Application Data Sheet
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Chlorine Measurement by Amperometric Sensor

Chlorine in aqueous solutions is used for a number of purposes such as disinfection, taste and odor control, bleaching, and as a powerful oxidizing agent in various manufacturing processes. Chlorine is a costly chemical and requires large amounts of energy to produce. About 3000 KWH are required to produce a ton of chlorine from brine, and the delivered cost ranges from $160 to $300 per ton. As energy becomes more expensive, so inevitably will chlorine.

If for no other reason than cost, it is important to measure and control chlorine concentration. Perhaps more important is the fact that the bleaching and disinfecting ability of chlorine depends on concentration. Too little chlorine is ineffective. Too much chlorine is wasteful and may create other problems in the process. A good illustration is the chlorination of drinking water. Underfeeding chlorine results in incomplete disinfection with consequent danger to the public health. Overfeeding chlorine may produce water with an objectionable odor. Overfeeding may also increase the levels of trihalomethanes (THMs) in the finished water. THMs are suspected carcinogens. In certain applications, such as the chlorination of drinking water, it is important to know the chemical form of the chlorine. Certain forms of chlorine are 80 to 100 times more effective in disinfecting water than other forms.

The reactivity of chlorine and its complex chemistry in aqueous solution make the measurement of chlorine difficult. Even under ideal laboratory conditions, results vary with the method used. With process instruments the situation is even more complicated. Calibration, drift, reliability and maintenance become important issues.

Emerson Process Management has developed a series of accurate, easy to use, low maintenance Rosemount Analytical amperometric sensors for the determination of chlorine. The sensors can be installed directly in the process piping or in low flow cells that require as little as 10 liters/hour of sample flow. Chemical reagents are not required.

The tip of the chlorine sensor consists of a membrane stretched over a noble metal cathode. The chlorine in solution diffuses through the membrane to the surface of the cathode. A voltage applied to the cathode reduces the chlorine to chloride. The process consumes electrons, which come from a second electrode (the anode) inside the sensor. The number of electrons consumed at the cathode, i.e., the current, is directly proportional to the concentration of chlorine in the sample.

The sensors are relatively free from interference. Manganese, iron, nitrate, and chromate--substances that interfere with other methods--have little influence on amperometric sensors. The sensors are fairly low maintenance, although they do require periodic cleaning to wash away solids that slowly accumulate on the membrane.

The chemistry of chlorine is complex, and we will confine ourselves in the following discussion to a summary of what happens when chlorine is added to water. For measurements in wastewater and/or processes with ammonia or sea water, refer to Application Data Sheet 4950-10.

Water is chlorinated by treating it with chlorine gas (Cl_2) or sodium hypochlorite (NaOCl) solution (bleach). When chlorine gas dissolves in water it produces hypochlorous acid (HOCl).

$$Cl_2 + H_2O = HOCl + H^+ + Cl^- \quad (1)$$

Sodium hypochlorite solution is a source of hypochlorite ions (OCl^-). Hypochlorous acid and hypochlorite ion are both forms of active chlorine and are related to one another by the following equation.

$$HOCl = H^+ + OCl^- \quad (2)$$

The important thing about equation 2 is that any solution of chlorine gas or bleach in water is a mixture of hypochlorous acid and hypochlorite ions. The relative amount of hypochlorous acid or hypochlorite present depends on pH and to a slight extent on temperature.

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At 25°C (77°F) and a pH of 7.5, half of the chlorine is present as OCl^- and half as HOCl. At higher pH values, the quantity of OCl^- increases at the expense of HOCl and at lower pH values, the shift is toward conversion of OCl^- to HOCl. At a pH of about 5, nearly all the chlorine is present as HOCl, and at pH 9 nearly all the chlorine is present as OCl^-. The graph in Figure 1 illustrates how the equilibrium changes with pH. Since many chemical and electrochemical methods used to determine chlorine concentration cannot distinguish between them, it is common to express the two together as free residual chlorine (FRC):

$$OCl^- + HOCl = FRC$$

Why then all the fuss? Because the form in which the chlorine exists is very important when used in specific applications. For example, in disinfecting potable water, hypochlorous acid (HOCl) has been reported to be 80 to 100 times more effective than hypochlorite (OCl^-). This means it takes 8 ppm of OCl^- to do the same job of disinfecting as 0.1 ppm of HOCl. Since the form of chlorine is important, providing adequate disinfection requires knowing both the chlorine level AND the pH level.

Rosemount Analytical's Model 499ACL-01 chlorine sensor can measure chlorine in the HOCl form and the OCl^- form. The sensor responds differently to each form, so determining the total FRC requires compensation for the sample pH and temperature. A RTD is mounted inside the Model 499ACL to measure temperature, and a separate pH sensor is used to provide the pH signal. Instruments such as the Model 1056 and 54eA contain sophisticated algorithms that convert the current to a reliable ppm level measurement.

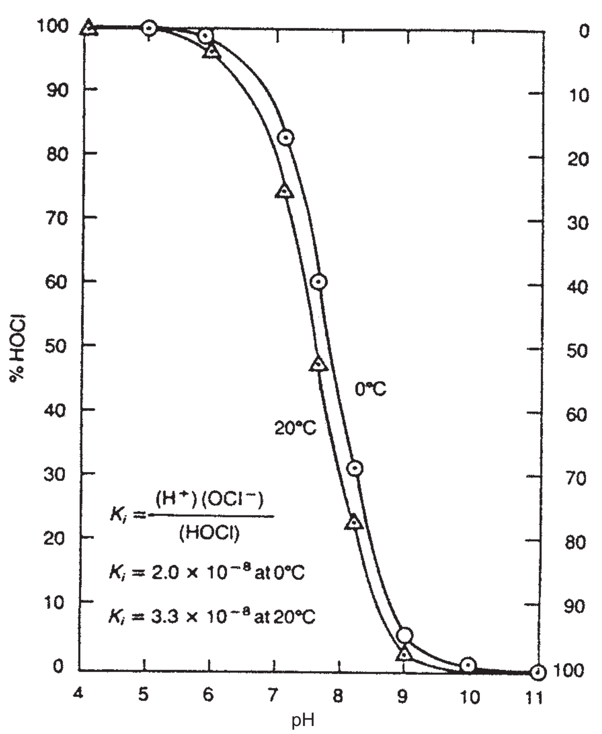

Figure 1. Equilibrium Changes with pH

% HOCL

pH	0°C	20°C
4	100	100
5	100	99.7
6	98.2	96.8
7	83.3	75.2
7.5	61.26	48.93
8	32.2	23.2
9	4.5	2.9
10	.5	.3
11	.05	.03

Figure 2. Tabular Data for HOCl from Figure 1.

INSTRUMENTATION

Chlorine measurement requires an amperometric sensor and an analyzer to convert the current signal to a ppm reading. Unless the pH never changes more than 0.2 pH units, a separate pH sensor is strongly recommended. The preferred installation is in a bypass line with the sensors installed in a low flow cell PN 24091-01. Other alternatives are installation in a 1-1/2 inch tee or submersed in a tank. The Model 499A sensor requires a minimum flow rate to provide a fresh sample for analysis.

For those desiring a complete solution the Model FCL-02 includes all necessary hardware for determination of free chlorine in water. This integrated system consists of a Model 499A free chlorine sensor, Model 399 pH sensor, Model 1056 dual-input analyzer, flow cells, and constant head flow controller all mounted on a back plate.

INSTRUMENTATION

Model 1056 Dissolved Oxygen Analyzer

- Single or dual DO input.
- NEMA 4X (IP65) weatherproof, corrosion-resistant enclosure.
- Onboard barometric pressure sensor.
- Two Isolated current outputs.

Model 54e Microprocessor Analyzer

- NEMA 4X (IP65) weatherproof, corrosion-resistant enclosure.
- Two independent outputs.
- Back-lit dot-matrix display.
- HART® and AMS® aware.
- Optional TPC relays and PID current outputs.
- Contains sophisticated algorithms that convert the current to a reliable ppm level measurement

Low Flow Cell PN 24091-01

- Properly directs sample flow across membrane
- Inlet nozzle keeps membrane clear of bubbles
- Accommodates 1/4” inlet and outlet lines

Model 499A Free Chlorine Sensor

- No messy and expensive reagents needed: Measure free chlorine without sample pretreatment.
- Replace sensor without running new cable using the Variopol connector option.
- Easily replaceable membrane: no special tools required.

pH Sensor Model 399

- Required for automatic pH correction of chlorine (wired to second analyzer input).
- Improved performance, increased life and minimized glass cracking with field proven AccuGlass® pH glass formulations.
- Eliminate cable twisting with quick cable-to-sensor release Variopol connector.

Model FCL-02 Free Chlorine System

- Complete system including sensors, analyzer, cables, and flow controller
- Automatic pH correction eliminates requirement for reagents and sample conditioning
- Intelligent analyzer with dual outputs, large display, and intuitive menus
- Measures free chlorine at pH up to 9.5

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