Ozone Sanitization of Ultrapure Water Systems
Innovations in Dissolved Ozone Measurement by UV Photometry

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Abstract

Sanitization of UPW Systems utilizing Ozone continues to garner increasing interest. The major drivers are reduced "carbon footprint", energy costs, safety and the enhanced efficacy of Ozone verses heat and/or chemical treatment. The "Dissolved Ozone Measurement" both pre and post UV are critical parameters. One of the key obstacles to future implementation of ozone as treatment is concern over accurate and stable dissolved ozone measurement. Ozone is primarily used in UPW for TOC, sterilization and biofilm control.

The paper will provide an overview on the drivers for the use of ozone. Basic ozone generation systems for UPW: UV, electrolytic and corona discharge are compared. The main dissolved ozone measurement methods: Colormetric (Indigo trisulfonate), polarographic (membrane), ORP (oxidation-reduction-potential) and UV Photometry are discussed.

A typical UPW Pharmaceutical Sanitization System utilizing Ozone will be presented. The principals of Ozone Measurement by UV Photometry are provided. Included is the history of Dissolved Ozone Measurement by UV Photometry in UPW for Pharmaceutical and Semiconductor Water Systems.

The data presented will show that properly designed instruments utilizing UV Photometry at 254nm will provide resolution down to the ppb levels, with low PM (preventive maintenance) requirements and relatively long service life. Typically, the units do not require recalibration.

Key Words: Dissolved, Ozone, UV photometry, measurement, UPW, Pharmaceutical, semiconductor

Introduction

Drivers for the use of Ozone:

Ozone has been used successfully to sterilize, reduce TOC and eliminate biofilms in UPW (Ultrapure Water Systems) for many years. Today, with the issues of green solutions, water savings, safety, increased efficacy and the reductions of carbon footprints, the use of Ozone for the Sanitization of UPW Systems where the treated UPW will be used in a process, i.e. pharmaceutical [1] and personal care products is expected to grow.

Why Ozone:

Ozone is a powerful oxidant. The hydroxyl radical is second only to Fluorine as an oxidizing agent [2].

Oxidizing Agent	EOP (ev)	EOP (x Cl_2)
Fluorine	3.06	2.25
Hydroxyl radical	2.80	2.05
Oxygen (atomic)	2.42	1.78
Ozone	2.08	1.52
Hydrogen peroxide	1.78	1.30
Hypochlorite	1.49	1.10
Chlorine	1.36	1.00
Chlorine dioxide	1.27	0.93
Oxygen (molecular)	1.23	0.90

Ozone in water creates the Hydroxyl radical (HO^o) which is typically the predominant reaction pathway.

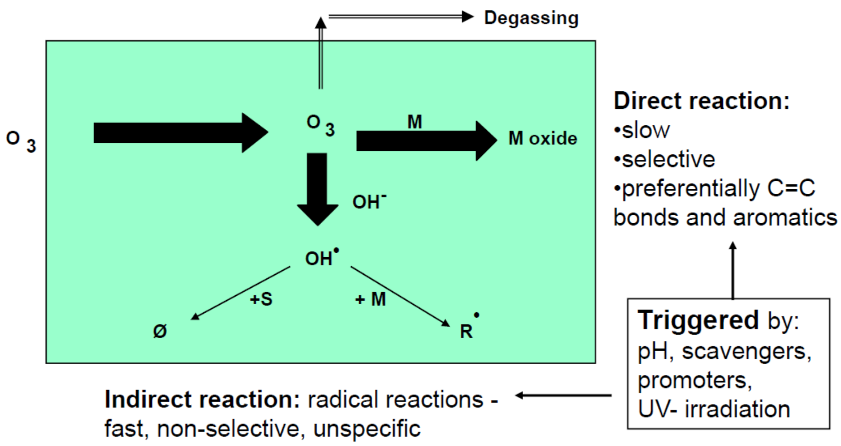


Figure 1. Chemical Reactions of Ozone (Hoigné & Bader)

Ozone is a strong Biocide. It kills by lysing the cell. The lysing process causes the cell wall to rupture, releasing the cell contents which are further oxidized to CO_2 & water. Conventional chemical and heat sterilization kill the cells, but leave the cellular material as food for further biological growth. The efficacy of Ozone in attacking viruses, spores, cysts and bacteria is well documented.

Ozone is considered a **GREEN CHEMICAL**. It is generated at point of use. There is no on-site storage or transportation required. Gaseous Ozone and dissolved ozone will decay over time ($2\ O_3 \longrightarrow 3\ O_2$). The decay rates will be a dependent on the pH of the water, temperature, scavengers, promoters, etc. The use of Ozone saves water by eliminating the necessity for rinsing necessary with chemical cleaning. It is less energy intensive than heat and safer. Data supports that Ozone provides improved efficacy in controlling TOC and Biofilms. Maintaining a continuous dissolved O_3 concentration of 0.020 to 0.050 ppm (20 to 50 ppb) offers the opportunity for continuous control with no water loss or downtime. There are reports of good results requiring only 0.020 ppm (20 ppb).

Methods of Ozone Generation:

There are three (3) primary methods for generating Ozone: UV Radiation, Electrolysis and Silent Electrical Discharge. For our discussion, Electrolysis and Silent Electrical Discharge are the typically used methods to produce ozone in UPW sterilization applications.

- **Ozone Generation** →

Reaction:	$O_2 + O$	—>	O_3
Electron Impact:	$O_2 + e^-$	—>	$O + O + e^-$
Photolysis (λ<200 nm):	$O_2 + h\nu$	—>	$O + O$
Trimolecular:	$O + O_2 + M$	—>	O_3 + M Collision

- **Ozone Decay:** ←

Electron Impact:	$O + O_2 + e^-$	<—	$O_3 + e^-$
Molecular collision:	$O_2 + M$	<—	O_3 + M (Thermal Decay)
Photolysis (λ > 250 nm):	$O + O_2$	<—	$O_3 + h\nu$
Recombination	O_2	<—	$O + O$
Atomic collision	$2\ O_2$	<—	$O + O_3$

Influenced by: Radical Concentration, Temperature, Concentration of potential Reaction Partners

Figure 2: Ozone Generation

For purposes of this paper, we will concentrate on the two methods of ozone generation currently being employed by the Pharmaceutical Industry.

A. **Electrolytic:** Utilizes the process of separating a water molecule into its component elements of Oxygen and Hydrogen. A solid electrolyte separates the anode and cathode, a DC current is fed to the cell which causes the UPW to split into ozone, oxygen and protons on the anode side and the reduction to hydrogen gas on the cathode side.
   1. High Purity water use only
   2. Water dissociated using a solid electrolyte
   3. Process water becomes oxygen source for the ozone generation
   4. No additional ionic contamination
   5. Produced ozone is dissolved into process water as soon as it is formed
   6. Minimal equipment required for the process
   7. Under pressure, relatively high ozone concentrations can be produced and dissolved

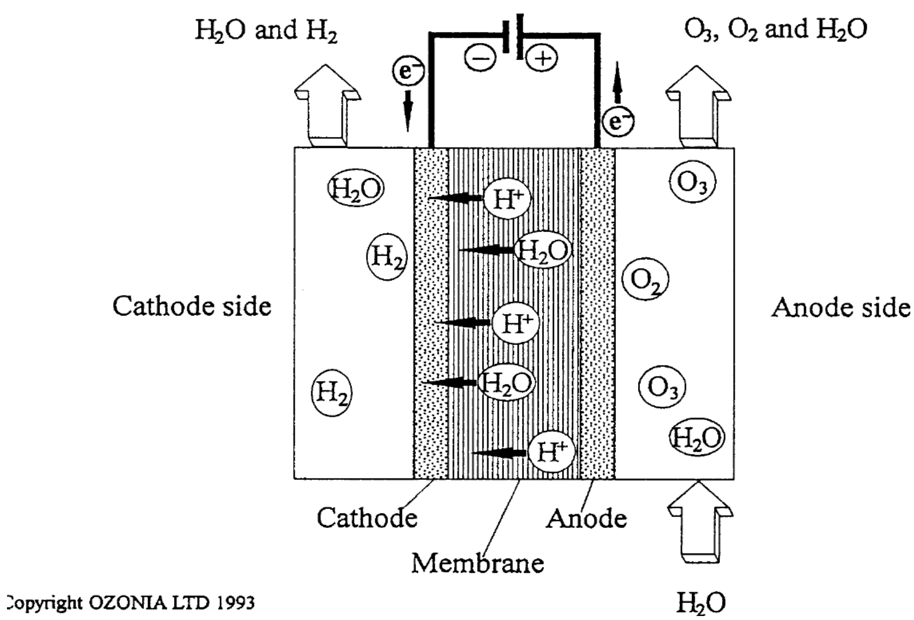


Figure 3: Electrolytic Ozone Cell

B. **Silent Discharge (Corona Discharge):** Ozone is produced by an electrical discharge in a gas stream containing oxygen. The energy conversion efficiency, ozone gas concentration levels and the purity of the resulting ozone gas stream can vary dramatically depending upon the ozone generator employed. Two (2) methods commonly in use today are *Volume Discharge* & *Surface Discharge*:

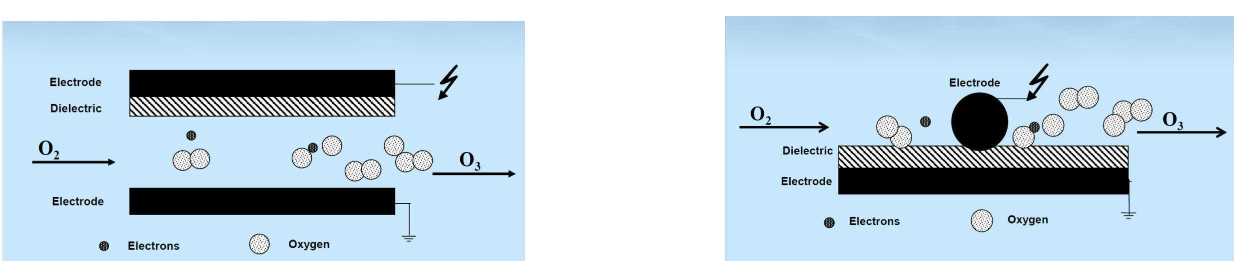


Figure 4: Comparison: Volume Discharge vs. Surface Discharge

In *volume discharge* the electrons must move across an air gap to reach the low voltage electrode. This causes inefficiencies in cooling which result in less than 20% of the energy employed being used to produce ozone with the balance generating heat. The heat generated and along with ozone destruction caused by material of construction issues (iron oxides act as catalysts in the destruction of ozone) limit the ozone concentration that can be produced. These phenomena necessitate the addition of nitrogen (as much as 10-15%) to the feed gas in order to reach higher ozone gas concentrations. (NO_x compounds are believed to sequester the FeO sites).

In *surface discharge* the high voltage electrode rests on the dielectric and heat removal (cooling) does not have to move across an air gap. Therefore the heat is removed more efficiently, allowing the ozone generator to operate at a lower temperature per unit of energy employed. The resulting geometry of the generator, the allowable higher oxygen content of the ozone generator feed gas (>95% O_2) and the materials of construction (no Fe containing materials in the ozone wetted path) mitigate against the necessity for N_2 additions and the resulting formation of NO_x compounds. The *surface discharge* units described here are relatively expensive compared to *volume discharge* and only make sense economically where high purity, high ozone gas concentration and little or no NO_x are tolerated. In the author's opinion this would include Sterilization of Pharma UPW Systems.

	Electrolytic	**Corona Discharge**
Method of Production	• From DI water at current densities • Creates ozone directly in the water	• Cold or current controlled electric discharge in a gas containing ozone
Concentration / Dosage Levels	• Relatively low flow rates • Low dissolve ozone concentrations • Typically adequate for the majority of small to medium sized systems	• No limit as function of the system design • Can be sized to handle large flows and high dose rates.
Production	• At present, available units appear to be limited to a production of 9 grams/hours. • Several units can be ganged to supply higher dosage requirements	No practical limits, from less than 1 gram/hour to over 250 kgs/hour
Contacting	• Not required • Creates dissolved ozone	• Very important to the efficiency of the system • Numerous contacting systems are available
Purity Issues	• High Purity • N_2 addition not required	• Excellent to poor dependent on the generator selected • Low NO_x generators available
Maintenance	• High – compared to corona discharge • Electrodes need to be replaced on a regular interval	Relatively Low – some suppliers offer 3 year warranties with little or no PM (Preventive Maintenance) needed
Capital Costs	Medium	Low to Medium High dependent on the ozone system employed
Operating Costs (based up 9 g/hr O_3 production)	Relatively high power usage compared to corona discharge: ~ 7 g/hr–O_3/kwh	Relatively low power usage compared to electrolytic: ~ 50 g/hr-O_3/ kwh
Comparison: 9 g/h – O_3 • Dimensions • Weight • Cost • Cooling	 • 30 x 29 x 14" • 146 lbs • $35,000 • Water	 • 15 x 7 x 6" • 14 lbs • $5,000 (generator only) • Air
General Remarks	• Mainstay in Pharma ozone sanitization • Good operating history • Preferred method for many companies	• > 100 year history in water treatment • High Purity ozone systems are available with good operating histories in semiconductor

Figure 5: Comparison Electrolytic vs. Corona Discharge

<u>Dissolved Ozone Measurement:</u>

There are several methods in use today for dissolved ozone measurement [3]:

1. Colormetric – Indigo trisulfonate (the indigo method) [4] is used both as an inexpensive method to measure dissolved ozone, but also as a verification of the instrumentation measurement [5].
2. Polarographic – requires a sensor and an electrolyte. Is used for both UPW and other types of water.

3. UV Photometry – Good history for dissolved ozone in clean water in the semiconductor industry. Relatively new to Pharmaceutical and other UPW applications. Requires Clean water (absence of constituents which absorb at 254 nm and/or matrixes in the water which could affected).
4. ORP (Oxidation Reduction Potential) – Inexpensive, but sensitive to oxidants such as chlorine in the water, which will give a false reading.

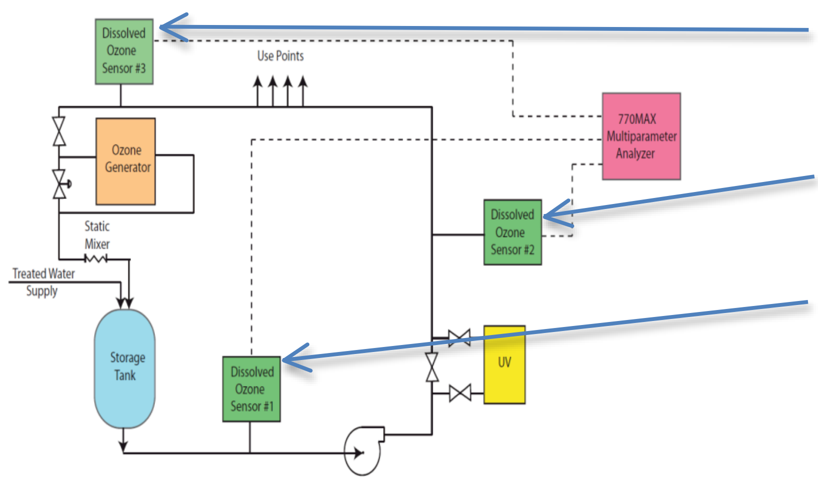
Methods 1, 2 and 3 are the most commonly used where the potential for false readings is possible.

Ozone Measurement by UV at 254 nm [6] is the method used by NIST for the NIST Standard Reference Photometer (SRP) for Ozone in Ambient Air Measurements. The NIST SRPs are located around the world to provide standards for Low Concentration Ozone Gas Measurements. Of late this responsibility has been transferred to France.

The IOA (International Ozone Association) Regulation 002/87 (F) recommends an extinction coefficient 3000 ltr /mol cm (at 1 atm/0^0 C) for ozone gas measurement utilizing UV_{254nm}.

The three (3) UV measurements typically employed are:
1. High Concentration Gas
2. Low Concentration Ambient
3. 3. Dissolved Ozone.

Three (3) Dissolved Ozone Measurements in a Pharmaceutical UPW System [7]:



 # 1 – Post-UV confirms that the sterilization has level was maintained over the entire loop or destroyed by UV.

 # 2 – To measure ozone levels post UV

 # 3 – Storage Tank to control & confirm the targeted concentration is achieved.

Figure 6: Dissolved Ozone Measurements
(Mettler-Toledo Thornton Application Note: An-0113)

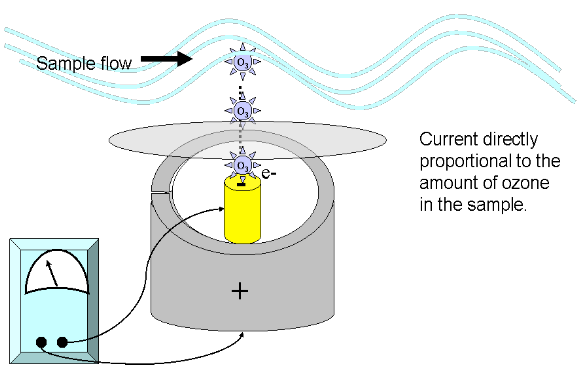
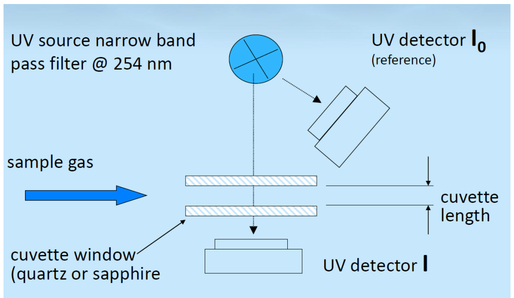


Figure 7: Polarographic Sensor

1. Molecules of O_3 pass through the cell membrane
2. O_3 reduced at the cathode to produce an electron.
3. The electron flows through the measurement cell as an electrical current.
4. The current is proportional to the number of ozone molecules which are directly proportional to the O_3 concentration of the sample
5. Requires an electrolyte

UV Photometry:
Most of the Ozone Photometers in use today, operate at 254 nm (Hartley Band)

At 254 nm ozone measurement is very sensitive. A low pressure Hg lamp is used as the source with only the line at 253.7 nm being used.



- The concentration is calculated by using the Bouguet-Lambert-Beer Law as shown below:
- $I = I_0 \, 10^{(-\alpha LC)}$

I = UV light intensity with ozone
I_0 = UV light intensity
α = absorption Coeff. by IOA of *"3000 l/mole cm"*
L = cuvette length
C = O_3 concentration

Cuvette Length:
The cuvette defines the measurement range and the sensitivity of the instrument. The cuvette length is inversely proportional to the ozone concentration to be measured [8].

RANGE	~ Cuvette Length
400 g/Nm^3	0.4 mm
200 g/Nm^3	0.8 mm
1 g/Nm^3	40.0 mm
1 ppm_v	300 mm

Measurement Ranges:
a. Dissolved ozone UPW (no interfering matrixes)
   - High concentration: 2 to > 200 ppm
   - Low concentration: < 20 ppb to over 100 ppb

b. Ozone gas
   - High concentration: > 300 g/Nm^3 (20 %wt/wt)
   - Low Concentration: < 1 ppm_v (100 to 300 ppb)

Enemies of ozone measurement by UV photometry are:
a. Dirt: Defined as anything which absorbs at 254 nm
b. Bubbles in dissolved senor will attenuate the light and provide a false reading (high or low) dependent on whether or not the light is diffused or focused.

Solutions are the regular zeroing of the instrument and the prevention of the formation of bubbles inside of the cuvette.

It has been stated that once biofilm is established, it is almost impossible to remove [9]. Europe and the USA have different approaches:

- Europe:
  - Continuous sterilization at 20 parts per billion (ppb)
  - Preference for electrolytic ozone over corona discharge
  - Early poor experiences with oxygen concentrators failing
- USA:
  - Intermittent sterilization at 50 to 100 parts per billion (ppb)
  - There does not seem to be preference between electrolytic & corona discharge

1. Mounted below UPW line.
2. Distance as short as possible
3. Recommended sample slow of 50 to 100 ml/min
4. Takes 30 reading per second.
5. Certificate of Calibration (error <0.5% of range)
6. Should be zeroed on regular basis as a precaution.

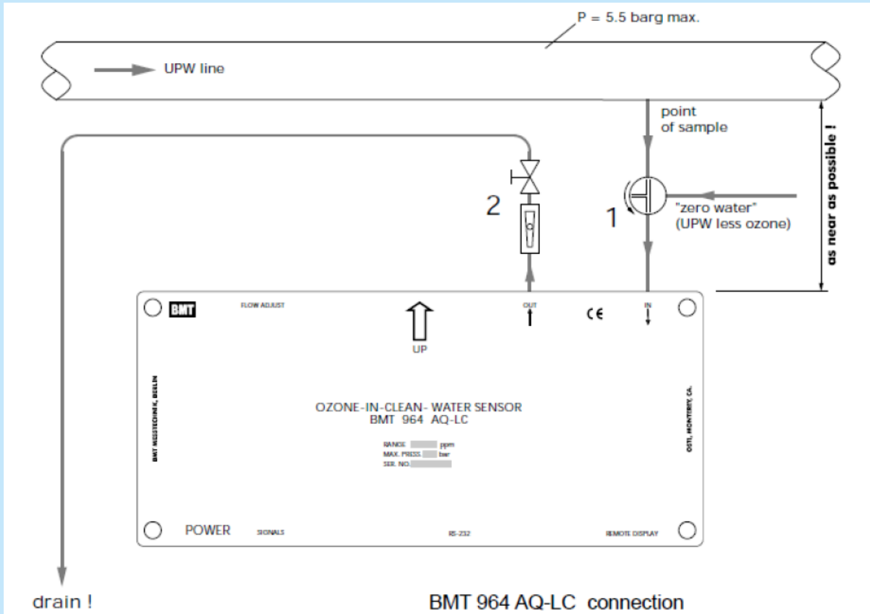


Figure 8: Installation of an Ozone-In-Clean Water Senor

Requiring a recommended sample flow of only 50 ml/min, this design would save 133,000 gallons/year of water verses the 1.0 l/min flow required by other measurement techniques. The unit can be installed inline and not require any water usage at all.

Actual Results in a Pharmaceutical Installation:

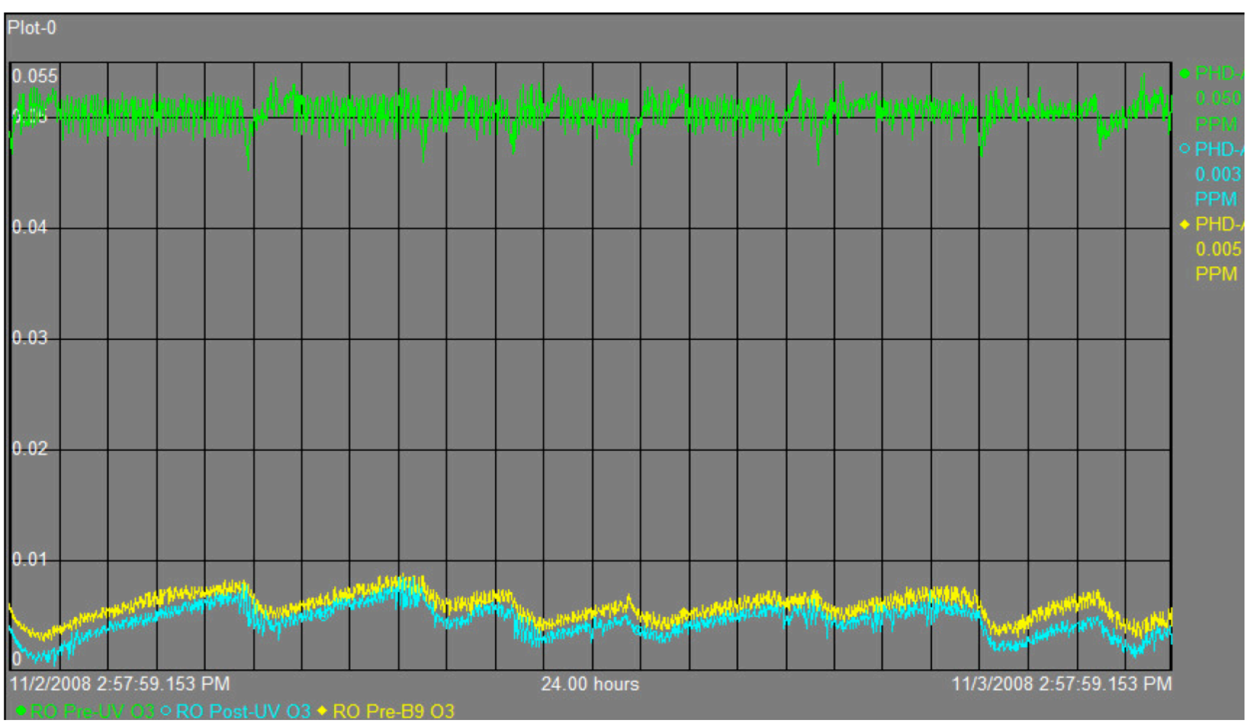


Figure 9: Three (3) Dissolved Ozone Measurements

The upper measurement shows the controlled sanitization measurement of 50 ppb. The periodic fluctuations are due to the makeup water dilution and the time element before the system goes back to the targeted dissolved ozone concentration. The control is 50 ppb ± 3 ppb.

The lower two (2) measurements are Post UV Destruct. The correlation between the two (2) sensors is approximately 1-2 ppb. This is an excellent result. The distance between the *dissolved ozone sensors is approximately 1500 feet.* They are both measuring within one (1) ppb and fluctuating within two (2) ppb of their designed range.

The data presented in Figure 10 was generated using the same three (3) x BMT 964 AQ-LC, range 0-0.75 ppm (750 ppb) instruments which provided the dissolved ozone concentrations shown in Figure 9. All of the instruments, some with up to 11,000 hours of operation, showed the electronics and UV lamps to be in excellent operation. As expected in a UPW installation, the Cuvette Dirty reading remained at 0.0%.

Under existing protocols, the Certificates of Calibration issued with each unit had to be reissued every twelve (12) months. Therefore, BMT 964 AQ-LC were to be returned every twelve (12) months for a “as received” calibration check, recalibrated and a new Certificate of Calibration issued. Since the time element was twelve (12) months, not twelve (12) months of operation, some units had been operated for shorter periods of time.

In Semiconductor UPW applications, the BMT 964 AQ (Ozone In Clean Water Sensor) has been operating for over fifteen (15) years with excellent performance as related to accuracy and reliability. The fundamental principles of Ozone Measurement by UV Photometry have employed successfully for both high and low concentration ozone gas measurement and for “dissolved ozone in clean water” in thousands of installations around the world.

Along with a *Certificate of Calibration*, the BMT 964 AQ-LC is available with *Certificates of Material Suitability* and *Certificates of Material Authenticity*. This allows the units be installed in line with no water usage at all or to drain with a recommended sample flow rate of only 50 ml/min. This offers considerable water savings over alternative sensor measurements.

Cal. Date	Unit	As Built Cal. Error	As Rec. Cal. Error	New Cal. Error	Operating hours	Comments: Diagnostics & Error/Event Logs indicate:
Oct 26 2009	A	< 0.2%	< 0.2%	< 0.2%	7,000	UV lamp & electronics are in excellent condition. The unit was zeroed ~ once every 2 weeks. Cuvette Dirty = 0.0%
Oct 14 2010	A	< 0.2%	< 0.5%	< +0.1%	11,000	UV lamp & electronics are in excellent condition. Since July of 2010, the unit was zeroed ~ once per month. Cuvette Dirty = 0.0%
Oct 21 2011	A	< 0.2%	< +1.9%	< +0.1%	19,350	UV lamp & electronics are in excellent condition Only zeroed every few months Cuvette Dirty = 0.0%
Dec 8 2009	B	< 0.2%	< +0.4%	< +0.1%	8,100	UV lamp & electronics are in excellent condition. The unit was zeroed ~ once per month. Cuvette Dirty = 0.0%
July 19 2010	B	< 0.2%	< +0.4%	< +0.1%	11,290	High voltage contact was disconnected UV lamp & electronics are in excellent condition Cuvette Dirty = 0%, very seldom zeroed
May 25 2011	B	< 0.2%	< +0.2%	< -0.1%	17,350	UV lamp & electronics are in excellent condition Zeroed once per month Cuvette Dirty = 0.0%
Feb 23 2010	C	< 0.2%	< +0.4%	< +0.1%	3,300	UV lamp & electronics are in excellent condition. The unit was operated for 4 months and zeroed 3 times. Cuvette Dirty = 0.0%
Mar 28 2011	C	< 0.2%	< +0.5%	< +0.1%	11,000	UV lamp & electronics are in excellent condition. Zeroed less than once per month. Cuvette Dirty = 0.0%

Cal. Date	Unit	As Built Cal. Error	As Rec. Cal. Error	New Cal. Error	Operating hours	Comments: Diagnostics & Error/Event Logs indicate:
Oct 18 2012	C	< 0.2%	< -0.1%	< -0.1%	27,430	UV lamp & electronics are in excellent condition Since Jan. 2011, zeroed very month Cuvette Dirty = 0.0%

Figure 10: Calibration Stability / Reliability Data (actual data from three x BMT 964 AQ-LC, Range: 0-0.75 ppm operating at a large pharmaceutical installation during a three year period. The units are sent back once a year for verification of the accuracy and issuance of a new Certificate of Calibration)

Ozone Measurement by UV Photometry is an accepted method:

- Used by NIST for the Standard Reference Photometer (SRP) for Ozone in Ambient Air. Approximately thirty (30) SRPs have been delivered to government agencies and standard bureaus around the world. Ownership of the maintaining the SRP has now been passed over to the French Bureau of Standards.
- IOA (International Ozone Association) recommends an Absorption Coefficient of 3000 l/cm mole for measurement by UV Photometry at 254 nm.
- Dissolved ozone measurement has been employed successfully in the semiconductor industry since 1996 with a very good operating history.
- Thousands of UV Photometers are employed around the world

Conclusions - Recommendations:

a. Ozone Systems:
   1. There are an assortment of ozone generation solutions and contacting systems available in the marketplace today.
   2. The technology has evolved dramatically over the last fifteen (15) years.
   3. High concentration ozone gas with O_2 as the feed gas will improve mass transfer efficiencies, reduce the introduction of NO_x compounds and the amount of gas injected into the system.
   4. Selection of the appropriate solution for the site specific application offers the opportunity for significant reductions in preventive maintenance, capital and operational costs.

b. Dissolved Ozone Measurement:
   1. Different O_3 measurement solutions are available today.
   2. The user needs to evaluate cost of ownership over time verses the initial costs.
   3. UV offers the potential for improvements in accuracy, reliability and reporting.

References:

1. International Society for Pharmaceutical Engineering (ISPE) *Good Practice Guide: Ozone Sanitization of Pharmaceutical Water Systems* (ISPE, Tampa, FL, 2012), p. 13 , section 2.2.
2. Stanley, Bruce T., *Electrolytic Ozone Generation and Its Application in Pure Water Systems*, Ozonia Ltd, Duebendorf, Switzerland (1993)
3. Gottschalk, C., Libra, J.A., and Saupe, A., *Ozonation of Water and Waste Water* (Wiley-Vch Verlag GmbH, Weinheim, Germany, 2000), p. 72
4. Masschelein, W.J. et al., Colorimetric Method for Manual Determination of Ozone Concentrations in Water*, Ozone Science & Engineering, Special Issuee on Quality Assurance in Ozone Practice* (1998), pp. 443-445
5. International Ozone Association (IOA), *Standardization Committee Report: Colorimetric Method for Determination of Traces of ozone in Water* (IOA, Scottsdale, AZ, 1989)
6. Wallner, F., High Concentration Photometric Ozone Measurement Primer, *Ozone News*, 35 (1), 20-26 (2007)
7. Bionshine, Todd, Dissolved Ozone in Pharmaceutical Water Systems: How and Where to Measure Dissolved Ozone, *Pharmaceutical Technology*, (April 2, 2006)
8. Christopher, Ralph, Accuracy of High Concentration Ozone Photometry, *Paper – IOA/IUVA World Congress,* Paris, France, May 2011.
9. Trager, H., Microbial Control, *Ulrapure Water*, 22, (May/June), pp.24-30 (2005)