Guideline for Measurement of Ozone Concentration in the Process Gas From an Ozone Generator

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Abstract

A joint meeting of members of the Quality Assurance Committees of the International Ozone Association Pan American Group (PAG), European-African Group (EAG), and Nippon Islands Group (NIG) was held in Oxford, Ohio on November 8 and 9, 1995. The purpose of the meeting was to establish a single, shared guideline for ozone concentration measurement in the gas phase and, in particular, from commercial ozone generators.

The ozone concentration reading of record may be determined by wet-chemistry only (Method A) or by a commercial UV meter verified by wet-chemistry (Method B). It should be noted that the methods are not necessarily listed in priority order: either may be used. For Method A, the ozone concentration reading of record shall be the average of at least three (3) wet-chemistry test results, and the standard deviation percentage (i.e., standard deviation ÷ average) for the measurements shall be less than ±2%. For Method B, the UV meter's displayed results shall be calibrated independently for sample cell temperature and pressure and also for gram molecular weight when the result is displayed as percent by mass (%wt). The UV meter shall be validated by wet-chemistry test results. A minimum of nine (9) UV meter versus wet-chemistry comparative tests shall be performed, and the relative percent difference for each comparative test shall be identified using the equation shown below. The UV meter shall be considered validated when the average percent difference of at least nine (9) comparative tests is within ±2%.

$$\% \ Difference \ = \ \left\{ \frac{UV \ Concentration}{Wet-Chemistry \ Concentration} \ - \ 1 \right\} \ x \ 100$$

Overview

Members of the International Ozone Association (IOA) Quality Assurance Committee of the Pan American Group (PAG) presented a draft guideline for ozone concentration in gas phase measurement at the IOA PAG Conference held in Pasadena, California in March 1992. Following the presentation, a workshop was conducted to obtain comments from the IOA membership in attendance. Responses to comments, received during the workshop and by mail after the conference, were published in the May/June 1993 issue of *Ozone News*, along with an update to the proposed ozone concentration measurement guideline. In that document a request was made for feedback from the IOA membership, at large, regarding the proposed guideline.

The predecessor organization of the Quality Assurance Committee of the IOA European-African Group (EAG) has published various "standards" for ozone gas and liquid phase measurement. These documents were used as reference materials for the PAG-developed document discussed above.

The IOA Nippon Islands Group (NIG) has published a document entitled "Measurements of Concentration of Ozone" that is written in Japanese. That document contains reference to both the PAG and EAG ozone concentration measurement papers.

Following the May/June 1993 *Ozone News* publication of the proposed IOA PAG guideline for ozone concentration measurement in a process gas, several supporting comments and some proposed alternatives for consideration were received by the PAG Quality Assurance Committee. Two primary considerations for change involved:

1)   reducing the tolerance for possible error from the proposed level of ±5%, and
2)   including an alternative method for ozone concentration measurement for the case when an ultraviolet (UV) ozone concentration meter is either not available at the plant site or is not selected for use in testing.

Both of these major considerations have been addressed in this paper.

At the IOA Ozone World Congress in Lille, France in May 1995, members of the PAG and EAG Quality Assurance Committees discussed the benefit of a singular guideline for ozone concentration measurement for the entire IOA. Toward this end, a joint meeting of members of the PAG, EAG and NIG was held in Oxford, Ohio on November 8 and 9, 1995. The purpose of the meeting was to establish a single, shared guideline for ozone concentration measurement in the gas phase and, in particular, from commercial ozone generators. The guideline agreed upon at this meeting is presented in this paper in sufficient detail for technicians to implement in field situations.

Proposed Gas Phase Ozone Concentration Measurement Methods

The focus of the proposed guideline is an ozone concentration measurement method for the ultimate purpose of determining the ozone production rate of commercial ozone generators. In this regard, the measured ozone concentration is combined with the measured gas flow rate to calculate ozone production. It was decided that the reference temperature and pressure for gas flow expression would be "normal" temperature and pressure of 0°C and one atmosphere pressure (101.3 kPa or 760 mm Hg). Further, it was emphasized that the proper gas flow rate must be coupled with the identified ozone concentration reading of record; otherwise inaccurate ozone production rates would be calculated. A separate section of this document is devoted to discussion of how to match the identified ozone concentration reading of record with the proper gas flow rate to correctly determine the ozone production reading of record.

The ozone concentration reading of record may be determined in one of two ways. Ideally, the selected methodology would be established by consensus agreement prior to the ozone production test or would be pre-established by the project specifications. Either Method A or Method B, described below, may be selected as the method for determining the ozone concentration reading of record. It should be noted that the methods are not necessarily listed in priority order.

METHOD A--WET-CHEMISTRY ONLY TEST METHOD

The iodometric wet-chemistry method (otherwise known as the KI method) appears to have a standard deviation percentage of 2% when performed in a careful manner using a prescribed procedure. A specific procedure is presented in this section of the paper, including discussion of areas where special precautions are necessary, such as quality control checks of the normality of the titrant used to obtain mass of ozone reacted and quality control checks of the totalized volume of process gas that passes through the gas washing bottle(s). For the wet-chemistry only test method, the ozone concentration reading of record shall be the average of at least three (3) wet-chemistry test results. Further, the standard deviation percentage (i.e., standard deviation ÷ average) for the three measurements shall be less than 2%.

Background of Ozone Wet-Chemistry Testing

The potassium iodide (KI) wet-chemistry method is based on the principle that iodide ion is oxidized by ozone to form iodine as the ozone gas is bubbled through a solution of KI. When bubbling is stopped, the KI solution pH is adjusted with sulfuric acid to pH 2, or lower, in order to complete the reactions. The liberated iodine is titrated to a starch endpoint with standardized sodium thiosulfate. The mass of ozone reacted is determined based on a theoretical ozone/iodine stoichiometry of 1.0.

Unfortunately, the ozone/iodine stoichiometry is not always 1.0, but can range from 0.65 to 1.5 (Birdsall, et al., 1952; Boyd, et al., 1970; Byers and Saltzman, 1959; Flamm, 1977; Gordon, et al., 1989; Wood, 1987), depending on testing methodology. Factors that affect the stoichiometry include: KI solution pH, buffer composition, buffer concentration, iodide ion concentration; sampling techniques; reaction time; and ozone gas flow rate.

Because of these influences on the desired stoichiometry of 1.0, the wet-chemistry test procedure must be implemented very carefully, using the prescribed procedure presented in the next section of this paper.

The necessary one-to-one stoichiometry is as follows:

$$O_3 + 2I^- + H_2O = I_2 + O_2 + 2(OH)^-$$
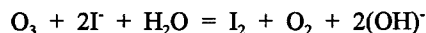
The iodine formed in the above reaction is titrated directly with thiosulfate ion:

$$I_2 + 2S_2O_3^{2-} = 2I^- + S_4O_6^{2-}$$
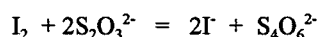
The reaction of ozone with iodide ion produces two moles of hydroxide ion for each mole of iodine. Hydroxide ion pre-existent in the absorption solution and/or formation of hydroxide ion in the reagent solution creates an inherent problem with the iodometric determination of ozone, because the reaction of ozone with hydroxide ion constitutes the initiation step of the ozone decomposition process in aqueous solution. The KI method and the NBKI$_e$ (IOA Standardisation Committee 001/87) methods are regarded as being better than other wet-chemistry methods because ozone decomposition and other side reactions are minimized, or at least are counterbalanced, in the subsequent acidification step so as to achieve the desired 1:1 stoichiometry during the sodium thiosulfate titration step. The NBKI$_e$ method, which is very weakly buffered, and the unbuffered KI method produce statistically equivalent results (Wood, 1987), having a 1:1 stoichiometry; and they are included as acceptable methods in this paper.

With the KI method, the iodide solution rapidly becomes basic and ozone decomposition potentially becomes a factor in the determination. Likewise, in the NBKI$_e$ modification, which is very weakly buffered, the local concentration of hydroxide ion might be expected to enhance the decomposition of ozone. Before the titration of iodine/thiosulfate, it is necessary to acidify the buffered solution to transform, back to iodine, any iodate ion that may have been formed.

The site-specific complications of the iodometric method most likely can be attributed to slight variations in the sampling parameters, assuming that the test equipment is properly calibrated and chemicals are properly prepared. For example, the flow rate of the gas sample bubbling through the KI or NBKI$_e$ solution has been shown to have an effect on the determination (Gordon et al., 1989). Ideally, the iodometric determination of ozone is reproducible when carried out under very strictly controlled conditions.

The detection limit of the KI and NBKI$_e$ methods is 0.1 mg/L. Specific chemical interferences include oxides of nitrogen, other oxidants capable of oxidizing iodide ion to iodine, and any inorganic impurities that might react with iodine itself. Generally, the interferences are minimal at the outlet of commercial ozone generators.

Ozone Wet-Chemistry Test Procedure

The wet-chemistry test results are inherently variable due to the complex chemical reactions that occur during the test and due to its sensitivity to analytical procedures. A definitive procedure for conducting the wet-chemistry test is presented here to enable the reader to obtain reasonably consistent results with an approximate 1:1 stoichiometry.

1. Equipment

1.1.   One or two standard gas washing bottles, 500 mL capacity, WITHOUT a fritted diffuser. A fritted diffuser may destroy the ozone.

1.2.   One totalizer-type wet-test gas meter equipped with integral manometer and thermometer capable of reading water temperature within ± 0.2 °C. It should be noted that the accuracy of the wet-test meter is critically important to the overall accuracy of the wet-test result. Toward this end, **the wet-test meter volumetric accuracy shall be within ±1%, as determined by an independent laboratory.**

1.3.   Tubing and connections of glass, stainless steel, aluminum, or Teflon. A small amount of Tygon tubing may be used to facilitate connections to glassware.

2. Reagents

2.1.   Use either unbuffered KI or slightly buffered KI (called $NBKI_e$). All other buffering formulations for KI are NOT acceptable.

2.1.1. Unbuffered KI

Potassium iodide stock reagent (2%): Dissolve 20 g KI in one liter of freshly boiled and cooled distilled water. Store in a brown bottle and refrigerate.

2.1.2. Slightly buffered KI ($NBKI_e$)

Potassium iodide stock reagent (2 %): Dissolve 20 g KI in one liter of freshly boiled and cooled distilled water. Add 7.3 g/L of disodium hydrogen phosphate ($Na_2HPO_4.2H_2O$) and 3.5 g/L of monopotassium dihydrogen phosphate (KH_2PO_4). Store in a brown bottle and refrigerate.

2.2.   Sulfuric acid (2 N): Add 56 mL concentrated sulfuric acid to 944 mL distilled water. Store in a reagent bottle.

2.3.   Sodium thiosulfate ($Na_2S_2O_3$) stock solution (1 N): Dissolve 250 g of sodium thiosulfate ($Na_2S_2O_3$) granules into one liter of freshly boiled distilled water. Store in a brown bottle and refrigerate.

2.4.   Prepare starch indicator solution by one of two methods listed below.

2.4.1. Zinc chloride starch indicator: To 4 g soluble starch, add a little cold distilled water and grind to a thin paste. Disperse the paste into 100 mL of distilled water which contains 20 g of zinc chloride ($ZnCl_2$). Boil the solution until the volume has been reduced to 100 mL. Finally, dilute this solution to a total volume of 1 L and

add 2 g of $ZnCl_2$. The indicator is stable for about one month when stored in the dark at room temperature.

2.4.2. Starch indicator: To 5 g soluble starch, add a little cold distilled water and grind to a thin paste. Pour into one liter of boiling distilled water, stir, and let settle overnight. Decant and refrigerate the clear supernate.

2.5. Sodium thiosulfate ($Na_2S_2O_3$) titrant (0.1 N): Add 100 mL of 1 N $Na_2S_2O_3$ stock solution to 900 mL freshly boiled distilled water. Standardize this solution each day, as discussed in Steps 3.1.1. and 3.1.2. below. It should be noted that other normalities may be used, as described in Step 3.7. below.

2.6. Potassium dichromate ($K_2Cr_2O_7$) (0.1000 N): Dissolve 4.904 g anhydrous $K_2Cr_2O_7$ (primary standard quality) in distilled water and dilute in a volumetric flask to one liter. Store in a reagent bottle.

2.7. Potassium periodate (KIO_3).

2.8. Distilled water: Distilled water quality is critical to results. Conductivity shall be less than 10 micromhos/centimeter.

3. Methodology

3.1. Standardize the 0.1 N sodium thiosulfate titrant using either method 3.1.1. or 3.1.2., below. This activity can be completed prior to the test, and shall be completed each day of the test.

3.1.1. To 150 mL distilled water in a 250 mL Erlenmeyer flask, add, with constant stirring, 1.0 mL concentrated H_2SO_4, 20.0 mL of 0.1000 N $K_2Cr_2O_7$ and 2.0 g KI. Cover and let mixture stand 6 minutes in the dark. Titrate with the approximate 0.1 N $Na_2S_2O_3$ titrant until the yellow color is almost gone. Add 1.0 mL of starch indicator solution and continue titrating carefully until the blue color just disappears. The normality of $Na_2S_2O_3$ titrant = 2.0 ÷ $Na_2S_2O_3$ mL consumed.

3.1.2. To 50 mL of distilled water in a 250 mL Erlenmeyer flask, add, with constant stirring, 0.05 g of potassium periodate (KIO_3) and 0.5 g of KI, followed by an additional 50 mL of distilled water. After mixing, add 10 mL of certified 0.1 N acid. The iodine formed is titrated with the approximate 0.1 N $Na_2S_2O_3$ titrant until the yellow color is almost gone. Add 1.0 mL of starch indicator solution and continue titrating carefully until the blue color just disappears. The normality of $Na_2S_2O_3$ titrant = 2.0 ÷ $Na_2S_2O_3$ mL consumed.

3.2.   Fill a 50 mL Class A burette with the $Na_2S_2O_3$ titrant that was standardized in Steps 3.1.1. and 3.1.2., above. Fill the burette just prior to adding ozone to the gas washing bottle (see Step 3.6.). Maintain fresh titrant in the burette (e.g., refresh daily).

3.3.   Add 400 mL of 2% KI or $NBKI_e$ solution to each gas washing bottle. Two bottles are suggested.

3.4.   Level the wet-test meter.

3.5.   Assemble the wet-test equipment for ozone product-gas measurements, as shown in Figure 1 below.
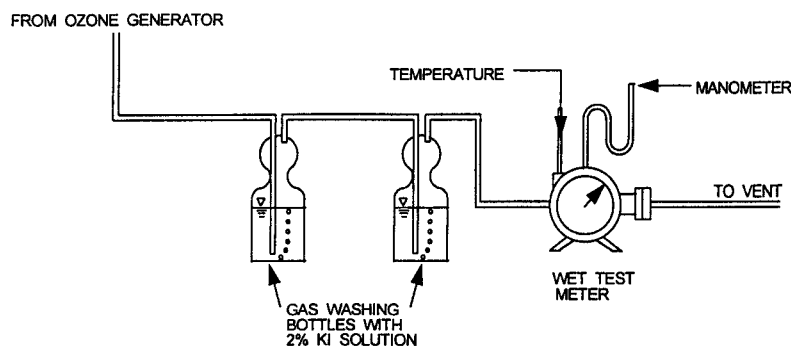

Figure 1.   Ozone concentration wet-test set-up for ozone generator product-gas.

3.6.   Bubble ozone through the KI solution and initiate recording the volume bubble through the KI by using either Step 3.6.1. or 3.6.2. below:

    3.6.1.   Safely purge the tubing from the ozone piping source to the gas washing bottle with fresh ozone before connecting the tubing to the bottle (e.g., purge into an off-line gas washing bottle). Then, connect the tubing that has been purged with ozone to the gas washing bottles and immediately begin recording the wet-test meter volume.

    3.6.2.   Allow the non-ozonated gas within the sample line to bubble through the test KI solution, in order to purge the sample line with sample ozone gas. Begin recording flow on the wet-test meter as soon as a yellow color is noticed at the point of entry in the gas washing bottle.

3.7.   Bubble 2 to 4 liters of ozone gas through the bottles at a rate of about 1 to 2 L/min, and record the exact volume of the wet-test meter as the uncorrected volume on the data sheet. The recommended gas volume to be collected depends on ozone concentration, titration volume, and $Na_2S_2O_3$ normality (see Figures 2 and 3 below). Better accuracy is obtained when the titration volume is at least 20 mL and the gas volume

is at least 2 L. Normality of the $Na_2S_2O_3$ titrant can be adjusted to achieve these conditions, as discussed in Step 2.5.
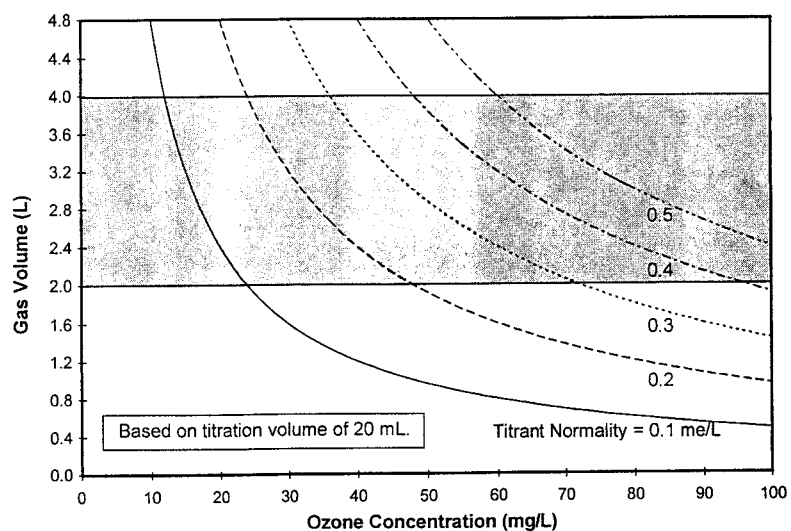

Figure 2.   Relationship among wet-test parameters for a titration volume of 20 mL.
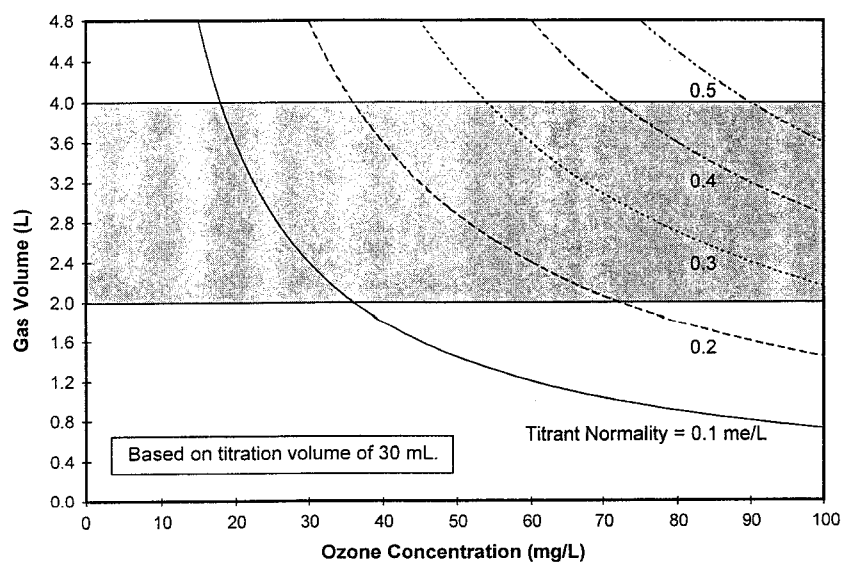

Figure 3.   Relationship among wet-test parameters for a titration volume of 30 mL.

3.8. After bubbling has stopped, quickly add about 10 mL of 2N H_2SO_4 to each gas washing bottle to lower the pH of the solution below pH = 2.

3.9. Transfer the liquid from each gas washing bottle to a 1- or 2-liter Erlenmeyer flask (use 2-liter for two gas washing bottles). Thoroughly rinse the gas washing bottles three times with distilled water, retaining all rinse water in the Erlenmeyer flask. When transferring contents, minimize splashing and aeration.

3.10. Read the initial volume of $Na_2S_2O_3$ titrant in burette. **NOTE: The titrant should have been standardized recently, as described in Steps 3.1.1. and 3.1.2.** Titrate with $Na_2S_2O_3$ until the solution becomes a pale yellow color.

3.11. Add about 5 mL of starch solution to the flask. A bluish color will form. Carefully continue the titration, drop by drop, until the blue color just disappears and the solution is clear.

3.12. Record the final burette reading and determine the total volume of titrant used. Record the volume of titrant used and the exact normality of the titrant from Steps 3.1.1. or 3.1.2. above.

3.13. Complete the calculations described in Step 4. below.

4. Determination of ozone concentration from wet-chemistry test procedure discussed in Steps 3.1. through 3.12.

4.1. Find temperature/pressure corrected gas volume using Equation [1].

$$V_{NTP} = V_a x \frac{(P_a - P_v - P_m)}{P_{NTP}} \ x \ \frac{T_{NTP}}{T_a} \qquad [1]$$

Where:

V_{NTP} = Gas volume in Liters (L_{NTP}) referenced to normal temperature and pressure conditions.

V_a = Uncorrected gas volume, in Liters, as measured by wet-test meter.

P_{NTP} = Normal, reference standard pressure (one atmosphere, which is 101.3 kPa or 760 mm Hg).

T_{NTP} = Normal, reference standard temperature (273.15 Kelvin = 0°C).

P_a = Barometric pressure in kPa or mm Hg.

P_v =   Vapor pressure in kPa or mm Hg, based on wet-test meter temperature. **(See Table 1, "Vapor Pressure Look-Up Table.")**

P_m =   Wet-test meter manometer pressure in kPa or mm Hg. **(NOTE: May have to convert from inches of water, using 1.868 mm Hg per inch of water and 0.1333 kPa per mm Hg. Typically, the wet-test manometer pressure is zero when testing the ozone generator product gas.)**

T_a =   Wet-test meter temperature in Kelvin, or 273.15 K plus wet-test meter temperature in °C.

4.2.   Find mass of ozone trapped in KI or $NBKI_e$, using Equation [2].

Mass   = $24 \times V_t \times N_t$

Where:

Mass   =   Mass of ozone trapped in KI or $NBKI_e$, in mg.

24   =   Conversion factor = 24,000 me/L per 1,000 mL/L.

V_t =   Volume of sodium thiosulfate titrate used, in mL.

N_t =   Normality of sodium thiosulfate, in mg/me.

4.3.   Find concentration of ozone in mg/L_{NTP} (Y_1) using Equation [3].

$$Y_1 = \frac{Mass\ from\ Equation\ [2]}{V_{NTP}\ from\ Equation\ [1]} \qquad [3]$$

4.4.   End of wet-chemistry test procedure.

METHOD B – INSTRUMENT (UV) METHOD VERIFIED BY WET-CHEMISTRY

The Method B approach for determining the ozone concentration reading of record shall be implemented using the following guidelines outlined below. It should be noted that ozone concentration readings from properly operating and calibrated UV meters (independently calibrated) have been shown to have a standard deviation percentage within ±2% of wet-chemistry test results (Rakness, et al., 1996 -- see following paper in this issue of OS&E).

1.   The UV meter's displayed results shall be calibrated independently. Specifically, the UV meter readings shall be corrected for sample cell temperature and pressure and for feed-gas gram molecular weight when the reading is displayed on a mass basis (i.e., %wt) and the meter's standard feed-gas gram molecular weight is different from the tested feed-gas gram molecular weight.

2.   The UV meter shall be validated by wet-chemistry test results (see Method A above for wet-chemistry test procedure).

   2.1.   A minimum of nine (9) UV meter versus wet-chemistry comparative tests shall be performed, and the relative percent difference for each comparative test shall be identified using Equation [4]:

$$\% \; Difference \; = \; \left\{ \frac{UV \; Concentration}{Wet-Chemistry \; Concentration} \; - \; 1 \right\} \; x \; 100 \qquad [4]$$

   2.2.   The UV meter shall be considered validated when the average percent difference of at least nine (9) comparative tests is within ±2%.

3.   The UV meter shall be verified at least once during the overall ozone generator testing program. However, wet-chemistry verification may be repeated at any time, if conditions dictate. It should be noted that UV meter calibration adjustments due to changes in sample cell temperature, pressure, or feed-gas gram molecular weight are not considered as a necessary reason for a separate wet-chemistry validation. The UV meter calibration adjustments for sample cell temperature, pressure, or feed-gas gram molecular weight are necessary adjustments for proper meter operation.

Background of UV Meter Operation

The International Ozone Association (IOA) Standardisation Committee - Europe has published several methods for measuring ozone concentration in the gaseous phase. Various references and literature sources are shown in the References section of this paper. The most common instrumental method in use is the UV measurement technique.

Gaseous ozone absorbs UV light with a maximum absorption occurring at 253.7 nm. At this wavelength, the commonly accepted gas-phase absorption coefficient for ozone is $3,000 \pm 30 \; L \; mol^{-1} \; cm^{-1}$, at 273 K and 101.3 kPa (AWWARF, 1991; Duguet, et al., 1986; Maurersberger, et al., 1986; Molina and Molina, 1986; Zurer, 1987).

Instruments for measuring the concentration of gas-phase ozone determine the light intensity without ozone and when ozone is present. The normal output is the difference between these two time-averaged readings, which is proportional to the actual number of ozone molecules present in the gas-phase (i.e., volume, temperature, and pressure sensitive measurement).

UV monitors normally are designed such that the displayed reading equals the concentration of ozone. If the temperature and pressure in the sample cell are known, the reading is directly proportional to the actual concentration of ozone in volumetric units (ppm, or grams per cubic meter), at an established reference temperature and pressure. By using the molar absorptivity value of $3,000 \pm 30 \; Lmol^{-1}cm^{-1}$ for gaseous ozone and under ideal, precision laboratory controlled situations, the ultraviolet measurement becomes an absolute measurement accurate to ±1 percent. In practical instrument applications, the accuracy has been shown to be within ±2% (Rakness and Henry, 1995).

There is minimal interference from other species that may be found in the output of ozone generators, such as nitrogen oxides, hydrogen peroxide, or nitric acid.

Commercially available gas phase UV ozone concentration monitors generally provide credible ozone concentration readings when suitably constructed and correctly installed. Meters may display ozone concentration readings on a volumetric basis (e.g., g/m^3, mg/L, or parts per million by volume) or mass basis (e.g., %wt). When displayed on a mass basis, the UV meter also must be calibrated for gas density.

The ozone concentration for a UV meter is determined by means of the Beer-Lambert Law, as shown in Equation [5], Equation [6], and Equation [7].

$$I = I_o e^{-\varepsilon l C} \qquad\qquad [5]$$

Where:

I_0 =   the light intensity in the absence of ozone, and

I =   the light intensity in the presence of ozone.

$$OD = \log\left(\frac{I}{I_o}\right) = \varepsilon l C \qquad\qquad [6]$$

Where:

OD is defined as the measured optical density.

$$C = \frac{OD}{\varepsilon l} \qquad\qquad [7]$$

Where:

ε = $3,000 \pm 30 \ M^{-1} cm^{-1}$ and

l =   the path length in cm

C =   ozone concentration in moles per liter

In order to obtain the concentration (C_{NTP}) from Equation [7], the temperature (T) and pressure (P) in the absorption cell are required, as shown in Equation [8].

$$C = \frac{OD}{\varepsilon l} \ x \ \frac{P_{NTP}}{P} \ x \ \frac{T}{T_{NTP}} \qquad\qquad [8]$$

The normal conditions are T_{NTP} = 273.15 Kelvin (K), P_{NTP} = 1.013 x 10^5 Pascals (Pa) corresponding to 0°C and 760 mm Hg. Equation [8] gives the ozone concentration in moles per liter (at NTP). In order to obtain the concentration in g/m^3 or mg/L (i.e., 1 g/m^3 = 1 mg/L), the concentration value as mole per liter must be multiplied by the factor 48,000 mg/mole.

The gas density adjustments are determined based on site-specific temperature and pressure, and when the displayed reading is on a mass basis, also for carrier gas gram molecular weight (GMW) when the meter's standard GMW is different from the tested carrier gas GMW. It is important to note that Method B requires that the UV meter **NOT** be calibrated using wet-chemistry test results. The UV meter shall be independently calibrated to account for changes in sample cell temperature, pressure, and carrier gas GMW. In the field, the integrity of the UV meter's installation shall be confirmed by wet-chemistry measurements.

Operating Principles of Commercial UV Meters

The operating principle of all commercial UV ozone monitors is similar; specific equipment features for individual units may be slightly different. The common attribute is the determination of the amount of UV light absorbed by the ozone in the gas as it passes through a fixed path-length sample cell. Specifically, it is the determination of the difference between the UV light absorption of the carrier gas without ozone *versus* the UV light absorption of the sample gas containing ozone. The difference is proportional to the number of ozone molecules (i.e., ozone volume) within the sample cell's path length. The instrument's electronics utilize the "difference" to calculate the ozone concentration.

Low concentration monitors (ozone destruction unit exhaust and ambient monitors) have a relatively long path length to increase the amount of UV absorbance for the lesser ozone concentrations. High concentration meters (ozone generator product gas or ozone contactor off-gas) have much shorter path lengths. UV monitors may display results as percent by volume (%vol), ppm by volume (ppm_v), percent by mass (%wt), ppm by mass (ppm_w), or mass/volume (i.e., g/m^3 or mg/L). Typically, high concentration monitors display results as %wt, or g/m^3.

The sample cell path length for a given ozone monitor is fixed. As the temperature and pressure within the sample cell changes, the number of total molecules passing through the sample cell changes. The correct ozone concentration will be displayed only when the direct ozone concentration reading from the sample cell is corrected to standard temperature and pressure conditions used by the monitor manufacturer. If not adjusted, a change in temperature or pressure will cause an incorrect ozone concentration to be displayed.

Some UV ozone monitors contain temperature and pressure instrumentation within the unit itself and display corrected readings automatically. Other UV monitors require independent temperature and pressure measurements, and require the operator to calculate meter correction factors and make adjustments, as necessary.

Monitors which display the ozone concentration on a mass basis (e.g., %wt) may require a third adjustment for carrier gas density. Typically, these monitors are set up for either air or oxygen as the carrier gas. If an "oxygen-based" meter is used when air is the

feed-gas, or *vice-versa*, then an adjustment is necessary for carrier-gas GMW. Or, if an oxygen recycle or oxygen enriched, air-fed ozone system is utilized, an adjustment is necessary to account for the actual GMW of the carrier-gas.

Other considerations for accurate ozone concentration readings include addressing time-dependent variations in UV bulb intensity and sample-cell sight-glass cleanliness. Various approaches are used to address these issues successfully. The overall goal is to obtain continuous, reliable, and accurate ozone concentration readings for several weeks or months without operator involvement to replace the UV bulb, clean the sample cell, or perform a wet-chemistry verification test.

UV Meter Temperature, Pressure, and Gas Composition Adjustments

Ozone monitors that display readings on a volume or mass/volume basis will specify a reference temperature and pressure. Monitors that display readings on a mass basis also will state the reference feed-gas, such as air or oxygen (i.e., GMW of 29 or 32, respectively). Meter reading adjustments are made automatically or manually according to Equation 9.

$$Adjustment\ Ratio\ =\ \frac{P_s}{P_a}\ x\ \frac{T_s}{T_a}\ x\ \frac{GMW_s}{GMW_a} \qquad [9]$$

Where:

P_s =   Meter's reference, absolute pressure.

P_a =   Actual sample cell, absolute pressure.

T_s =   Meter's reference temperature in Kelvin.

T_a =   Actual sample cell temperature in Kelvin.

GMW_s =   Meter's reference gas GMW.

GMW_a =   Actual feed-gas GMW.

Validating the UV Meter With Wet-Chemistry Tests

Ozone concentration may be determined by using the iodometric wet-chemistry method as a means of confirming the trustworthiness of the installed UV ozone monitors. *It is important to note, however, that the UV monitor reading be established independently of the wet-chemistry result. Monitor temperature, pressure, and gas composition adjustments shall be determined using the procedure discussed in the preceding section.* The wet-chemistry test result should be utilized only as an independent comparison of UV monitor results. If the comparative ozone concentration exceeds ±2%, then this provides a clue that something is wrong with the UV monitor installation or with the wet-chemistry test procedure. Both the UV meter and wet-chemistry test procedures then should be

re-evaluated to ensure that they are being performed correctly. The meter may be repaired or replaced if it is not functioning properly.

The procedure for completing a UV meter *versus* wet-chemistry test comparison is as follows:

1.   Arrange the ozone generator product-gas sample flow to the UV meter and gas washing bottles, as described below, so that truly comparative ozone concentration readings are obtained.

>   1.1.   Provide a sample tap to the gas washing bottle from the same sample line to the UV meter. If the UV meter reading is not affected when ozone is bubbled through the KI solution, simultaneously read the UV meter reading, or readings, while bubbling ozone. The UV meter reading is not affected when sufficient pressure exists to force the gas flow to both the gas washing bottles and the UV meter without affecting flow to the UV meter.

>   1.2.   If the UV meter reading is affected when ozone is bubbled through the KI solution, read the UV meter for a short period of time before and after bubbling ozone. However, it is important to confirm that the ozone generator production rate and associated ozone concentration do not change when switching from one test method to the other.

2.   Establish that the UV meter is displaying an ozone concentration that properly takes into account the sample cell temperature and pressure and also feed-gas composition when the reading is displayed on a mass basis (i.e., %wt). Make calibration adjustments to the UV meter for sample cell temperature and pressure and feed-gas composition, as necessary.

3.   Independently perform the wet-chemistry test. If the UV meter reading changes during the course of bubbling ozone into the gas washing bottle, collect several UV meter readings and average the results.

4.   Determine the percent difference between the UV meter ozone concentration (average of several UV meter readings, if applicable) and wet-chemistry ozone concentration using the equation that follows below. Be sure that the ozone concentrations are properly determined, as discussed below.

$$\% \ Difference \ = \ \left\{ \frac{UV \ Concentration}{Wet\text{-}Chemistry \ Concentration} \ - \ 1 \right\} x \ 100$$

>   4.1.   If the UV meter reading is displayed in mg/L, ensure that its reference temperature and pressure are the same as those used for determining the wet-chemistry ozone concentration (e.g., mg/L_{NTP}).

>   4.2.   If the UV meter reading is displayed in %wt, convert the wet-chemistry reading in mg/L to mass basis, using Equation [10]. It should be noted that in Equation [10], the term 0.5 Y_1 V_m / 48 effectively accounts for the

fact that three oxygen molecules form two ozone molecules within the ozone generator and that the weight percent calculation must involve the determination of ozone generator product-gas density. It is incorrect to use feed-gas density in the denominator of Equation [10].

$$Y_1' = \frac{100 \ Y_1}{W_{fg}\left(1000 + \dfrac{0.5 Y_1 V_m}{48}\right)}$$ [10]

Where:

Y_1'	=	Ozone concentration, percent by weight
Y_1	=	Ozone concentration, mg/L_{NTP}
100	=	Conversion of mass ratio to percent expression
V_m	=	Molar volume (22.4 LNTp/mol)
48	=	Gram molecular weight of ozone, g/mol
W_{fg}	=	Density of feed gas, g/L_{NTP}, as shown in Equation [11]

$$W_{fg} = \frac{(V_{O_2} x GMW_{O_2}) + (V_{N_2} x GMW_{N_2}) + (V_{Ar} x GMW_{Ar})}{V_m}$$ [11]

V_{O2}	=	Oxygen concentration in feed-gas (~20.94% vol for air)
V_{N2}	=	Nitrogen concentration in feed-gas (~78.12% vol for air)
V_{Ar}	=	Argon concentration in feed-gas (~0.94% vol for air)
GMW_{O2}	=	Gram molecular weight of oxygen, at 32.00 g/mol
GMW_{N2}	=	Gram molecular weight of nitrogen, at 28.01 g/mol
GMW_{Ar}	=	Gram molecular weight of argon, at 39.95 g/mol
NOTE:		Other gases present in air or in the feed-gas may be included if desired, but typically would result in a minor adjustment, at most.

OZONE PRODUCTION CALCULATION CONSIDERATIONS

Ozone concentration is multiplied by gas flow to obtain ozone production rate. It is very important to use the correct gas flow with the ozone concentration reading of record, or an incorrect ozone production rate will be obtained.

When the ozone concentration reading of record is expressed on a volumetric basis as g/m^3 or mg/L, the ozone generator product-gas flow rate (L or m^3) must be used as the gas flow rate reading of record. The ozone generator feed-gas flow shall not be used; otherwise an incorrect ozone production rate would be determined. The ozone generator product-gas volumetric flow rate shall incorporate the proper adjustments for temperature, pressure, and gas composition, considering the fact that ozone is contained in the product-gas flow.

When the ozone concentration reading of record is expressed on a mass basis as %wt, the conversion from g/m^3 or mg/L to %wt shall be performed using Equation [10]. Then, the mass flow rate of the ozone generator feed-gas may be determined and multiplied by the %wt ozone concentration to obtain the ozone generator product-gas ozone mass flow rate. In general, this method of determining ozone production rate is less complicated, because the gas composition of the generator feed-gas composition generally does not change, whereas the ozone generator product-gas composition would change constantly as ozone concentration changes.

TABLE I. LOOK-UP TABLE FOR VAPOR PRESSURE

Temp C	V.P. mm Hg	Temp C	V.P. mm Hg	Temp C	V.P. mm Hg	Temp C	V.P. mm Hg	Temp C	V.P. mm Hg
10.0	9.21	15.0	12.79	20.2	17.75	25.4	24.33	30.6	32.93
10.2	9.33	15.2	12.95	20.4	17.97	25.6	24.62	30.8	33.31
10.4	9.46	15.4	13.12	20.6	18.20	25.8	24.91	31.0	33.69
10.6	9.58	15.6	13.29	20.8	18.42	26.0	25.21	31.2	34.08
10.8	9.72	15.8	13.46	21.0	18.65	26.2	25.51	31.4	34.47
11.0	9.84	16.0	13.63	21.2	18.88	26.4	25.81	31.6	34.86
11.2	9.98	16.2	13.81	21.4	19.11	26.6	26.12	31.8	35.26
11.4	10.11	16.4	13.99	21.6	19.35	26.8	26.43	32.0	35.66
11.6	10.24	16.6	14.17	21.8	19.59	27.0	26.74	32.2	36.07
11.8	10.38	16.8	14.35	22.0	19.83	27.2	27.05	32.4	36.48
12.0	10.52	17.0	14.53	22.2	20.07	27.4	27.37	32.6	36.89
12.2	10.66	17.2	14.71	22.4	20.32	27.6	27.70	32.8	37.31
12.4	10.80	17.4	14.90	22.6	20.56	27.8	28.02	33.0	37.73
12.6	10.94	17.6	15.09	22.8	20.81	28.0	28.35	33.2	38.15
12.8	11.08	17.8	15.28	23.0	21.07	28.2	28.68	33.4	38.58
13.0	11.23	18.0	15.48	23.2	31.32	28.4	29.01	33.6	39.02
13.2	11.38	18.2	15.67	23.4	21.58	28.6	29.35	33.8	39.46
13.4	11.53	18.4	15.87	23.6	21.84	28.8	29.70	34.0	39.90
13.6	11.68	18.6	16.07	23.8	22.11	29.0	30.04	34.2	40.34
13.8	11.83	18.8	16.27	24.0	22.38	29.2	30.39	34.4	40.80
14.0	11.99	19.0	16.48	24.2	22.65	29.4	30.74	34.6	41.25
14.2	12.14	19.2	16.68	24.4	22.92	29.6	31.10	34.8	41.71
14.4	12.30	19.4	16.89	24.6	23.20	29.8	31.46		
14.6	12.46	19.6	17.10	24.8	23.48	30.0	31.82		
14.8	12.62	19.8	17.32	25.0	23.76	30.2	32.19		
15.0	12.79	20.0	17.53	25.2	24.04	30.4	32.56		

To convert from mmHg to kPa, multiply by 0.1333 kPa/mmHg.

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Key Words

Résumé

Une réunion de délégues des différents comités assurance qualité de l'Association International pour l'Ozone (PAG, EAG, NIG) s'est tenue à Oxford (Ohio, USA) les 8 et 9 Novembre 1995. Le but de cette réunion était d'établir un document commun pour la mesure de la concentration en ozone dans un gaz et, en particulier, à la sortie d'un générateur d'ozone.

Cette concentration en ozone peut être déterminé soit en utilisant seulement la méthode chimique par voie aqueuse (Méthode A), soit en utilisant un appareil commercialisé de mesure UV (Méthode B), lui même vérifié par la méthode chimique. Il convient de noter que les méthodes ne sont pas listées dans un ordre prioritaire: elles peuvent être utilisées l'une ou l'autre.

Pour la Méthode A, la concentration en ozone retenue doit être la moyenne d'au moins 3 (trois) mesures et le pourcentage de déviation standard (déviation standard : moyenne des résultats) doit être inférieur à ±2%. Pour la méthode B, les résultats de l'appareil UV doivent être calibrés en tenant compte de la pression et de la température de la cellule de mesure, ainsi que de la masse molaire si le résultat est exprimé en pourcentage de masse (% m/m). L'appareil de mesure UV doit être validé par la voie chimique aqueuse. Un minimum de 9 (neuf) tests de comparaison devra être effectué, et la différence relative en pourcentage sera calculé, pour chacque test, en utilisant l'équation suivante:

$$\% \ Difference = \left[\frac{Concentration - UV}{Concentration - chimique} - 1 \right] x \ 100$$

L'appareil UV sera validé si la moyenne des différences en pourcentage d'au moins neuf tests est comprise entre ±2%.

Zusammenfassung

An 08.11.1995 wurde in Oxford, Ohio (USA) eine gemeinsame Sitzung der Mitglieder des Qualitätssicherungskomitees der IOA Pan-Amerika Gruppe (PAG), der Europa-Afrika Gruppe (EAG) und der Nippon-Island Gruppe (NIG) abgehalten. Das Ziel war die Einführung einer einzigen Richtlinie zur Messung der Ozonkonzentration in der Gasphase, insbesondere beim Einsatz kommerzieller Ozonerzeuger.

Die ausgewählten Meßmethoden beruhen entweder nur auf der Naßchemie (Methode A) oder auf einem kommerziellen UV-Meßgerät geeicht mit Naßchemie (Methode B). Es ist zu betonen, daß die Methoden nicht nach irgendeiner Priorität in A und B aufgeteilt sind, sondern sie sind völlig gleichwertig. Für die Methode A soll der angegebene Meßwert der Durchschnittswert der letzten drei naßchemischen Messungen sein, wobei die Standardabweichung (Standardabweichung ÷ Durchschnitt) der Messungen kleiner als ±2 Prozent sein soll. Bei der Methode B sollen die im UV-Gerät angezeigten Werte unabhängig von Zelltemperatur, Druck und Moleculargewicht geeicht sein, wenn das Ergebnis in Massenprozent angegeben wird. Das UV-Gerät soll mittels naßchemischer Verfahren geeicht sein. Mindestens neun Vergleichstests sollen zwischen UV-Messung und naßchemischer Methode durchgefürt werden und die relative prozentuale Abweichung

für jeden Vergleichstest soll gemäß nachstehender Gleichung angegeben werden. Das UV-Meßgerät gilt als geeicht, wenn die mittlere prozentuale Abweichung von mindestens neun Vergleichstests innerhalb von ± 2 Prozent liegt.

$$\%\text{-}Differenz \; = \; \left\{ \frac{UV\text{-}Konzentrationsmessung}{Nasschemische\;\;Messung} \; - \; 1 \right\} \; x \;\; 100$$