

Accuracy of High Concentration Ozone Photometry

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Abstract

An introduction to ozone photometry is provided. The principle and the inner workings of an ozone analyzer are explained, together with the different units available to express measurement results. Sources of error in an ozone analyzer are identified and quantified on a component basis. Some practical advice is given for operating an ozone analyzer in an industrial environment, including drying of wet sample gas. A manufacturer of ozone analyzers has to provide a self made Primary Standard. An error budget is shown for such a standard. Three Primary Standards were made and compared among each other and also to a 20 year old standard used in production.

Keywords: Ozone, UV-photometry, accuracy, ozone analyzer, cuvette, extinction, absorption

Introduction

UV Ozone photometry has become the method of choice for the measurement of process ozone in recent years for many applications. It allows a continuous measurement of ozone concentration, making easy control of ozone generators and ozone residual possible. With commercial concepts like "ozone-over-the fence" accuracy and reliability of these measurements is becoming more and more important, also economically.

This paper gives a short introduction into ozone photometry, and then focuses on sources of errors in an ozone analyzer. Some practical advice for operation is given. Calibration is a very important subject and quite problematic, because there are no national standards for high concentration ozone to trace calibration to. In this regard, accuracy of calibration completely depends on the quality of Primary Standards made by the manufacturer of the analyzer.

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 two beam photometer [1], 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. 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 °C and 40 °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 bar_{abs} and then at 1 bar_{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 informa-

tion 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 reaches the detector.

Other possible units are ppm_v and percent by weight, which is “mass of ozone per mass of sample”:

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

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 $200 \text{ g}/\text{Nm}^3$, an analyzer set to oxygen as carrier gas will display 13.37 %wt, when set to air it will display 14.46 %wt. The relationship between %wt and g/Nm^3 is nonlinear, because the denominator in (3) changes with concentration.

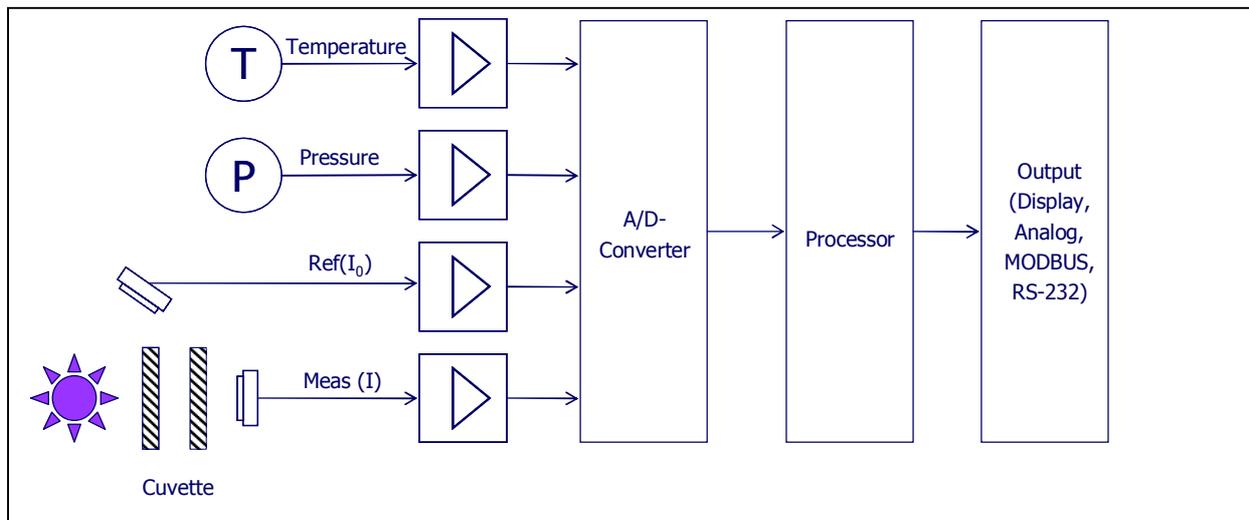


Figure 1. Block diagram of an ozone analyzer

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 [2]. 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 over wavelength 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. 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 a 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 thoroughly 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. A good analyzer 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.

Hint: If the operator worries that the dirt in the cuvette, the gas filter, or even in corroded steel pipes connecting the analyzer could destroy ozone, a simple test, at least in larger systems where flow rate through the analyzer is not relevant to generator concentration, is to reduce flow rate through the analyzer to e.g. 50 % of the prescribed value. Displayed concentration should not drop.

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, nitric oxides are formed in the electrical discharge, predominantly dinitrogen pentoxide (N_2O_5). This oxide has a melting point of 30 °C and accumulates as a solid in operating ozone generators^[3]. Reports from customers lead us to the conclusion that before service, during generator purge and warm up, some of this material could move down the sample line into the ozone analyzer, soiling the cuvette.

Hint: Shut off the sample line to the analyzer during pre-service generator purge and unpressurized standby. This will also protect the ozone destruct of the analyzer from contamination with nitric oxides, which could poison the catalyst. It will also prevent moisture from entering a standby generator "backwards" through the analyzer.

Hint: Some analyzers come with an ozone destruct for the sample gas. The gas leaving the destruct contains nitric oxides, which together with ambient air humidity forms nitric acid (HNO_3). In order to prevent corrosion of sensitive equipment it is advisable to connect a tube to the catalyst outlet and lead away the gas to a location where it can not cause any damage.

In off-gas measurement application the sample gas is humid, which means that condensation of water could be possible. Reliable photometric operation is not possible with water droplets in the cuvette. This situation has to be avoided by all means.

Condensation will occur if dew point temperature of the sample gas is higher than temperature of the materials in contact with the gas, e.g. tubing from sample point to analyzer, or the cuvette itself. If condensation occurs in the sampling tube, a larger drop of water could develop which eventually closes the inner diameter of the tube and then rapidly moves towards the instrument. Dew point temperature of the sample gas usually is the temperature of the tank water.

Hint: When planning an ozone system where humid sample gas has to be measured, make sure that under any circumstances sample gas dew point temperature is always below the temperature of sample gas tubing and analyzer. If this is not the case or if in doubt, use a sample gas dryer. Sometimes vent-gas is measured after passage through a heated catalytic ozone destruct. Heating gas does not in any way change its dew point temperature! Depending on temperatures involved, the problem may also exist at this point of measurement.

A very convenient and maintenance-free way of drying sample gas is to cool it down to about 1°C with a Peltier cooler and have the humidity condensate in the cooler.

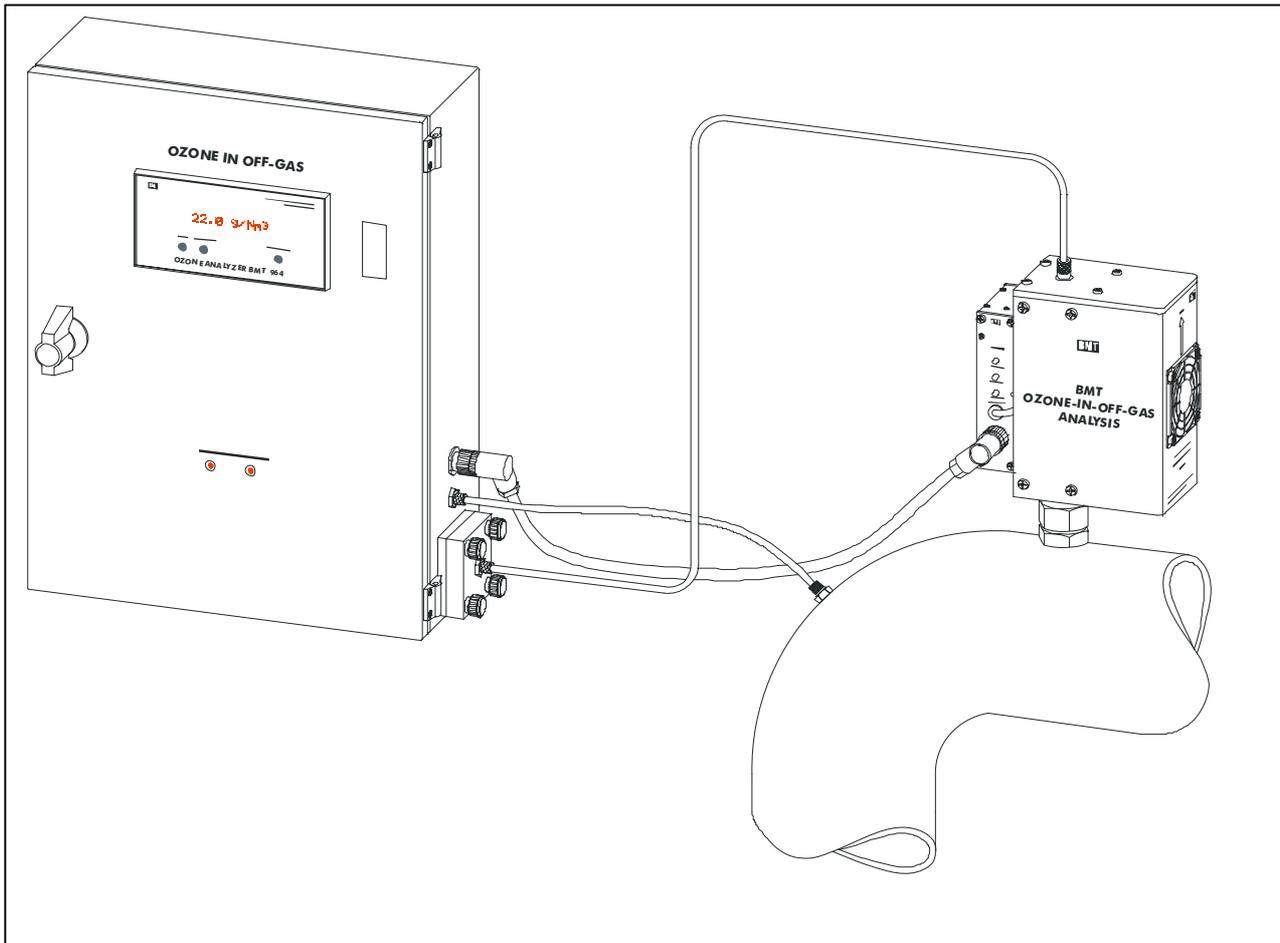


Figure 2. Off-Gas Ozone Measurement

Figure 2 shows an ozone analyzer with a gas dryer. The ozone analyzer houses the power supply for the dryer and an ozone resistant sample gas pump plus flow meter. The measured sample gas is returned to its origin via a second tube, so no ozone destruct is necessary. It is very important, that the dryer is installed vertically on the sample point, so that condensate can drop back into the tube or tank.

This principle does not influence measurement accuracy, because no ozone is destroyed during drying. It can even be used for very low (ambient) ozone concentrations.

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 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. 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 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 done 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.

Output errors can be completely avoided by using fieldbus technology like MODBUS, which will also simplify system setup, because multiple wiring of analogue and error signals is not necessary.

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 max. 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 [4].

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 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 ^[5] can be calculated as

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

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 %) ^[6].

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 ^[7]. 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 ^[8]. Hearn ^[9] 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 precision 1 mm block gauges. 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 a row, so that ozone leaving the first analyzer would enter the second analyzer. In order to provide the very stable ozone supply necessary, a 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):

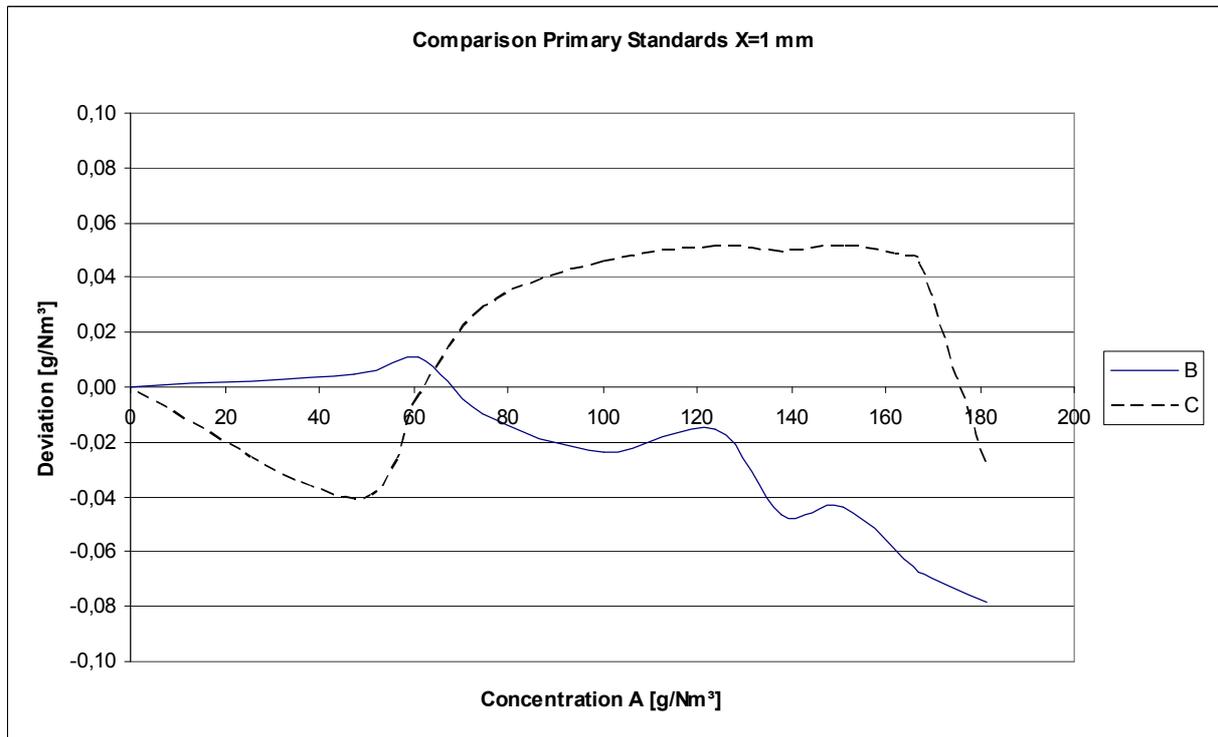


Figure 3. Comparison of three Primary Standards

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. Optical and electrical design 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 PrimaryStandard

Max. 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.

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