

Rev. 8/02

ChemScan® Method Summary #121 Total Chlorine in Water or Wastewater

Standard Chlorine Analysis

Chlorination of water or wastewater is performed to destroy microbiological organisms and also to oxidize nitrogen or sulphur compounds, metals and organic substances. Interactions between chlorine and various forms of nitrogen found in or intentionally added to water are complex and are generally classified as "combined" chlorine analysis. Other ChemScan Method Summaries address analysis of specific forms of "combined" chlorine (See ChemScan Method Summary #122, Chloramines in Water or Wastewater) or free chlorine (See ChemScan Method Summary #49, Free Available Chlorine in Water). This publication discusses analysis of chlorine under conditions where the total "residual" may be in the form of combined chlorine, free chlorine or both.

Upon introduction to water, chlorine gas will form hypochlorous acid (HOCl) and hypochlorite ion (OCl-). The relative percentage of these forms of chlorine is pH dependent, as shown in Figure 1. The term "free available chlorine" refers to the concentration of hypochlorous acid plus hypochlorite ion in the water.

Free chlorine readily reacts with free ammonia to form combined chlorine. The specific form of combined chlorine will depend on pH, reaction time and the chlorine to nitrogen ratio. Three types of chloramines are formed in aqueous solutions. Free chlorine is first converted to monochloramine at pH of 7 to 8 while the ratio of chlorine to ammonia is 5 to 1 by weight or less. As the ratio of chlorine to ammonia is increased, dichloramine and nitrogen trichloride (trichloramine) is formed. Thus, in water that contains substantial free ammonia, such as wastewater effluent, it is actually possible for an increased free chlorine dose to result in a reduced total chlorine residual, until the "breakpoint" has been surpassed. (See Figure 2)

Typical laboratory methods for total chlorine analysis are selected based on the tolerance for known interferences in the water to be analyzed. Specific methods include idiometric techniques (based on the liberation of free iodide from potassium iodide, measured using titration procedures or ion electrodes), amperometric titrations, DPD ferrous titrations and colorimetric procedures using DPD reagents. The DPD method may be subject to interference from monochloramine unless special precautions are taken. On-line methods are typically an automated version of one of the standard methods. Care should be taken to select a method of analysis that is appropriate for chlorine analysis in the presence of

known or expected interference from other oxidizing agents, turbidity, color and organic contaminants as the above methods do not perform equally under all conditions.

ChemScan Analysis Methods

1. Amperometric Analysis

The method of choice for applications where the main issue is the absolute concentration of total chlorine (rather than the specific form of chlorine) is Amperometric analysis using the ChemScan A-2000 analyzer. This analyzer provides continuous analysis of a single sample line using polarographic principles and is not affected by turbidity, color or other oxidants in the sample. A sample flow is introduced into a mixing chamber together with a constant regulated flow of buffer solution in the form of white distilled vinegar. A small amount of potassium iodide is added with the vinegar for analysis of total chlorine. The mixing chamber contains a gold measurement electrode and a copper reference electrode. The buffered sample is continuously stirred within the mixing chamber, which also contains inert mixing spheres to aid agitation and to clean the electrodes. This method is an improved version of standard method 4500-Cl-C and D and is capable of analysis at total chlorine concentrations as low as 0.00l mg/l or as high as 50.0 mg/l.

2. Idiometric Analysis

This is the method of choice where the application requires control of the specific forms of combined chlorine, such as water chloramination monitoring and control (See ChemScan Application Summary # 86, Water Chloramination Process Control). This method is based on the principal that free and combined chlorine will proportionally liberate free iodine from potassium iodide. Free iodine has a strong UV absorbance signature, such that a full spectrum analyzer like the ChemScan UV-2150 can be used to detect the liberated iodine, plus compensate for other oxidizing or reducing agents or interferences in the background (including monochloramine - which can be independently detected), and calculate the resulting concentration of total chlorine. This is also the method of choice if multiple sample lines are being monitored or if other parameters are analyzed in addition to total chlorine. Typical range is 0.05 mg/l to 10.0 mg/l, but can be altered based on path length selection.

Monitoring System Requirements

Sample extraction points are a function of the process being monitored. If the best control signal is desired, careful sample point selection, short sample lines and frequent measurement intervals are best.

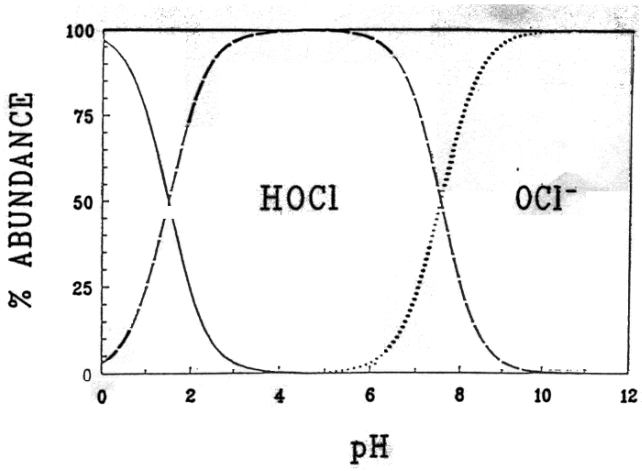

Figure 1

Percent Distribution of Aqueous Chlorine Species with Changes in pH

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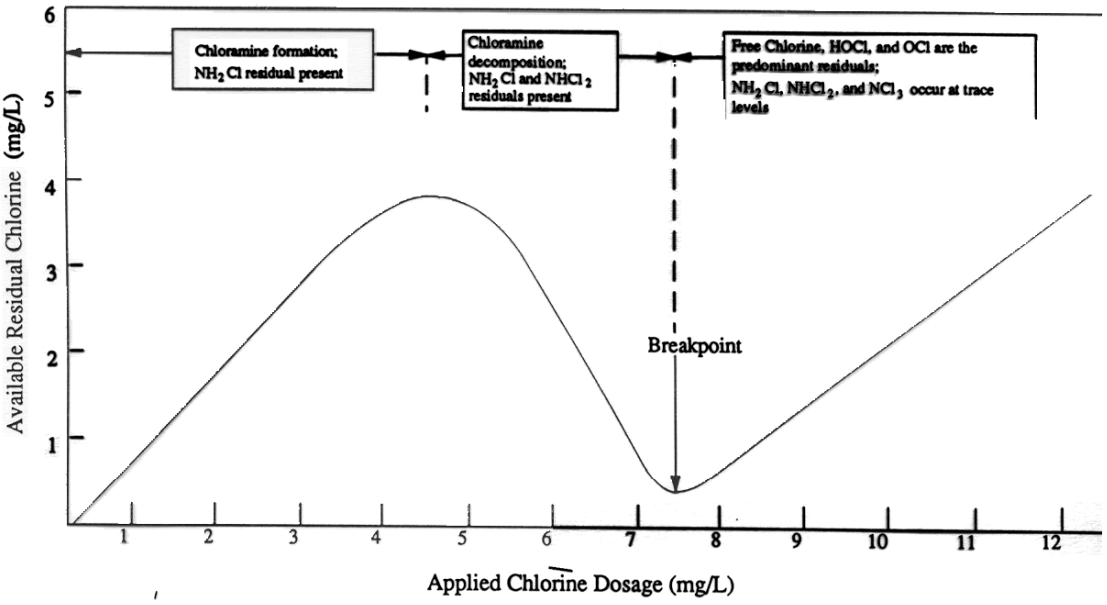

Source: Wolfe et al. 1984

Figure 3.6 Theoretical breakpoint chlorination scheme (1.0 mg/L ammonia-nitrogen; pH 7; temperature 25°C; contact time 2 hours)

Figure 2
Spectral Shift of Free Chlorine Absorbance with Change in Sample pH