The influence of sample tubing material on accuracy of low ozone concentration measurement

Dr.-Ing. Andreas Scholz[1], Dr.-Ing. Franz Wallner[1]

1. BMT Messtechnik GmbH, Güterfelder Damm 87-91, 14532 Stahnsdorf / Germany

Abstract

The aim of this study was to investigate the applicability of different sample tubing materials for low ozone concentration measurement. Ozone is a very unstable gas. The materials used in a measurement system have to be selected carefully. Otherwise ozone decomposition could occur on the surface of the materials, especially inside the tubing. Due to the toxicity of ozone, workplace concentration monitoring is mandatory in many countries. Any destruction of ozone on its way from the point of sample to the ozone monitor has to be prevented. Otherwise the safety monitoring system fails.

Two stainless steel (SS) tubing materials were compared with a sample gas tubing made of FEP (fluorinated ethylene propylene). The FEP tubing showed no measurable ozone decomposition and thus is the material of choice for low ozone concentration measurement. On the other hand the measurements showed alarming results for the stainless steel tubing. Inside the tubing up to 100% (!) of the ozone was destroyed. For safety monitoring this is a catastrophe.

The paper gives recommendations for a proper installation.

Key-words: ozone decomposition, ozone measurement, UV photometry, stainless steel tubing, workplace safety, ambient ozone measurement, vent-gas measurement

Introduction

Measurement of low ozone concentration is trace analysis. UV photometry is the standard measurement principle for this task. Ozone is a very unstable gas. To determine the exact amount of ozone in a sample, decomposition of ozone on its way from the sample point to the ozone monitor has to be prevented [1]. Therefore, the materials used in a measurement system have to be selected carefully. The measurement system consists of the ozone monitor itself, the particle filter, the tubing etc.. This paper focuses on the material of the sample gas tubing.

In many industrial applications, e.g. drinking water treatment plants, the use of stainless steel tubing for ambient or vent ozone measurement is still mandatory, although the risk of ozone decomposition on metal surfaces has often been described [2].

Ozone is a toxic gas. In many countries regulations require the workplace ozone concentration never to exceed 0.1 ppm_v. In the United States OSHA has established a Permissible Exposure Limit (PEL) of 0.1 ppm_v TWA (8 hour Time Weighted Average) [3]. In addition OSHA recommends a STEL (15 minute Short Term Exposure Limit) of 0.3 ppm_v. Normally the STEL is used for an ozone generator power shutdown [4]. Ambient ozone monitors are used for TLV (Threshold Limit Value) monitoring.

Another typical application of low ozone concentration measurement is often referred to "Vent-Gas Measurement". In a water treatment plant the off-gas from the ozone contactor will be destroyed by a heated catalytic destruct. This vented "off-gas post destruct" or vent-gas must also comply with OSHA standard. Elevated ozone concentration in the vent-gas indicates a failing destruct unit.

Both measurements, the safety monitoring and the vent-gas measurement as well, depend on accurate and reliable ozone concentration measurement. The paper will show how the use of inappropriate tubing material could cause dramatic decomposition of ozone in the sample gas line.

Material and Methods

Tubing Specimens

Different types of stainless steel and FEP tubing were used for the study (*Table 1*). The stainless steel tubing specimens were cleaned for oxygen service by the manufacturers.

specimen no.	manufacturer	material	tube OD	tube wall	specification
1	Dockweiler	stainless steel 316L (1.4401)	1/4" (6.35mm)	0.065" (1.65mm)	TCC, chemical cleaned (ASTM A632-S3)
2	Swagelok	stainless steel 316Ti (1.4571)	1/4" (6.35mm)	0.065" (1.65mm)	oil-free
3	SMC	FEP	1/4" (6.35mm)	0.047" (1.2mm)	transparent

Table 1: Tubing specimens

Experimental Setup

Figure 1 shows the experimental setup used for the study. Ozone was produced from room air by a small ozone generator using a UV lamp with a wavelength of 185 nm (BMT AOS-1). Two measurements - upstream (A) and downstream (B) of the tubing - were used to evaluate the ozone decomposition inside the tubing. The measurements were taken by an ambient ozone monitor BMT 932-3 (three channel). The use of a single multichannel ambient monitor removed the possibility of any differences in measurements at point A and point B to be attributed to two different monitors.

The particle filter upstream of sample point A prevents contamination of the tubing inner wall. The particle filter is one of the most important elements of an ambient or vent-gas ozone monitoring system. Every decontamination or impurity, e.g. dust, inside the tubing could cause dramatic decomposition of ozone. The result would be a partial or complete malfunction of the monitoring system.

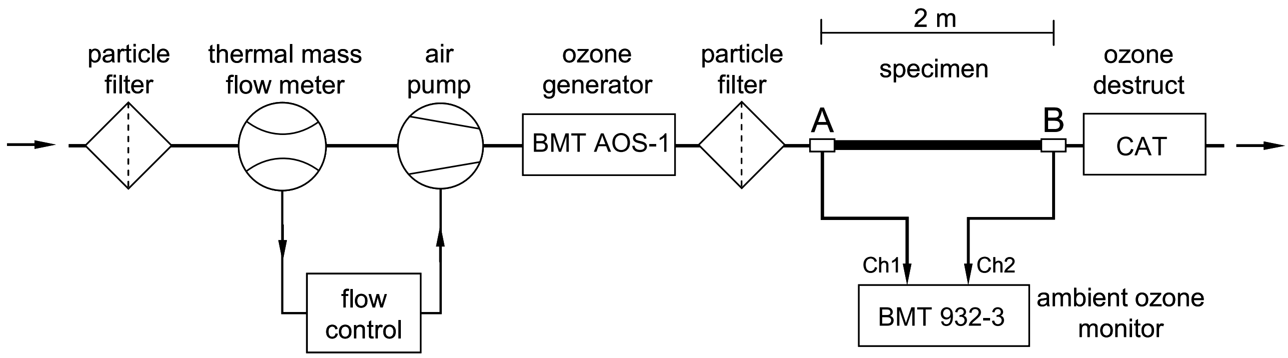

Figure 1: Experimental setup

The results of the measurements will be discussed in the next paragraph. The following ratio will be displayed in the figures:

$$ratio = \frac{ozone\ measurement\ outlet\ (B)}{ozone\ measurement\ inlet\ (A)}$$

If the ratio equals 1, no ozone was destroyed inside the tubing.

The decomposition of ozone could be calculated by:

$$ozone\ decomposition = 1 - \frac{ozone\ measurement\ outlet\ (B)}{ozone\ measurement\ inlet\ (A)} = 1 - ratio$$

Results and Discussion

Stainless Steel vs. FEP

Figure 2 shows a comparison of the measurements for stainless steel tubing vs. FEP tubing. Tubing length was 2 m. In this experiment an ozone level of 170 ppb_v and a flow rate of 1.6 L/min were used. All tubes were unused before the measurements.

The FEP tubing showed no measurable ozone decomposition. From the start of the experiment the measured ozone concentration downstream the tubing (B) equals the value upstream the tubing (A).

On the other hand both types of stainless steel tubing showed significant differences concerning ozone decay between inlet A and outlet B. Within the first minutes of the measurement the ozone decomposition inside the stainless steel tubing No. 1 (Dockweiler) was about 90% (!) with a steady decrease. Even after 15 minutes the decomposition was about 43%. Stainless steel tubing No. 2 (Swagelok) showed an initial ozone decomposition of about 75%! That means, at the start the measured value at sample point B is less than 25% of the "true reading" (= sample point A). After 15 minutes the ozone decomposition inside the stainless steel tubing No. 2 was still about 37%.

Concerning safety reasons this is a catastrophe. The ambient or vent-gas ozone monitor would detect elevated ozone concentrations immediately if FEP tubing would be used. In case of stainless steel tubing safety monitoring of the ozone is impaired or even impossible.

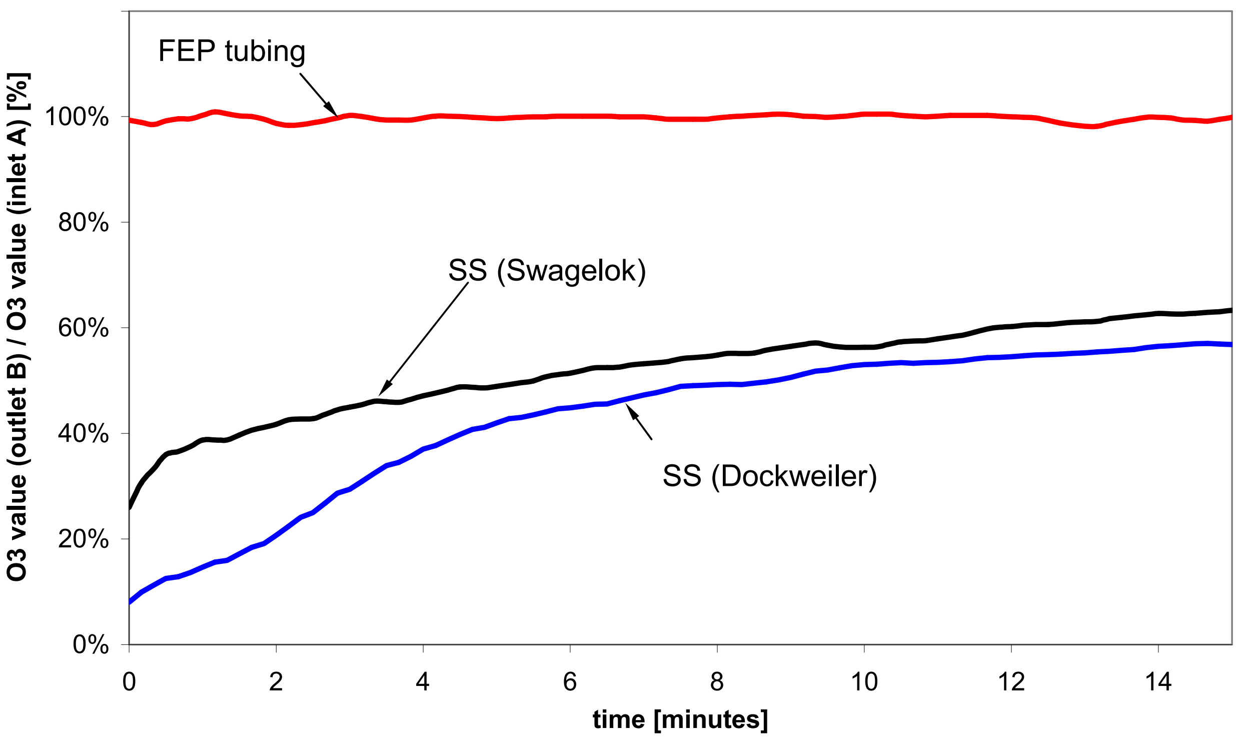

Figure 2: Influence of tubing material on the ozone measurement downstream of the tubing, ozone level: 170 ppbv, tubing length: 2m

Conditioning of Stainless Steel Tubing

From the data in *Figure 2* one could conclude, that the stainless steel tubing requires a period of ozonation, often called conditioning or passivation, of the surface before the "true reading" is achieved.

McElroy et al [5] recommend to expose the sample lines and filters of an ozone measurement system "to high concentrations of ozone (> 400 ppm) for at least 30 minutes".
For this study the stainless steel tubing No. 1 (Dockweiler) was treated with a much higher ozone concentration: 200 g/Nm³ for 2 hours (1 g/Nm³ equals 466 ppm$_v$!). The results of this conditioning are shown in *Figure 3*.
The test series that started only one hour after the end of the passivation showed a relatively stable ratio of the measured ozone value at the outlet (B) of the tubing to the ozone value at the inlet (A) of the tubing. Nevertheless a relatively constant ozone decomposition of about 5 % occurred inside the pre-treated stainless steel tubing.
The passivated tubing was sealed for three months and the measurement then was repeated. The data in *Figure 3* show that the passivation is not permanent. Even after 15 minutes of ozonation the value of the "freshly" conditioned specimen was not reached. Three month after the pre-treatment the measured initial ozone concentration downstream the tubing (B) was only about 65% of the value at sample point A.
From these results it becomes obvious that passivation will not overcome the disadvantages of the stainless steel tubing compared with the FEP tubing.

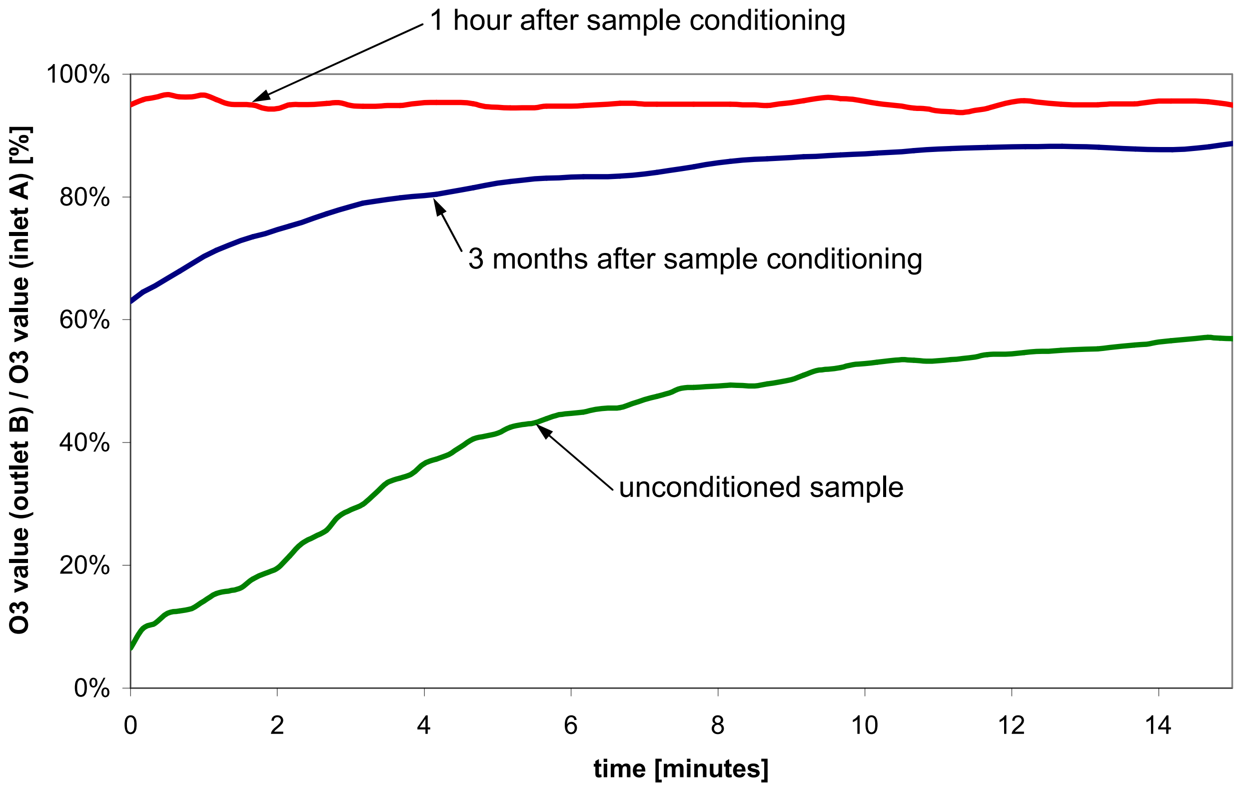

Figure 3: Influence of sample tubing conditioning on the ozone measurement downstream of stainless steel tubing No. 1 (Dockweiler), conditioning: 200 g/Nm³ of ozone for 2 hours, measurement conditions: ozone level: 170 ppbv, tubing length: 2m

Influence of Tubing Length

The results of the previous paragraphs were obtained by using tubing specimens with a length of 2 m. In a real installation the sample gas lines could be up to 20 m. *Figure 4* compares the measurement results for a 20 m FEP tubing vs. 2 m and 4 m long stainless steel tubing. All specimens were unused prior the measurements.

It is obvious that the ozone decomposition inside the stainless steel tubing will rise with rising length of the sample line. *Figure 4* shows an alarming result for the stainless steel tubing 4 m long: At the start of measurement the measured value at sample point B (outlet of the tubing) is 0% of the "true reading" (=sample point A) for more than 5 minutes! The ozone monitor will show 0 ppb although the real ozone concentration at the sample point exceeds the Permissible Exposure Limit (PEL). The safety monitoring system will not work if stainless steel tubing is used!
On the other hand, even at a length of 20 m, the FEP tubing showed no measurable destruction of ozone inside the tubing.

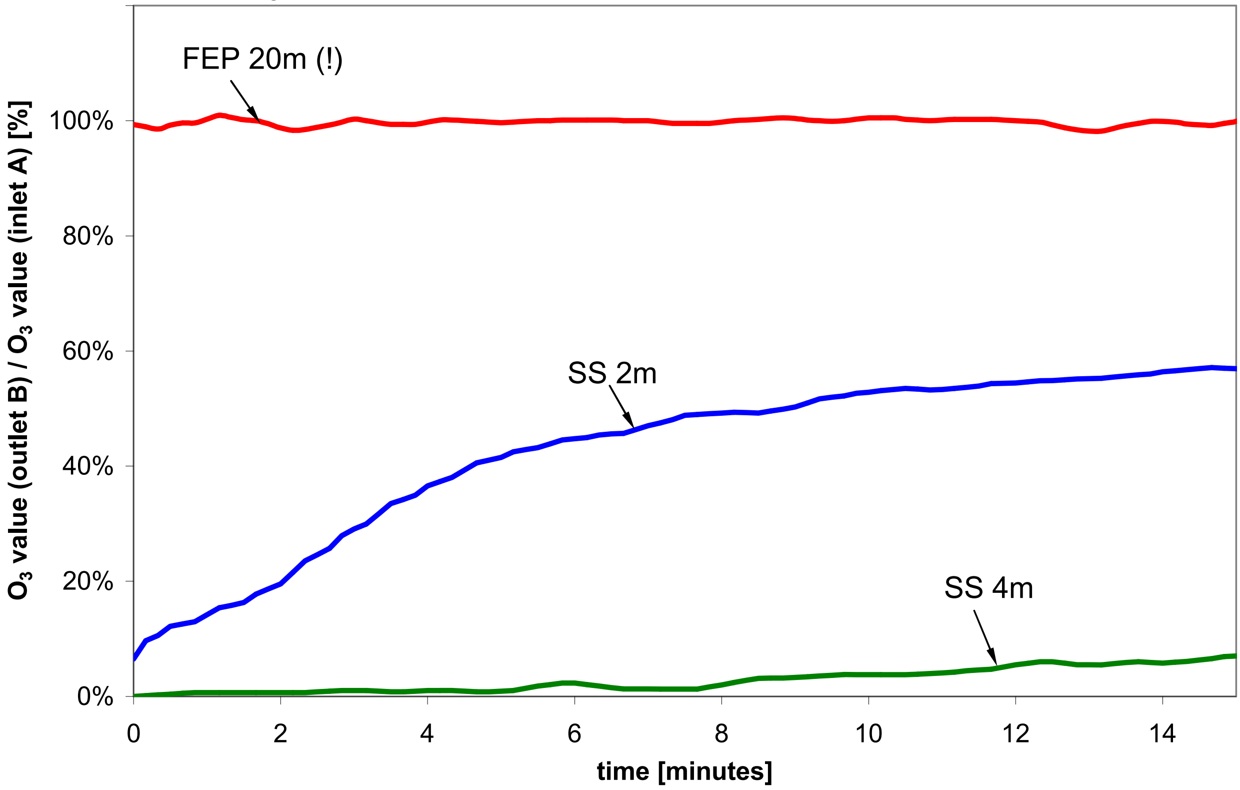

Figure 4: Influence of tubing length on the ozone measurement downstream of the tubing, ozone level: 170 ppbv

Recommendations for a Proper Installation
Based on the results of this study, the authors suggest to comply with the following recommendations:

1. One of the most important parts of an ozone measurement system is the particle filter. The filter should always be placed <u>upstream</u> the sample gas line. This is the only way to protect the sample gas tubing <u>and</u> the analyser from contamination. The filter inserts have to be replaced on a regular basis to prevent ozone decomposition inside the filter.

2. FEP is the material of choice for low ozone concentration measurement. From experience of the authors PTFE tubing will show comparable results to FEP tubing. The disadvantage of PTFE is that it is not transparent. The use of FEP tubing offers the possibility of visual inspection of the tubing. Dirt or water droplets will be visible immediately.

3. Stainless steel is not an appropriate tubing material for low ozone concentration measurement!

4. If metallic tubing is mandatory for the installation, one should use a conduit, well known from electrical wiring, made of stainless steel, aluminium or copper with a wide inner diameter. A sample gas line made of FEP should be inserted into the metallic protective tubing. The FEP tubing should be replaceable.

Conclusions

The main objective of this work was to investigate the influence of tubing material on low ozone concentration measurement. Tubing made of FEP and 316L and 316Ti stainless steel were used for this study.
The results of this research are clearly showing that the use of inappropriate tubing material - namely stainless steel - will cause dramatic decomposition of ozone in the vent-gas and ambient air sample gas lines.
Ozone may be dangerous and harmful, even at low concentration. Ozone decomposition inside the sample tubing will cause dramatic measurement error of threshold limit value (TLV) monitoring. This will affect workplace safety.

Based on the results of this study it could be summarized, that FEP is the material of choice for low ozone concentration measurement.
The authors strongly recommend to review the installation specifications for ambient and vent gas ozone measurement. The paper gives recommendations for these installations.

References

1. WMO World Meteorological Organization, Guide to Meteorological Instruments and Methods of Observation , WMO-No. 8, 2008 edition, updated 2010.
2. Song, W. et al, Ozone decomposition in a downer reactor, The 12th international conference on fluidization - new horizons in fluidization engineering, 2007.
3. OSHA Occupational Safety & Health Administration, Exposure limits and health effects of ozone, https://www.osha.gov/dts/chemicalsampling/data/CH_259300.html (accessed March 19, 2015).
4. Rakness, K. L., Ozone in Drinking Water Treatment: Process Design, Operation and Optimization, AWWA, 2005.
5. McElroy, F., Mikel, D., Nees, M., Determination of Ozone by ultraviolet analysis - quality assurance handbook for air pollution measurement systems, final draft 1997, http://mattson.creighton.edu/Ozone/OzoneEPAMethod.pdf (accessed December 5, 2014).