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

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METHOD 334.0

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1. 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.

2. 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.

3. 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.

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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

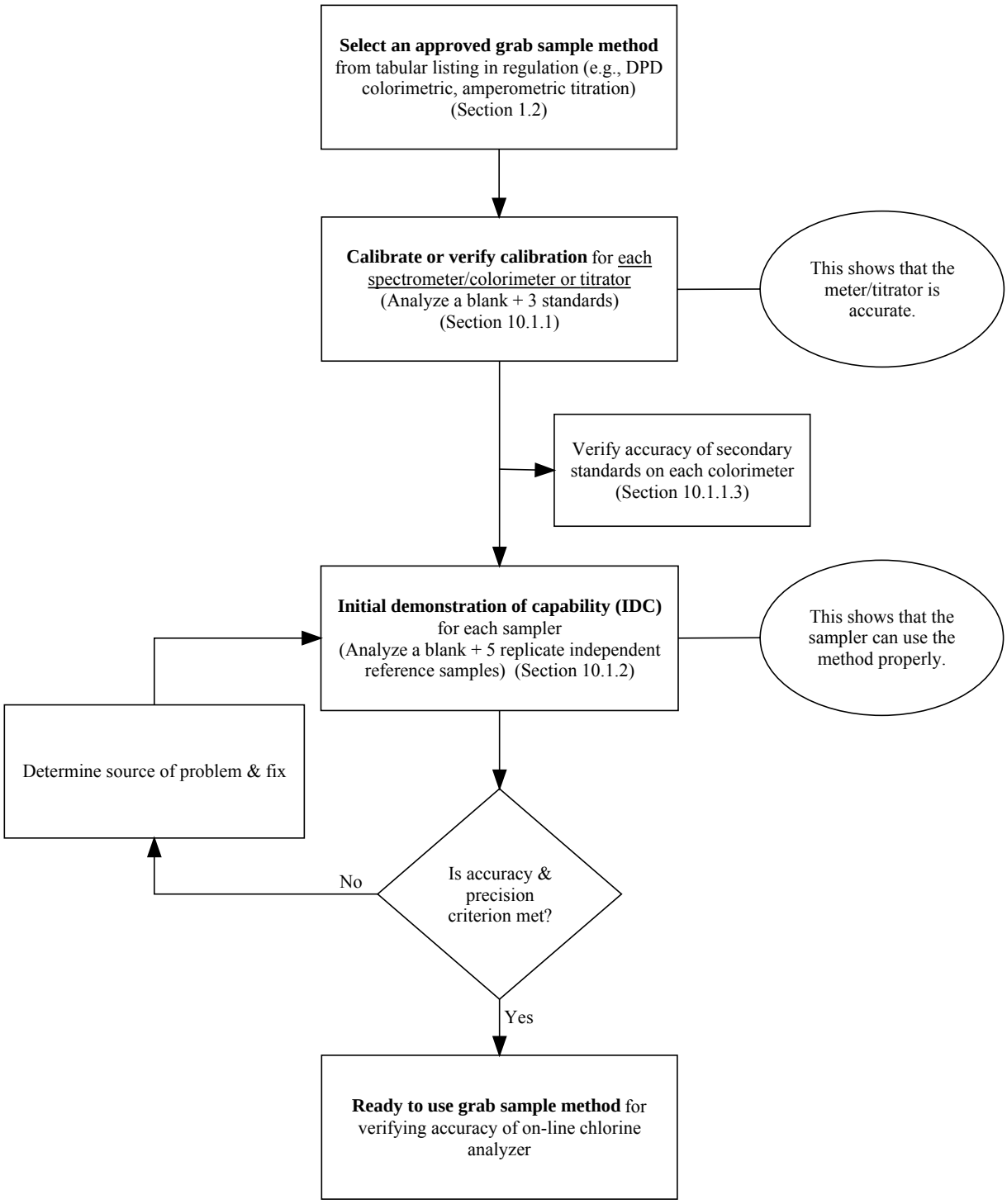
Table 3. Routine QC for Grab Sample Methodology

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

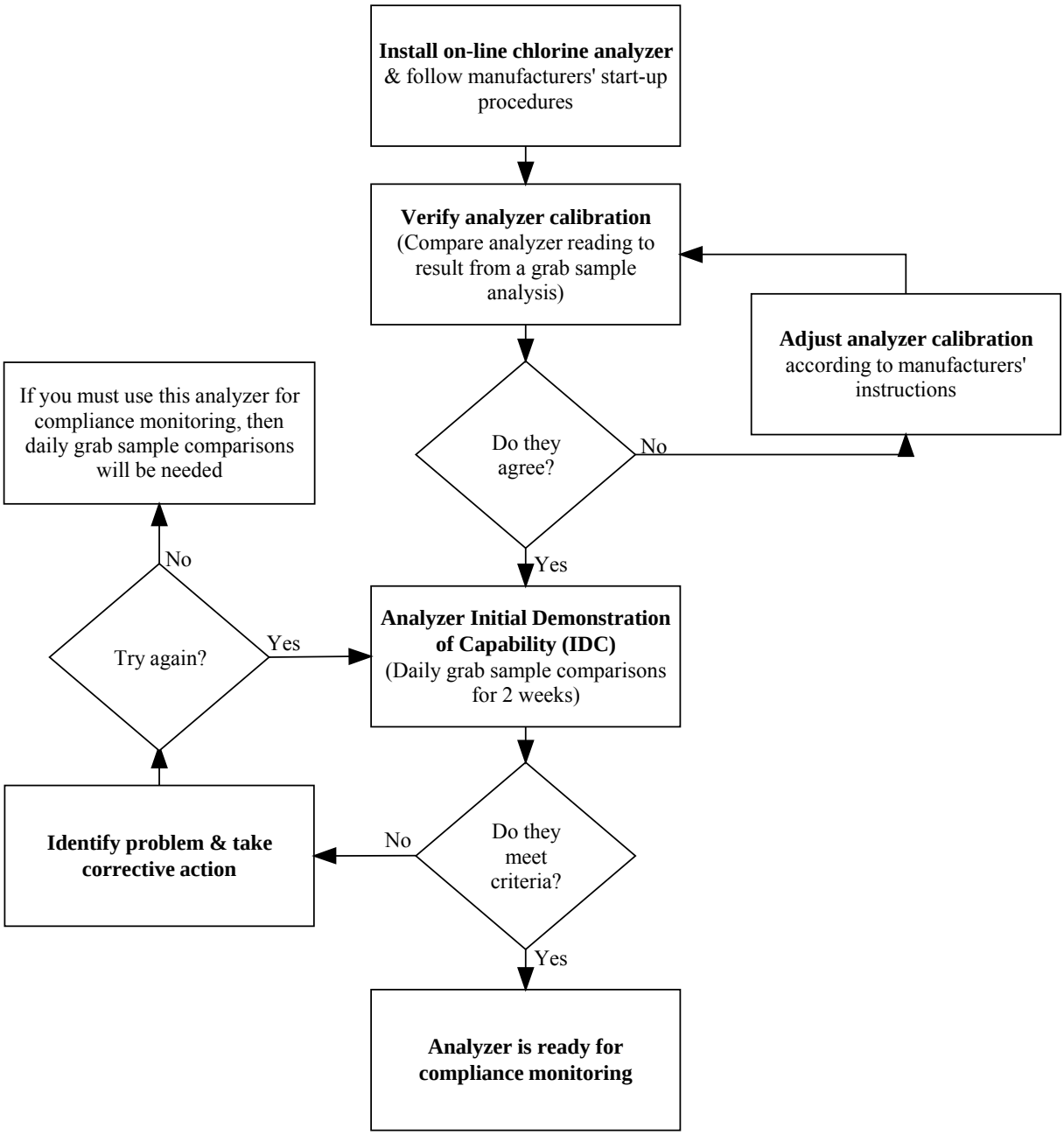
Table 4. QC for On-line Chlorine Analyzer

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

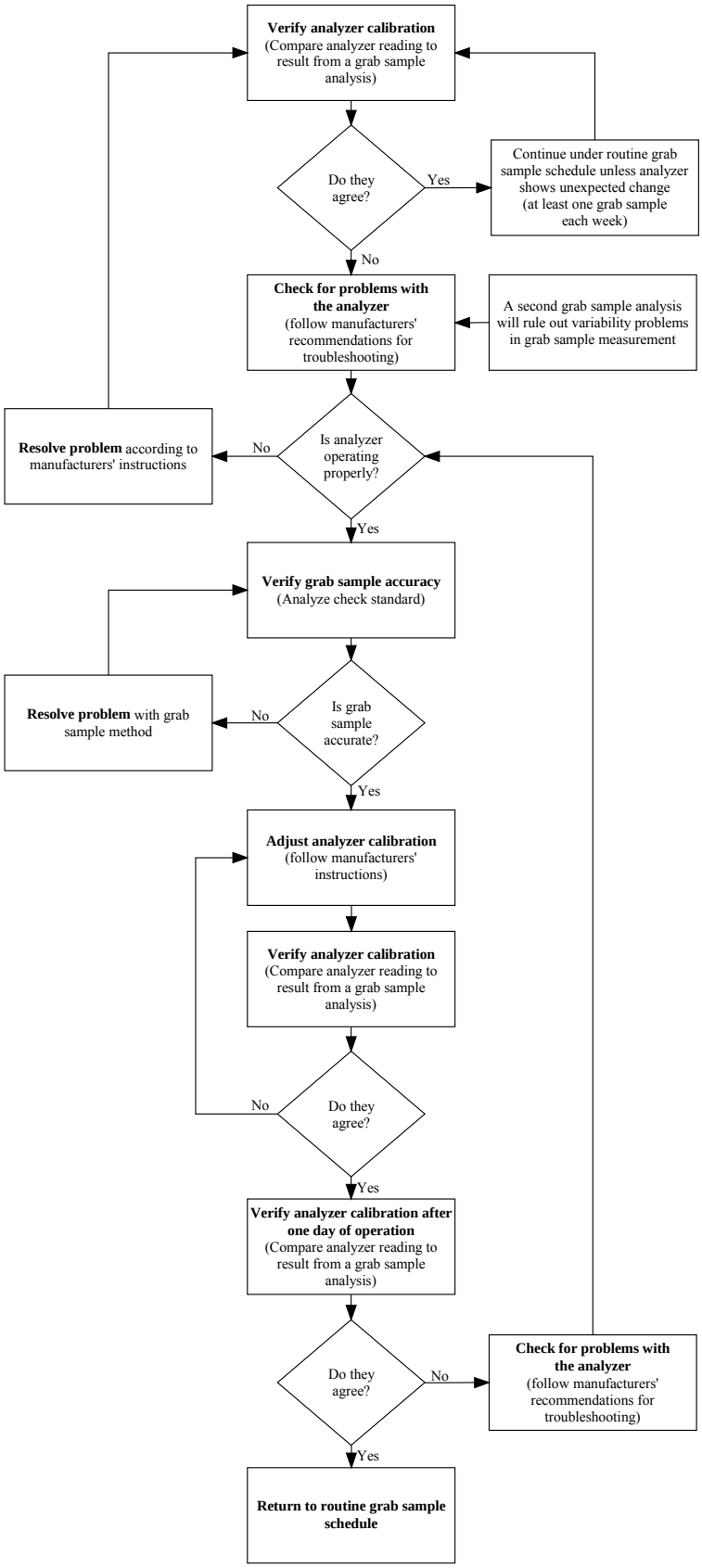
Flowchart 1. Start-up Procedure for Grab Sample Method



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



Flowchart 3. Routine QC for On-line Chlorine Analyzer



METHOD 334.0 APPENDIX A

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

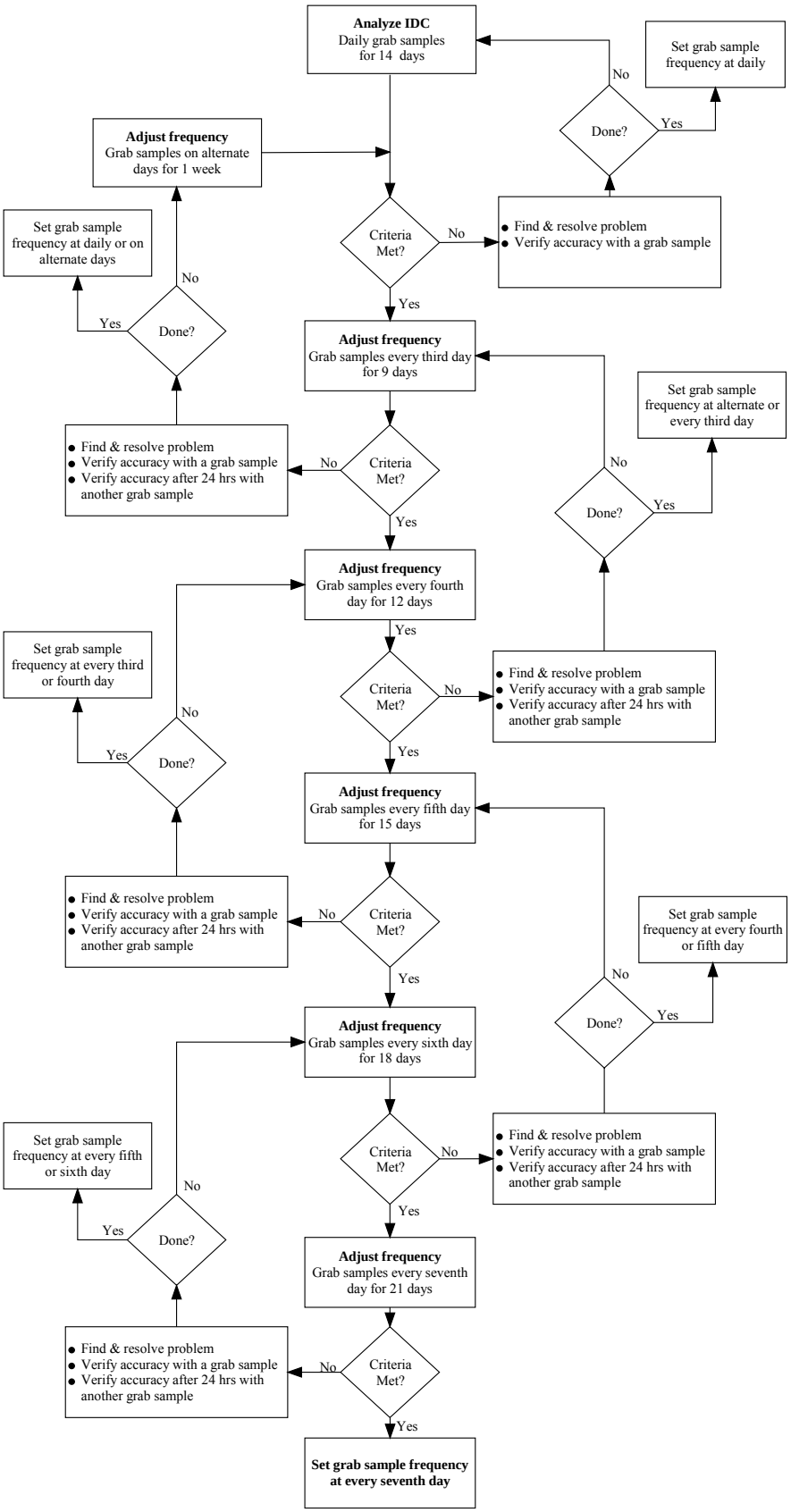
A. Historical data can be used to establish a routine schedule for comparing grab sample measurements to the results from the on-line chlorine analyzer. The data must demonstrate that the grab sample measurements are frequent enough to detect problems with the analyzer within a reasonable period of time 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