Chlorine Dioxide

For water and wastewater **DPD and Chlorophenol Red Methods**

Introduction

Chlorine Dioxide is a deep yellow gas that is generated directly for on-site use as a bleaching agent in industrial processes, such as the manufacture of pulp and paper. It is used increasingly for special treatment objectives in municipal water treatment because, unlike chlorine, chlorine dioxide does not form trihalomethanes (THMs) in reaction with certain organic compounds. Two colorimetric methods for chlorine dioxide at low levels are used in Hach procedures. Hach also offers a high range method that directly measures the yellow color of the chlorine dioxide gas dissolved in the sample water.

The DPD method is an extension of the N,N-diethyl-p-phenylenediamine (DPD) method for determining free and total chlorine. Glycine is used to eliminate chlorine interference.

The Chlorophenol Red (CPR) method reacts specifically with chlorine dioxide.

Chemical reactions

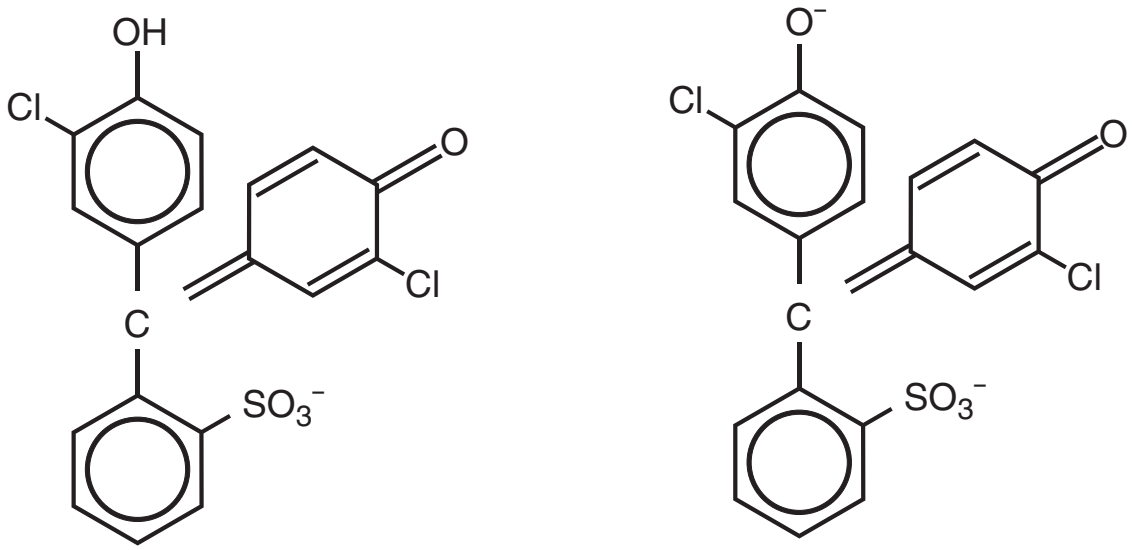
DPD Method

Chlorine dioxide reacts with the DPD (N,N-diethyl-p-phenylenediamine) Indicator Reagent (to the extent of one-fifth of its total available chlorine content corresponding to the reduction of chlorine dioxide to chlorite) to form a pink color. The color intensity is proportional to the ClO_2 in the sample. Chlorine interference is eliminated by adding glycine, which converts free chlorine to chloroaminoascorbic acid, but has no effect on chlorine dioxide at the test pH.

Chlorophenol red method

Chlorophenol Red (CPR) indicator reacts specifically with chlorine dioxide with a distinct color change; no interference is experienced form other mild oxidants, including hypochlorite, chlorite, chromate, permanganate, ferric iron, or low levels of chloramines. One mole of CPR reacts with two moles of chlorine dioxide to form a colorless product with a net decrease in absorbance at 570 nm. The discoloration of CPR is linear to approximately 0.6 mg/L, although concentrations to approximately 1.0 mg/L are easily determined. The reaction of CPR with ClO_2 is reproducible. No equation for this reaction will be suggested; however, the reaction may result in the formation of an ion-pair complex.

The reaction of CPR with chlorine dioxide is pH-sensitive. A pH of 7.0 has been suggested for the spectrophotometric method. Hach researchers found the optimum pH for this reaction is actually 5.2. It was also determined that the sensitivity is improved if the solution is buffered to near pH 10 after the initial reaction. The reagents for this method are contained in three convenient solutions. Reagent 1 is a buffer which adjusts the sample to the optimum pH, 5.2. Reagent 2 is a special formulation of CPR which is added after the pH adjustment. Reagent 3 is a pH 10 buffer added after CPR to increase sensitivity. Blanks for standardizing the spectrophotometer are prepared by adding dechlorinating agent to a 50-mL sample, thereby destroying up to 35 mg/L of ClO_2.



Yellow (acid color) Red (base color)

Figure 1 Chlorophenol Red structures