

# ChemScan<sup>®</sup>

## PROCESS ANALYZERS

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### ChemScan<sup>®</sup> Method Summary #49 Free Available Chlorine in Water

#### 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 “combined” chlorine (See ChemScan Method Summary #121, Total Chlorine in Water or Wastewater) or Chloramine (See ChemScan Method Summary #122, Monochloramines). This publication discusses analysis of free available chlorine under conditions where the total “residual” is always in the form of free available chlorine.

Upon introduction to water, chlorine gas will form hypochlorous acid (HOCl) and hypochlorite ion (OCl<sup>-</sup>). 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.

Typical laboratory methods for chlorine analysis include idiometric methods (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. 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 most applications 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. 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 chlorine concentrations as low as 0.001 mg/l or as high as 50.0 mg/l.

## 2. Idiometric Analysis

This method is based on the principal that 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, compensate for other oxidizing or reducing agents or interferences in the background, and calculate the resulting concentration of free chlorine. This is the method of choice if multiple sample lines are being monitored or if other parameters are analyzed in addition to free chlorine. Typical range is 0.05 mg/l to 10.0 mg/l, but can be altered based on path length selection.

## 3. Spectrophotometric Analysis

Hypochlorite ion has a strong absorbance signature in the ultraviolet wavelength range with a peak absorbance at 292 nm, while hypochlorous acid has a weaker absorbance signature with a peak at 236 nm. As the pH of the sample is altered, the absorbance signature will rotate at 254 nm as the form of free chlorine is exchanged between HOCl and OCl<sup>-</sup> forms, as shown in Figure 2.

Multiple wavelength absorbance data can be used to characterize the concentration and relative form of free chlorine in a sample of known or stable pH. If the pH is not known or is variable, sample pH can be adjusted to the 4-5 range, where HOCl is 100% of the form or to the 10+ range where OCl<sup>-</sup> is 100% of the form. Multiple wavelength absorbance spectrometry can also be used to compensate for the effects of any organics, nutrients or metals that may be present in the sample.

This is the method of choice for very high concentrations of free chlorine, above 25 mg/l.

### 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.

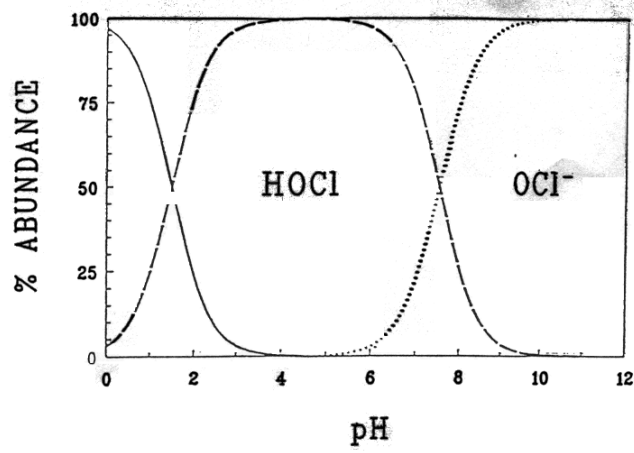


Figure 1

Percent Distribution of Aqueous Chlorine Species with Changes in pH

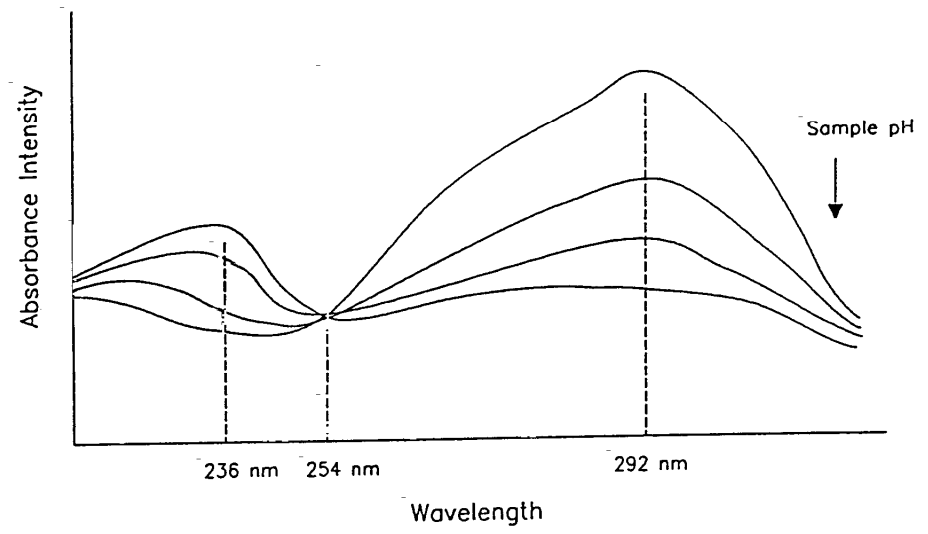


Figure 2

**Spectral Shift of Free Chlorine Absorbance with Change in Sample pH**