Application Note D-102

A New Method for On-Line Measurement of Dissolved Ozone and Other Gases

Lawrence B. Kilham

Eco Sensors, Inc.
Santa Fe, New Mexico, USA
E-mail: larry@ecosensors.com

Abstract

There has long been a need for a simple, low-cost and compact device to remove dissolved gases from a liquid stream to make measurements using conventional gas measurement instruments. Larry Kilham and his associates at Eco Sensors, Inc. approached this challenge by devising a new way to mechanize gas removal from solution within the limitations predicted by Henry's law.

The gas stripper is compact, low-cost, sensitive and fast-reacting. Patents have been applied for in many countries. Eco Sensors has developed an instrumentation package for dissolved ozone using its ozone instrumentation technology, and a partner firm has done the same for dissolved VOC detection using FID and other analyzers.

Key Words

Ozone; Dissolved Ozone Measurement; Dissolved VOC Measurement; Gas Stripping; On-line Dissolved Gas Measurement

Introduction

There has long been a need for a simple, low-cost and compact device to remove dissolved and entrained gases from a liquid stream in order to make measurements using conventional gas measurement instruments. Membranes, trickling towers and other approaches have all had problems including clogging and sluggish response rates. For dissolved ozone measurement, the challenge was to make a better and lower cost instrument for users such as water bottlers and public water supplies where ozone is used for sterilization. The problem with conventional on-line instruments has been that the delicate probe is usually in contact with the water, and water degrades the sensor.

For measuring dissolved VOCs the problems are similar, except that many VOC applications require much greater sensitivity than required for the dissolved ozone application. Less than 25 ppb is a typical requirement. Current dissolved VOC applications include cooling tower water contamination and ground water pollution.

We at Eco Sensors, Inc. decided to strip the gas from the water before measuring it to avoid the clogging problems of membrane-based probes. The foundation of gas stripping is the gas-water partitioning principle known as Henry's law. It is the theoretical underpinning of Eco Sensors' novel approach to mechanizing the gas release from water. The result is a dissolved gas measurement system that is simple, sensitive, low-cost and easily adaptable to many field conditions. We will describe tests against established dissolved gas measurement techniques for ozone, an oxidizing gas, and benzene, a volatile aromatic hydrocarbon.

Current Methods for Measuring Dissolved Ozone Concentrations

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

1 - ORP (Oxidation reduction potential 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.

2 - 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 mainstream. It has a wide dynamic range, usually into the 10's 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.

3 - "Indigo" test such as the Hach colorimeter. No on-line 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 is easily misperformed and there is a constant waste product of broken glass ampules.

First Developments with Ozone

There was a clear need for a device that first stripped the dissolved ozone from the water matrix, and then analyzed the gas. This approach was theoretically feasible because the Henry's Law (dimensionless) constant for ozone is a relatively high value of about 4, indicating a propensity for ozone to move into the gaseous state (Sanders, 1999).

The apparatus uses a compact, low flow sparger instead of a trickling tower or membrane to strip dissolved and entrained gases and volatiles from the water. The gas is continuously stripped out of a small water flow using a proprietary device and released into a sampling headspace where it is removed by a continuous are flow in and out..

Our experimental apparatus is shown in Figure 1. The Eco Sensors instrument strips ozone from a .15 L/min water flow side stream using a proprietary process. To do this, the stripper section requires 2 bar (28 psi) water pressure. The connection to our instrument is a 1/4" NPT female port or compression fitting. The sensing instrument itself uses a heated metal oxide semiconductor sensor. The instrumentation package includes a water strainer, pressure regulator, and stripping chamber which is 50 mm in diameter and 300 mm in height (an early design shorter unit is shown in Figure 1).

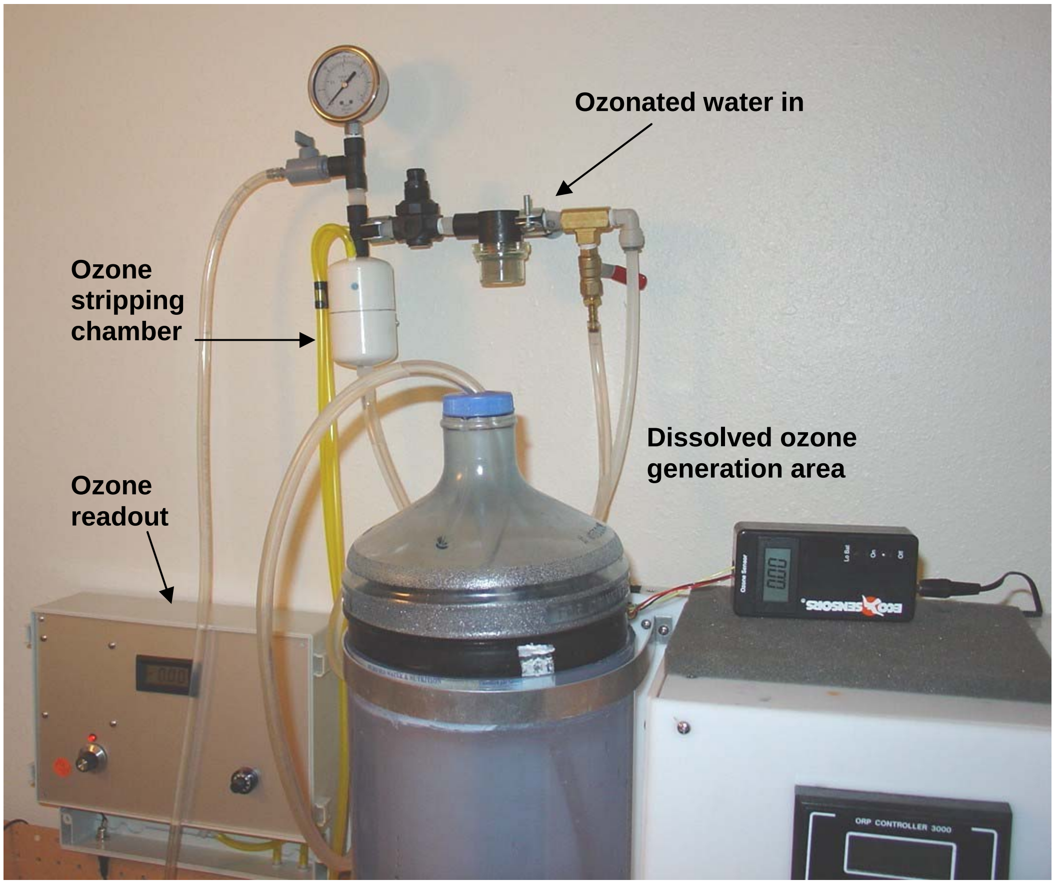

FIGURE 1 Experimental apparatus for ozone

Results of an early trial of our engineering prototype over the 0-0.8 ppm range against tests of the same water by a Hach Model 850 Colorimeter are shown in Figure 2. A linear regression of the data yielded good results with a correlation of $r^2 = 0.9980$

First Field Test with Ozone

Late in the summer of 2003, instruments were sent out to selected users for beta site testing. Results were better than we hoped for. Preliminary top interest was 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. Testers commented about the ease of use and reliability.

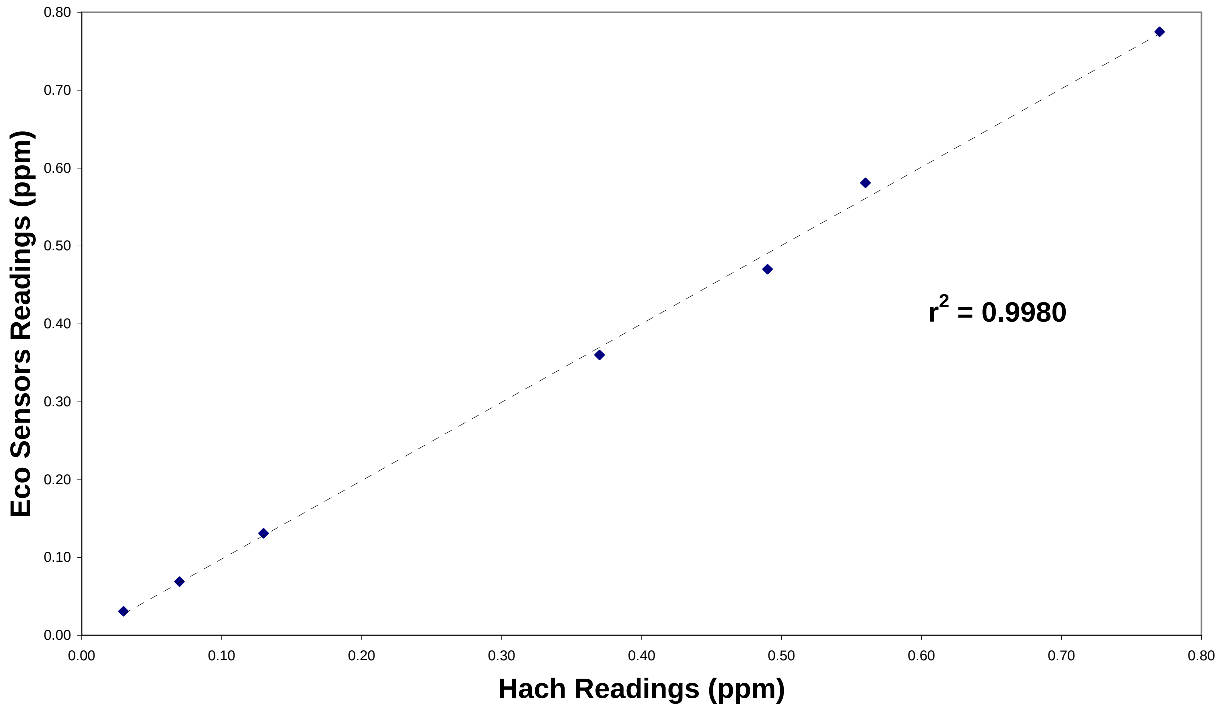

FIGURE 2 Correlation with Hach Colorimeter for Concentration of Ozone

Other applications of current interest are municipal water works, measuring ozone residual in food rinse water, cooling tower water, plant process water treatment, and ozonated water analysis in subterranean remediation. These all can be characterized by water with dissolved and suspended solids and other agents that can quickly foul the membrane-based probes of electrochemical dissolved ozone analyzers.

After the ozone instrument was formally introduced at the IOA World Congress in 2003 in Las Vegas, orders have come from such diverse locations as China, Japan, Israel, Sweden, Australia, Ecuador and Angola. Consistency and ease of operation have been key points reported.

Tests for Dissolved VOCs

Dissolved VOC quantification is potentially a much larger market than the initial application of dissolved ozone. Applications include checking source water for drinking, recirculating water in cooling towers, manufacturing process water and ground water remediation. With this in mind, Eco Sensors approached Baseline-Mocon (Lyons, Colorado, USA), a leading manufacture of VOC measuring instruments. Baseline-Mocon had an immediate project to develop an instrumentation package to monitor for VOCs in cooling tower water, so it was decided to apply this new measurement approach to that application.

Historically, a method utilizing a dynamic or flow-through system for air stripping a sample of cooling tower water has been used that was developed for use by El Paso Products in the early 70’s (Vernon et al., 1981). An experiment was designed to evaluate the effectiveness of the traditional El Paso method and the new Eco Sensors method. Evaluation was based on response, response time, minimum detectable quantity, and stability. Both methods used a Baseline 8800 H flame ionization detector to analyze the effluent from the stripper.

Benzene was chosen as the experimental analyte for two main reasons. First, because of its slight water solubility (0.18 g/100 mL), the generation of known standards was a simple dilution. Also, because of its relatively low dimensionless Henry’s Law Constant ($k_{H\ inv}$ = 0.227 gas/aq); benzene would tend to stay in the aqueous phase more so than other common VOCs such as propylene, 1,3-butadiene, and butene isomers ($1.022 \leq k_{H\ inv} \leq 9.732$) (Sander, 1999).

VOC Measurement Method Descriptions

The traditional El Paso Method uses an air stripping apparatus to air-strip highly reactive VOC’s from a water matrix. In our experiment, the main chamber was a 914 mm chamber with an internal diameter of 76 mm, which is constructed of clear, heavy-walled glass. This chamber was packed with 6-8 mm berl saddles to a height of 660 mm, and capped with non-reactive end caps. Stainless steel and Teflon tubing were used to transport gas and water throughout the system. Following the main air stripping column, a glass knock-out filter was used to prevent any liquid from entering the analyzer, and a bubbler was used to visually display an excess of stripped gas supply to the analyzer. In the experiment, a heated flame ionization detector was used to prevent problems caused by condensing water in the sample lines.

The Eco Sensors approach uses a very low flow sparger instead of a trickling tower to strip the dissolved and entrained gases and volatiles from the water. The sparging unit used was in a 25 mm diameter X 75 mm in height enclosed chamber with the carrier air pumped in and out by flexible tubing.

VOC Measurement Results

Figure 3 shows the response of the instrumentation using the Eco Sensors stripper vs. the El Paso stripper. A linear regression of the data showed good linearity, $r^2 = 0.9993$. Both methods are equally good in accuracy.

The response times for the two methods was markedly different. These are plotted in Figure 4. The Eco Sensors method shows a sharply defined response while the El Paso method responds slowly and asymptotically. The Eco Sensors method response time is several 10's of seconds vs. several hundred seconds for the El Paso method.

More comparative data from the test of the two methods is shown in Table 1.

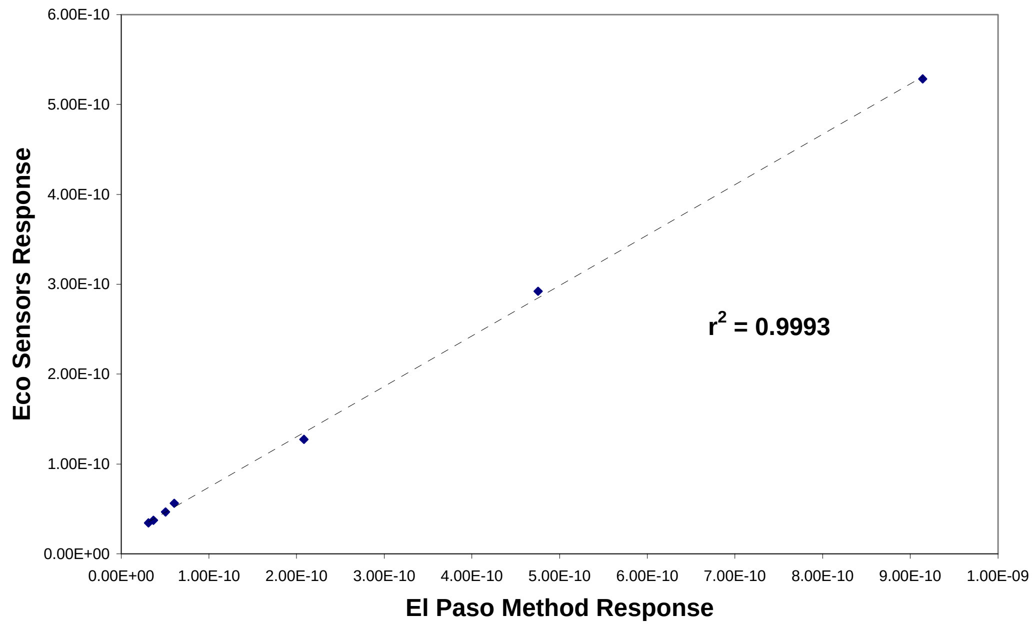

FIGURE 3 Benzene Response (0-10 ppm), El Paso Method vs. Eco Sensors Method

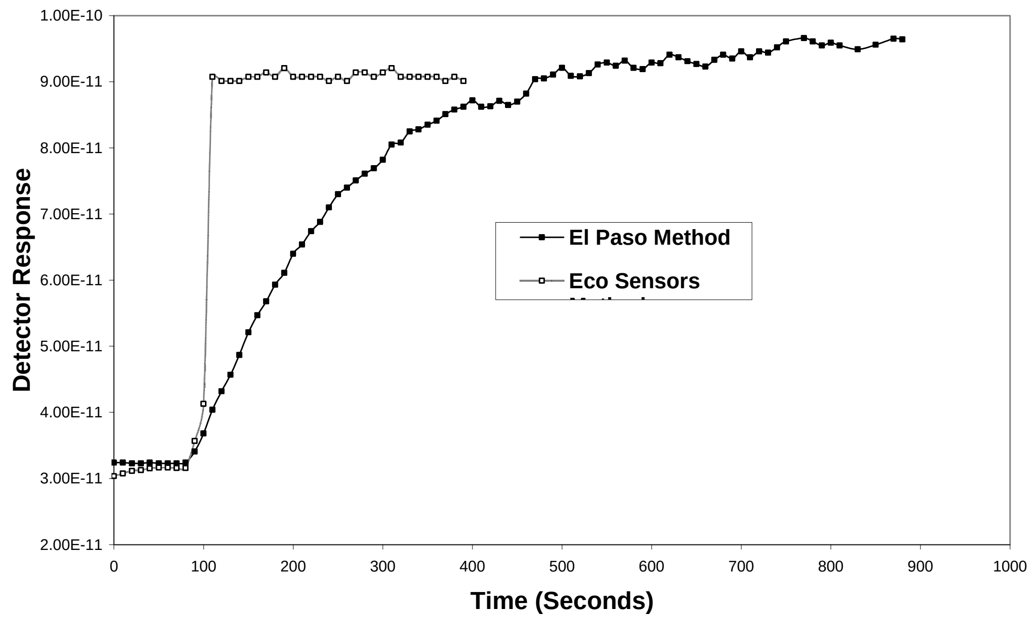

FIGURE 4 Respnse Rate to Benzene (1.0 ppm)

TABLE 1 Comparative Summary of the Two Measurement Methods

	Eco Sensors	**El Paso Tower**
Background	**29.7 pA**	**31.2 pA**
Gain	**64 pA/ppm**	**89 pA/ppm**
Noise (Ten minutes)	**1.57 ppb**	**3.39 ppb**
Minimum Detectable Quantity (3 X Noise)	**4.71 ppb**	**10.16 ppb**
Response Time (90% span signal)	**29 seconds**	**300 seconds**
Stability (Coefficient of variance or % RSD)	**0.46%**	**1.49%**

The largest differences between the two systems are the stability of the signal and the response time. This can be seen in Figure 4, and is also reflected by the coefficient of variation for the equilibrated systems in Table 1. The major variables that determine the response time are the volume of water in each system and the Henry's Law constant of the analyte in question. The Eco Sensors stripping method contains less than 100 mL of water at any given time in the stripping chamber, while the El Paso method contains over 2 L of water. Therefore, for any given analyte, the Eco Sensors chamber will respond significantly more quickly than the El Paso stripper. In the case of this experiment, the difference was a factor of 10.

Conclusions for VOC Use

The Eco Sensors stripping method has many advantages over the traditional El Paso trickling tower method. The most significant is the response time. Due to the large volumes of water in the El Paso tower, it is slow to respond to volatiles that do not readily transfer to the gas phase. The alternative air stripping method overcomes this by minimizing the amount of water in the Eco Sensors chamber. The Eco Sensors method was also much more stable than the El Paso method, which made the Eco Sensors stripping method more sensitive despite being slightly less efficient. Another advantage of the Eco Sensors stripping method is its size; it is much smaller than the El Paso Tower, which also translates to a more cost effective system. The set-up and use of the systems was equal, neither presented a significant problem.

Long-term maintenance and ruggedness of the instrument are also important. The El Paso method, if contaminated, must be broken down and cleaned. This would expose the glass components of the system to possible breakage. Also, the packing material in the main stripper column (berl saddles) may need to be periodically replaced as they become contaminated. The clear glass may also allow the growth of algae and bacteria, which may compromise the accuracy of the system. The Eco Sensors air stripping method uses rugged components, which should not break unless severely mishandled. The stripping chamber is made of an opaque material, which would prevent algal growth. Its low cost allows throwaway replacement to be the simplest maintenance solution.

Temperature Considerations

A dissolved gas concentration measuring instrument using the Eco Sensors stripper is as accurate as the gas sensor connected to it. Operated within its recommended parameters, the stripper does not introduce significant inaccuracies. The principle variable that affects calibration is temperature. The temperature-dependent expression of Henry's Law predicts a strong positive correlation as a function of temperature. As long as the instrument is operated indoors where the temperature is stable, this should not be a problem. For outdoor use and advanced systems, we are developing microprocessor based sensing instrumentation that will automatically adjust the calibration for temperature changes.

Summary

The Eco Sensors stripping method was evaluated for both dissolved ozone and benzene quantification. Correlation between measurements by established techniques was >0.99 in both cases. The new method is both faster in response, and achieved with a simple and compact stripper. The stripper can be used as the sampling apparatus with most conventional gas sensing instruments.

The Eco Sensors stripping method and hardware combined with suitable sensing instrumentation is lower in cost than most competing systems. The resulting instrumentation should be very maintenance free because the sensors are not immersed in the water, and the components that do contact water are compact and economically replaced ...

Patents have been applied for in many countries.

References

(1) Sander, R. "Compilation of Henry's Law Constants for Inorganic and Organic Species of Potential Importance in Environmental Chemistry (Version 3) http://www.mpch-mainz.mpg.de/~sander/res/henry.html (1999)

(2) Vernon, W.D. et. al., "A Device for Measuring Volatile Organic Carbon Emissions from Cooling Towers Water," *Journal of Air Pollution Control Association*, December: 1280-1282 (1981).

(3) Kilham, L.B., Pietrykowski, T."A New Method For On-Line Measurement of Dissolved Gases", *Gases and Technology*, 2(6):14-18 (2003)