reported by the monitor.
    a. If the values differ by more than 0.05 NTU,* adjust the recorder.
    b. If the values differ by 0.05 NTU,* or less, no adjustment of the recorder is needed.

* If the comparison is conducted when turbidity levels are above 1.0 NTU, you may accept differences of up to 10% when comparing the results of two turbidimeters and of up to 5% when comparing the recorder results with that of the turbidimeter.

Regardless of which method you use to check the calibration of the online turbidimeter, you must recalibrate the unit using primary standards if the unit is not providing an accurate reading.

Chlorine Residual Analyzers

If you are using a manual method to test your disinfectant residuals, you must check the accuracy of your instrument and method at least once every 30 days. This check must be conducted using a chlorine solution with a known concentration, a chlorine standard, or a similar method recommended by your instrument manufacturer. If the instrument and method are not providing an accurate reading, you must recalibrate the instrument (if possible) or take other corrective action to improve the accuracy of the results.

If you are using an online disinfectant analyzer to collect data that you report to us, you must calibrate the instrument at least once every 90 days using a chlorine solution with a known concentration or a similar method recommended by the instrument manufacturer in the instrument's owner's manual. You must also check the accuracy of your instrument and method at least once every 30 days using a chlorine solution with a known concentration or by using the following procedure:

1. Record the chlorine residual reading shown on the online monitor.
2. Collect a sample from the inlet of the online monitor.
3. Measure and record the chlorine residual of the sample collected from the online monitor using an EPA-approved manual method such as:
    a. titration (for example, DPD-ferrous)
    b. colorimetry (for example, Hach DR100)
    c. spectrophotometry (for example, Hach DR2000)
4. Compare the two chlorine residual readings.
    a. If the values differ by more than 10% or 0.10 mg/L, whichever is greater:
        i. Follow the manufacturer's instructions and recalibrate the online chlorine residual monitor.
        ii. Repeat Steps 1–3. If the values still differ by more than 10% or 0.10 mg/L, whichever is greater, contact the instrument's manufacturer for further instructions.
    b. If the values differ by no more than 10% or 0.10 mg/L, whichever is greater, a complete calibration of the online monitor is not required.
5. If a continuous recorder is used, compare the value reported by the recorder with the value reported by the monitor.
    a. If the values differ by more than 0.10 mg/L, adjust the recorder.
    b. If the values differ by 0.10 mg/L or less, no adjustment of the recorder is needed.

pH Meters

If you are using a benchtop pH meter, you must calibrate the unit in accordance with the manufacturer's specifications at least once each day using at least two buffers. You must also check its calibration with at least one buffer each time you run a series of samples. If the pH meter is not accurately reading the buffer, you must recalibrate the unit.

If you have an online pH meter, you must calibrate the unit in accordance with the manufacturer's specifications at least once every 30 days. The calibration of online pH meters must also be checked at least once each week with a buffer solution

or by comparing the results from the online unit with the results from a properly calibrated benchtop unit. If necessary, the online unit needs to be recalibrated with primary standards.

Thermometers

We have not established any minimum calibration procedures for checking the calibration of your thermometer. However, we recommend that you check it about once each 90 to 180 days by stirring the thermometer in an ice bath; after two minutes or so in the ice bath, the thermometer should read 0ºC (32ºF).

Flowmeters

You must check the calibration of your raw and treated water flowmeters at least once every 12 months. The flowmeters can be checked using a pitot tube, a calibrated ultrasonic flowmeter, or similar calibration device. The accuracy of the meters can also be checked by filling or draining a known volume with water into (or from) a basin. If the meter is not reading within the accuracy range specified by the manufacturer, you must repair, recalibrate, or replace the meter.

7.3 LABORATORY RECORDS

Records Retention

Our record-keeping requirements vary depending on the type of data being collected. Although there are other records (such as your CT approval letter, your engineering drawings, and others) that you must maintain, the following are some of the important *laboratory* records you must keep.

- You must retain all your calibration records for at least three years.
- IFE turbidity readings must be maintained for at least three years.
- CFE turbidity readings must be kept for at least 10 years.
- Copies of the SWMOR must be kept for 10 years.
- A copy of the up-to-date laboratory-approval form must be maintained with your approved monitoring plan.

Laboratory-Approval Form and Instructions

The current requirements for laboratory approval are contained in the TCEQ's Regulatory Guidance 384: How to Develop a Monitoring Plan for a Public Water System. Please refer to that document for detailed instructions on completing the form.

A copy of the laboratory-approval form must be attached to the system's monitoring plan. For information on monitoring plans and laboratory approval forms, contact the TCEQ's Drinking Water Quality Team at 512-239-4691 or by e-mail at <PWSCHEM@tceq.texas.stateailt>. On the monitoring plan, the system must attach documentation showing that any outside labs it uses are approved or accredited, as appropriate.

If you send approved-lab analytes to a commercial lab, that system's lab must be approved by the TCEQ to conduct the appropriate analysis. You must attach a copy of that lab's Laboratory Approval Form to your monitoring plan.

7.4 ROUNDING NUMBERS ON YOUR SWMOR

Your plant can probably measure water quality data to a very high level of precision. However, we do not want the SWMOR or SWMOR2 to show so many decimal places that we cannot read the report. Still, you should probably record as many decimal places as possible on your daily log, and you may enter as many digits as you can when entering data in the two spreadsheets.

To ensure that we can read the form when you submit it, the SWMOR and SWMOR2 are both designed to automatically round any value you enter to the proper number of decimal places. Don't be surprised if your spreadsheet doesn't show or print all of the decimal places that you entered when you filled out the report. Table 7.3 shows how the two spreadsheets round the values that you enter.

The two spreadsheets also do some additional rounding when they perform some of their automatic determinations. For example, if you enter a reading for filtered-water turbidity of <0.346> NTU, your report will display and print a reading of 0.35 NTU, but it will not count the reading as being above 0.3 NTU, since the actual value that you entered was not higher than 0.35 NTU. Therefore, it is beneficial to enter actual results and let the spreadsheet program do all the rounding for you.

Drinking Water Laboratory Approval Form

Public Water System Name: _____ **Plant Name or Number:** _____

PWS ID No.: _____ **Date:** _____

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.

Operator's Signature:* _____

Certificate No. and Grade:* _____

* Or, for Labs, the Lab Analyst's signature, name, title, and phone number.

Analyte	Method (& Analyzer Type)	Accuracy		Calibration	
				Frequency	Method
Turbidity		±	NTU		
pH		±	pH unit		
Temperature		±	C		
TOC		±	mg/L		
UV_{254}		±	cm -1		
Alkalinity		±	mg/L		
Disinfectant					
Free Chlorine		±	mg/L		
Total Chlorine		±	mg/L		
Chlorine Dioxide		±	mg/L		
Chlorite at point of entry		±	mg/L		
Calcium		±	mg/L		
Phosphate		±	mg/L		

Please see reverse for brief instructions.

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Figure 7.1. Laboratory-approval form.

Table 7.3. How the SWMOR and SWMOR2 round the readings you enter.

Type of Value	The Reports Round to Nearest …	Examples		Comments
		Entered Value	Displayed Value	
Raw-water turbidity	1 NTU	124.3 75.834	124 76	
Settled-water turbidity	0.1 NTU	3.43 1.856	3.4 1.9	
Filtered-water turbidity	0.10 NTU	0.544 0.546 1.044 1.046 2.043 2.053	0.54 0.55 1.04 1.05 2.04 2.05	• For values less than 0.1, round to the nearest 0.01 NTU. • For values that exceed a trigger level, the SWMOR counts only those values that are above that trigger level based on the value you entered and after rounding—not the values displayed.
Treated water turbidity	0.1 NTU	0.349 0.350 1.049 1.050	0.3 0.4 1.0 1.1	• For values less than 0.1, round to the nearest 0.01 NTU. • For values that exceed a limit, the SWMOR counts only those values that are above that limit based on the values you entered and after rounding—not the values displayed.
Chlorine or chloramine residual	0.1 mg/L	0.445 0.75	0.4 0.8	
Chlorine dioxide residual	0.05 mg/L	0.45 0.12	0.5 0.1	
Ozone Residual	0.02 mg/L	0.43 0.12	0.44 0.12	
pH	0.1 unit	7.843 8.456	7.8 8.5	
Temperature	0.1ºC	14.74 26.55	14.7 26.6	Convert temperatures measured in degrees Fahrenheit to degrees Celsius.
Time	0.25 hour	35 min 40 min	0.50 hour 0.75 hour	
Percentage	0.1%	5.045 5.052	5.0 5.1	