By Lawrence B. Kilham, EcoSensors, Inc.

Measuring Dissolved Ozone

Company develops new method of measurement for bottled water plants

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A new technology shows promise for measuring dissolved ozone and can be used in applications such as bottling plants, water stores and food and beverage plant process water treatment.

Shake a bottle of beer, uncap it, and the dissolved gases spray out. Sounds like a promising start for measuring the concentrations of dissolved gases in water. That's essentially the breakthrough. The new method efficiently mechanizes this gas-water partitioning principle long known to chemists as "Henry's law." Mechanizing gas release from water using Henry's law is not new. The approach is. The result is a new dissolved ozone monitor that overcomes many nagging problems with existing technologies.

Current Methods for Measuring Dissolved Ozone Concentrations

By way of review, the common current methods for measuring dissolved ozone include

- **Oxidation reduction potential** (ORP), also known as Redox. ORP reacts to any oxidizing influences in the water such as chlorine. ORP is simple, rugged and inexpensive, but it is not ozone-specific, and its range for ozone is rarely much above 1 ppm. ORP in many cases is the right measurement where total oxidizing ("germ killing") power is of interest such as some swimming pool and drinking water systems that combine chlorine and ozone.

- **Electrochemical cell** (polarographic). This is a chemical reactive cell protected by a special membrane. The cell can be in a sample stream or sometimes in the main stream. It has a wide dynamic range, usually into the 10s of ppm and reads to high precision. Electrochemical cells and instruments are fairly expensive, and abuse to the cell membrane by particulates, salts, mishandling, etc., often requires frequent costly maintenance.

- **"Indigo" test** (i.e., Hach colorimeter). No online version. These are packaged reagent ampules of indigo trisulfonate that is bleached by ozone. The results are read by a colorimeter, usually digital. When carefully done, the procedure is quite accurate, but it easily can be misperformed, and there is a constant waste product of broken glass ampules.

Figure 1. Experimental Apparatus During Tests

It was time to devise a better way to measure dissolved ozone concentration. After much trial and error a satisfactory design was achieved. (Experimental apparatus is shown in Figure 1.) The new instrument strips ozone from a .15 L/min (3 gal/hr.) sidestream using a proprietary process. To do this, the stripper section requires 14 psi (1 bar) water pressure. There is a ¼-inch NPT female port or a hose barb connection to the instrument. A heated metal oxide semiconductor sensor is used by the sensing instrument itself. The DOM-1 instrumentation package includes a water strainer, pressure regulator and hardware to mount everything to the plant wall. Easy calibration to a laboratory reference is created. Replacement parts are low cost and easily replaceable by plant personnel.

An early trial of the engineering prototype against tests of the same water by a Hach Model 850 Colorimeter are shown in Figure 2. The linearity is good, and the r^2 correlation is .9968.

The first generation of instrumentation is for the 0–2 ppm dissolved ozone range. It should prove to be well-suited for monitoring and control applications in bottled water plants, swimming pools and various industrial processes such as food washing.

Ozone Beta Tests

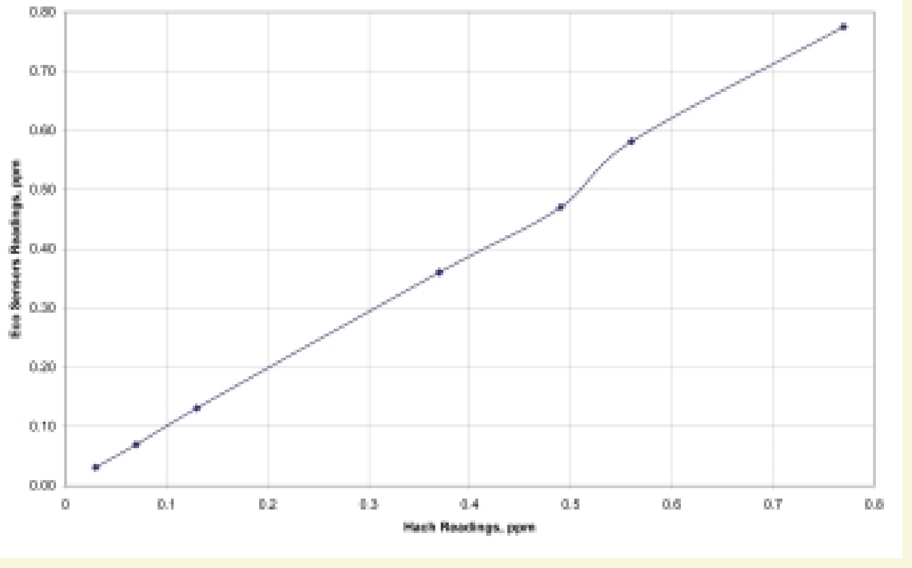
In the early summer of this year, instruments were sent out to selected customers for testing ("beta sites"). Results have been better than hoped for. Preliminary top interest is for bottled water plants where operators want to be sure there is enough ozone in the water for effective sterilization and yet not so much as to cause a bromate ion problem. Other applications of current interest are small water companies, jug water stores and food and beverage plant process water treatment.

Consistency and ease of operation have been key points reported. The beta testers have found that analysis and experimentation is required to find the best point in the plant flow stream to connect the instrument. Also, the connection line from the plant pipe to the instrumentation should be short in order to minimize ozone half-life loss.

Also Works Well for Dissolved VOCs

One of the beta site testers checked the operation of the gas stripper for VOCs such as benzene dissolved in water. This is important because the feed water or process water for many systems must be free of organics, petrochemical derivatives, solvents, etc. Most of these are collectively known as VOCs (volatile organic compounds). The stripper's output fed a standard flame ionization detector detecting benzene. The results were sensitivity below 10 ppb and very high accuracy. Applications

Figure 2. Correlation with Hach Colorimeter



* *Patents for the technology described in this article have been applied for in the United States and many foreign countries.*

About the Author

Lawrence B. Kilham has a master's degree from the Sloan School of Management at MIT. He holds three patents in instrumentation and received the IR 100 award for technical innovation. Kilham has published numerous technical articles and addresses professional societies. He also published a book, *Great Idea to a Great Company: Making Inventions Pay*. Kilham has been in sales, engineering and management positions in high tech companies since 1965. Currently, he is owner of Eco Sensors, Inc., a rapidly growing instrument company in Santa Fe, N.M., and is a director of several start-up companies. He can be reached at larry@ecosensors.com.

could include checking source water to drinking water plants, recirculating water in cooling towers, recycled manufacturing process water and ground water remediation.

General Considerations

The instrument is as accurate as the gas sensor, which is coupled to the stripper. The stripper itself is very precise. The only variable that affects calibration is temperature as you can verify by the much greater amount of gas released from shaken warm beer vs. that released from cold beer. (This is all predicted by Henry's law.) As long as the instrument is operated indoors where the temperature is stable, this is not a problem. For outdoor use and advanced systems, microprocessor-based sensing probes are being developed that will automatically adjust the calibration for temperature changes.

The first version of the technology for ozone was designed to be easily understood by plant mechanics and plumbers. Fittings are standard NPT, and there are such features as strainers for stray particles, which are a problem for other kinds of sensors. The filters are quickly removed, rinsed off and replaced.

The first model to be introduced to the market will have an LCD digital readout, set-point controlled relay for controlling alarms and generators and a 4–20 mA loop output to plant data systems. Next generation designs are planned to be microprocessor-based with output in factory data LAN formats.

The new instrument is lower in cost than electrochemical and ultraviolet-based systems. It is essentially ozone-specific compared to the lower cost ORP instruments that are sensitive to all oxidants in the water. Due to the probe not being immersed in the water, the instrument virtually is maintenance free. However, as is the case for all new technology developments, unforeseen problems can arise. WQP

Helpful Definitions

Henry's Law—An expression for calculating the solubility of a gas in a fluid-based on temperature and partial pressure.

Oxidant—A chemical substance capable of promoting oxidation such as oygen, ozone or chlorine.

Oxidation—The loss of electrons from the reducing agent.

Oxidation-Reduction Potential—Electrical potential needed in order to transfer electrons from one element to another.

Ozonation—The feeding of ozone to a given water supply for decolorization, disinfection, deodorization and oxidation.

Ozone destruction—The step in which a component unit of an ozonation system destroys all of some of the ozone present in the off-gas being vented.

Ozone Half-Life—The period of time for 50 percent of a given quantity of zone to decompose at a specific tempaerature and pressure.

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