Chlorine Monitoring Compliance Review

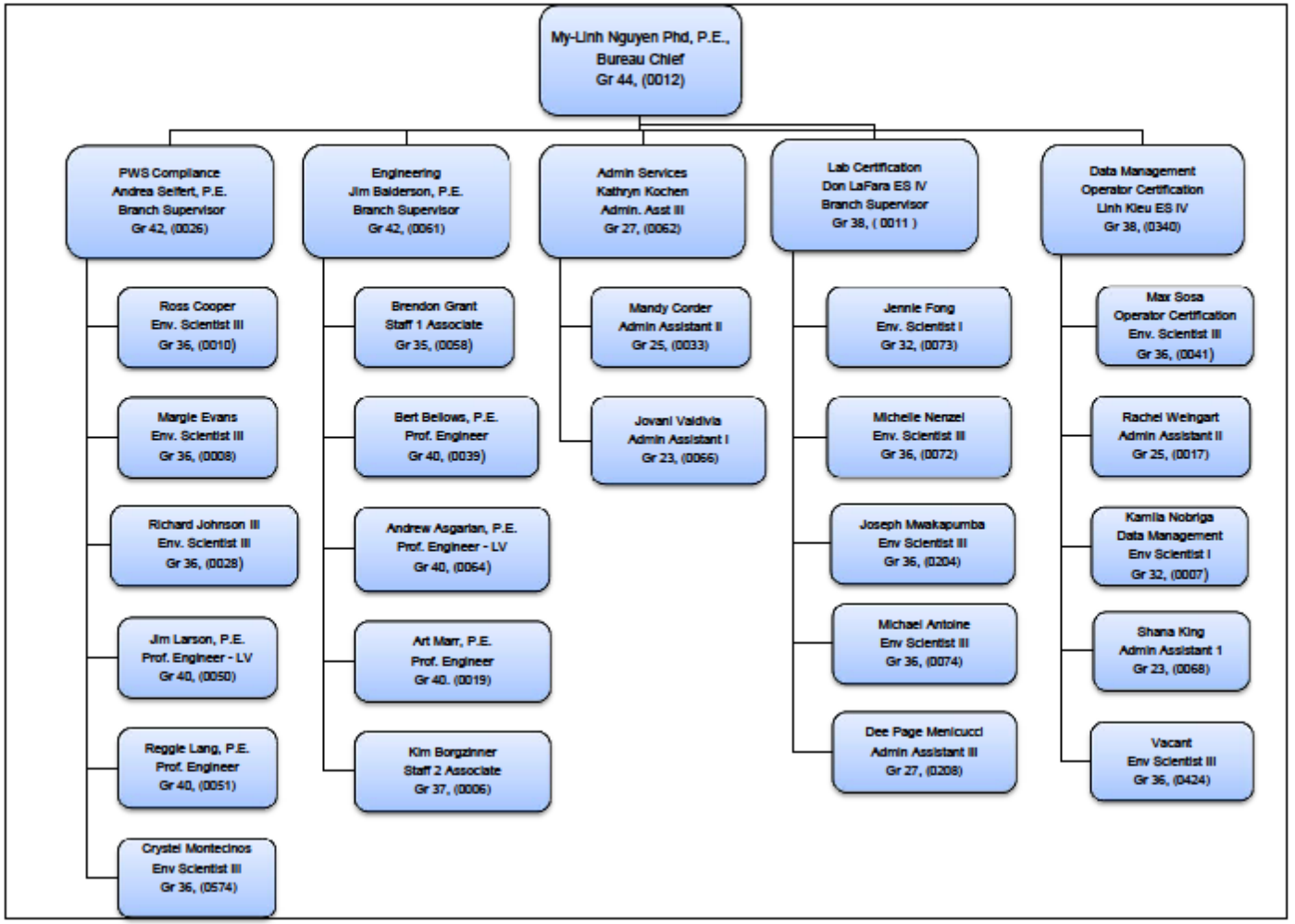
Bureau of Safe Drinking Water

Presented by:

Reggie Lang

Introductions and Organizational Chart

DIVISION OF ENVIRONMENTAL PROTECTION
Bureau of Safe Drinking Water – December 05, 2016



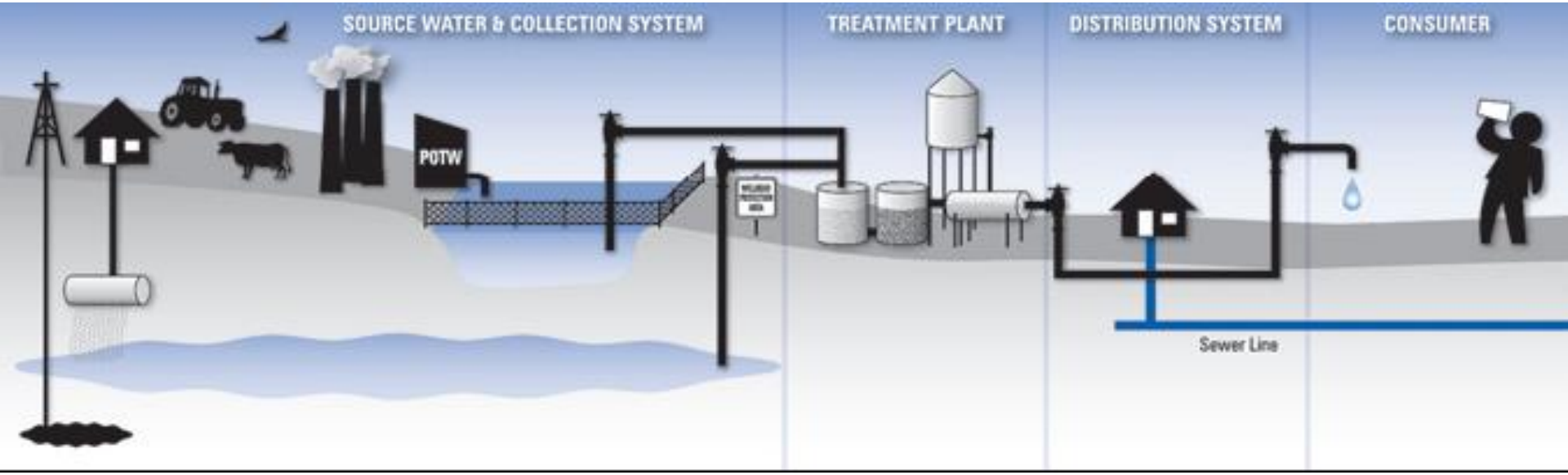
Presentation Overview

* Method 4500-Cl G
  * Who does this impact?
  * Regulation Review
  * Procedural Review
  * Common EPA Approved and Unapproved Units
* Standard Operating Procedure
  * Utilizing Secondary Gel Standards
  * Performing an Initial Demonstration of Capability (IDC)
  * Routine Calibration Verification Standard
  * Reporting Results to BSDW
* Ensuring Compliance
  * Take back to your water system
  * Sanitary Survey and BSDW Checklist

Overview- EPA Method 334.0

* 1. Calibration of Hand-held Analyzer
* 2. Initial Demonstration of Capability (IDC)
  * On-line and Hand-held are Same Chemistry
  * On-line and Hand-held are Different Chemistry
* 3. Quarterly Calibration Verification
* 4. Routine Calibration Check Every 5 or 7 days

Keep This in Mind
From Source to Tap



Method 4500-Cl G

* Who does this impact?
  * Systems Utilizing DPD Colorimetric Test Kits for Compliance Monitoring
    * Maximum Residual Disinfectant Level for Chlorine and Chloramines
      * Community & Non-Transient Non-Community
      * Chlorinated or Chloraminated Water Systems
    * Treatment for Pathogens & Grab Samples
      * All Public Water Systems
* Why Now?
  * Review and comments from EPA on our primacy package for the Stage 1 DBP Rule.
  * Provide process to ensure that field data obtained for compliance is equivalent to certified lab data.

Method 4500-Cl G Regulation Review

Distribution

* Stage 1 Disinfectant/Disinfection Byproducts Rule
  * Monitoring Requirement
    * NAC 445A.4525, 40 CFR §141.132(c)
    * Chlorine and Chloramines
    * Requires chlorine residual monitoring at same time and place as Coliform monitoring (Routine and Repeat).
  * Surface Water Treatment Rules
    * Monitoring Requirement
    * NAC 445A.527, 40 CFR §141.72

Method 4500-Cl G Regulation Review

Distribution

* Stage 1 Disinfectant/Disinfection Byproducts Rule
  * Analytical Requirement
    * NAC 445A.458 (4)-Conduct of Analysis ⟶ 40 CFR 141.131 (c)
      * (2) If approved by the State, systems may also measure residual disinfectant concentrations for chlorine, chloramines, and chlorine dioxide by using DPD colorimetric test kits.
        * Chlorine and Chloramine-4500-Cl G
        * Chlorine Dioxide-4500 ClO_2 D
      * (3) A party approved by EPA or the State must measure residual disinfectant concentration.
      * Free chlorine or total chlorine may be measured for demonstrating compliance with the chlorine MRDL and combined chlorine, or total chlorine may be measured for demonstrating compliance with the chloramine MRDL.

Method 4500-Cl G Regulation Review

Distribution

* Surface Water Treatment Rule
  * Analytical Requirement
  * NAC 445A.527-Requirements for Monitoring → 40 CFR 141.74(a)(2)
    * If approved by the State, residual disinfectant concentrations for free chlorine and combined chlorine also may be measured by using DPD colorimetric test kits.
    * In addition States may approve the use of the ITS free chlorine test strip for the determination of free chlorine. Use of the test strips is described in Method D99–003, "Free Chlorine Species ($HOCl^-$ and OCl^-) by Test Strip," Revision 3.0, November 21, 2003, available from Industrial Test Systems, Inc.

Method 4500-Cl G Regulation Review

TREATMENT

* Surface Water Treatment Rule
* Monitoring Requirement- Procedure applies for Grab Samples
  * NAC 445A.527 ⟶ 40 CFR §141.74
  * Requires chlorine residual monitoring to determine contact time and Entry Point to the Distribution System Monitoring.
  * If continuous monitoring fails, grab sampling every 4 hours can be used to determine compliance.

Method 4500-Cl G Regulation Review

TREATMENT

* Ground Water Rule
* Monitoring Requirement- Procedure applies for Grab Samples
  * NAC 445A.4525 ⟶ §141.403(b)(3)(i)
  * (A) Population >3300
    * Must continuously monitor
    * The ground water system must maintain the State-determined residual disinfectant concentration every day the ground water system serves water from the ground water source to the public.
    * If there is a failure in the continuous monitoring equipment, the ground water system must conduct grab sampling every four hours until the continuous monitoring equipment is returned to service.
    * Must resume continuous residual disinfectant monitoring within 14 days.

Method 4500-Cl G Regulation Review

TREATMENT

* Ground Water Rule
* Monitoring Requirement-Procedure applies for Grab Samples
  * NAC 445A.4525 ⟶ §141.403(b)(3)(i)
  * (B) Population ≤ 3300
    * Must take a daily grab sample during the hour of peak flow or at another time specified by the State.
    * If any daily grab sample measurement falls below the State-determined residual disinfectant concentration, the ground water system must take follow-up samples every four hours until the residual disinfectant concentration is restored to the State-determined level.
    * Alternatively, may monitor continuously and meet the requirements of paragraph (b)(3)(i)(A) of this section.

Method 4500-Cl G Regulation Review

TREATMENT

* Surface Water Treatment Rule and Ground Water Rule
  * Analytical Requirement
    * NAC 445A.4525, 445A.458, 445A.527 ⟶ 40 CFR 141.74 (a)
    * NAC 445A.4525 ⟶ 40 CFR 141.403 ⟶ 40 CFR 141.74 (a)
      * (2) Public water systems must measure residual disinfectant concentrations with one of the analytical methods in the table or
      * If approved by the State, residual disinfectant concentrations for free chlorine and combined chlorine also may be measured by using DPD colorimetric test kits.
      * In addition States may approve the use of the ITS free chlorine test strip for the determination of free chlorine. Use of the test strips is described in Method D99–003, "Free Chlorine Species ($HOCl^-$ and OCl^-) by Test Strip," Revision 3.0, November 21, 2003, available from Industrial Test Systems, Inc.

Method 4500-Cl G Regulation Review

* NAC 445A.458 Conduct of analysis.
  * **1. Except as otherwise provided in this section, each analysis required by NAC 445A.4525 to 445A.457, inclusive, must be performed by a laboratory certified pursuant to NAC 445A.542 to 445A.54296, inclusive.**
  * 2. Turbidity measurements may be made by a laboratory certified pursuant to NAC 445A.542 to 445A.54296, inclusive, or by public water system personnel utilizing an instrument capable of meeting the requirements of 40 C.F.R. § 141.74(a)(1), as adopted by reference pursuant to NAC 445A.4525.
  * **3. Chlorine residual measurements to comply with 40 C.F.R. §§ 141.72 and 141.74, as adopted by reference in NAC 445A.4525, must be made by public water system personnel utilizing an instrument and methods capable of meeting the requirements of 40 C.F.R. § 141.74(a)(2), as adopted by reference in NAC 445A.4525.**

Method 4500-Cl G Regulation Review

* NAC 445A.458 Conduct of analysis.
  * **4. Chlorine, chloramines or chlorine dioxide residual measurements to comply with the maximum residual disinfectant level must be made by public water system personnel using an instrument and methods capable of meeting the requirements of 40 C.F.R. § 141.131(c), as adopted by reference in NAC 445A.4525.**
  * 5. Temperature and pH measurements must be made by the public water system utilizing an instrument and methods capable of meeting the requirements of 40 C.F.R. § 141.23(k)(1), as adopted by reference in NAC 445A.4525.
  * 6. Public water systems may direct the laboratory which analyzes water samples to submit the results of the sample to the Division or the appropriate district board of health.

Method 4500-Cl G Regulation Review

Analytical Methods—40 CFR 141.131 (c) Table

Methodology	SM (19th or 20th ed)	SM Online[2]	ASTM method	Residual Measured		
				Free Cl_2	Combined Cl_2	Total Cl_2
Amperometric Titration	4500–Cl D	4500–Cl D–00	D 1253–86 (96), 03	x	x	x
Low Level Amperometric Titration	4500–Cl E	4500–Cl E–00				x
DPD Ferrous Titrimetric	4500–Cl F	4500–Cl F–00		x	x	x
DPD Colorimetric	**4500–Cl G**	**4500–Cl G–00**		**x**	**x**	
Syringaldazine (FACTS)	4500–Cl H	4500–Cl H–00		x		

Method 4500-Cl G Procedural Review

* Why is this important?
  * Chlorine Residual results must be obtained in a manner consistent with Laboratory Methods.
  * Holding Time for Chlorine is immediately (15 minutes).
  * Field Colorimeters developed to comply with Method 4500-Cl G are acceptable for compliance reporting.
  * Legal defensibility.

Method 4500-Cl G Procedural Review

* What will I need to do differently?
  * Utilize EPA approved Colorimeter(s) that meets Method 4500-Cl G criteria.
    * Wavelength must be 490-530 nm with light path > 1 cm (SM 4500-Cl G 2.a. 2)
  * Develop and implement a Standard Operating Procedure (SOP).
  * Perform an Initial Demonstration of Capability (IDC).
  * Utilize Secondary Standards to verify the calibration of your Colorimeter.
    * These are NOT the Secondary IOC's sampled for triennially
  * Be prepared to defend your data!

Method 4500-Cl G Procedural Review

* Why do I need an SOP?
  * Creates consistency when a process is performed
  * Provides a format that is easy to follow
  * Reduces the possibility of human error
  * Ensures data is Legally Defensible
* BSDW created a Template that you can tailor to fit your system.

Method 4500-Cl G Procedural Review

* What are Secondary Standards? Why are they important?
  * Secondary Standards are used to perform the IDC and to quickly check the accuracy of your colorimeter.
  * Colorimeters are factory calibrated. The calibration can shift and should be verified with Secondary Standards each day a Chlorine Residual is obtained.

* What is an Initial Demonstration of Capability?
  * A procedure to confirm the operator can properly perform a particular method. Subsequently performed with any significant changes (new instrument, new operator, new standards, new/revised methods).

Common EPA Approved Field Instruments

Hach Pocket Colorimeter II

Hach DR890 Colorimeter

LaMotte 1200-CL Colorimeter

Non EPA Approved Units

Color Wheels

Non DPD Colorimeters

Method 4500-Cl G
Standard Operating Procedure

Standard Operating Procedure (SOP)

* Template created by BSDW
* Available for download
  * www.ndep.nv.gov/bsdw/forms
* Addresses the following items:
  * Sample Handling
  * Interferences
  * Equipment and Supplies
  * Secondary Gel Standards
  * Initial Demonstration of Capability (IDC)
  * Routine Calibration Verifications
  * Routine Procedure for collecting a Chlorine Residual
  * Reporting of Results
  * Operator Ethics Statement

SOP Sections 1-5

* Tailor our example to fit your system.
* Fill in items in **RED**.
* Sections 1-4 are basic items.
* Section 5: May need an SOP for each Brand of Colorimeter
* Secondary Gel Standards (Section 5c):
  * Verify values on Certificate of Analysis (COA) with Colorimeter(s)
  * Known Concentrations
  * Do not expose Gel standards to extreme temps

SOP Section 6- Definitions

* Initial Demonstration of Capability (Section 6):
  * Very simple procedure that shows each operator is capable of performing analysis.
  * Also ensures the accuracy of your colorimeter.
  * What does Relative Standard Deviation mean?
    * Standard Deviation is simply a measure of how spread out the numbers are in a given set of data.
  * What is % Recovery?

$$\frac{\text{Amount Obtained (recovered)}}{\text{Starting Amount}} \times 100 = \%R$$

OR:

    * How much Stuff you ended up with / How much Stuff you started with x 100 = percent recovery of Stuff

SOP Section 6

* Initial Demonstration of Capability (Section 6):
  * Procedure for Performing
    * Step by step instructions for excel spreadsheet
    * Analyst and Witness should sign
      * Witness Affiliation shows BSDW that the witness is knowledgeable in the procedure
    * Keep this on file for review during a Sanitary Survey

Cl Residual IDC Tool.xlsx - Microsoft Excel

Residual Chlorine Initial Demonstration of Capability SM 4500-Cl G

Revision 1, April 9, 2012

Enter data in blue spaces only. The spreadsheet will automatically calculate % Recovery and Relative Standard Deviation (RSD).

Analyst: (Use full name)

Method No: 4500-CL G

Analysis: Residual Chlorine

SOP No/Rev No:

Matrix: (e.g. Water, Wastewater)

Instrument/Meter Manufacturer:

Serial #:

Date of Analysis:

Gel Calibration Check Standards: (e.g. Manufacturer or Brand Name)

Lot # & Expiration date:

Enter your readings in the blue boxes below

Analyte	Known Conc. *	Units	Read 1	Read 2	Read 3	Read 4	Average Avg	%Rec	%RSD	Acceptance Criteria Avg % Recovery	%RSD
Low Residual Chlorine	0.23	mg/L	0.24	0.23	0.23	0.24	0.24	102.17	2.46	85-115	≤ 15
Medium Residual Chlorine	0.93	mg/L	0.91	0.93	0.93	0.92	0.92	99.19	1.04	85-115	≤ 15
High Residual Chlorine	1.61	mg/L	1.62	1.62	1.63	1.63	1.63	100.93	0.36	85-115	≤ 15

Signature of Analyst:

Analyst Title:

Signature of Witness:

Witness Affiliation/Title:

* Refer to step 5c in the SOP.

Sample Blank
Ready
120%

SOP Section 7

* Routine Calibration Verification Standards (Section 7):
  * Perform prior to collecting a chlorine residual for compliance.
    * Perform before leaving office or treatment plant for the day.
      * Gel Standards are temperature sensitive
    * Perform prior to sampling and again following the final sample analysis of the work day.
      * More Defensible especially for systems collecting a large number of samples

SOP Section 7

* Routine Calibration Verification Standards (Section 7):
  * Ensures your Colorimeter is reading within range.
  * Rule of thumb- Use standard that is ½ the expected Cl2 residual.
  * Reading should be ≤ 15% of Known Concentration.
  * Notice trending towards ≥ 15%.

SOP Section 8

* Analytical Procedure (Section 8)
  * This is what you all know how to do better than us!
  * Be aware of minor details associated with:
    * Low Range vs. High Range
    * Free Chlorine vs. Total Chlorine
    * Write these details into your SOP

SOP Section 9

* Recordkeeping (Section 9)
  * Describe your internal procedure for Recordkeeping
  * May include:
    * Writing result on Chain of Custody
    * Maintaining a Log of results and date analyzed
    * Creating a Spreadsheet

SOP Section 9
Reporting Results -Distribution System

* Reporting Results (Section 9)
  * Describe your internal procedure for Reporting Data
  * Compliance Data
    * Utilize "Disinfectant Residual Data Quarterly Report" Form

    * Report values to BSDW by the 10th of the month following each quarter
  * Operational Data
    * Provide to supervisors and other staff
    * Providing data to next shift operator
    * Providing data to management

SOP Section 9 cont. Reporting Results - Surface Water Treatment Rule

* Reporting Results (Section 9)
* Monthly Report-Routine Monitoring (NAC 445A.527)
  * Daily Chlorine Parameters
    * Minimum chlorine residual at entry point to distribution system
    * Minimum Contact Time
    * Residual in distribution system cannot be undetectable in more than 5% of the monthly samples
* As soon as possible-no later than next business day (NAC 445A.538)
  * If your online chlorine analyzer fails
    * Take Chlorine Residual Grab Samples every 4 hours, no more than 5 working days following equipment failure.
  * Failure to meet minimum Contact Time

SOP Section 9 cont. Reporting Results - Ground Water Rule

* Reporting Results (Section 9)
* As soon as possible-no later than next business day

  NAC 445A.4525 ⟶ 40 CFR 141.405(1)
  * If water system fails to meet minimum chlorine residual for more than four hours.
* Every 3 months NAC 445A.5405
  * Sampling log verifying that treatment plant treating in accordance with the state regulations

SOP Sections 10-12

* Safety: DPD is Toxic. Refer to the MSDS.
* References: Utilize your Owners Manual!
* Ethics Statement: Referenced in NAC 445A.54278 and just good business practice.
* Each operator should read the SOP and Sign and Date.
  * Keep these copies on file for review during a Sanitary Survey.

Ensuring Compliance

Ensuring Compliance

* Take this back to your water system and implement a procedure, conduct Initial Demonstration of Capabilities, train your other operators.
* What to expect on an Inspection
  * Have SOP and completed IDC forms ready for your Sanitary Survey.

Ensuring Compliance

* You've spent a lot of time obtaining accurate and defensible results—Ensure you Report the Data Correctly
* Distribution System-Maximum Residual Disinfectant Level
  * Utilize Quarterly report form to report values to BSDW
  * Total Coliform Rule and Chlorine Residuals reported to our office go hand in hand.
    * Collect a residual at each Total Coliform sample site.
    * # of samples on this form must match samples taken for compliance with Total Coliform Rule.
    * Report Chlorine Residuals for Routine & Repeats required under the Total Coliform Rule.

Ensuring Compliance

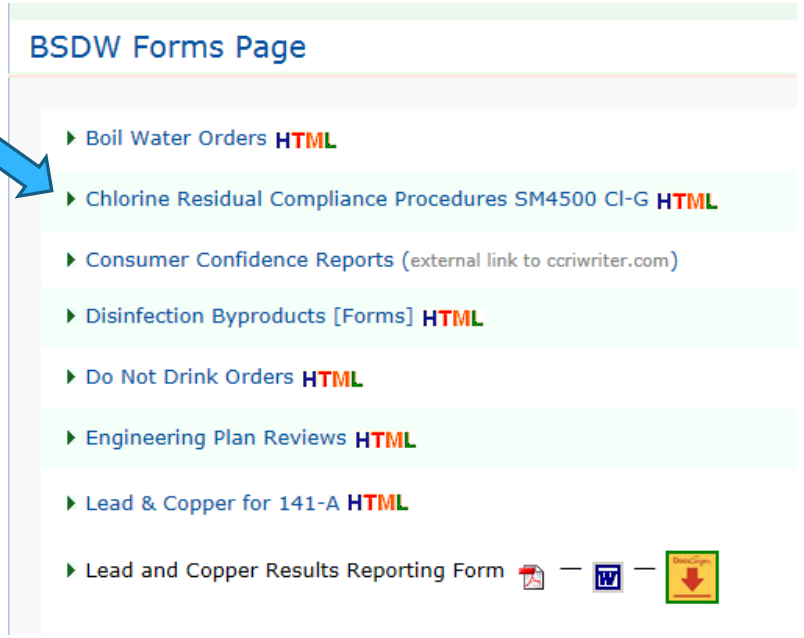
* Distribution System-Maximum Residual Disinfectant Level (Continued)
  * Compliance is based on the Running Annual Average-4.0 mg/L
  * Labs include individual residuals on reports as a courtesy
    * These values may be transposed or omitted by the lab
      * Example: 0.38 accidentally becomes 0.83.
      * If omitted we don't always receive a copy of your Chain of Custody
  * Results are due by the 10th of the month following each Quarter

Ensuring Compliance

* Surface Water Treatment & Ground Water Treatment
  * Contact BSDW if not in compliance
    * Note: After hours call line
      * 888-331-6337 (Calling from within Nevada)
      * 775-687-9485 (Calling from Anywhere)
  * Submit monthly reports on time

Ensuring Compliance

* On our web site:
  * Example SOP
  * Example IDC spreadsheet
  * Disinfectant Residual Data Quarterly Report
* www.ndep.nv.gov/bsdw/forms



EPA Method 334.0

EPA Method 334.0 Overview

* 1. Calibration of Hand-held Analyzer
* 2. Initial Demonstration of Capability (IDC)
  * On-line and Hand-held are Same Chemistry
  * On-line and Hand-held are Different Chemistry
* 3. Quarterly Calibration Verification
* 4. Routine Calibration Check Every 5 days

EPA Method 334.0- Calibration

* The Calibration Curve of the online analyzer must be verified in one of two ways:
  * 1. Comparing the on-line analyzer with grab sample readings obtained on a hand-held Colorimeter (like those just discussed).
  * 2. With aqueous standards. (Auxiliary plumbing and fittings would need to be installed.) Gel standards are not applicable.
* Calibration process is based on the chemistry utilized in the on-line analyzer and the hand-held Colorimeter.

EPA Method 334.0 - Summary

* Section 2.1: An on-line chlorine analyzer is used by some facilities to continuously monitor the chlorine concentration at a drinking water sampling point. The instrument is **calibrated** using aqueous standards **or** the results from duplicate grab sample analyses that are collected at the same location and time. The grab samples are analyzed for chlorine (free or total) using a method that is approved for drinking water compliance monitoring (e.g. SM4500 Cl G).

  The accuracy of the on-line analyzer is periodically verified/adjusted based on results from grab sample analyses.

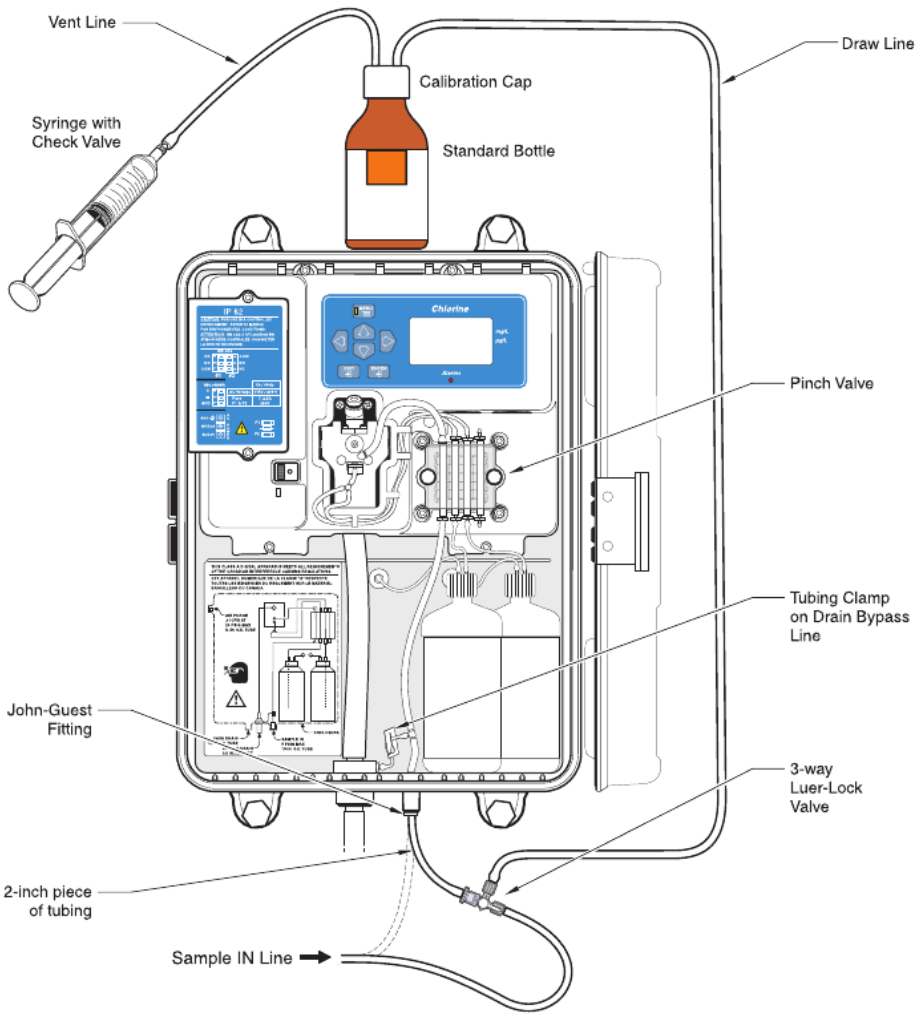
Calibrating with Aqueous Standards

The Cl-17 OLA can be re-configured to allow introduction of standard solutions.

Auxiliary plumbing and fittings would need to be installed:

- **In-let Tubing**
- **Guest Fitting**
- **3-way Valve**
- **Bypass tubing**
- **Clamps**
- **Pinch Valve**
- **Syringe with Check Valve**
- **Vent line**
- **Calibration Bottle with Modified cap**

Figure 4 Calibration/Verification Assembly Mounted on a New Style CL17



What is a Grab Sample?

* An independent measurement of other another measurement method.
* A single sample taken at a specific time. A snapshot of the water at a specific point and time, so is not representative of the entire flow.

* Typical EPA Methods require daily analysis of field blanks, reagent blanks, calibration standards, calibration check standards, second source standards or QC samples, fortified blanks, matrix spikes, duplicates etc. With each batch of samples!
* These QC samples may be useful and may be included as part of an SOP
* Not necessary when the grab sample measurement is being compared to an on-line analyzer because the comparison of the two measurements serves as a QC check.

* Method 334.0 requires Calibration Grab Sample using an approved DPD colorimetric method (SM 4500 Cl-G). The analyses of the grab samples verify the accuracy of the on-line analyzer.

Calibrating your Online Analyzer

Readings from an Online Analyzer

Are Compared to :

Readings from your Hand-Held Unit

Grab Sample Comparisons

* The online analyzer must be calibrated with a Primary Aqueous Standard (3 separate concentrations).
  * 1) Lowest standard must be ≤ 0.2 mg/L
  * 2) Standards must span concentration range expected to be observed in grab samples.
  * 3) Also prepare a Method Blank (reagent water)
* An additional Second Source Standard equal to the midpoint of the Calibration Curve is then used to verify the calibration.

Calibration Verification
EPA 334.0
Residual Chlorine

Enter data in blue spaces only. The spreadsheet will automatically calculate % Recovery and RSD.

Method No:	EPA 334.0			
SOP Revision # & Date:	EPA 334.0 Rev. 1.0 5/9/12			
Analyst/Operator	D.E. LaFara	**Signature:**		**Date:**
Matrix:	Water			
Colorimeter Manufacturer & Model:	HACH Colorimeter II	**Serial #**		
On-Line Analyzer Manufacturer & Model	HACH Cl-17	**Serial #**		
Calibration Spiking Solution Source:	HACH Volutte 63.9 ug/ml			
Lot # & Expiration date:	Lot A2096 Expires 12/31/13			
Date of Analysis:	6/2/2013			
2nd source calibration check standard:	Siemens Primary Cl Standard			
Lot # & Expiration date:	Lot 79011 Expires 3/31/13			

Enter your readings in the boxes below

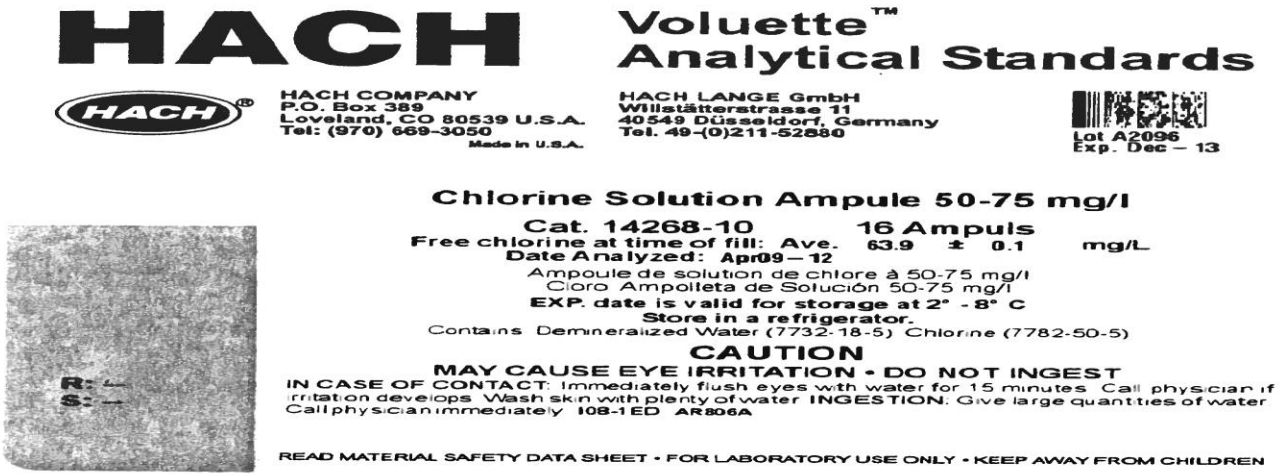
	Conc.	Units	Read 1	Read 2	Read 3	Avg	Average %Rec	Acceptance Criteria: Avg % %RSD	Recovery	%RSD
Acceptable Range 1.50 +/- 15%	1.38-1.63									
Residual Chlorine Known Value	1.50	mg/L	1.56	1.45	1.50	1.50	100.2	3.66	85-115	≤ 15

Witness; please record the following information:	Y/N	
DH_2O Blank Reading or Value	0.04 mg/L	Must be ≤ .07mg/L
Stds spiked near mid-point of the calibration curve	Y	This needs to come from a source different from the calibration standards.
Recoveries (accuracy) inside correct limits ± 15% R	Y	
Acceptable Precision ≤ 15% RSD	Y	
Witnessed by:		Date:

Why so many standards?

* Scenario: Insert mechanical scenario here similar to when your car won't start that conveys the "Right, Wrong Answer" theory. (i.e. using one standard for the calibration and one to verify the calibration).
* Or a Wine Tasting scenario such as comparing Napa Valley Wines to Sierra Foothills Wines to determine the best region for growing grapes. To do this you couldn't only compare two wines from the same winery- they would have to be separate… IDK. ☺

Purchasing Aqueous Standards- Option #1



HACH

Voluette™ Analytical Standards

HACH COMPANY
P.O. Box 389
Loveland, CO 80539 U.S.A.
Tel: (970) 669-3050
Made in U.S.A.

HACH LANGE GmbH
Willstätterstrasse 11
40549 Düsseldorf, Germany
Tel. 49-(0)211-52880

Lot A2096
Exp. Dec – 13

Chlorine Solution Ampule 50-75 mg/l

Cat. 14268-10 **16 Ampuls**
Free chlorine at time of fill: Ave. 63.9 ± 0.1 mg/L
Date Analyzed: Apr09 – 12
Ampoule de solution de chlore à 50-75 mg/l
Cloro Ampolleta de Solución 50-75 mg/l
EXP. date is valid for storage at 2° - 8° C
Store in a refrigerator.
Contains Demineralized Water (7732-18-5) Chlorine (7782-50-5)

CAUTION
MAY CAUSE EYE IRRITATION • DO NOT INGEST
IN CASE OF CONTACT: Immediately flush eyes with water for 15 minutes. Call physician if irritation develops. Wash skin with plenty of water. **INGESTION**: Give large quantities of water. Call physician immediately. **108-1ED AR806A**

READ MATERIAL SAFETY DATA SHEET • FOR LABORATORY USE ONLY • KEEP AWAY FROM CHILDREN

Purchasing Aqueous Standards- Option #1

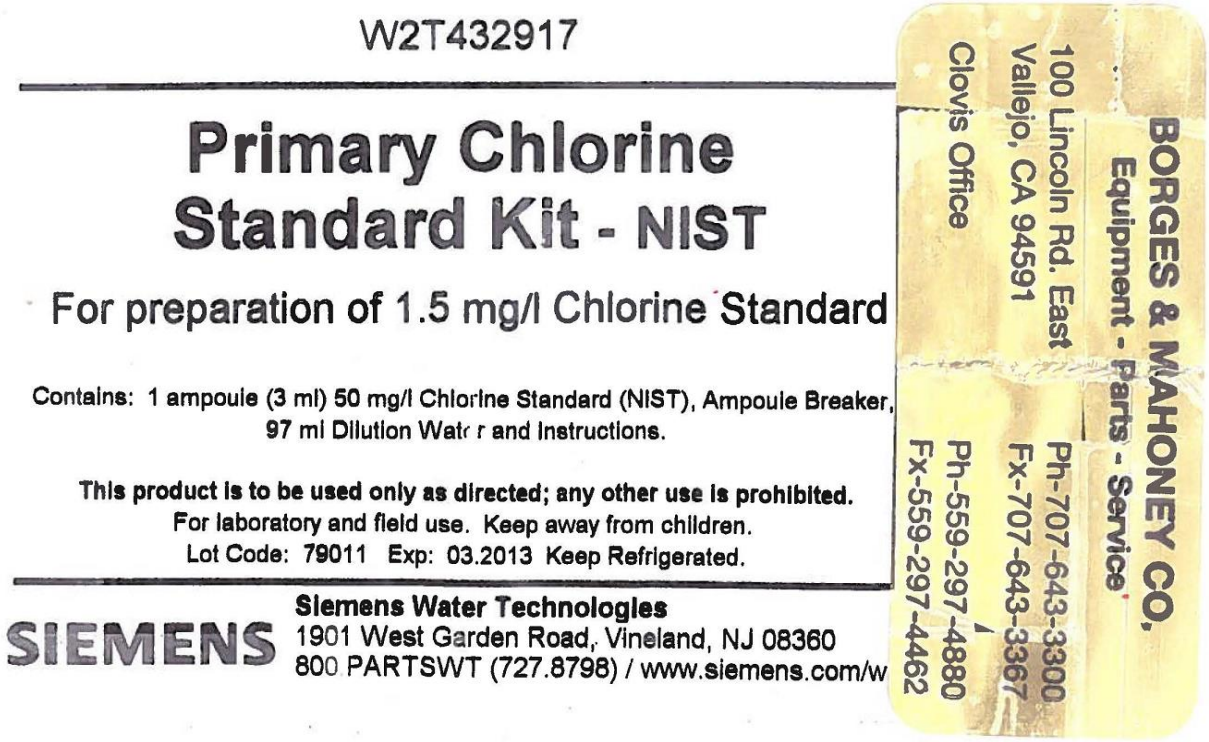
* **Example #1:**

  Hach Chlorine Standard Solution, 50-75 mg/L as Cl2, pk/16 - 10 mL Voluette Ampules (NIST) $46.35 USD

Purchasing Aqueous Standards- Option #2

* **Example #2:**

Second Source Standard-50 mg/L (ug/ml)
Siemens Primary standards kit
W2T432917 $32.94 USD



Purchasing Aqueous Standards- Option #2

INSTRUCTIONS FOR USE

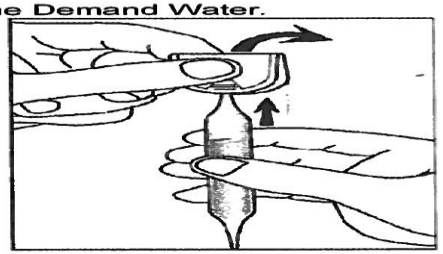
SIEMENS

Primary Reference Standard (NIST)

This self contained kit will allow preparation of a 1.5 mg/L chlorine standard without the use of additional pipettes or other glassware. Carefully follow all instructions for best results.

Procedure

1. Open the bottle containing precisely 97 mL of Zero Chlorine Demand Water.
2. While holding the double-tipped ampoule in a vertical position, snap the upper tip using the tip breaking tool (see illustration).
3. Invert the ampoule and position the open end over the bottle. Snap the upper tip and allow the contents to drain into the bottle. Tap the bottom opening of the ampoule against the neck of the bottle to transfer all of the contents to the bottle.
4. Securely Cap the bottle and invert to mix. (Do not shake) The concentration of diluted solution = 1.50 mg/L Cl_2.
5. **IMPORTANT!** Due to the inherent instability and temperature dependence of the mixed chlorine standard, use as soon as possible (within 30 minutes). Actual results can range ±15% of 1.50 mg/L Cl_2 (1.38 – 1.63 mg/L Cl_2).
6. Dispose of the empty ampoule and its tips in a safe refuse container to prevent injury.



Siemens Water Technologies
1901 West Garden Road. Vineland, NJ 08360
800.PARTSWT (727.8798) / www.siemens.com/water

Preparation of Aqueous Chlorine Standards

Equipment Needed:

64 mg/L Primary Chlorine Standard

Independent Reference Standard

10 & 25 ml Volumetric Flasks

1 & 5 ml Serological Pipettes

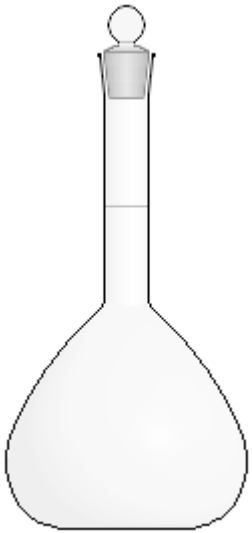
Pipette bulb or Pipette Helper

Distilled H_2O

250 ml Wash (squirt) Bottle

Preparation of Aqueous Chlorine Standards

10 & 25 ml Volumetric Flasks



1 & 5 ml Serological Pipettes

Wash (squirt) Bottle

Pipette Helper

6.4 Calibration Standard Solutions- Terminology

* **A concentrated Stock Standard solution should be purchased from a commercial source. The purchased stock standard must be traceable to NIST 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 (DH2O) to obtain calibration standard solutions in the range of 0.2 mg/L to 4.0 mg/L. Calibration standards should be prepared fresh each day unless the manufacturer's instructions specify otherwise.**

* **Terms: Stock Standard is used to prepare the Primary Standard which is used to prepare the Aqueous Standards which are the Calibration Standards**

* **A Second Source or Independent Reference Standard is used to verify the accuracy of the Calibration Standards. This is our Quality Control (QC) Check Standard**

Why can't we use Gel Standards?

Hello Don,
You must use aqueous standards. Gel (secondary) standards can't tell you anything about the chemistry of the method they can only give you information about colorimeter performance. I know that some companies are selling standards that are easy to dilute. Here's an example from one manufacturer and there are probably others. Note that even though the meter is certified as pre-calibrated you STILL NEED TO CHECK THE CALIBRATION WITH AN AQUEOUS STANDARD.

Steven C. Wendelken Ph.D.
U.S. EPA, OGWDW-TSC
26 W. Martin Luther King Dr.
Cincinnati, Ohio 45268
Phone: (513) 569-7491
Fax: (513) 569-7191
wendelken.steve@epa.gov

IDC for Method 334.0- Same Chemistry

* If the on-line analyzer utilizes the same chemistry as the hand held unit (i.e. DPD) an IDC must be performed.
* The IDC requires five readings, not four.
* Must be performed with the 2nd source standard so you are verifying the calibration with a source other than the one you calibrated with.

Initial Demonstration of Capability
EPA 334.0
Residual Chlorine

Enter data in blue spaces only. The spreadsheet will automatically calculate % Recovery and RSD.

Method No:	EPA 334.0
SOP Revision # & Date:	EPA 334.0 Rev. 1.0 5/9/12
Analyst/Operator	D.E. LaFara
Signature:	Dor LaFara
Date:	6/2/12
Matrix:	Water
Colorimeter Manufacturer & Model:	HACH Colorimeter II
Serial #	
On-Line Analyzer Manufacturer & Model	HACH Cl-17
Serial #	
Calibration Spiking Solution Source:	HACH Volutte 63.9 ug/ml
Lot # & Expiration date:	Lot A2096 Expires 12/31/13
Date of Analysis:	6/2/2013
2nd source calibration check standard:	Siemens Primary Cl Standard
Lot # & Expiration date:	Lot 79011 Expires 3/31/13

Enter your readings in the boxes below

	Conc.	Units	Read 1	Read 2	Read 3	Read 4	Read 5	Avg	Average %Rec	Acceptance Criteria Avg % %RSD	Recovery	%RSD
Acceptable Range 1.50 +/- 15%	1.38-1.63											
Residual Chlorine Known Value	1.50	mg/L	1.56	1.45	1.63	1.55	1.50	1.54	102.5	4.40	85-115	≤ 15

Witness; please record the following information: Y/N

DH_2O Blank Reading or Value	0.04	mg/L Must be ≤ .07mg/L
Stds spiked near mid-point of the calibration curve	Y	This needs to come from a source different from the calibration standards.
Recoveries (accuracy) inside correct limits ± 15% R	Y	
Acceptable Precision ≤ 15% RSD	Y	

Witnessed by: Ibegood Water Date: 6/2/12

IDC for Method 334.0- Different Chemistry

* If the on-line analyzer utilizes a different chemistry from the hand-held unit (i.e. amperometric) the IDC is slightly different.
* It consists of 14 consecutive business days of comparing grab samples on the hand-held to the on-line analyzer.
* Still have to perform the daily CVS with the gel standards.

Can I use it now?

* Section 10.2.3: Upon successful completion of the IDC, the analyzer can be put into service for compliance monitoring.
* Section 10.2.4: A routine schedule for grab sample comparisons should then been established. Minimum per the DBP Rule is once every 5 days. (Method 334.0 says 7, therefore the Rule trumps the Method)

Quarterly Calibration Verification

* If the calibration of the on-line analyzer is adjusted or a minimum of once Quarterly the calibration must be checked
* Utilize the Second Source and prepare an aqueous standard equal to the expected concentration of your chlorine residual.
* Read standard on hand-held and reading must be w/in 15% of expected value.
* Run a grab sample from on-line analyzer outfall on hand-held. Value must be w/in 0.1 ppm of on-line reading.

Purchased Stock Chlorine Standard 63.9mg/L

PPM = 1 minute in 2 Years PPB = 1 minute in 32 years PPT = 3 seconds in 100,000 years

64mg/L = 64 PPM = 64ug/ml = 64 PPM = 64ng/ul = 64 PPM

There are several ways to express parts per million, for the ease of calculation, we will use ug/ml.

Calculations:

From the Stock Standard, Prepare a Primary Dilution Standard @ 10.22ug/ml Cl

To prepare the Primary Standard: Use the Squirt Bottle and add 5-10 ml of DH2O to the 25ml volumetric flask

Use the 5 ml Serological Pipette and transfer 4ml of the 63.9ug/ml Stock Standard and dilute to 25ml with DH_20 = 10.22ug/ml

Where: $\frac{(4\ ml)(63.9\ ug/ml)}{25ml} = 10.22ug/ml$

Serial Dilutions

Using the 10.22ug/ml Primary Standard you just prepared; Prepare Calibration Standards @ approximately 0.2; 1.0; 2.0; and 4.0 ug/ml

Prepare them one at time using the same glassware, have labeled plastic or glass containers ready to store the prepared Calibration Standards. Rinse glassware between preparations with DH20.

Using the formula $\frac{(xml)(10ug/ml)}{10ml} = 4.0ug/ml$

Where: 4 X 10 = 40/10 = 4

Using the 5 ml Pipette;

Pipet 4 ml of the 10.22 ug/ml Primary Dilution Standard and dilute to 10 ml with DH_20 = 4.08 ug/ml

Pipet 2 ml of the 10.22 ug/ml Primary Standard and dilute to 10 ml with DH_20 = 2.04 ug/ml

Using the 1 ml Pipette;

Pipet 1 ml of the 10.22 ug/ml Primary Standard and dilute to 10 ml with DH_20 = 1.02 ug/ml

Pipet 0.2 ml of the 10.22 ug/ml Primary Standard and dilute to 10 ml with DH_20 = 0.20 ug/ml

Using a bound paginated notebook document your Standard Preparation(s)
Primary (64ug/ml) Standard Info.
Include: Manufacturer & Part #
Concentration
Lot #
Date Received
Date Opened
Expiration Date

Include the Dilution Information: Primary Dilution Standard

Pipette 4ml of the 64ug/ml Primary Standard and dilute to 25ml with DH_20 = 10.2 ug/ml

Where: $\frac{(2\text{ ml})(50\text{ ug/ml})}{10\text{ml}}$ **= 10 ug/ml**

Include the Dilution Information: Calibration Standards

Pipet 4 ml of the 10 ug/ml Intermediate Standard and dilute to 10 ml with DH_20 = 4.0 ug/ml
Pipet 2 ml of the 10 ug/ml Intermediate Standard and dilute to 10 ml with DH_20 = 2.0 ug/ml
Pipet 1 ml of the 10 ug/ml Intermediate Standard and dilute to 10 ml with DH_20 = 1.0 ug/ml
Pipet 0.2 ml of the 10 ug/ml Intermediate Standard and dilute to 10 ml with DH_20 = 0.2 ug/ml

Prepared 4/10/12

by _____ DOB_____ SSN_____ Allergies_____

An alternative to keeping a *Standard Preparation Logbook* and writing the recipe each time a standard is prepared, you can put the preparation directions in the SOP. You will still need to document;

What was prepared and from what (Stock Std Information)
Date Prepared
Lot Numbers (Stock Std & DH2O)
Expiration Date(s)
Prepared by

As long as the standards are prepared the same way every time you can reference the SOP e.g.;

A 10ug/ml Primary Cl Std was prepared from the 63.9ug/ml Stock Cl Std Lot # A2096 per page 7 of the 334.0 SOP Rev. 001 (June 1, 2012). Calibration Stds @ 0.2, 1.0, 2.0 & 4.0ug/ml are prepared per page 8 of the 334.0 SOP.

For the data generated with these standards to be legally defensible, the Std prep must be traceable and reconstructable. This is accomplished with complete and thorough documentation.

I strongly recommend using a Standards Prep. Logbook.

Legal Defensibility

Use indelible blue ink. Blue ink is a fraud deterrent.

Never use whiteout or obliterate mistakes.

Draw a single line through the mistake
~~15ml(500ug/ml)~~ DEL 6/3/12 Initial and Date the correction
1.5ml(50ug/ml) Re-enter the correct information

Avoid blank pages. If a page is left blank note on the page
"This page intentionally left blank"

If using pre-printed forms avoid blank spaces. Line out or write NA.

CHLORINE METER CALIBRATION LOG

Date	Time	Initials	Meter #	Blank (mg/L)	STD 1 (mg/L)	STD 2 (mg/L)	STD 3 (mg/L)
6-1-12	0615	[R]	12120	.05	.24	.52	1.56
6-2-12	0610	[R]	12120	.03	.28 ~~.56~~	.56	1.60
		White Out			Obliteration		
6-1-12	0615	[D]	12/20	[R] .5 6-1-12	~~.56~~ 6-1-12 [R] .28	.56	1.56
NA	NA	NA	NA		NA	NA	NA
6-2-12	0610	[R]	12120	.03	.28	.56	1.60
W	E	E	K	—	E	N	D
6-5-12	0600	[R]	12120	.02	.25	.54	1.55
NOTHING			ELSE	FOLLOWS		NA	NA
6-5-12	0815	[R]	Prepared 1.5 ppm Cl Std. for 2nd source std. 3ml (50ug/ml) ⇒ 100ml DH2O = 1.5 ug/ml STOCK STD - SIEMENS LOT # 7901I Exp. 3/31/13 SIEMENS ZERO CHLORINE H2O LOT # L02A Exp. 2/28/14				

D. LaTour 6/5/12

SUPERVISOR SIGNATURE: DATE:

QA SIGNATURE: DATE:

Questions?

Contact Info:

* Andrea Seifert, (775) 687-9526, aseifert@ndep.nv.gov
* Reginald Lang, (775) 687-9528, rlang@ndep.nv.gov
* Don LaFara, (775) 687-9491, dlafara@ndep.nv.gov