

TechNote TN-1

High Concentration Photometric Ozone Measurement Palimpsest

Rev. 10/2011

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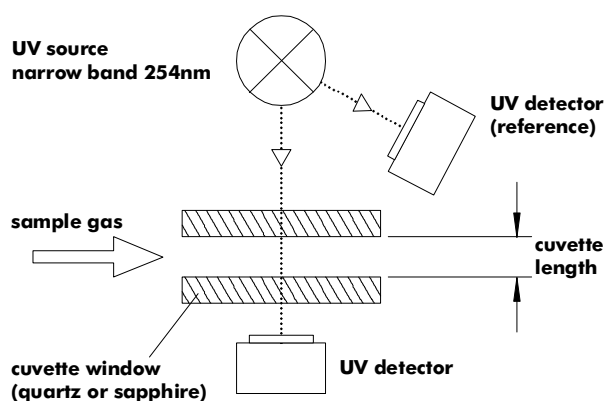
**1. Ozone Photometer:
Principle of Operation**

Ozone photometers are narrow band instruments measuring ozone at the wavelength of 254 nm (in the Hartley band between about 200 and 300 nm), or at about 590 nm (in the Chappuis band between about 500 and 700 nm). Namely at 254 nm ozone measurement is very sensitive.

The principle of measurement is quite simple: The source of radiation is a low pressure mercury lamp (in a UV photometer). Only the mercury line at 254 nm wavelength is used for measurement. To exclude the other spectral lines, narrow band UV detectors are used, or narrow band filters (one at the UV lamp, or one at each of both UV detectors).

The sample gas (ozone plus carrier gas, usually oxygen or air) flows between two parallel windows which are transparent for 254 nm radiation. These cuvette windows are made of quartz or sapphire. The distance between the cuvette windows (the cuvette length) defines the measurement range and the sensitivity of the instrument. For

e.g. the range of $200 g/m^3$ the cuvette length is typically only 0.8 mm, for the range of $400 g/m^3$ it is typically 0.4 mm.



The UV radiation is measured electrically by two different UV detectors. One detector, which is called the reference detector, measures the radiation before its passage through the cuvette, and the other detector measures the radiation after the passage through the cuvette and through the sample gas contained in the cuvette.

From both electric signals the instrument calculates the degree of extinction produced by the ozone contained in the cuvette. The carrier gas does not produce any extinction, as long as it is clean oxygen or air.

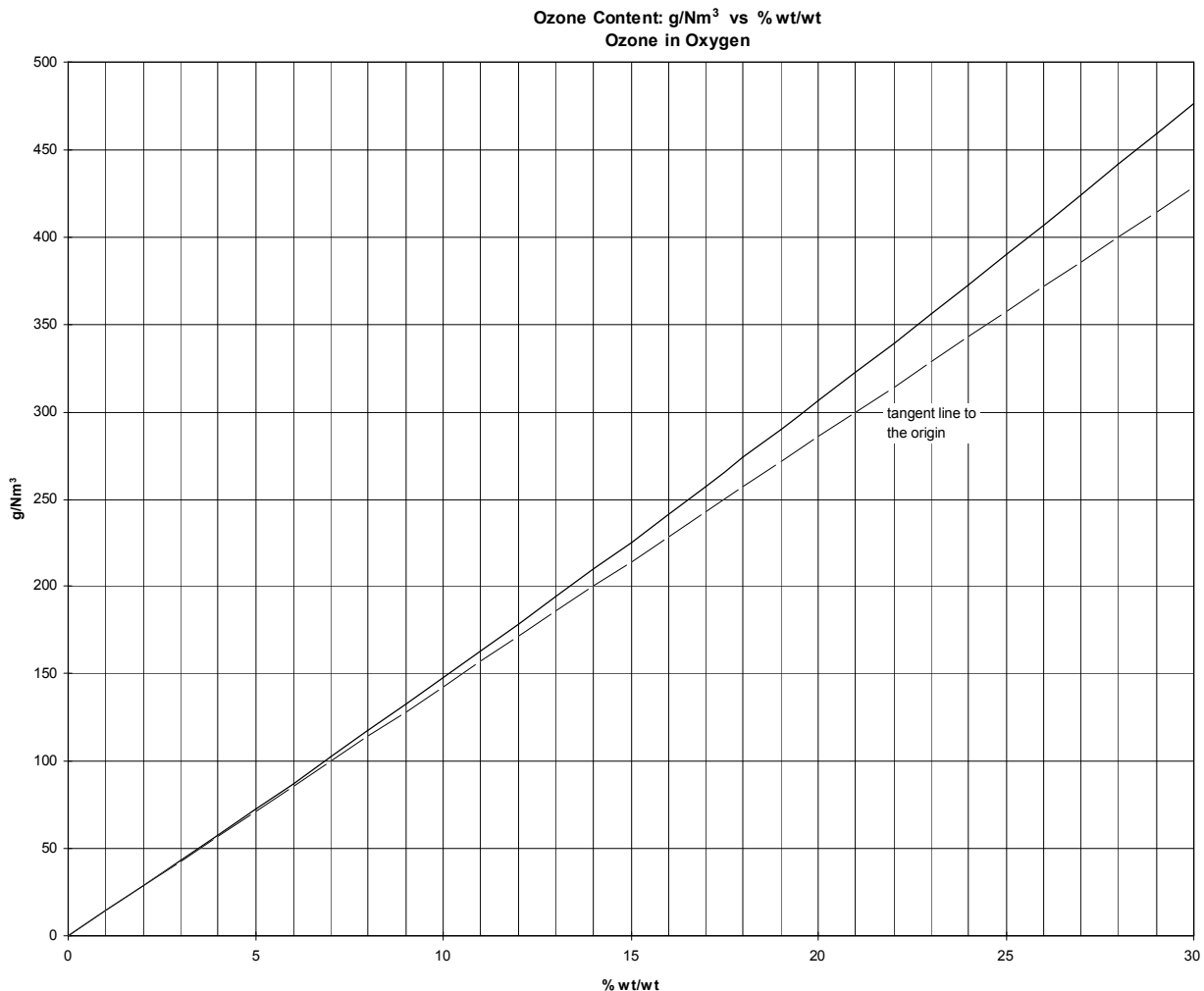
2. What an Ozone Photometer Really Measures

Ozone photometers "see" the ozone only, but they are "blind" to air or oxygen. This is the reason why they can measure ozone content in the sample only as "mass of ozone per volume of the sample". The dimension is g/m^3 (or e.g. mg/l). No information about the mass of the carrier gas actually is contained in this quantity!

Ozone photometers also cannot "see" the temperature and the pressure of the sample gas. To correct for this blindness, ozone photometers have to be equipped with a temperature

and a pressure sensor which give additional information about the mass of the carrier gas. An ozone analyser is an ozone photometer with an additional temperature sensor, an additional pressure sensor, and a computational unit which calculates the "mass of ozone per normal (or standard) volume of sample gas" at the arbitrary temperature and pressure of the sample gas, in g/Nm^3 .

One Nm^3 is the mass of sample gas contained in one cubic metre at $0^\circ C$ and 1 atm. It is an important fact that the gas mixture (ozone and carrier gas) changes density with changing ozone content because the oxygen (one oxygen molecule has two atoms) "shrinks" when it is transformed to ozone (one ozone molecule has three atoms). In the quotient g/Nm^3 both are changing with the ozone content, the numerator, and the denominator, as well, making the relationship between g/Nm^3 and %wt/wt nonlinear!



When the nature of the carrier gas is known (which is usually the case, e.g. dry air or oxygen) ozone content can also be calculated in "mass of ozone per mass of sample". The dimension is %wt/wt. But the instrument needs an additional

Ozone in Oxygen

g/Nm ³	% wt/wt	% wt/wt	g/Nm ³
10	0,70	1	14,3
20	1,39	2	28,8
30	2,08	3	43,3
40	2,77	4	57,9
50	3,46	5	72,7
60	4,14	6	87,5
70	4,82	7	102,4
80	5,50	8	117,5
90	6,17	9	132,6
100	6,84	10	147,8
110	7,51	11	163,2
120	8,17	12	178,6
130	8,83	13	194,2
140	9,49	14	209,9
150	10,14	15	225,6
160	10,79	16	241,5
170	11,44	17	257,5
180	12,09	18	273,6
190	12,73	19	289,9
200	13,37	20	306,2
210	14,01	21	322,7
220	14,64	22	339,3
230	15,28	23	356,0
240	15,90	24	372,8
250	16,53	25	389,7
260	17,15	26	406,8
270	17,77	27	424,0
280	18,39	28	441,3
290	19,01	29	458,8
300	19,62	30	476,3
310	20,23		
320	20,84		
330	21,44		
340	22,04		
350	22,64		
360	23,24		
370	23,83		
380	24,43		
390	25,02		
400	25,60		
410	26,19		
420	26,77		
430	27,35		
440	27,92		
450	28,50		
460	29,07		
470	29,64		
480	30,21		
490	30,77		
500	31,33		

information about the nature of the carrier gas. The reason is that the density (at given temperature and pressure) is different for different carrier gasses, of course. The density of oxygen is about 10.5% higher than that of dry air.

3. Accuracy - As We Understand It

The extinction coefficient of the ozone at the wavelength of 254 nm is not known better than to an uncertainty of about 1% (see regulation 002/87F of the International Ozone Association, IOA). In this regulation the extinction coefficient (to the base of 10) is given as **3000 ltr/cm mol at 0°C/1 atm**. We are using this extinction coefficient in our UV ozone analysers to calculate the ozone content in the ozone gas.

The uncertainty of 1% mentioned above is the least systematic error of every ozone photometer, of any manufacturer.

The design of our ozone instruments adds another 0.5% uncertainty to this systematic uncertainty. This means that repeatability plus reproducibility plus systematic errors of our analysers are in total not higher than 0.5%.

4. Gain Stability

The stability of the gain - or sensitivity - of an ozone photometer depends upon the stability of: the cuvette length, the UV detectors, the transmission of radiation from the UV lamp to the detectors, and the photometric calculation.

When the calculation is performed numerically by a digital system like a microprocessor, stability is out of question.

The cuvette length in our ozone photometers is given by a stainless steel spacer between both quartz cuvette windows. It is quite unlikely that this spacer will ever change its length.

The UV detectors used in our ozone photometers are silicon photodiodes which are extremely linear concerning UV input and signal output. Linearity is excellent over more than eight orders of magnitude. But the sensitivity of the detectors could be subject to drift. And the UV lamp is not stable concerning the shape and structure of the UV emitting plasma leading to fluctuations in the transmission of the UV radiation from the lamp to both UV detectors.

The photometric calculation is in essential the logarithm of the quotient of both UV intensities, before and after the cuvette. To set a photometer to zero means to set the quotient to exactly the amount of one at no ozone in the cuvette (note that log 1 = 0). This is done electrically by

changing the gain of one of the UV signals (from the UV detectors) so that this signal exactly equals the other signal. To zero an ozone photometer thus means to re-calibrate it at the same time. In other words: Each time an ozone photometer is zeroed (at no ozone in the cuvette) it is also re-calibrated.

5. Connection of the Analyser to the Ozone System: Full Flow, Bypass, Vent Mode

The ozone analyser has to be connected to the ozone system so that enough sample gas flows through the cuvette. The velocity of flow has a lower limit and an upper limit.

The lowest limit theoretically is given by the decomposition of the ozone on its way to the cuvette. But the rate of decomposition is so low that it does not play any role, practically, as long as the instrument has not become dirty inside. More important is the time delay between the withdrawal of the sample from the ozone system and the ozone measurement in the cuvette. This dead time is important e.g. for an automatic control system controlling the concentration output of an ozone generator.

The upper limit of the flow velocity is given by the inevitable pressure drop of the sample during its passage through the very narrow gap between the cuvette windows. Since the pressure of the sample gas during the photometric ozone measurement has to be detected with a pressure transducer at the inlet or at the outlet of the cuvette, any pressure drop inside the cuvette results in an uncertainty of the measured pressure which ideally should be that inside the cuvette. If the uncertainty of the pressure measurement has to be less than e.g. 0.3%, and if the pressure would be about 1 atm, pressure drop between inlet and outlet of the cuvette must not be higher than 0.6% of 1 atm, or about 6 mbar (because the pressure inside the cuvette lies approx. in the middle between the inlet pressure and the outlet pressure of the cuvette).

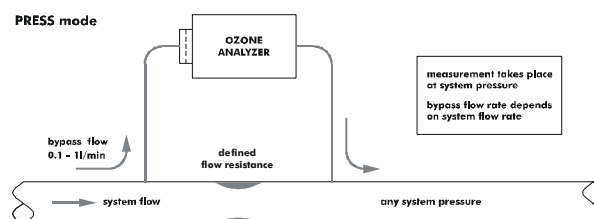
For BMT ozone analysers we recommend a flow rate of the sample gas of about 0.1 to 1 litre per minute. If the distance

between the point of withdrawal of the sample and the analyser is short, e.g. only 50 cm, even a flow rate of less than 0.1 l/min would be possible. The shorter the length and the lower the internal diameter of the connecting tubing is, the lower the flow rate may be. The internal volume of a cuvette for the measurement range of e.g. 200 g/m³ is about 50 microlitres. To replace the sample gas inside the cuvette ten times a second would require a flow rate of only 0.03 litres per minute. But the time delay would be quite long: with a length of 50 cm of the connecting tubing having an ID of 3 mm, the delay would be about 7 seconds. At 0.3 litres per minute the time delay would be only 0.7 seconds (see 7.).

Full flow connection of an ozone analyser means that the total ozone gas flowing in the ozone system is lead through the analyser. We recommend that full flow connection should be used for system flow rates of up to about 1 litre per minute.

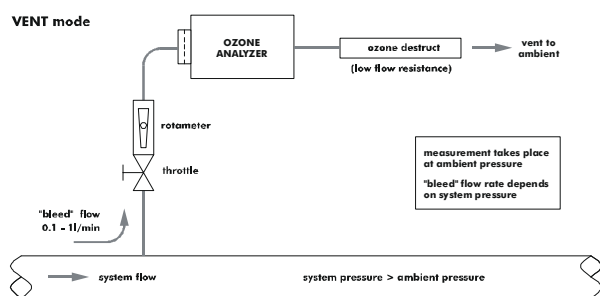
When the system flow rate is higher, e.g. between 1 and 10 litres per minute, the best solution would be to connect the ozone analyser in a bypass to a small flow resistance in the ozone line. Pressure drop at this flow resistance should be in the order of a few millibars to allow enough sample gas to flow through the analyser.

Both modes of connecting the analyser to the ozone system, full flow and bypass, as well, of course need an analyser



equipped with an internal pressure transducer which is resistant against ozone. The pressure range of the pressure transducer, and the range of pressure compensation performed by the internal microprocessor, have to be fitted to the range of the pressure which could actually occur in the ozone system. We are offering pressure ranges 0.5 - 1.5 to 0.5 - 4.0 bars absolute.

Connecting the ozone analyser in the vent mode is recommended when the flow rate in the ozone system is high enough to spend a bit of the ozone gas, e.g. 0.3 litres per minute, to only feed the ozone analyser for measuring the ozone content, and afterwards destroy the ozone in an ozone destruct. Since the ozone gas usually is under an elevated pressure, the vent connection usually is made via a needle valve and a flow meter to adjust and monitor the sample gas flow rate through the analyser. Behind the analyser an ozone catalyst, or some other ozone destruct, has to be installed.



Full flow ozone analysers are offered on the market with a flow capacity elevated to 5 or 15 litres per minute equipped with fittings for 1/4" tubing. They are called in-line analysers. Actually they have an internal bypass, of course. The drawback is that the internal cuvette alone cannot be protected from dirt by a filter. In-line analysers are restricted to applications with very clean ozone gas without any dirt, e.g. in semiconductor manufacturing.

6. The only Real Enemy of an Ozone Analyser: Dirt

By our experience with thousands of ozone analysers and over more than two decades we know that the vast majority of service problems with ozone analysers are due to only one reason: dirt which had come inside the instrument via dirty sample gas. The best one can do to his ozone analyser is to prevent dirt from getting into the instrument!

Dirt is everything which could soil the cuvette windows with a layer of optically active substance (at the wavelength of 254 nm at which the ozone photometer "sees" the ozone).

The least problem is water vapour. When the dew point temperature of the water vapour contained in the sample gas is higher than the temperature of the cuvette windows, water will condensate on the windows. The temperature of the

cuvette windows is about 10 K higher than the ambient (around the analyser) due to the heat produced by the UV lamp and by the electronic circuitry inside the instrument. When the ambient temperature is around 20°C the dew point temperature of the sample gas should not be higher than about 25°C. If pure water has condensated on the cuvette windows, the problem will vanish when the vapour content of the sample would drop.

Much worse are hydrocarbons contained in the sample. The high intensity of the UV radiation used for the ozone measurement leads to a transformation of fluidic or even gaseous hydrocarbons when they get onto the cuvette windows. They tend to "burn in". To remove such burnt-in layers is possible only by dismantling the instrument, and sometimes only by replacing the cuvette windows.

7. How to Retain Water Vapour

Water vapour in an ozone sample gas practically does not interfere with the ozone measurement, not even at very low atmospheric ozone concentrations. Water vapour should be reduced only when condensation has to be expected at some point in the ozone measuring system.

Water vapour may not be removed by desiccants like silica gel because the contact with these substances can destroy part of the ozone to be measured. Only in a laboratory situation calcium chloride could be used for drying ozone gas.

The only rational method to reduce the dew point temperature of the water vapour is to cool the sample gas down in order to let some of the water vapour condensate at the walls of a cold vessel. The simplest means would be a washing bottle which is cooled from the outside with tap water or even with ice.

For continuous cooling and drying ozone sample gas, we are offering instruments named Sample Gas Dehumidifier DH3 and DH5. The heart of this type of instrument is a vertical stainless steel tube with an ID of 8 mm and a length of 160 mm which is electrically cooled down by a Peltier cooler to about +1°C. This tube has to be mounted on top of the ozone reaction vessel from which the wet ozone sample gas usually has to be withdrawn. The wet gas flows upwards through the cold tube and part of the water vapour now condensates on the walls of the tube. The condensate runs

down at the inner walls of the tube and drops back into the ozone reaction vessel. Hence the condensate is removed continuously and automatically, and condensation in the sample gas tubing now is avoided, which is the only purpose of drying the sample gas.

8. How to Retain other Kinds of Dirt

Particulate and dust can be retained by an appropriate filter. Our ozone analysers are equipped with such a sample gas filter at the inlet. The filter insert is a sheet of pure glass fibre felt, 25 mm in diameter. Additionally we offer a sample gas filter of 50 mm diameter (SGF 50).

When higher quantities of fluids may be expected to occasionally appear in the sample gas, a washing bottle is recommended which may retain and store these fluids, and particulate, too. We offer such bottles with 25 and 100 ml volume (DIRT TRAP 25 and DIRT TRAP 100).

When a Sample Gas Dehumidifier DH3 or DH4 is used to remove water vapour, it may be expected that also e.g. gaseous hydrocarbons will be removed, at least partially.

9. Connecting Tubing, Time Delay of Measurement

Inside our ozone analysers we use PTFE tubing 2,5 mm ID. This size is more than wide enough for the low sample gas flow we recommend.

To our experience, our customers usually tend to use too wide tubing to connect the analyser to their ozone system, e.g. 4 mm ID, or even more. As a compromise the external fittings of our instruments are for 3 mm ID PTFE tubing (3 mm ID x 5 mm OD, or 1/8" x 3/16").

If a wider connecting tubing is desired, e.g. for mechanical reasons, an adaptor may be used. We offer an adaptor from 3 x 5 mm to 4 x 6 mm tubing (AD 3x5-4x6).

From the point of view of time delay of the ozone measurement, we recommend to use only tubing of 3 mm ID.

Time delay at a given flow rate is proportional to the length and the internal cross section area of the connecting tubing. At a sample gas flow rate of e.g. 0.3 l/min and with a tubing ID of 3 mm, the time delay due to the limited velocity of the gas flow is about 1.4 seconds per meter of connecting tubing. If the time delay has to be reduced, we recommend to use a higher flow rate of the sample gas (but not more than about 1 l/min!), or to reduce the ID of the connecting tubing (please contact factory). If wider tubing (ID higher than 3 mm, e.g. for mechanical reasons) must be used, a good idea is to put a second, but thinner, PTFE tubing inside the wider tubing in order to reduce the effective internal cross section area.

10. Ozone Destruction after Measurement in the Vent Mode

After measurement in the vent mode the sample gas usually has to be let to the ambient. To remove the ozone in the sample gas, some kind of ozone destruct has to be used.

Ozone may be destroyed by several means. One is heating to about 350°C for about 3 seconds. This method is not economic for the low sample gas flow from an ozone analyser. Another means is activated carbon. But activated carbon can burn, or even explode. It must not be used for destruction of ozone in oxygen!

The method usually used for destruction of the ozone contained in the sample gas is an ozone destruct filled with an appropriate quantity of a special ozone catalyst containing heavy metal oxides, namely manganese dioxide. We offer the Catalyzing Cartridge CAT-R for this purpose.

The ozone catalyst has some drawbacks which have to be considered. It produces dust, which in our CAT-R is retained by glass fibre filters on both sides: inlet and outlet. More important is the fact that the ozone catalyst can be "poisoned" by substances occasionally contained in the sample gas. Such substances e.g. are water, nitrogen oxides, chlorine, halogenes, and even hydrocarbons.

11. Materials for Ozone Systems

Materials well suited for high concentrated ozone are: stainless steel, quartz, sapphire, borosilicate glass, PTFE, PFA, FEP, FFKM (KALREZ® CHEMRAZ®), AFLAS®,

FLUORAZ®, silicon, Al₂O₃ ceramic, and anodised aluminium. Silicone rubber and FKM (VITON®), though they are generally stable, may not be used for ozone. At a low concentration of up to about 50 g/Nm³ PVDF or PVC are acceptable, namely when the ozone gas is wet.

12. How to Measure System Flow Rate

For a quantitative analysis of an ozone process not only knowledge about the ozone concentration is required, but also an information about the flow rate of the ozone gas.

Gas flow measurement usually is made by a rotameter type of flow meter, or by a thermal mass flow meter.

Calibration of a rotameter depends upon the nature of the gas, its temperature, and namely its pressure. If e.g. a rotameter calibrated at 1 bar abs would be used at 2 bars abs, the flow rate would be displayed about 30% too low! An approximate correction can be made by multiplying the displayed mass flow rate (e.g. Nl/min, or Nm³/h) by the square root of the quotient of the actual pressure divided by the calibration pressure.

Calibration of a thermal mass flow meter practically only depends upon the nature of the gas.

Since the nature of ozone gas varies with its ozone content, neither one of these flow meters can be used for precise measurement of flow rate. The thermal mass flow meter has two additional drawbacks: The high temperature of its sensor element, usually about 90°C, leads to some degree of exothermic (!) ozone destruction during measurement the heat of which disturbs the thermal measurement principle of the instrument. Decomposition of the ozone (with oxygen atoms in statu nascendi) now tends to destroy the internal capillary tube of the thermal mass flow meter, namely when traces of nitrogen are present in the ozone gas.

These are the reasons why the flow rate must not be measured in the ozone gas. Precise measurement of the flow rate of an ozone gas is possible only indirectly in the pure carrier gas (usually oxygen or dry air), either in front of the ozone generator, or after destruction of the ozone.

13. Calculation of Ozone Mass Flow Rate

For calculating the ozone mass flow rate, two informations are necessary: the flow rate of the carrier gas (see 12.), and its ozone content.

The flow rate of the carrier gas may e.g. be given in Nm³/h or in g/h. The dimension Nm³/h actually means a mass per unit of time, as it is the case with g/h. When the carrier gas is oxygen, 1 Nm³/h equals 1428.97 g/h.

The ozone content of the ozone gas may be given in g/Nm³ or in %wt/wt.

The simplest way of calculating ozone mass flow is multiplying the g/h (carrier gas) by %wt/wt (ozone content of the ozone gas). At e.g. an oxygen flow rate of 100 g/h and an ozone content of 8 %wt/wt the ozone mass flow is 8% of 100 g/h or 8 g/h.

More complicated is the situation when the ozone content is given in g/Nm³, since the mass contained in one Nm³ of ozone gas depends upon the ozone content (because the oxygen "shrinks" when it is converted to ozone, see 2.). Ozone mass flow may not be calculated by simply multiplying Nm³/h (carrier gas) by g/Nm³ (ozone content). One should have in mind that one Nm³ of oxygen represents a given and constant mass, whilst one Nm³ of ozone gas contains more or less mass depending upon the ozone content. In other words: The Nm³ in the carrier gas flow is not the same as the Nm³ in the ozone content!

For calculating the ozone mass flow by multiplying the carrier gas flow in Nm³/h and the ozone content in g/Nm³ a correction factor has to be used. This correction factor is $1/(1 + \mu C)$, where C is the ozone content in g/Nm³, and $\mu = 2.333 \times 10^{-4}$ Nm³/g for ozone in oxygen as the carrier gas. Without this correction the ozone mass flow would be calculated too high, the error rising with the ozone content:

2.3% at 100 g/Nm³, 4.7% at 200 g/Nm³, 7.0% at 300 g/Nm³, and 9.3% at 400 g/Nm³.

14. Ozone in Water

Pure water is nearly transparent for UV radiation at 254 nm (the wavelength at which ozone can be measured). This is the reason why ozone dissolved in water can be measured

the same way as ozone in gas - as long as the water is really clean.

One problem with measuring ozone dissolved in water may be the presence of gas bubbles in the water. When a gas bubble enters the cuvette the photometric measurement is severely disturbed. This is the reason why the measurement must not be made behind a throttle which reduces the pressure of the water. Pressure reduction would lead to outgassing.

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