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Methods for measuring ozone concentration in ozone-treated water

***Abstract**. The ozone measurements are gaining in importance as the area of environmental ozone applications to liquids and especially to water grows. Some a few methods can be enumerated, and each of them has only limited area of applications. The comparison of the methods shows that there still is a need for rugged, reliable, ozone-specific, direct measurement methods and sensors for measuring ozone concentration in ozonated water.*

***Streszczenie.** Przyrządy i metody do pomiaru stężenia ozonu w cieczach, a zwłaszcza w wodzie, nabierają coraz większego znaczenia w miarę rozszerzania się obszarów zastosowań ozonu ze względu na ochronę środowiska. Porównano kilka współcześnie stosowanych metod i wykazano, że każda z nich posiada tylko ograniczony obszar przydatności. (**Metody pomiaru stężeń ozonu w wodzie ozonowanej**)*

Keywords: water ozonation, dissolved ozone concentration measurement, water disinfection systems.
Słowa kluczowe: ozonowanie wody, pomiary stężeń rozpuszczonego ozonu, układy do dezynfekcji wody.

Introduction

The global increase in pollution of surface fresh water as well as seawater is mainly caused by human industrial activity. This problem is even more urgent in highly populated areas of developed countries, since the environment becomes ecologically damaged – and this degradation is a factor enhancing e.g. the risk of water-spread epidemies [1]. On the other hand, consumers require from the manufacturers better quality of water and food for realizing healthy lifestyle. For these reasons, an intensive search for fast and efficient methods of water purification without residual taste, odour or toxic by-products is continued. The method of water ozonation seems to satisfy these requirements to highly promising degree [2].

Although ozone was discovered in 1839 (by C. F. Schonbein) and used for tap water treatment in the Netherlands (1880's), Nice (1907) and St. Petersburg (1910) [3], the water ozonation process is still widely investigated [4, 5]. This research was intensified after 1982, when the US Food and Drug Administration (FDA) recognized safe status for ozone usage in bottled water, and later for liquid food and beverages processing (in 1997). The designing of optimal water ozonation system is a complex task because of unique features of gaseous ozone technology as chemical agent. Firstly, the ozone generators can operate on either air (the output is 1-3% ozone) or pure oxygen (the output is ca. 6 % ozone) – if the corona-discharge or other high voltage-based generator is used The UV or VUV generator outputs are insufficient (0.5% ozone or less). So, the gaseous concentrations are small.

Secondly, ozone is a highly unstable gas which cannot be stored [6]. The half-life time of ozone in distilled water is ca. 20 minutes [7] (in raw potable water ca. 10 min.), It facilitates the problem of excess ozone utilization, but enforces the installation of the ozone generator as integral part of the ozonation plant [8, 9].

Thirdly, the solubility of ozone in water is rather low – approximately 10 times lower than solubility of chlorine [10] (for this reason, chlorine is still used; although the ozone killing power of microorganisms is 400 times stronger than chlorine). Therefore, a special chamber (bubble column, or contact tank, or contactor) is necessary to allow diffusing the ozone gas into water [11]. The ozone (mixed with the air or oxygen from the generator) is injected into the water in fine gas bubbles, and the turbulent mass transfer (by diffusion) occurs. Higher temperatures mean decrease in ozone solubility, but increase in reaction rates. Since the bubbles contain a few percents of ozone, and the solubility is low, the mass transfer and, in consequence, the reaction rates are moderate, even for such powerful oxidant as ozone (only fluoride exhibits higher oxidation potential) [10].

When the ozone is dissolved in water, there is a need of measuring the ozone concentration at the inlet. The concentration level of the applied ozone depends on the kind of microorganisms or inorganic pollutants to be destroyed, and on the required reduction ratio (expressed in logarithmic scale). This level also depends on the designed treatment time; the disinfection standards take into account both factors (e.g. exposure to 4 ppmw ozone concentration for 4 minutes is required) [5]. In practice, the applied ozone exhibits concentrations from 0.2 ppmw to 10 ppmw; only some processes in wafer technology require ultra-pure water treated with 30 ppmw ozone.

A long-term exposure of the personnel to 0.2 ppmw is harmful for lungs and respiratory tract. A person who doesn't work around ozone, may smell in air the concentration 40 $\mu gO_3/1\ m^3 air$ (i.e. 18.7 $ppmvO_3$, or 0.03 $ppmwO_3$= 30 $ppbwO_3$) – "sniff test". Ca. 0.1 ppmv ozone is present in the ambient air; so for workspace the US Occupational Safety and Health Administration limits the allowable ozone concentration to 0.1 ppmv. For these reasons, the residual dissolved ozone in the exit water should be checked and maintained at 5-50 ppbw; if necessary, it should be decomposed using UV radiation of ca. 250 nm wavelengths [6, 11].

Methods for measuring dissolved ozone in water

The methods for measuring ozone in water can be categorized as specific or not specific to ozone. The dissolved ozone-specific methods are: the UV absorption method, the indigo method, the amperometric-membrane method, and the stripping and gas phase detection method. The dissolved-ozone not specific methods are: the potassium iodide method and the amperometric-bare method. The absolute method for measuring ozone concentration is based on the change in volume which accompanies the ozone decomposition:

$$2O_3 \rightarrow 3O_2; \quad (1)$$

the alternative manometric method is based on change in pressure at fixed volume. Unfortunately, these methods are time-consuming, and inaccurate because of minute changes at low concentrations.

The UV absorption method was developed mainly for measuring the ozone concentration in air, but it is also applicable to dissolved ozone in water – because the UV radiation at 254 nm wavelength is absorbed only by ozone; air, water or oxygen are "transparent" to this radiation of low-pressure mercury lamp. The main equation [12] is as follows:

$$O_3(ppmw) = \frac{10^6 T}{273 Pkl} \log \frac{I_0}{I_t}, \quad (2)$$

where: T – the absolute temperature; P – the total pressure; k – the extinction coefficient of ozone; I_0 – the intensity for the ozoneless medium; I_t – the intensity with ozone present; l – the pathlength (in cm).

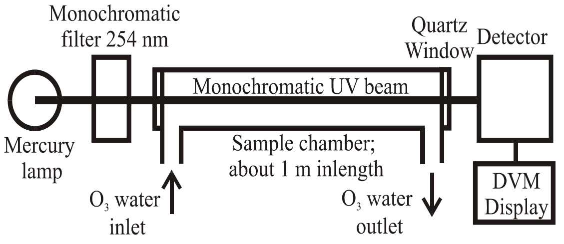

Fig.1. Schematic of the single beam arrangement of UV method

The arrangement for measuring ozone in water is shown in Fig.1; other setups (dual beam or splitted beam) are possible. The corrections for temperature and pressure inside the sample chamber are necessary for measurement in air; for water these corrections can be neglected. The UV absorption method is sensitive to bubbles in water or other impurities; the sample should be filtered and protected from degassing.

In 1953, the first colorimetric oxidant recorder was elaborated. Only in 1978 in Switzerland, the indigo method was invented. The indigo "blue jeans" dye was chosen because the selective rapid reaction of ozone with the double bond of indigo is useful for its simplicity and lack of interferences. The decolourization of indigo trisulfonate (ITS) under ozone influence causes linear drop in absorbance with increasing ozone concentration. The indigo method is recommended when the UV absorption method cannot be performed or the concentration is lower than 100 ppbw. The main drawback of indigo method is its off-line performing. The equation applied to calculate the ozone concentration is expressed as [13]:

$$O_3(ppmw) = \frac{100 \cdot \Delta A}{fbV}, \quad (3)$$

where: ΔA – the difference in absorbance between sample and blank solution; b – the pathlength of the cuvette in cm; V – the volume of sample added into the ampoule, normally 90 mL); f – the experimentally obtained factor (0.42).

The amperometric bare-electrode sensors use the ozonated water as the electrolyte. The oxidants present in the water are reduced at the cathode, and the generated current is linearly dependent on the concentration of all oxidants present in the water. These sensors require removing of all oxidants but ozone first or correcting for oxidants other than ozone.

These drawbacks can be got around by using an ozone-specific membrane which is wetted with the flow of ozonated water; the ozone diffuses through the membrane. The diffusion rate is linearly proportional to the ozone concentration in the water (Fig.2).

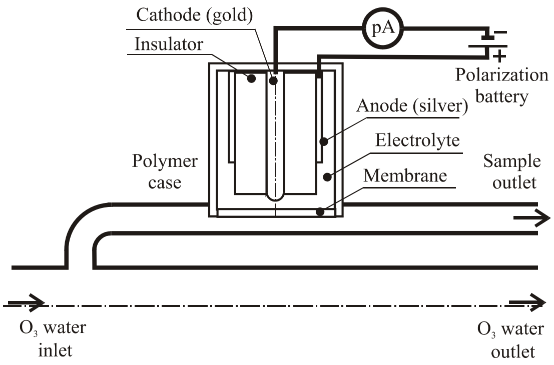

Fig.2. Schematic of a membrane-type amperometric ozone sensor

The membrane-type ozone sensors are either amperometric or polarographic electrochemical cells which transform the measurement in water into measurement in air. The headspace of the sensors should be periodically filled with air and the ozone-containing air after the measurement should be removed.

The stripping and gas phase method is similar to the membrane-type sensors, but the process of stripping the ozone from the water can be realized either by bubbling an inert gas like nitrogen (or air) through the sampled water or by intensive shaking a vessel containing the sample – in order to derive the dissolved gas by turbulent flow of water. Thin film semiconductor heated metal oxide sensors (HMOS) use the change in resistivity on the grain boundaries evolved by the ozone adsorbed on the surface of the semiconductor for sensing the ozone concentration.

The theoretical support of the stripping process is Henry's law which states that the concentration of a gas dissolved in the water is linearly proportional to the partial pressure of that gas in the air over the surface of the water is Higher pressures increase the solubility; according to the so called unitless Henry's law:

$$p = H_u \cdot c, \quad (4)$$

where: p and c are in the same concentration units (e.g mg/L) for air (p) and water (c), and H_u is the unitless Henry's constant - for ozone H_u =3.71 (gas/aq) at 20ºC. The law is observed for equilibrium (or steady) state; in practice, that condition is not met, and the stripping process does not strictly agree with Henry's law what in turn influences the accuracy of that method.

Comparison of different dissolved ozone measurement methods

The electrochemical or HMOS sensors can be calibrated using both the indigo and the UV methods – but the whole range is covered only by the UV method. The sensors can be calibrated against spectrophotometers or UV absorption analyzers – but these instruments themselves must be calibrated against reference solutions or chemical methods like gas-phase titration or iodometry, which are cumbersome and require very skillful staff. For testing if an ozone sensor is still responsive to ozone ("bump test") portable ozonators are used.

For reporting low concentrations of ozone dissolved in water the ppmw (part per million weight by weight) or the ppbw (part per billion weight by weight) units are used. On the other hand, low concentrations of ozone in air are given in ppmv (part per million volume by volume) or ppbv units. In many cases the abbreviation ppm (or ppb) is used which can cause confusions. Especially when the membrane-type or gas stripping sensors are used, the concentration unit must be carefully explained. As the concentration in air is temperature- and pressure-dependent, one should check if the results displayed are recalculated by the instrument to standard conditions.

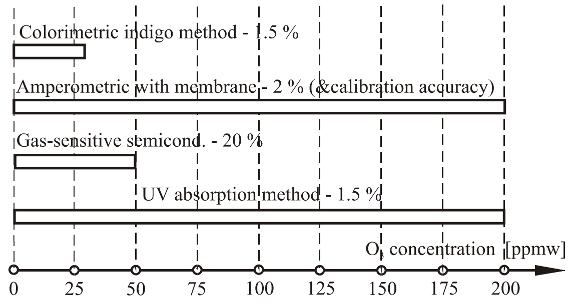

Fig.3. The dissolved ozone measurement range of different methods (in ppmw) – average accuracies are shown over the bars

In recent years, a tendency for expanding the measurement range toward lower limits of measurable ozone concentrations can be observed. This is caused by reducing the allowable concentrations in workplaces as well as adjusting the values of residual ozone at the outlet of the ozonation plant.

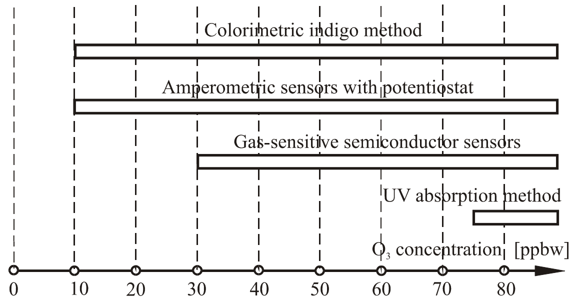

Fig.4. Lower limits of measurement range of different methods (in ppbw)

The UV method and the indigo method offer the response time of about one order faster than the amperometric sensors for dissolved or stripped ozone. However, the long-term trend aimed at shortening of the sensors' response time can be noticed.

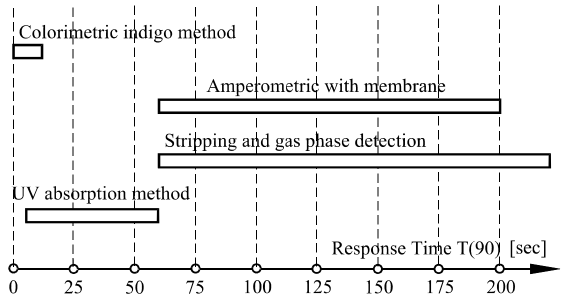

Fig.5. Response times of different methods for measurements of the concentration of dissolved ozone

Conclusions

The general trend toward low allowable levels of ozone in air or its residuals in water claims for designing new meters or sensors for the range of a few tens of ppbw.

For better control of ozonation plants, there is a need for sensors of short response time, allowing fast reaction to unexpected events within the installation.

For better metrological characteristics of ozone sensors, active sampling should be introduced to improve the contact of the sensing device with the sample.

The great problem is the calibration of the instruments for measuring dissolved ozone concentration. The UV method is most reliable as the reference method, but the trouble is to compose accurate reference solutions to check the UV analyzers. The same concerns the indigo method.

Unfortunately, there are not reference standards for calibrating instruments for measuring dissolved ozone. Some attempts to calibrate the membrane-type amperometric ozone sensors against reference gas mixtures containing oxygen are made. Oxygen is not unstable like ozone, and its concentration in air is well known all over the world. However, the measurements of the gaseous ozone from a sample are not as reliable as of the dissolved ozone, obtained directly in water.

There still is a need for rugged, reliable, ozone-specific, direct measurement methods and sensors for measuring ozone concentration in ozonated water.

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