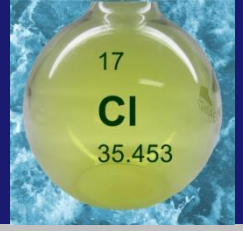
Chlorine Analyzers

Free and Total Chlorine Residual (Amperometric)

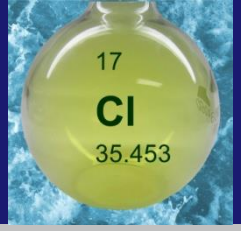
Presented by:

Electro-Chemical Devices



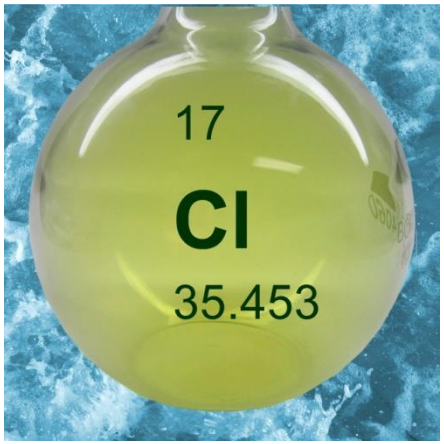
Introduction to Chlorine

- Chlorine, Cl_2, is a Diatomic Gaseous Element
- It is a strong oxidizer (wants electrons)
- The High Oxidation Potential makes it an efficient Sanitizer and Disinfectant.
- When combined with water it hydrolyzes to form hypochlorous acid and hypochlorite ion, depending on the pH.
  - HOCl
  - OCl^-



What is Free Chlorine?

- Free Chlorine is the sum of the Hypochlorous acid and Hypochlorite ions in the sample.
- Hypochlorous acid, HOCl, is the dominant species in solutions with the pH below 7.5 pH
- Hypochlorite ion, OCl^-, is the dominant species in solutions with the pH above 7.5 pH
- Free Chlorine is typically a measurement of the chlorinating strength of the solution, a process control parameter.



What is Total Chlorine?

- Total Chlorine is defined as the sum of the Free Chlorine and Combined Chlorine in the sample.
- Combined Chlorine is formed by the reaction of Free Chlorine with Organic Compounds, Ammonia or other nitrogen compounds.
- Two of the most common forms of Combined Chlorine are Monochloroamine (MCA) Dichloroamine (DCA)
- Total Chlorine is typically a regulatory measurement in wastewater to satisfy discharge requirements.

How is Chlorine Measured?

- DPD Method (N, N-diethyl-p-phenylenediamine sulfate)
- One of the most widely used testing methods for Free and Total Chlorine
- Forms a pink color with an intensity proportional to the chlorine concentration
- The testing can be automated or handheld measuring the intensity of the color formed
- FAS-DPD testing (pink to clear with addition of thiosulfate drops)
- DPD is not specific for chlorine it responds to most oxidizers

How is Chlorine Measured?

- Colorimetric Systems Advantages:
  - High pH is not a limiting Factor.
  - EPA Approved DPD Method
- Colorimetric System Disadvantages:
  - Uses Reagents
  - Must use pumps valves, and small tubing
  - Can only generate a new chlorine reading every 2.5 minutes
  - High Maintenance

How is Chlorine Measured?

- Amperometric and Polarographic Analyzers
  - Measure current between two polarized electrodes
  - No Reagents are needed
- Complete system should consist of the following
  1. Flow control (Constant Head Flow Controller)
  2. pH Sensor in Flow Cell with sample port
  3. Chlorine Sensor in Flow Cell
  4. Analyzer
  5. Spray Cleaner solenoid (optional)

How is Chlorine Measured?

- Amperometric and Polarographic Analyzers Advantages:
  - Ease of use
  - Low maintenance
  - No reagents
  - Flow control
  - pH compensation

How do they Work? (FC)

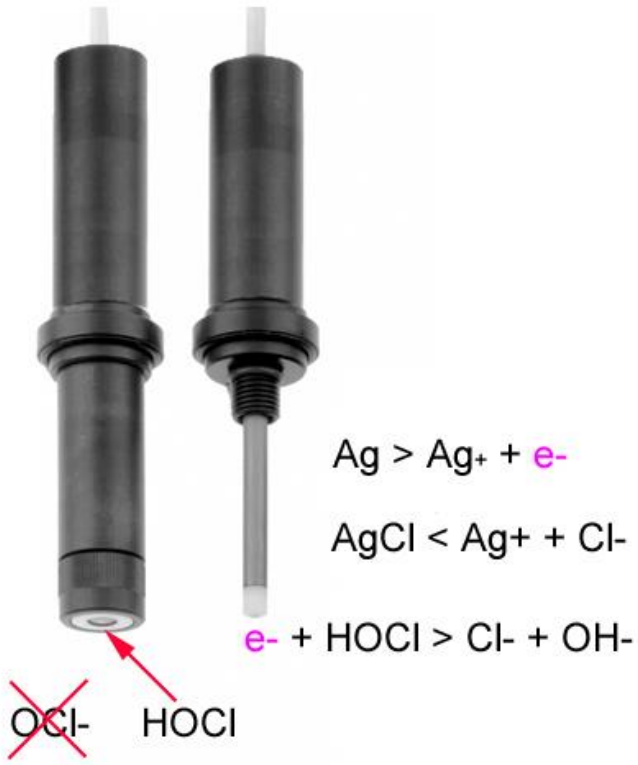
- The instrument applies a fixed voltage between the anode and cathode.
- This polarization voltage generates a polarization current in the sensor
- The current consumes all oxidants in the sensor and the sensor stabilizes at the “zero point current.”
- The initial polarization takes about 30-60 minutes.
- The Chlorine sensor is then ready to use.

Free Chlorine Sensors

- Polarographic Design
  - Gold Cathode
  - Silver-Silver Chloride Anode
  - The Cathode/Anode are Externally polarized by the Analyzer
- Replaceable rugged Teflon Membrane
  - Allows only uncharged molecules to pass through
  - No salts or other ions
- Refillable Electrolyte
  - Typically Potassium Chloride
- Outer body PVC or similar plastic

Free Chlorine Sensors

- The Polarization voltage oxidizes silver from the anode freeing up electrons for the cathode.
- Hypochlorous acid, HOCl, diffuses through the membrane and is reduced (gains electrons) at the cathode to form chloride.
- The added chloride facilitates more silver dissolving, freeing up more electrons.
- The current flow is proportional to the Free Chlorine concentration.

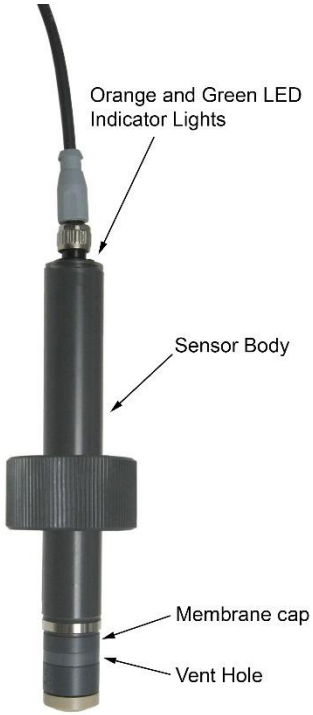


How do they Work? (TC)

- The instrument applies a fixed voltage across the sensor referenced to the 316SS counter electrode.
- This polarization voltage generates a polarization current in the sensor.
- The current consumes all oxidants in the sensor and the sensor stabilizes at the “zero point current.”
- The initial polarization takes about 60 minutes.
- The Chlorine sensor is now ready to use.

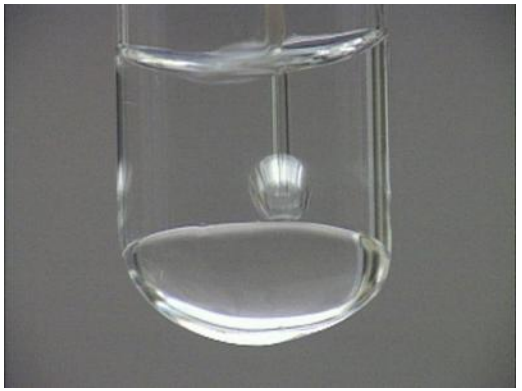
Total Chlorine Sensor

- Amperometric Design
  - Externally polarized by the analyzer
  - Gold Cathode
  - Silver-Silver Halide Anode
  - 316 SS Counter Electrode
  - Digital communication
- Replaceable Micro Porous Teflon Membrane
- Refillable Potassium Iodide Gel Electrolyte
- PVC outer body

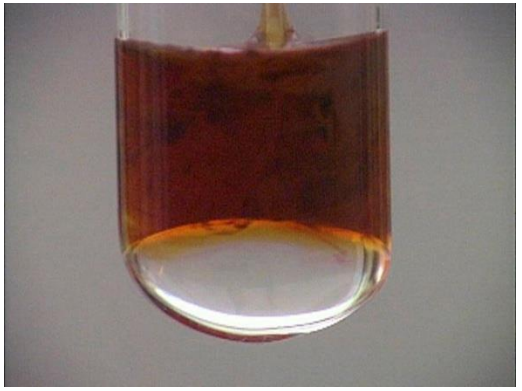


Total Chlorine Sensors

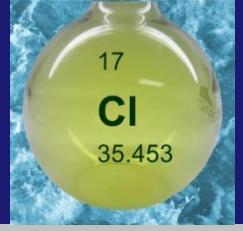
- The Micro Porous membrane allows all oxidizers to pass through.
- When an oxidizer diffuses through the membrane it oxidizes the iodide to iodine, reducing the Chlorine compound to Chloride
- Iodine is then reduced at the cathode back to iodide.
- Silver is oxidized off the anode in response to the chloride and iodide ions.
- The current flow from the oxidation and reduction reactions is proportional to the Total Chlorine concentration.



Potassium Iodide (KI)



KI plus Chlorine yields Iodine

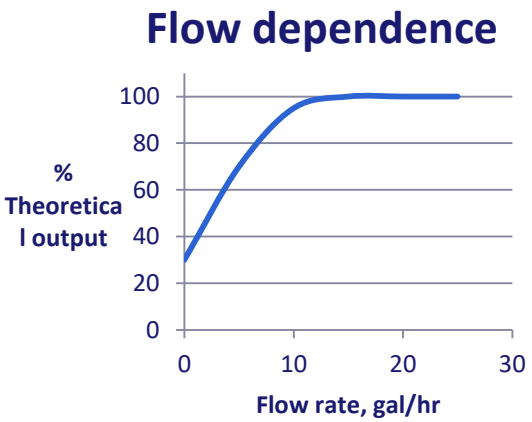


Measurement Influences:

- Flow Sensitivity
- pH
- Temperature
- Coatings

Measurement Influences: Flow

- Flow Sensitivity
  - The Chlorine sensors consume chlorine depleting the area around the sensing tip
  - Flow replenishes the chlorine supply
  - Constant flow is required for a stable measurement
  - Low flow = Low reading
  - Chlorine readings are unchanged with flow rates above 0.5 ft./sec

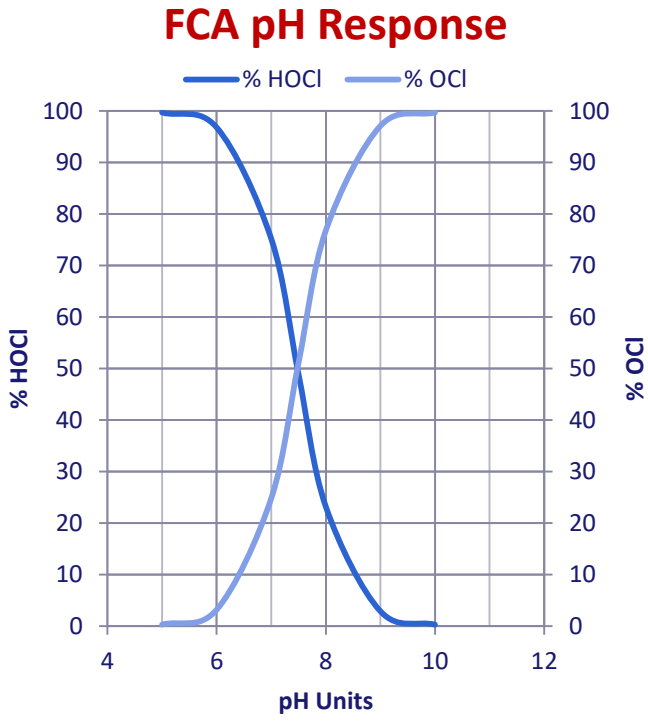


Constant Head Flow Controller

- The Constant Head Flow Controller (CHFC) eliminates the need for Pressure Regulators and Rotameters to control the flow by the sensor.
  - CHFC has ¼” ports
  - No small orifices to clog
- The unique overflow design maintains a constant flow at the sensor with incoming variations between 8 and 80 gal/hr.

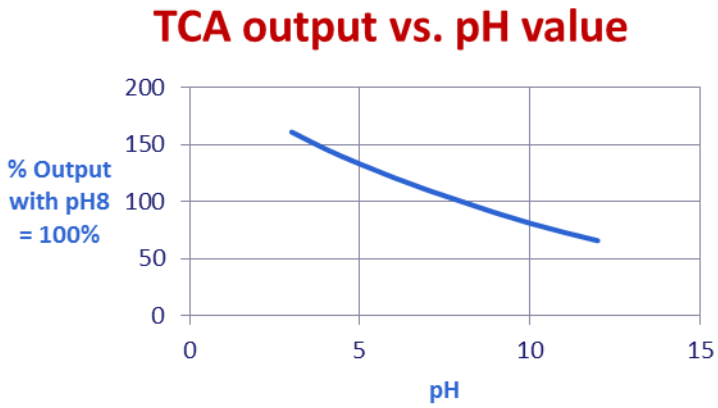
Influences: pH Free Chlorine

- Only HOCl is directly measured by the Free Chlorine sensor
- The Teflon membrane allows only neutrally charged molecules to pass through it.
  - HOCl is neutral and will pass the membrane.
  - OCl^- is charged and won't pass.
- OCl^- is calculated by the T80 analyzer using the pH value and the dissociation curve for chlorine.
- The sum of the two species is reported as the Free Chlorine concentration.



Influences: pH Total Chlorine

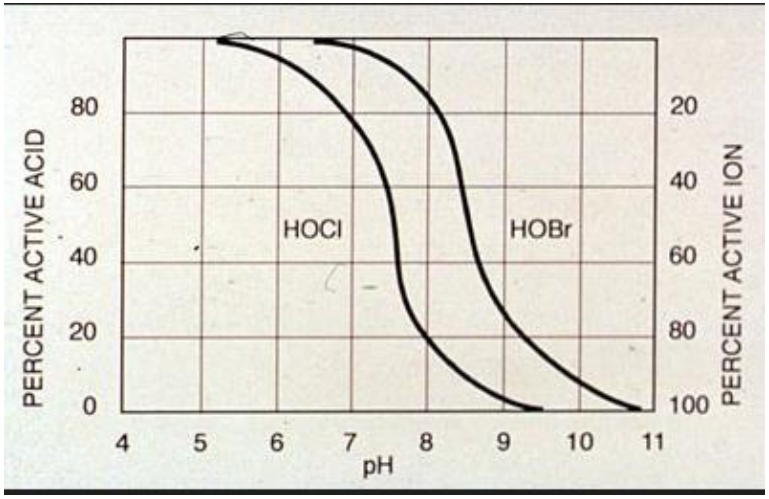
- The Total chlorine concentration is not affected by the pH of the solution.
- The Total Chlorine sensor is affected by the pH of the solution, about -5% per pH unit
- The Total Chlorine concentration does not change with changes in pH but the output of the sensor increases as the pH gets lower.
- The sensor's equilibration time to pH changes is typically 3-5 minutes, T90 < 30 seconds



pH Sensor or Reagents?

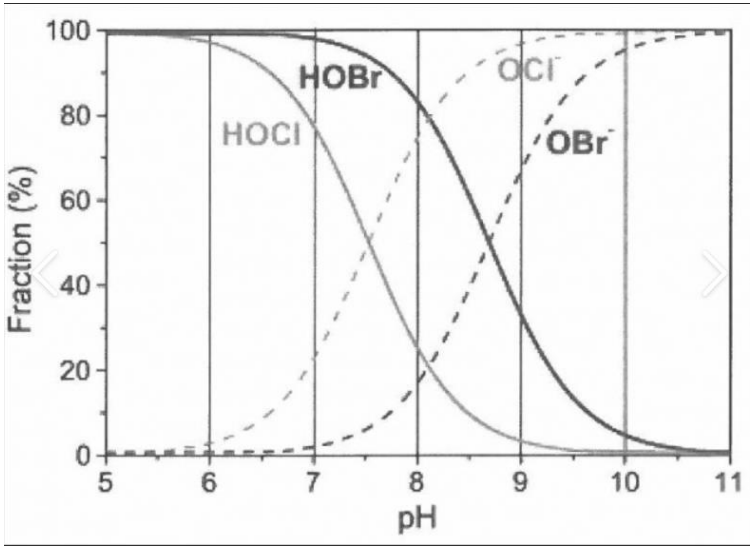
- pH influences both Free Chlorine and Total Chlorine
- The pH must be controlled by adding reagents, typically acetic acid (vinegar) or
- The pH must be measured and used to calculate the interaction

Chlorine for Seawater



- Seawater contains around 60-90 ppm of dissolved bromides. When you put chlorine into seawater, it displaces the bromine into bromide and turns into chloride. Meaning, total bromine (free and combined bromine) is the disinfection.
- The amperometric sensor only measures either the HOCl or HOBr of the process. With a pH sensor, you can determine the remaining Ocl or Obr. The transmitter with the embedded charts will perform a calculation to determine the residual chlorine or in seawater, total bromine of the process.

Chlorine for Seawater

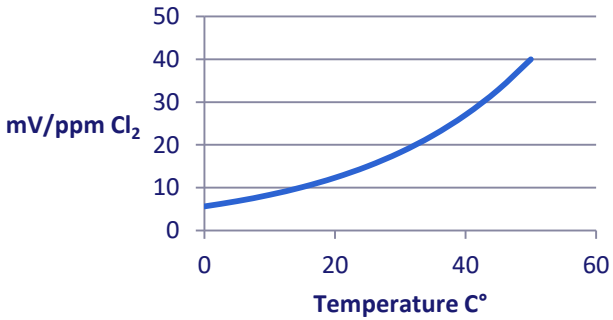


- Since, typically **residual** or **free** chlorine is known as the disinfecting agent, saying the **total** bromine is the disinfecting agent is still not well known. Due to this, we can measure based on the chart above, and move the pKa of the chlorine into the HOBr path and display for the customer as a free chlorine measurement.
- DPD analysis in seawater can be a bit confusing. DPD 1 measures free chlorine and total bromine. Calibrating against a DPD 1 to a free chlorine or free bromine can yield high errors due to confusion as typical DPD 1 measure “FREE/RESIDUAL”, and not TOTAL. Therefore, one must take into account what they calibrate the analyzer to.

Measurement Influences: Temperature

- Temperature Sensitivity
  - Output increases with temperature, 4-6 % per C°
  - Primarily due to the increased permeability of the membrane at higher temperatures
  - Output decreases with cooling.
- Some Sensors have the temperature compensation built in, like the TC80, which sends a temperature compensated reading
- Others send a temperature signal to the Analyzer to perform the compensation, like the FC80

Temperature Dependence, 4%/C°



Measurement Influences: Coating

- Iron and Manganese precipitate from some waters after chlorination
- Bio-Films grow on most surfaces when little to No chlorine is present
- Mud and silt can settle out from some sample waters
- Regular cleaning is necessary
  - Manually with a squirt bottle and rag or
  - Automatically with the Spray Cleaning option
  - Period and duration controlled solenoid with 40+ psi water or air back flushes the system

Maintenance

- All Analytical Instrumentation requires regular Maintenance
- Weekly DPD verification of grab sample
- Verify pH is correct weekly, standardize the reading if more then 0.2 pH off
- Visually inspect for sedimentation or fouling in lines

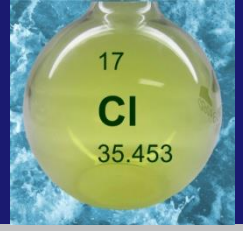
Maintenance

- FC80 yearly replacement of electrolyte and membrane
- TC80 replace electrolyte every 4-6 months and membrane cap yearly
- pH electrode replacement every 6-12 months depending on water quality.

Meet EPA Requirements?

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

EPA
United States Environmental Protection Agency



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