Water Authority Tries Free Chlorine Measurement

A system requiring no reagents and no pH sensor

By José Diego Lebrón

The question of how best to measure free chlorine in drinking water has been an issue for some years. Should you use a reagent-based method or a reagent-free method with the inherent pH dependence problem? The experience of a major aqueduct and sewage authority in the Southeast shows the economic advantages of an approach that is both reagent-free and pH-independent.

Measuring free chlorine

Most water plants are required by the U.S. Environmental Protection Agency to continuously monitor free chlorine in the product water. Two types of process monitors are available for the job: colorimetric and amperometric.

In the colorimetric method, chemicals added to the sample react with chlorine to produce a color. The darkness of the color is proportional to the amount of chlorine. The process instrument measures the color and converts the result into a parts per million chlorine reading.

The amperometric method is electrochemical. The sensor produces a current directly proportional to the concentration of chlorine in the sample. The analyzer measures the current and converts it into a parts per million chlorine reading. Amperometric chlorine instruments all share a common problem—the response of the sensor depends on pH.

The pH dependence exists because free chlorine is a mixture of hypochlorous acid and hypochlorite ion. The proportion of each depends on pH. Because the sensor responds only to hypochlorous acid, pH variations cause the sensor current to change even if the concentration of free chlorine remains constant. Thus, if the pH of the sample varies from the value it had when the sensor was calibrated, the chlorine reading will be in error. The error can be quite large, as much as a 20% per unit change in pH (see Figure 1).

There are two ways to solve the pH problem. One is to treat the sample with acid. Acid converts hypochlorite to hypochlorous acid, the form of free chlorine the sensor measures. The other is to measure the pH of the sample and use a pH-correction algorithm in the analyzer to calculate the true concentration of free chlorine.

Using colorimetric analyzers

Until about a year ago, this Southeastern water authority used the colorimetric method exclusively; however, the method has a number of drawbacks. One is reagent consumption. Reagents last a month and, for a single system, cost between $750 and $1,000 a year. The authority has more than 200 water supply systems, so annual reagent costs were around $200,000.

Approach

provides solution for a utility

The big cost of a reagent-based system, however, is not in materials alone. It is in the manpower required to change the reagents, order, store and track them. Many of the water authority's systems are not close to main roads, so the time required just to get to the site is not trivial. In addition, the colorimetric analyzers have a sample conditioning system (a pump to inject reagents, tubing to carry them and a mixing device). These parts require regular monthly maintenance, including cleaning, inspecting and replacing tubing, as well as calibrating and verifying the system.

Interestingly, the water authority also discovered a hidden but considerable cost associated with the colorimetric analyzers. When the reagent ran out, the residual chlorine drifted below the regulated level, and the system went into alarm mode.

The telemetry system showed the plant was not meeting local and federal requirements, leaving the authority potentially subject to fines and penalties. Improving the reliability of the chlorine monitors that used a major goal when the authority decided to upgrade its infrastructure and analytical instrumentation.

Amperometric methods

The authority investigated the amperometric instruments on the market. Reagent-based instruments that used acid to adjust pH were rejected because they gave no real advantage over colorimetric analyzers. Reagent-free amperometric instruments that use a pH measurement to correct the sensor reading were considered, but these instruments required that a pH sensor be purchased with every unit. The pH sensor constituted both upfront and continuing maintenance costs.

FIGURE 1: Percent change in sensor current as function of sample pH.

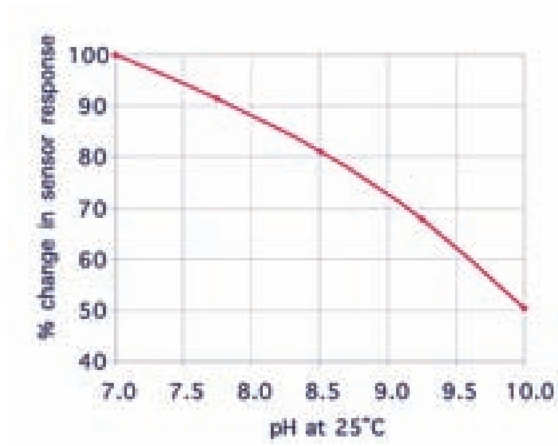

FIGURE 2: Internal pH correction in new sensor technology.

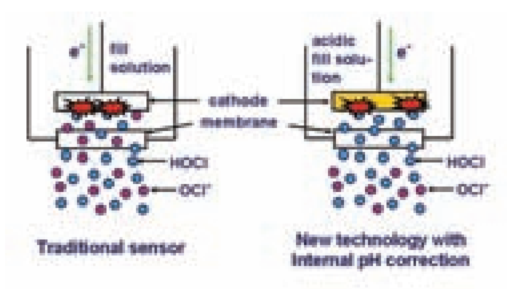

FIGURE 3: The Rosemount Analytical Model FCLi measures free chlorine without reagents or the need for pH correction.

The best of both worlds

After an extensive evaluation, the water authority settled on a new technology that provides sample pH adjustment inside the sensor. The system does not require reagents or a pH sensor.

Figure 2 compares the new technology with a traditional amperometric free chlorine sensor. As the figure shows, the sample contains hypochlorous acid (HOCl) and hypochlorite ion (OCl-). Both diffuse into the sensor, but in the traditional sensor only HOCl contributes to the sensor current. Any variation in sample pH will alter the amount of HOCl, and thus, the sensor current. In the new technology, the acidic fill solution inside the sensor converts all the OCl- to HOCl, making the sensor response independent of sample pH.

The pH-independent chlorine sensor needs some maintenance. The fill solution and membrane require replacement about every three months. The job takes only five minutes, which is a dramatic reduction in maintenance time compared with the previous requirement. Less maintenance time, combined with elimination of reagent costs (about $760 per system) saved the water authority more than $61,000 per region per year. This did not include the cost of gasoline and other vehicle operation expenses.

The water authority has improved the reliability of a critical parameter in the safe distribution of drinking water to 3.7 million people. Noncompliance violations have stopped. Maintenance frequency has been reduced by 75%, reagent costs have been eliminated and analytical results have met all requirements.

To the question, "Should a water plant choose to use reagents or purchase pH sensors to measure free chlorine?" this major water utility has clearly answered, "Neither." WWD

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