Total Residual Chlorine Testing Methods

For: Northern Michigan Wastewater Operators Seminar
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Regional Sales Manager – Michigan
Outline

• Regulatory Criteria and Definitions
• Some Options for Ultra-Low Range (ULR) Total Residual Chlorine (TRC) Testing
  ➢ Colorimetric
  ➢ Amperometric
  ➢ Ion Selective Electrode
• Lab Practice Reminders
Issue: Measurement Uncertainty

• Is my reading right?
• Am I using the correct method, instrument?
• Am I in compliance?
• Will my lab results hold up if questioned?
Regulatory Criteria

• Most Michigan NPDES Discharge Permits for Total Residual Chlorine (TRC) to Surface Waters have a limit of **0.038 mg/L or 38 ppb**

• Per MDEQ, testing **method & instrument** must be:
  1. NPDES-Permit compliant for Wastewater
  2. Appropriately accurate and sensitive
  3. Verifiable with proper QA/QC procedures
Definitions

• **Limit of Detection (LOD)** – the lowest concentration that can be determined to be statistically different from a blank with 99% confidence. LOD’s are matrix, method, and analyte specific.

• **Limit of Quantification (LOQ)** – the level above which quantitative results may be obtained at a specified degree of confidence; mathematically equal to 10 x the Standard Deviation of the results for a series of replicates used to determine a justifiable LOD.
Definitions, cont’d.

- **Method Detection Limit (MDL)** – the minimum concentration measured with 99% confidence that an analyte is greater than zero; are matrix, instrument, and analyst specific and require well defined analytical methods.
  - Used to judge the significance of a single measurement of a future sample.
  - Determined by testing a minimum of seven (7) aliquots of the sample.
  - Calculated from the Standard Deviation of the replicate measurements.
Definitions, cont’d.

• **Instrument Detection Limit (IDL)** – the concentration equivalent to a signal, due to the analyte of interest, which is the smallest signal distinguished from background noise by a particular instrument.

• Refer to USEPA Method Detection Limit procedure in Title 40 CFR Part 136, Appendix B, revision 1.11)

• When in doubt, discuss with your local MDEQ contact
Practically Speaking

- **Precision**: How reproducible are the measurements?

- **Accuracy**: How close are the measurements to the true value.
Repeatedly Hitting the Target

- Low accuracy, Low precision
- Low accuracy, High precision
- High accuracy, Low precision
- High accuracy, High precision
Options for Chlorine Measurement

- Ultra-Low Range (ULR) Colorimetric Methods
- Ultra-Low Range (ULR) Amperometric Titration Methods
- Ultra-Low Range (ULR) Ion Selective Electrode Methods
**Colorimetric Method**

**Estimated Level of Detection**

**Chlorine Total**

USEPA DPD Method\(^1\)

2 to 500 µg/L Cl\(_2\)

**Pour-Thru Cell and OriFlo™ Filtration**

**Scope and application:** For testing trace levels of chlorine and chloramines in treated domestic and industrial wastewater. USEPA accepted for reporting in wastewater analysis. This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.

\(^1\) USEPA accepted for reporting in wastewater analysis. Adapted from *Standard Methods for the Examination of Water and Wastewater.*

**Table 1 Instrument-specific information**

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Sample cell orientation</th>
<th>Pour-Thru Kit</th>
<th>Adapter</th>
</tr>
</thead>
<tbody>
<tr>
<td>DR 6000</td>
<td>The flow path is to the right.</td>
<td>LQV157.99.200002</td>
<td>—</td>
</tr>
<tr>
<td>DR 3800</td>
<td></td>
<td>5940400</td>
<td>LZV585 (B)</td>
</tr>
<tr>
<td>DR 2800</td>
<td></td>
<td>5940400</td>
<td>LZV585 (B)</td>
</tr>
<tr>
<td>DR 2700</td>
<td></td>
<td>5940400</td>
<td>LZV585 (B)</td>
</tr>
<tr>
<td>DR 1900</td>
<td></td>
<td>LZV899</td>
<td>—</td>
</tr>
<tr>
<td>DR 5000</td>
<td>The flow path is toward the user.</td>
<td>LQV479</td>
<td>—</td>
</tr>
<tr>
<td>DR 3900</td>
<td></td>
<td>LQV157.99.100002</td>
<td>—</td>
</tr>
</tbody>
</table>
Colorimetric Method, cont’d.

- Measured on Spectrophotometer
- Methods are pre-programmed
- Uses liquid DPD buffer & indicator solutions
- Uses Pour-Thru Cell & 3-micron filter – following DPD reaction
Colorimetric Method, cont’d.

1. Start program 86 Chlorine Total, ULR. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.

   Note: Although the program name can be different between instruments, the program number does not change.

2. Flush the Pour-Thru Cell with at least 50-mL of deionized water.

3. Remove the cap from the OriFlo plunger assembly. Make sure that the O-ring is seated correctly in the cap.

4. Install a new, 3-micron filter (white) into the cap recess. Wet the filter with drops of deionized water. Reassemble and hand-tighten the cap onto the plunger.

5. Open one ampule of ULR Chlorine Buffer Solution.

6. Use a TenSette Pipet with a clean tip to add 1 mL of buffer from the ampule to a clean and prepared 50-mL mixing cylinder.

7. Open one ampule of DPD Indicator Solution for Ultra Low Range Chlorine.

8. Use a TenSette Pipet with a clean tip to add 1 mL of indicator from the ampule to the same mixing cylinder.
9. Swirl to mix. Continue to the next step within 1 minute.

10. Prepared Sample: Prevent extra agitation while carefully filling the cylinder to the 50-mL mark with sample.

11. Put the stopper on the mixing cylinder. Carefully invert the mixing cylinder twice to mix.

12. Start the instrument timer. A 3-minute reaction time starts. Complete steps 13–18 during this period. Measure the reacted sample 3–6 minutes after mixing the sample and reagents.

13. Push the valve button on the OriFlo barrel assembly in (“closed” position). Put the barrel assembly into its stand.

14. Pour approximately 50 mL of the original sample into the barrel. The lower ring on the barrel assembly shows about a 50-mL volume.

15. Insert the plunger into the barrel and slowly push the plunger down with even pressure until the plunger is fully seated.

16. Pour the filtered, unreacted sample from the plunger reservoir into the Pour-Thru Cell.
Colorimetric Method, cont’d.

17. When the flow stops, push ZERO. The display shows 0 µg/L Cl₂.

18. Pull the barrel valve button out to the "open" position. Pull the plunger up to separate it from the barrel assembly. Discard the remaining unfiltered sample. A new membrane may be necessary for very turbid samples. Alternatively, use a second Quick Filter unit with a new membrane filter installed.

19. Push the barrel valve button to the "closed" position. Put the barrel assembly into its stand.

20. When the timer expires, pour the contents of the mixing cylinder into the barrel.

21. Insert the plunger into the barrel and slowly push the plunger down with even pressure, until the plunger is fully seated.

22. Pour the filtered, reacted sample from the plunger reservoir into the Pour-Thru Cell.

23. When the flow stops, push READ. Results show in µg/L Cl₂. If the sample contains a dechlorinating agent (e.g., sulfite or sulfur dioxide), the sample result (corrected for the reagent blank) will read "0" or a slightly negative value.

24. Flush the Pour-Thru Cell with at least 50-mL of deionized water immediately after use.
Colorimetric Method, cont’d.

Determine the blank value

1. Start program 86 Chlorine Total, ULR. For information about sample cells, adapters or light shields, refer to Instrument-specific information on page 1.

   **Note:** Although the program name can be different between instruments, the program number does not change.

2. Flush the Pour-Thru Cell with at least 50-mL of deionized water.

3. Collect approximately 100 mL of deionized or tap water in a clean, 250-mL beaker.

4. Use a TenSette Pipet to add 1.0 mL of Blanking Reagent to the beaker. Swirl to mix. The Blanking Reagent removes chlorine and chloramines from the water.

   **Note:** Use this solution in step 11.
5. Start a timer for 5 minutes.

6. Open one ampule of ULR Chlorine Buffer Solution.

7. Use a TenSette Pipet with a clean tip to add 1 mL of buffer from the ampule to a clean and prepared 50-mL mixing cylinder.

8. Open one ampule of DPD Indicator Solution for Ultra Low Range Chlorine.

9. Use a TenSette Pipet with a clean tip to add 1 mL of indicator from the ampule to the same mixing cylinder.

10. Swirl to mix. Continue to the next step within 1 minute.

11. Fill the cylinder to the 50-mL mark with dechlorinated water from step 4. Keep the remaining dechlorinated water for step 14.

12. Put the stopper on the mixing cylinder. Invert the mixing cylinder two times to mix.
13. Start the instrument timer. A 3-minute reaction time starts.

14. During the reaction period, flush the Pour-Thru Cell with the remaining dechlorinated water from step 4.

15. When the flow stops, push ZERO. The display shows 0 μg/L Cl₂.

16. When the timer expires, pour the contents of the cylinder into the Pour-Thru Cell.

17. Push READ. Results show in μg/L Cl₂.

18. Subtract this value from the sample results received in this procedure. Refer to the instrument documentation for more information on blank adjustment.

19. Flush the Pour-Thru Cell with at least 50-mL of deionized water immediately after use.
### Consumables and replacement items

#### Required reagents

<table>
<thead>
<tr>
<th>Description</th>
<th>Quantity/test</th>
<th>Unit</th>
<th>Item no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ULR Chlorine Reagent Set (approximately 20 tests), includes:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ULR Chlorine Buffer Solution, 1.5-mL ampules</td>
<td>1 mL</td>
<td>20/pkg</td>
<td>2493120</td>
</tr>
<tr>
<td>DPD Indicator Solution for ULR Chlorine, 1.5-mL ampules</td>
<td>1 mL</td>
<td>20/pkg</td>
<td>2493220</td>
</tr>
<tr>
<td>Blanking Reagent for ULR Chlorine</td>
<td>1 mL</td>
<td>29 mL</td>
<td>2493023</td>
</tr>
</tbody>
</table>

#### Required apparatus

<table>
<thead>
<tr>
<th>Description</th>
<th>Quantity/test</th>
<th>Unit</th>
<th>Item no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ULR Chlorine Apparatus Set, includes:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Filter, membrane, 25-mm, 3-micron</td>
<td>1</td>
<td>25/pkg</td>
<td>2594025</td>
</tr>
<tr>
<td>OniFlo™ Assembly</td>
<td>1</td>
<td>each</td>
<td>4966000</td>
</tr>
<tr>
<td>PourRite® Ampule breaker</td>
<td>1</td>
<td>each</td>
<td>2484600</td>
</tr>
<tr>
<td>Beaker, 250-mL</td>
<td>1</td>
<td>each</td>
<td>50046H</td>
</tr>
<tr>
<td>Mixing cylinder, graduated, 50-mL, with glass stopper</td>
<td>1</td>
<td>each</td>
<td>189641</td>
</tr>
<tr>
<td>Pipet, TenSette®, 0.1–1.0 mL</td>
<td>1</td>
<td>each</td>
<td>1970001</td>
</tr>
<tr>
<td>Pipet Tips, for TenSette® Pipet, 0.1–1.0 mL</td>
<td>2</td>
<td>50/pkg</td>
<td>2185696</td>
</tr>
</tbody>
</table>
## Colorimetric Method, cont’d.

### Interferences

<table>
<thead>
<tr>
<th>Interfering substance</th>
<th>Interference level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bromine, Br₂</td>
<td>Interferes at all levels.</td>
</tr>
<tr>
<td>Chlorine Dioxide, ClO₂</td>
<td>Interferes at all levels.</td>
</tr>
<tr>
<td>Chloramines, organic</td>
<td>Can interfere.</td>
</tr>
<tr>
<td>Copper, Cu²⁺</td>
<td>More than 1000 µg/L.</td>
</tr>
<tr>
<td>Iodine, I₂</td>
<td>Interferes at all levels.</td>
</tr>
<tr>
<td>Iron (Fe³⁺)</td>
<td>More than 1000 µg/L.</td>
</tr>
<tr>
<td>Manganese, oxidized (Mn⁴⁺, Mn⁷⁺) or Chromium, oxidized (Cr³⁺)</td>
<td>1. Adjust sample pH to 6-7 with 1.000 N Sulfuric Acid. 2. Add 9 drops Potassium Iodide (30 g/L) to an 80-mL sample. 3. Mix and wait 1 minute. 4. Add 9 drops of Sodium Arsenite¹ (5 g/L) and mix. 5. Analyze the treated sample as described in the procedure above. 6. Subtract the result of this test from the original analysis to obtain the correct concentration.</td>
</tr>
<tr>
<td>Nitrite, NO₂⁻ (uncommon in clean waters)</td>
<td>mg/L nitrite</td>
</tr>
<tr>
<td>2.0 mg/L</td>
<td>3 µg/L</td>
</tr>
<tr>
<td>5.0 mg/L</td>
<td>5 µg/L</td>
</tr>
<tr>
<td>10.0 mg/L</td>
<td>7 µg/L</td>
</tr>
<tr>
<td>15.0 mg/L</td>
<td>16 µg/L</td>
</tr>
<tr>
<td>20.0 mg/L</td>
<td>18 µg/L</td>
</tr>
<tr>
<td>Ozone</td>
<td>Interferes at all levels.</td>
</tr>
<tr>
<td>Peroxides</td>
<td>Can interfere.</td>
</tr>
<tr>
<td>Extreme sample pH or highly buffered samples</td>
<td>Adjust to pH 6–7.</td>
</tr>
</tbody>
</table>

¹ Samples that are treated with sodium arsenite will contain arsenic and may require special disposal consideration. Refer to the current MSDS/SDS for safe handling and disposal instructions.
Colorimetric Method, cont’d.

- Reproducible optics of Pour-Thru Cell yield more stable readings
- Sample color is compensated by zeroing
- Reagents are packaged in ampules & sealed under argon gas for stability
- Reagents Blank values are subtracted from sample readings
- Measurement wavelength is 515 nm
Colorimetric Method, cont’d.

• Perform analysis on Standard Solution within the Method range; 0.040 mg/L, for example
• WW samples must be tested ASAP
• Ensure glassware is chlorine-demand free
• Tubing and Cell must be very clean; use 5.25 N Sulfuric Acid
• Do NOT skip, improvise method steps!
Colorimetric Method, cont’d.

- If the Spectrophotometer used does not have direct read-out, a \( \text{Abs} \) vs. Concentration curve may need to be generated.
Amperometric Method

Total Chlorine

Based on 4500-CI D in Standard Methods for the Examination of Water and Wastewater

Amperometric Forward Titration
0.003 – 5.00 mg/L as Cl₂

1. Introduction

This application note follows method number 4500-CI D in “Standard Methods for the Examination of Water and Wastewater” (20th Edition).

The scope of this application note is to determine the total chlorine concentration (= Free Chlorine Conc. + Combined Chlorine Conc.) in water or wastewater samples.

Total chlorine corresponds to the chlorine derived from all its possible forms in solution including free elemental chlorine (Cl₂), hypochlorous acid (HOCl), hypochlorite (OCl⁻) ion, and chloramines (NH₂Cl, NHCl₂, etc.) among other types.

Two applications for total chlorine determination are available with a different increment size to increase accuracy and reduce titration time:

- **High range**: for a sample concentration between 0.05 and 5 mg/L
- **Low range**: for a sample concentration between 0.003 and 0.08 mg/L
Amperometric Method, cont’d.

- Forward Titration
- Uses Phenylarsine Oxide (PAO) Titrant
- Acetate pH 4 Buffer
- Potassium Iodide (KI)
- Platinum Redox Probe
- Results are highly accurate
Amperometric Method, cont’d.

- Volume of titrant used corresponds to the concentration of chlorine present; Equivalent Point
- Can also use Backward Titration Method with Iodine as Titrant
- Can use Backward Titration to measure Bisulfite concentration
Amperometric Method, cont’d.

Forward Titration

Backward Titration

Titration curve: Current [µA] vs. volume of titrant [mL]:

- Left graph: Current [µA] vs. Titrant (PAO) volume [mL]
- Right graph: Current [µA] vs. Titrant volume I2 [mL]
• Limit of Detection = 10 ppb
• Uses Potassium Iodate for calibration solution
• Uses Iodide & Acid reagents
• Chlorine reacts with iodide to form iodine, which is measured with probe
Ion Selective Electrode (ISE) Probe, cont’d.

- Electrode response is non-linear at low levels
- Ferric interference can occur
What About Method 8167?

Chlorine, Total

USEPA DPD Method

0.02 to 2.00 mg/L Cl₂

Scope and application: For testing residual chlorine and chloramines in water, wastewater, estuary water and seawater; USEPA-accepted for reporting for drinking and wastewater analyses. This product has not been evaluated to test for chlorine and chloramines in medical applications in the United States.

1 Adapted from Standard Methods for the Examination of Water and Wastewater.
2 Procedure is equivalent to USEPA and Standard Method 4500-CI G for drinking water and wastewater analysis.

Estimated Level of Detection
What About Method 8167, cont’d.

- Not recommended because –
  1. Resolution – Hach Method 8167/Program #80 yields only two (2) decimal places
  2. Interference – DPD in powder form can produce turbidity interference
  3. Level of Detection – 20 ppb; repeatability 3X LOD or 60 ppb; >38 ppb Discharge Limit
Lab Practice Reminders

• Always run a Standard first to ensure your instrument and reagents are reliable
• Don’t use reagents past their expiration dates
• Run at least one reagent blank per lot
• Glassware cleanliness is very important
• Don’t use your finger/thumb as a stopper
• Follow your QA/QC procedures
• Clearly document your results; reflect proper units
“Bummer of a birthmark, Hal”
Questions?

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