Technical Note 500

Thermo Scientific Orion Chlorine XP How it Works

Water Analysis Instruments, Thermo Fisher Scientific

Key Words

On-line chlorine monitoring, DPD method, Chlorine XP, total chlorine, free chlorine, combined chlorine measurement.

Goal

The following technical note describes how the Thermo Scientific™ Orion™ Chlorine XP™ Water Quality Analyzer quickly and accurately measures free, total and combined chlorine in water.

Introduction

Continuous monitoring of water quality can provide operational advantages and improve public health protection. Being able to closely monitor chlorine levels is critical for facilities in the municipal drinking water, wastewater treatment, and food and beverage markets. Real time information can improve an operator's ability to control water treatment processes such as disinfection and turbidity removal – ultimately ensuring that the water is safe. Plants treat water with chlorine to keep the water free of bacteria and harmful organisms, but too much chlorine in the water can also be hazardous.

The Chlorine XP continuously monitors a process stream using an automated DPD test for free and optionally total chlorine. Based on the results of these tests, the controller determines if and how much additional chlorine to add to the water. This procedure is repeated periodically, as often as every 2 minutes, depending on user entered settings and chlorine level stability.

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DPD Colorimetric Method

The DPD (N, N-diethyl-p-phenylenediamine) method for residual chlorine was first introduced by Arthur Thomas Palin in 1957. It has become the most widely used method for determining free and total chlorine in water and wastewater. When DPD reacts with small amounts of chlorine at a near neutral pH, the dye is the principal oxidation product. The DPD dye color is measured photometrically at wavelengths ranging from 490 to 555 nanometers (nm).

The Chemical Test

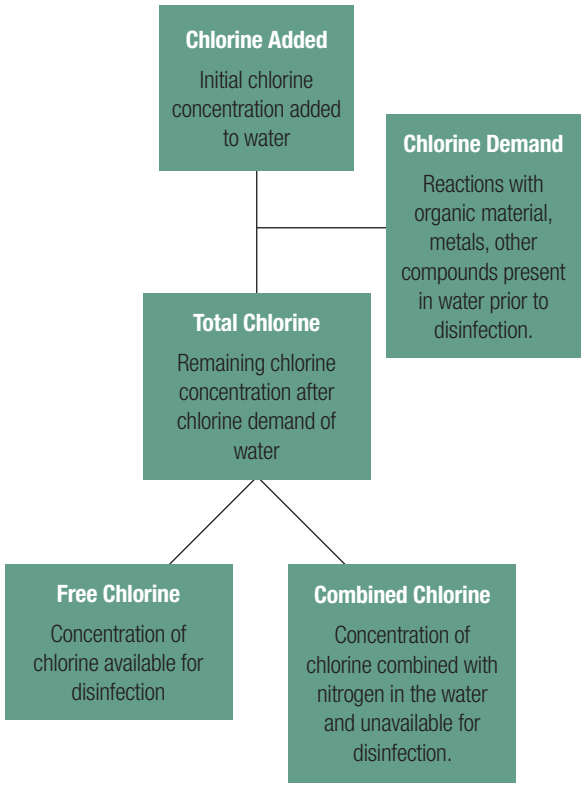
Free Chlorine (hypochlorous acid + hypochlorite ions) reacts with the Free Chlorine Indicator (DPD 1) causing a color change in the sample from clear to red. The buffer is used to ensure reaction at a consistent pH. The more free chlorine that is present, the darker the red color that forms. The color intensity is converted to PPM employing the Beer-Lambert Law.

Total chlorine is most often used for monitoring combined chlorine (chloramines) levels, which cannot be directly measured. Combined chlorine is the difference between the total chlorine and free chlorine.

Total Chlorine = Free Chlorine + Combined Chlorine

When one wishes to measure Free Chlorine and Total Chlorine in sequence, Total Chlorine Indicator (DPD 3) is added to the sample already containing the Free Chlorine Indicator (DPD 1) and Buffer. The combined chlorine reacts with the Total Chlorine Indicator causing an increase in the red color. The total chlorine is determined from the color change and the combined chlorine is calculated from the difference between the total and free chlorine.

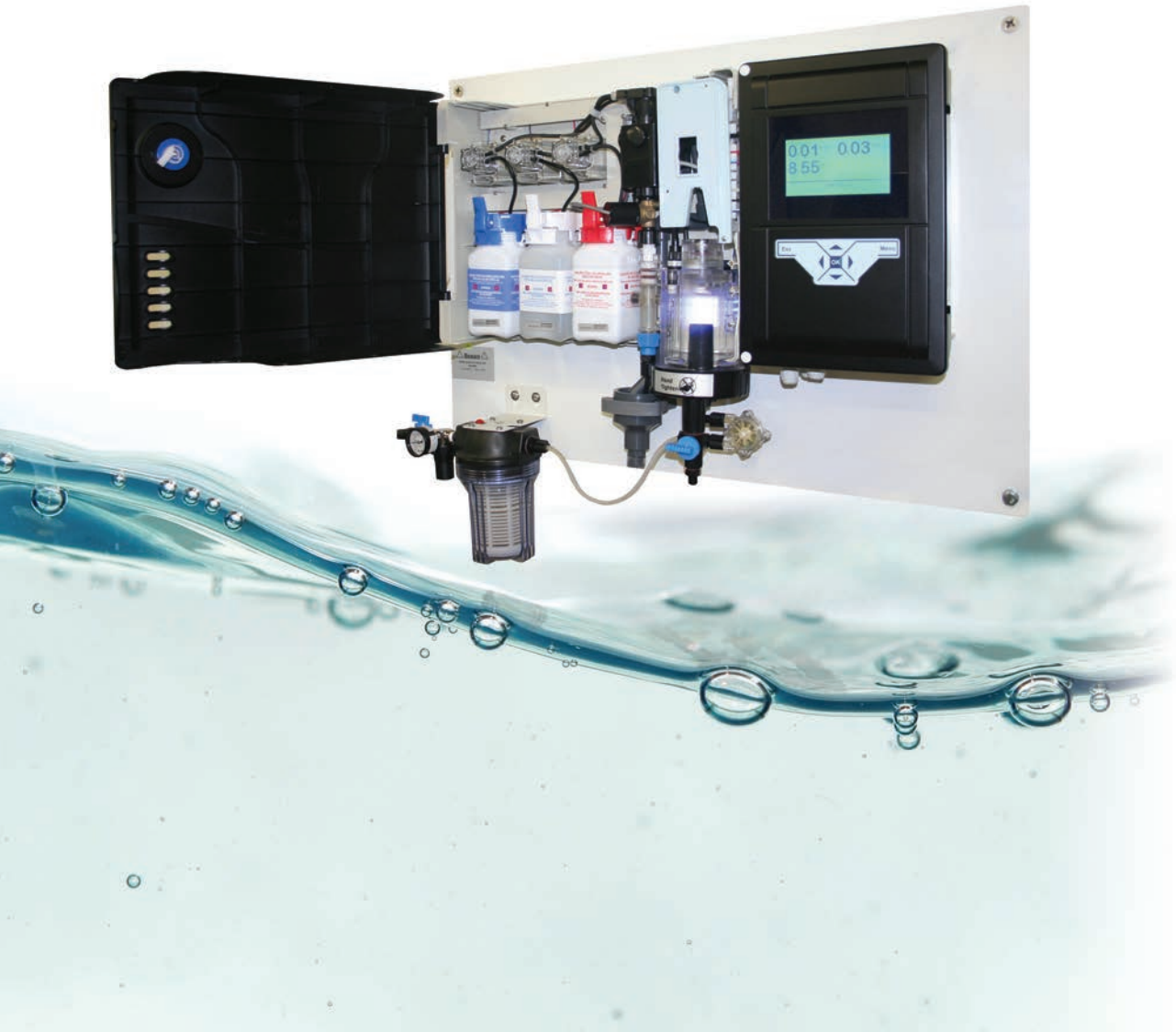
When only total chlorine test is needed the Total Chlorine Indicator (DPD 4) will be added to the sample causing color change and the levels of total chlorine will be determined.



Chlorine Testing Sequence

1. Water flows in the bottom of the colorimeter and drains from an opening near the top. Periodically, the inlet valve closes, and a precise amount of water is trapped in the Chlorine XP.
2. A piston moves through the water sample to remove any air bubbles and an initial set of absorbance readings are taken. These initial readings provide the baseline value, or zero, for use in the calculation of chlorine level.
3. Precise amount of Free Chlorine Indicator (DPD 1) and Free Chlorine Buffer solutions are pumped into the Chlorine XP and the piston mixes the sample. A chemical reaction between the Free Chlorine Indicator and any free chlorine (hypochlorous acid + hypochlorite ions) induces a color change from clear to red.
4. A second absorbance reading is taken and compared with the initial, zero, reading and the amount of free chlorine is determined. This value is then presented in PPM (parts per million or mg/L).
5. If total chlorine is also tested, DPD 3 is added to the solution already containing the Free Chlorine Indicator and Buffer (DPD1). When only measuring free chlorine, go to Step 7.
6. Precise amount of Total Chlorine (DPD 3) solution is pumped into the Chlorine XP and the piston mixes the sample. A chemical reaction between the solutions already containing the DPD 1 solution reacts with the DPD 3 solutions any total chlorine induce additional color change.

   Note: *It will add about 30 seconds to the cycle time to measure both free and total chlorine in sequence. For instance, if a 2 minute cycle time is selected for the free chlorine reaction it will take an additional 30 seconds for the total chlorine to react, resulting in 2:30 minute cycle time.*
7. A third absorbance reading is taken and the amount of total chlorine is determined. This value is then presented in PPM (parts per million or mg/L).
8. The inlet valve is reopened and fresh water flows through the Chlorine XP and the piston moves again to clean the analyzer and prepare for the next reading.



Chlorine XP Work Flow Diagram

Water source from line / reservoir / surface is fed to Chlorine XP.

Water flows to the sampling cell where optional ORP, DO and temperature measurements are available.

At user-selectable intervals (2 -10 minutes), the solenoid opens, allowing the sample to flow into the colorimeter reaction cell.

Clean water can be returned to source or dumped.

The valve automatically closes to capture the sample being measured.

An automatic zero calibration compensates for turbidity, background color or dirt buildup on the optics.

Free chlorine reagent is added using pumps - delivering them to the colorimeter reaction cell.

A piston mixer activates to homogenously mix the reagent and sample. This step also cleans the reaction reaction chamber.

Light source is activated again to read the free chlorine concentration

Total chlorine reagent is added using pumps - delivering them to the colorimeter reaction cell.

Light source is activated again to read the total chlorine concentration. Combined chlorine is calculated (by difference).

The solenoid valve opens to flush the colorimeter reaction cell with a fresh sample, further reducing cleaning and maintenance.

The solenoid valve closes. Movement of the piston cleans the optics and reduces maintenance.

The chlorine measurement cycle is complete.

Summary

The Chlorine XP offers ease-of-use and low total cost of ownership. It is recommended as a general purpose chlorine measurement analyzer along with other parameters – pH, temperature, ORP, and flow in water quality measurement applications.

Visit www.thermoscientific.com/chlorinexp for more information.

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