

An Alternative Method for the Verification of High Concentration Ozone Gas Measurement (UV Photometry vs. KI)

Vince Ciufia, OSTI, Inc., PO Box 3320, Monterey, CA 93942 USA

Abstract

In 1995, a joint meeting of members of Quality Assurance Committees of IOA-PAG, IOA-EAG and IOA-NIG was held in Oxford, OH. 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. This resulted in 1996 in the issuing of by the IOA Quality Assurance Committee Revised Standard Procedure 001/96, "*IODOMETRIC METHOD FOR THE DETERMINATION OF OZONE IN A PROCESS GAS*" and the publication of "*GUIDELINES FOR MEASUREMENT OF OZONE CONCENTRATION IN THE PROCESS GAS FROM AN OZONE GENERATOR*". The IODOMETRIC METHOD is described.

The relative costs, accuracy and merits of using the Iodometric (KI) Method versus UV photometry to determine ozone concentration in a process gas from an ozone generator is discussed. The conclusions support that the implementation of a properly designed High Concentration Ozone Gas Analyzer will provide improved accuracy, lower verification costs and enhanced repeatability compared to the KI Method.

An introduction to ozone photometry is provided. The principle and inner workings of an ozone analyser are explained. Sources of error are identified and quantified on a component basis. Since no Primary Standard for High Concentration Ozone Measurement exists, it is necessary for an ozone analyser manufacturer to provide a self made Primary Standard. The error budget for such a standard is given. A comparison of Three Primary Standards is shown.

Keywords: Ozone, UV-photometry, KI, Iodometric, accuracy, measurement, ozone analyzer, cuvette, extinction, absorption, ozone generator

Introduction

In 1995, a joint meeting of members of Quality Assurance Committees of IOA-PAG, IOA-EAG and IOA-NIG was held in Oxford, OH. 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. In the design, performance and acceptance specification for an ozone system, it is necessary to confirm that the ozone system meets the output criteria. In this case, the verification of the ozone measurement in the gas phase, in particular, from commercial ozone generators ^[1] is an important element in the acceptance of the ozone system by the user.

Guidelines state: 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 a 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 $\pm 2\%$. 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 results 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 $\pm 2\%$.

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

Following the May/June 1993 *Ozone News* publication of the proposed IOA PAG guideline for ozone concentration measurements 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 $\pm 5\%$, 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 were addressed in the new Guidelines issued in 1996. The guidelines agreed upon were presented 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 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 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 of reading of record; otherwise inaccurate ozone production rates would be calculated. A separate section of the Guidelines is dedicated 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 the Guidelines including discussion of areas where special precautions as 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 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 upon principle that iodide ion is oxidized by ozone to form iodine as the ozone gas is bubbled through a solution of KI. When the bubbling is stopped, the KI solution pH is adjusted with sulfuric acid to pH 2, or lower 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.

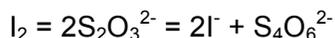
Unfortunately, the ozone/iodine stoichiometry is not always 1.0, but can range from 0.65 to 1.5 (Birdsall, et al., 1952); Boyd, et al., 1970; Byers and Saltzman, 1959; Flamm, 1977; Gordon, et al., 1989; Wood, 1987), depending on testing methodology. Factors that affect the stoichiometry include: KI solution 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 the paper. (Bold and underline done by author.)

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



The iodine formed in the above reaction is titrated directly with thiosulfate ion:



The reaction of ozone with iodine 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_c (IOA Standardization 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_c 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_c 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_c solution has been shown to have an effect on the determination (Gordan, 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_c 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.

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 the ozone concentration readings from properly operating and calibrated UV meters (independently calibrated) have been shown to have a standard deviation percentage within $\pm 2\%$ of wet-chemistry test results ^[2].

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 the feed-gas gram molecular weight when the reading is displayed 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 tests results (see Method A 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 the equation shown below:

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

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

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 the 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.

Verification of High Concentration Ozone Gas Measurement by UV Photometry

Ozone Photometry

UV Ozone photometers measure the absorption of light of a wavelength of 254 nm that passes through a cuvette with a defined length, which is filled with the sample gas. The light source usually is a low-pressure mercury cold-cathode UV lamp. In a dual beam photometer ^[2], UV radiation is measured by two different detectors. One is called the reference detector and measures the light coming directly from the lamp (I_0). The other detector measures radiation passing through the cuvette (I), which will be more or less attenuated by ozone, see Figure 1. The carrier gas has no influence on the extinction, as long as it is clean oxygen or air.

With these two light intensities, the molar extinction coefficient A of $3000 \text{ l mol}^{-1} \text{ cm}^{-1}$, cuvette length d and the formula

$$I = I_0 \cdot 10^{-Acd} \quad (1)$$

of Lambert-Beer the ozone density c in mol/l can be calculated. This “density” is subject to change due to influence from pressure and temperature of the sample gas. If we run the same sample of ozone through different cuvettes which are at temperatures of e.g. $20 \text{ }^\circ\text{C}$ and $40 \text{ }^\circ\text{C}$, we get results that would differ by about 7 %. Pressure has an even bigger influence. If we would take a sample, measure it at $2 \text{ bar}_{\text{abs}}$ and then at $1 \text{ bar}_{\text{abs}}$, result of the second measurement would only be 50 % of the first!

This is why an ozone analyzer always has to have a pressure sensor and a temperature sensor, both being able to track temperature and pressure inside the cuvette accurately. With the information from these sensors, ozone density can be calculated into “mass of ozone per normal (or standard) volume of sample” at the arbitrary temperature and pressure of the sample gas.

The real life equation an ozone analyzer has to solve is:

$$C = \log \frac{I_0}{I} \cdot G \cdot \frac{T}{T_N} \cdot \frac{P_N}{P} \quad (2)$$

Usually, ozone analyzers are calibrated by comparison to a Primary Standard of the manufacturer. G is determined at calibration and sets sensitivity of the analyzer, so that the equation calculates concentration as g/Nm^3 , normalized to $T_N = 273.15 \text{ K}$ and $P_N = 1.01325 \text{ bar}$. At full range, I_0/I usually is about 10, which means, that only 10 % of the UV light (I_0) reaches the detector.

Another commonly used unit is percent by weight, which is “mass of ozone per mass of sample” [3]:

$$C[\%wt] = \frac{M_{O_3}}{M_{O_3} + M_C} \cdot 100 \quad (3)$$

As can be seen in (3), in this case the analyzer has to know the molecular weight of the carrier gas, which could be oxygen or air. At 200 g/Nm^3 , an analyzer set to oxygen as carrier gas will display 13.37 %wt, when set to air it will display 14.46 %wt. An incorrect setting of the carrier gas would introduce an error of over 7%. The relationship between %wt and g/Nm^3 is nonlinear, because the denominator in (3) changes with concentration.

A unit often used for lower concentrations is ppm_v , which is proportional to g/Nm^3 ($466.43 \text{ ppm}_v = 1 \text{ g/Nm}^3$).

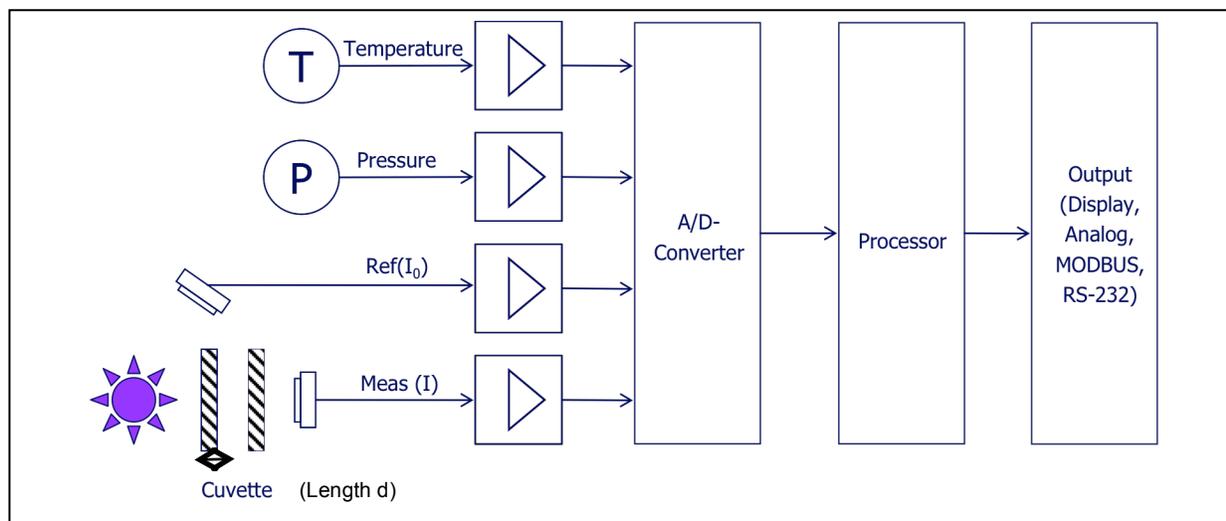


Figure 1. Block diagram of an ozone analyzer

Figure 1 shows the block diagram of an ozone analyzer: Signals from the two UV sensors, the pressure sensor and the temperature sensor are first amplified. Then these analogue signals enter a multi-channel analogue-to-digital converter. The processor fetches converted data from the A/D-converter and calculates concentration, does error checking and controls the output signals.

Without any ozone in the cuvette, I and I_0 will be at some arbitrary values, and (2) will not result in zero, as it should. This is why an ozone analyzer has to be zeroed with ozone-free gas from time to time. During zeroing, the processor will calculate a factor to be multiplied with I in the following measurements, so that $I_0/I = 1$ without ozone ($\log 1 = 0$).

Sources of Error in an Ozone Analyzer

Three kinds of errors have to be considered:

- Offset error
- Sensitivity error
- Nonlinearity

Offset errors manifest themselves in a deviation from zero, when there is no ozone present, and in a constant measurement error at different concentrations. Offset errors that originate from the optical system (lamp, UV sensors, cuvette soiling) can be corrected by zeroing the analyzer with ozone-free gas.

Sensitivity errors will lead to a difference between true and measured concentration, which is proportional to ozone concentration.

Nonlinearity means that the calibration curve of an analyzer does not follow a straight line.

The following sections will present an overview of error sources on a component level and will give some advice for ensuring reliable operation of an ozone analyzer.

Spectral filtering and UV lamp

A low-pressure mercury lamp will emit about 92 % of its light at the desired wavelength of 254 nm, the rest goes into wavelengths of e.g. 313 nm, 365 nm, 405 nm, 436 nm, and 546 nm^[4]. This is called stray light. Without any filtering this means that 8 % of the light coming from the lamp will pass the cuvette without absorption by ozone. Assuming that 8 % of the light is not absorbed, (2) becomes

$$C = \log \frac{I_0 \cdot (1 + 0.092)}{I + I_0 \cdot 0.092} \cdot G \cdot \frac{T}{T_N} \cdot \frac{P_N}{P} \quad (4)$$

With a cuvette length of 0.8 mm an instrument with detectors having uniform sensitivity on the different wavelengths would measure

True Conc. [g/Nm ³]	Meas. Conc. [g/Nm ³]	Error [%]
10	9.1	-9.0
50	44.5	-11.0
200	151.1	-24.5

Table 1. Error without spectral filtering

This error is nonlinear, with decreasing sensitivity at higher concentrations. In practice, the error would be even more severe, because the sensitivity of photodiodes peaks at much longer wavelengths than 254 nm, where it is only about 10 % of its maximum. Their sensitivity for stray light is higher than for UV at 254 nm. For a maximum error of 0.1 % in this example, stray light must be kept below 0.023 %.

The light source in a UV lamp is a plasma, which is inherently unstable, i.e. brightness is not distributed uniformly, and areas of different brightness can move through the lamp, influenced by temperature and ageing. Depending on the optical design of an ozone analyzer, it is possible that the cuvette and reference detector do not focus exactly on the same spot in the plasma. This leads to a change in radiation ratio on the two detectors, which creates an offset error.

Example: in an instrument with a 0.8 mm cuvette, a change of 0.13 % in light intensity of one channel would lead to an offset error of 0.1 g/Nm³. Apart from mistakes made during zeroing (e.g. with ozone), these lamp fluctuations are the main reason for “honest” analyzers sometimes displaying negative concentrations.

Cuvette and Zeroing

A properly designed cuvette will not change its length, which means that sensitivity will not change.

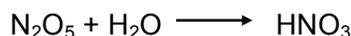
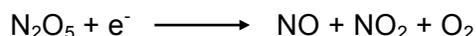
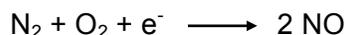
The only real enemy of an ozone analyzer is dirt. Dirt is any substance deposited in the cuvette, which absorbs UV light at 254 nm. Such soiling will create an offset error, which is visible, when the cuvette is purged with ozone-free gas: the instrument will display a positive concentration.

The offset error caused by a soiled cuvette can be corrected during operation by zeroing the instrument with ozone-free gas. Some ozone analyzers come with a complete purge mechanism, consisting of a solenoid valve and an air pump, and do a complete automatic zero in fixed time intervals, e.g. every 24 h. Analogue and digital outputs in our analyzers remain at the last measured concentration during the auto zero, so a connected control system does not become aware of it. Analyzers are available which will inform the user about cuvette status and give an alarm, if the cuvette becomes too dirty.

Soiling of the cuvette should not decrease accuracy of the ozone analyzer out of its specified values, as long as there is no alarm. Resolution will be decreased, because of quantization in the A/D-converter (see section below).

The best way to deal with dirt is to prevent it from reaching the cuvette. Introduction of particle filters at the instruments' input port gave a massive improvement regarding the "cuvette dirty" failure rate. Gas filter inserts should be replaced as necessary.

Feed gas of ozone generators is either air or oxygen. Generators running on oxygen are usually "doped" or "spiked" with small amounts of nitrogen to increase efficiency. In both cases, whether air or oxygen feed, nitrogen oxides are formed in the electrical discharge^[5]. The following reactions are suggested to occur in corona discharge generators.



Moisture has always been considered a serious problem for ozone generators operating on air due to the tendency to form nitric acid. The formation of nitric acid is a primary cause of corrosion problems and of dielectric failure in both municipal and industrial ozone applications. Nitrogen doping of a system with air can create serious problems if organics (hydrocarbons) present in the air. The plasma in the generator could turn these hydrocarbons into water, therefore generating nitric acid.

Sensors and Amplifiers

Good silicon photodiodes are extremely linear concerning UV input and signal output, over more than eight orders of magnitude. Sensitivity and dark current of the sensors is subject to temperature drift, which can create an offset error. With high quality components this is marginal compared to lamp drift.

Errors in pressure and temperature measurement will result in a sensitivity error of the analyzer, see (2). The error is proportional to absolute pressure and inverse proportional to temperature on the Kelvin scale. Again, using the best components will minimize these errors.

The amplifiers that are used to match the sensor signal to the A/D-converter also can have offset and gain drift, but with the right choice of components, these errors are negligible.

A/D-Converter

The analogue-to-digital converter translates the analogue sensor signals into digital information that the processor can work with. An important characteristic of an A/D-converter is its resolution. A 12-bit converter e.g. can distinguish 4096 voltage levels, while a 14-bit converter can encode 16384 levels. This is called quantization. Because of the exponential behaviour of I vs. concentration (1), converter resolution becomes quite important for instrument concentration resolution at high concentrations with strong absorption. If I_0 is close to end of span (voltage range) of the A/D-converter, instrument resolution can be calculated as:

$$r = C - \log \frac{I_0}{I - \frac{I_0}{2^b - 1}} \cdot G \cdot \frac{T}{T_N} \cdot \frac{P_N}{P} \quad (5)$$

where b is the number of bits of the converter.

The following table shows examples for resolution of instruments with 12 and 14-bit converters and a cuvette length of 0.8 mm at different concentrations:

Concentration [g/Nm ³]	Res. 12 bit [g/Nm ³]	Res. 14 bit [g/Nm ³]
50	0.04	0.01
100	0.07	0.02
180	0.17	0.04
200	0.21	0.05

Table 2. Resolution of different A/D-Converters

Processor

The processor fetches the digitized sensor data and computes the output result. Accuracy of these calculations depends on the math library used in software development. With today's libraries supporting floating point precision of at least seven decimal points the processor does not have any influence on accuracy or resolution.

Output

Ozone analyzers have analogue outputs, so the measurement result computed by the processor has to be converted to an analogue signal again. This is accomplished by a digital-to-analogue converter. This converter also has a limited resolution. In an instrument with a 12-bit converter the analogue output has a resolution of 0.024 %, which is linear over concentration. All components in the analogue output signal chain (D/A-converter, isolation amplifier, 4-20 mA converter) have parameters like offset and gain, that are subject to influence by temperature. With the choice of the right components the overall output error over the specified temperature range of the ozone analyzer can be limited to 0.1 % of instrument range. When using analogue signals, also the errors contributed by the inputs of a PLC / SCADA system have to be considered.

System Noise

Noise sources in an ozone analyzer are fast fluctuations of the lamp and thermal noise of the electronics. Lamp fluctuations will at least partially cancel out due to the ratiometric principle of dual-beam photometry. Analogue low-pass filtering and software averaging techniques allow limiting system noise down to the quantization thresholds mentioned above. Immunity against radiated or conducted disturbances is an important characteristic.

Temperature drift

Accuracy of an ozone analyzer has to remain within the specified limits over the full specified temperature range, e.g. 0-50 °C. The following temperature dependency of the zero value of a BMT analyzer with range 200 g/Nm³ was observed when ambient temperature was changed in an oven:

Temperature [°C]	Concentration. [g/Nm ³]
20	0.0
30	-0.1
40	-0.2
50	-0.3

Table 3. Temperature Zero Drift

The test was repeated with the photocurrents from the photodiodes being replaced by constant currents from a stable current source. The maximum observed offset drift was 0.1 g/Nm³. This means that most of the zero drift over temperature can be attributed to geometrical changes in the lamp plasma. Because this is an offset error it can be corrected by zeroing the instrument.

Most of the sensitivity error caused by temperature can be traced to the pressure sensor, which can have a maximum error of 0.3 % over the temperature range of 0-50 °C.

Calibration of Ozone Analyzers

For ambient ozone up to 1 ppm_v, UV photometry is a worldwide standard. NIST plays a leading role in providing National Standards for ambient ozone to many nations. Unfortunately, there is no such National Standard available for high concentration ozone.

For modern high accuracy ozone analyzers the use of the wet-chemistry method (IOA 001/96) is not sufficient because of its limited repeatability of at least 2% and limitation to a range of 200 g/Nm³ [6].

Although the extinction coefficient of ozone that the industry agreed on has an uncertainty of about 1 %, an alternative is the use of accurate ozone photometry as a calibration standard as long as its contribution to the overall uncertainty is kept to a minimum. A big advantage of this method is that the calibration process and its documentation can be automated. Because tracing ozone concentration to a national standard is not possible, each manufacturer has to design and use a self made Primary Standard, which should have the highest quality possible. Three physical measurements have to be traceable to National Standards in such a Primary Standard:

- Cuvette Length
- Pressure
- Temperature

The following quantifies the errors found in a BMT Primary Standard.

Maximum deviation from nominal size for e.g. a 0.5 mm cuvette spacer is 20 nm (0.004 %). Planarity of the cuvette windows also has to be considered. Here typical tolerances are 125 nm for each window, giving 0.05 % max. for both windows. The Primary Standard will use equation (2) for calculation of concentration, with G as a constant that was calculated from the extinction coefficient and cuvette length.

An often overlooked phenomenon in photometers is Fresnel reflection. A beam of light passing a boundary where the index of refraction changes, e.g from gas to quartz glass, will be partially reflected. When passing through the air-quartz boundary at normal incidence, reflectance [7] can be calculated as

$$R = \left(\frac{n - 1}{n + 1} \right)^2 \quad (6)$$

where n is the index of refraction of quartz glass. This index is dependant on wavelength and at 255 nm it has a value of 1.505, giving a reflection coefficient of R = 0.0406 (4.06 %) [8].

A beam of light passing through the cuvette is partially reflected on the surfaces of the window on the detector side back into the cuvette. This reflected light will again be reflected partially towards the detector by the other window [9]. Because the partially reflected light has crossed the cuvette two times additionally, cuvette length for this portion of the light is doubled, leading to an effective cuvette length

that is larger than the mechanical length. The error resulting from this phenomenon is nonlinear, because with higher concentration the reflected portions of light will be absorbed stronger than the light passing the cuvette only once. The largest error occurs at low concentrations with a magnitude of a few tenth of a percent of concentration. It is possible to decrease this error, either by design or by calculation, but the question remains if the scientists, who had determined the absorption coefficient of ozone in the past, took these reflections into account. There is no mention of it in the original article of Tanaka and Inn^[10]. Hearn^[11] mentions the problem but unfortunately does not elaborate on how he solved it.

Inaccuracy of pressure measurement is 0.3 mbar, which adds 0.03 % to the error budget. Pressure measurement has to reflect the real pressure inside the cuvette. This can easily be checked by varying flow rate of a gas with constant ozone concentration. The concentration displayed by the standard should not change when changing flow rate.

Temperature is measured with an inaccuracy of 0.15 K, adding another 0.05 % of error.

Not accounting for the uncertainty in knowledge of the absorption coefficient of ozone and neglecting Fresnel reflections, and adding up the errors mentioned above, the error in ozone concentration measurement of our Primary Standard is limited to 0.134 %.

Experimental

A prerequisite for relying on self made Primary Standard is that this standard can be reproduced so that all instruments do not deviate from each other (reproducibility of measurement results). Three Primary Standards with a range of 200 g/Nm³ were made. Electronics were taken from the BMT 964 series of ozone analyzers. The cuvette was slightly modified with an additional high accuracy PT5000 temperature sensor, so that temperature calibration was improved. Cuvette length was determined by a precision 1 mm gauge block. Temperature and pressure measurements were calibrated to the highest possible precision.

Two Primary Standards were compared against a third. For each of the two measurement series, two analyzers were connected in series, so that ozone leaving the first analyzer would enter the second analyzer. In order to provide the very stable ozone supply necessary, a specially designed 30 g/h ozone generator (BMT) was used, the output of which was led through a 100 ml glass bottle, which served as a low-pass filter against concentration fluctuations coming from the generator. Gas flow rate was 0.5 NI/min.

In each measurement series, time stamped concentration data from the serial interfaces of both instruments was recorded on a computer in 1 s intervals. Concentration was varied, so that 10 different ozone concentrations were recorded, with allowing each concentration level to become constant over time. In an Excel sheet, 12 measurements were selected for each concentration level on each instrument and averaged. The following diagram shows the comparison of time averaged data of one instrument (A) against two others (B, C):

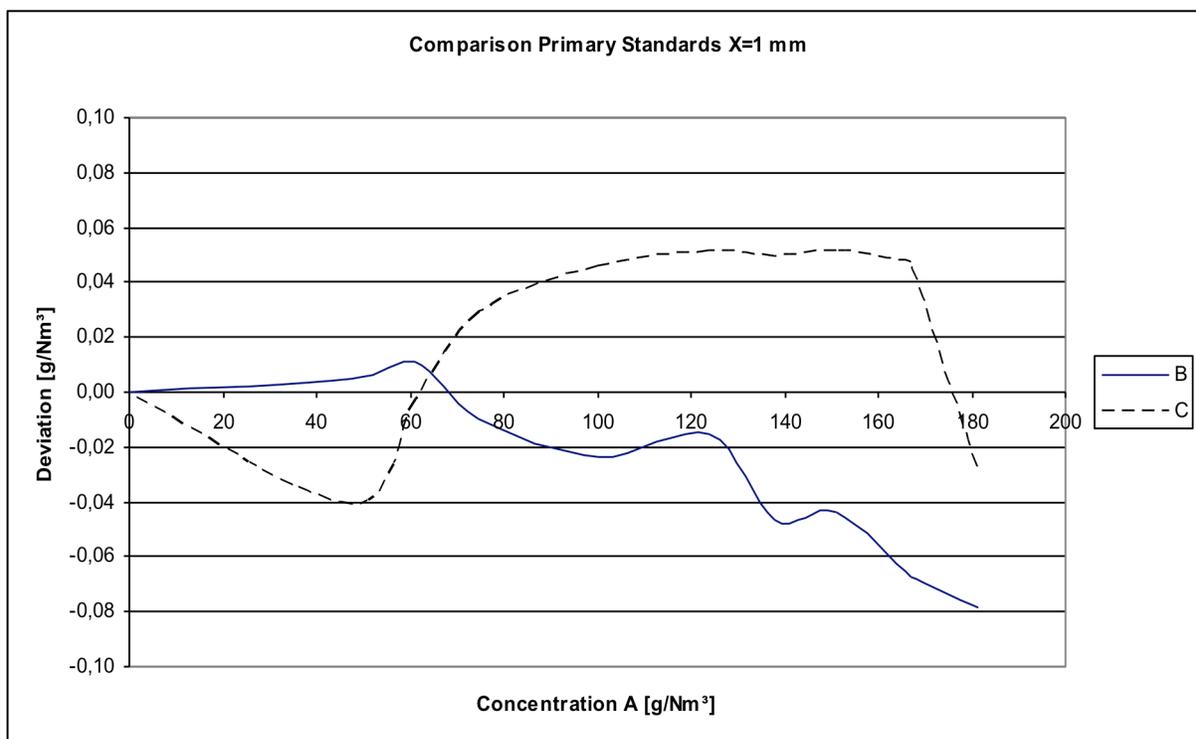


Figure 3. Comparison of three Primary Standards

Error remains well below the theoretical value of 0.134 % calculated above. Above 150 g/Nm³ quantization probably becomes the major source of error.

In another test, one of the newly made Primary Standards (A) was compared to the Primary Standard used in ozone analyzer production, which, apart from minor modifications, remained the same since its construction about 20 years ago. The optical and electrical design of the older Primary Standard is quite different from the design of the new standard.

Concentration. [g/Nm ³]	Deviation [g/Nm ³]
80	-0.1
130	-0.05
180	-0,1

Table 4. New against old Primary Standard

Maximum deviation is 0.125 %.

Conclusions

Calculation of error budget in a high concentration Primary Standard and experimental comparisons of three new standards among each other and comparison to a 20 year old production standard show that errors in these standards can be kept quite small, allowing calibration of high concentration ozone analyzers having an accuracy of 0.4% of measurement + 0.1% of scale.

The largest uncertainty in photometric ozone measurement originates from the uncertain knowledge of the extinction coefficient of ozone. Further research is necessary in this respect. It would be quite

beneficial for the ozone industry, if national high concentration ozone standards would be made available by National Standards institutes.

The results using a properly designed UV Photometer compare quite favorable with the time, expense, accuracy and uncertainty surrounding the "Wet-Chemistry Method".

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