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PRESENT USED METHODS FOR MEASURING DISSOLVED OXYGEN CONCENTRATION AT WASTEWATER TREATMENT PLANTS

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Summary

The article presents common used methods for measuring dissolved oxygen concentration at wastewater facilities. The described methods include Winkler titration and instrumental measurements, such as electrochemical sensors and more recent developed optical ones. The principles, analysis procedures as well as advantages and drawbacks of the methods were discussed. Furthermore, the valid ISO and PN-EN standards for dissolved oxygen measurements were shortly presented with emphasis on the recent changes concerning standards for the optical sensor method. As the results of a survey conducted among wastewater treatment plant operators in southern Poland reveal, optical sensors are being currently preferred in on-line applications due to their enhanced properties in comparison to other measurements methods.

Key words: dissolved oxygen, wastewater analysis, optical DO sensors, electrochemical DO sensors

INTRODUCTION

Dissolved oxygen (DO) concentration is one of the most important parameter which describes the quality of waters of all kinds (drinking waters, natural waters, waste waters etc.). In case of wastewater treatment plants the information of DO concentration in sewage at various points of the technological line is essential for controlling the processes of nitrification and denitrification as well as some others (Dojlido and Zerbe 1997; Application Note, AN-D1 2004). There are several methods of DO determination, which vary from chemical laboratory tests (Winkler titration method) to measurements by means of instruments equipped with sensors sensitive to DO concentration in a sample (Wierzbicki 1997). In modern applications the accuracy and reliability of the method, as well as its maintenance complexity, are of crucial importance. Furthermore, continuous monitoring of DO concentration has become a necessity at most wastewater treatment facilities. This is why new instruments designed for improving the standards of DO measurements, such as optical sensors, are being employed at wastewater treatment plants, in recent years (Younos and Parece 2015).

The main aim of this work was to present methods used for measuring dissolved oxygen concentration at wastewater treatment plants in regard to valid ISO and PN-EN standards. In addition, the study includes an analysis of methods and devices used currently in wastewater treatment facilities located in southern Poland. The analysis is based upon the results of a short survey conducted among wastewater treatment plant managers.

WINKLER TITRATION

The most commonly applied chemical method for DO analysis is known as the Winkler titration or iodometric method. Developed in 1888 by L.W. Winkler, a Hungarian chemist, has long been the standard for accuracy and precision when measuring DO. It is a titrametric procedure based on the oxidizing property of DO. Water samples have to be collected in a specific bottles, designed to seal without trapping air inside. An excess of manganese(II) salt, iodide (I^-) and hydroxide (OH^-) ions is added to a sample causing the formation of a white precipitate of $Mn(OH)_2$, which is then oxidized by the DO in the sample into a brown manganese(IV) compounds. In the next step, in acidified solution manganese(IV) ions oxidize iodide ions (I^-) to iodine (I_2), which is then titrated with a thiosulfate solution using starch indicator (Winkler 1888; Minczewski and Marczenko 2011).

The Winkler titration is liable to interferences resulting from the presence of other compounds in a sample, which can influence the redox reactions due to their reducing or oxidizing properties. The prior knowledge of the sample is required to apply the right modification of the method, for instance adding appropriate chemicals during the sample preparation or submit the sample to other operations (such as coagulation) prior to analysis (Wierzbicki 1997).

While the Winkler method is still recognized standard for analysing DO it has some drawbacks which cause replacing this method with instrumental measurements in nowadays applications. Titration is time-consuming, requires appropriate equipped laboratory, is subject to human errors, inaccuracies, sample contaminants and interferences mentioned above. The long analysis procedure excludes this method from applications in controlling the biological processes (such as nitrification/denitrification) at the wastewater treatment plant, not mentioning continuous monitoring of DO in waters (Dojlido and Zerbe 1997). The Winkler titration remains still a reference method for checking linearity and sensor calibration in instrumental DO measurements methods, however (PN-EN 25814 1999).

The Winkler method has been standardized. The latest edition in Poland, still valid, was issued in 1997 as PN-EN 25813. The norm implements the EN 25813:1992, which is based upon the ISO 5813 issued in 1983. The Polish Standard PN-EN 25813:1997 apart from presenting the typical Winkler titration procedure gives in details the instructions to be followed in a case of interfering compounds presence in the sample.

ELECTROCHEMICAL DO SENSORS

The first DO oxygen sensors which could be applied in field measurements of natural or waste waters were developed in early 1960s, soon after Leland Clark (professor of biochemistry at Antioch College in Yellow Spring, Ohio) invented the electrode sensitive to oxygen concentration (Younos and Parece 2015). There are two types of electrochemical DO sensors: galvanic and polarographic. Both types use two polarized electrodes, an anode and a cathode, submersed in an electrolyte solution. The electrodes and electrolyte solution are isolated from the sample by a thin, semi-permeable membrane. Oxygen enters through the membrane by diffusion, in the amount proportional to the pressure of oxygen in the water, and is reduced and consumed at the cathode. The hence created electrical current is directly related to the oxygen concentration, which can be expressed by the following equation (Dojlido and Zerbe 1997):

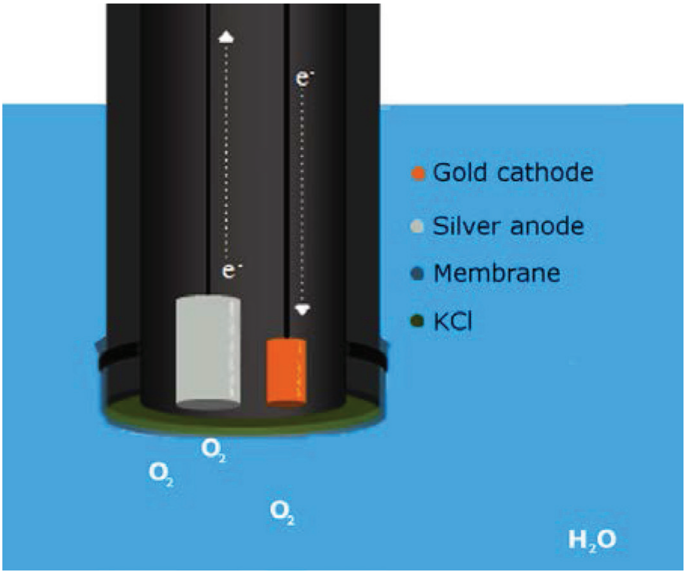
$$i_d = \frac{4 \cdot F \cdot P_m(t) \cdot A \cdot p_{O_2}}{d} \tag{1}$$

where:
i_d – current produced
F – Faraday’s constant
$P_m(t)$ – permeability of the membrane as a function of temperature
A – surface area of cathode
p_{O2} – partial pressure of oxygen
d – membrane thickness

Since the oxygen molecules are consumed at the cathode it is necessary to stir the sensor in the analysed water sample until the dissolved oxygen readings no longer increase. This applies to still water or laboratory measurements –

flowing waters ensure the appropriate oxygen access to the sensor in most cases (Application Data Sheet ADS 4950-01 2009).

Interferences in this method may results from the presence of other gases or vapours which affects the electrochemical reaction. These could be chlorine, hydrogen sulphide, amines, iodine or bromine. The other factors which have influence on the measured current or has to be taken into consideration while calculating the results are temperature, atmospheric pressure and salinity (Dojlido and Zerbe 1997).



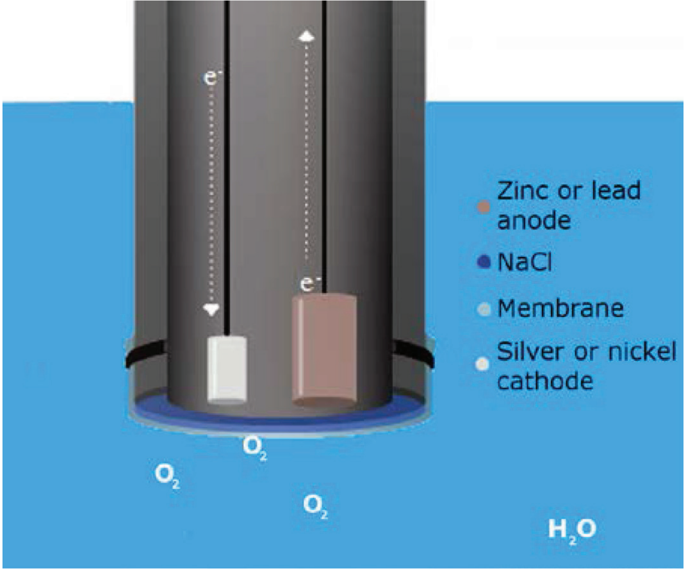
Source: own illustration (based upon Dojlido and Zerbe 1997)

Figure 1. Cross section of a polarographic DO sensor

Polarographic sensors (Fig. 1) consists of a silver anode and a noble metal (such as gold or platinum) cathode in a KCl solution. Prior to calibration or measurement the electrodes have to be polarized – the warm-up time varies from several minutes to approx. 1 hour, depending on the instrument. The polarizing potential is held constant while the sensor detects changes in the current caused by the DO reduction. The more oxygen passes through the membrane, the greater the electrical current read by the instrument. The overall reaction is as follows:

$$O_2 + 2H_2O + 4KCl + 4Ag = 4AgCl + 4KOH$$

Noticeable is the fact that during the reaction a AgCl coating is formed, which has to be removed from the electrode if its accumulation decrease the sensor's performance. Apart from proper electrode cleaning the membrane maintenance is of great importance as it is vulnerable to mechanical damages or contaminants present in the analysed water.



Source: own illustration (based upon Dojlido and Zerbe 1997)

Figure 2. Cross section of a galvanic DO sensor

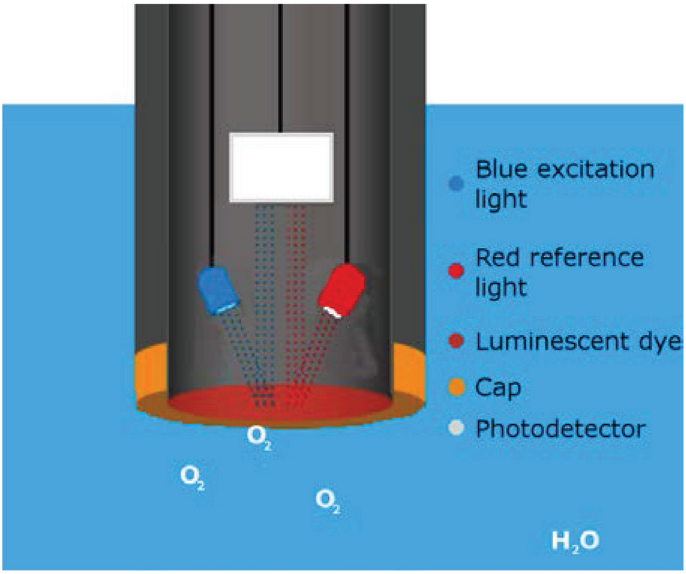
In galvanic sensors (Fig. 2) the electrodes are dissimilar metals, e.g. zinc or lead as an anode and a noble metal (silver, gold) as a cathode. The electrochemical reaction in galvanic sensor is very similar to the reaction in polarographic sensors, yet without the need for a separate constant potential. The dissimilar electrodes self-polarize, no warm-up time is required. In the case of zinc anode the overall reaction occurs as follows:

$$O_2 + 2H_2O + 2Zn = 2Zn(OH)_2$$

The zinc hydroxide produced in the reaction is visible as a white precipitate in the electrolyte solution. Unless its amount become excessive and interfere with the ions' ability to carry current between the cathode and the it does not affect the sensor's performance (Younos and Parece 2015).

There has been many individual solutions developed by instruments manufacturers based upon the general idea of en electrochemical sensor described above. In some applications the third electrode is added to the system as the reference. In pulsed polarographic sensors turning on and off the circuit every few seconds reduce the flow dependence and the sample does not need to be stirred. It enabled more efficient unattended continuous water quality measurements (Minczewski and Marczenko 2011).

The DO measuring procedure by means of en electrochemical sensor as well as calibration, sample preparation and calculating the results are presented in the Polish Standard PN-EN ISO 5814:2013-04 (based upon the ISO 5814:2012). According to the standard the probe (or sensor) has to be either galvanic type lead/silver or polarographic type silver/gold. It has to be equipped with the temperature sensitive compensating device. The valid standard, in contrary to the preceding one (PN-EN 25814:1999, based upon EN 25814:1992), does not require the linearity check versus Winkler method and accept the calibration at saturation performed in water vapour saturated air, which is far more simpler than previous procedure based on comparison with results from Winkler method tests. The calibration at zero needs the preparing of water free from oxygen (the procedure described in the standard), but it has not to be checked daily, as it is required in case of calibration at saturation. According to the standard the electrochemical probe method is suitable for drinking waters, natural waters, waste waters and saline waters (correction for salinity has to be taken into consideration). It is preferred for highly coloured and turbid waters and also for analysis of waters not suitable for the Winkler titration method because of the iron or iodine fixing substances, which can interfere in the iodometric method.



Source: own illustration (based upon Younos and Parece 2015)

Figure 3. Cross section of an optical DO sensor

OPTICAL DO SENSORS

Optical sensors are the most advanced technological solution for the water monitoring. They offer several advantages over electrochemical sensor, particularly in terms of calibration stability and antifouling capability. Optical DO sensors become widely available in mid-2000s (Younos and Parece, 2015).

A typical sensor (Fig. 3) consists of a semi-permeable membrane, sensing element, light-emitting diode (LED) and photoreceptor. The measurement principle is based upon the interaction between oxygen and certain luminescent dyes present in the sensing element. When exposed to the blue light of a LED the dye becomes excited and emit red light as the electrons return to their normal energy state (luminescence). This light is detected by the photoreceptor. The dye's ability to luminescence is quenched in the presence of oxygen, however (Younos and Parece 2015; Bell *et al.* 2012). The measured effect is inversely proportional to the partial pressure of oxygen, as shown by the Stern-Volmer equation modified for DO (Chu *et al.* 2011):

$$\frac{I_0}{I} = 1 + k_q \cdot t_0 \cdot [O_2] \tag{2}$$

where:
I_0 – intensity or lifetime of dye luminescence without oxygen
I – intensity or lifetime of dye luminescence with oxygen present
k_q – quencher rate coefficient
t_0 – luminescence lifetime of the dye
$[O_2]$ – oxygen concentration as a partial pressure

The equation presented above is an approximation of a real correlation between measured and computed parameters, which is not linear in the whole range of DO concentrations. To calculate requested data correctly the measuring instruments' software requires an input of pre-determined sensor constants which are specific to each applied sensor cap.

Stability and accuracy of the sensor is increased by using a secondary reference red LED. The red light will not cause luminescence, but simply be reflected back by the dye to the photoreceptor.

Optical DO sensors are suitable for long-term monitoring due to the significantly low maintenance requirements. These sensors exhibit little calibration drift (significantly less than the electrochemical sensors) and remain stable and accurate for many months. They do not require any warm-up time or stirring when taking a measurement. Over a long period of time the dye degrades and the sensing element and membrane will need to be replaced, but this replacement is very infrequent compared to electrochemical sensor membrane replacement (Chu *et al.* 2011).

However, optical DO sensors usually require more power than an electrochemical sensor. They used also to exhibit less accuracy at low oxygen concentrations and longer response time than their electrochemical predecessors but the progress in optical sensors constructing within last few years has enabled to decrease significantly the response time and to reach the sub-mg·kg^{-1} accuracy, which is required in such advanced applications as monitoring of DO in technological water at nuclear power plants (Bell *et al.* 2012).

Although already in use in water monitoring and at wastewater treatment plants, optical sensor method for DO concentration measurement was not standardised in Europe until recently. The ISO standard concerning the optical DO sensors was issued in June 2014 as ISO 17289:2014 and was implemented by DIN in December (DIN ISO 17289:2014-12). The presumable reason for a delay in standardizing this method was the fact that results from optical sensors in past were not always comparable between manufacturers. The progress in materials engineering and sensor constructions proved that instruments manufactured today are of best quality and can be applied in the standardized method for DO concentration measurements. By issuing the standard ISO legitimised the use of optical DO sensors which were already in common use at that time.

The ISO 17289:2014 standard recommends the optical probe method for the same conditions as stated in the ISO 5814:2012 standard for electrochemical DO sensors (drinking, natural, waste and saline waters; preferred method for highly coloured and turbid waters and also for analysis of waters not suitable for the Winkler titration method). It indicates the fact that the both instrumental methods are complementary. In the optical probe method there are no interferences in the water, however. The standard describes the same calibration procedures as in the case of the ISO 5814:2012 standard, advising to choose the method for zero setting which is most suitable for materials from which the sensor is made (it should be stated in the instruments' manual). Similarly to electrochemical probe method, while calculating the results from measurements by an optical sensor factors such as temperature, atmospheric pressure or salinity has to be taken into consideration.

The ISO 17289:2014 standard has not been implemented in any Polish Standard yet, one may presume that in near future the Polish Committee for Standardization will issue the appropriate document.

METHODS FOR MEASURING DO CONCENTRATION APPLIED AT WASTEWATER TREATMENT PLANTS IN POLAND

A survey concerning DO measurements among the wastewater treatment plants operators in southern Poland brings about that in most wastewater treatment facilities optical DO sensors are in common use (in 10 out of 12 examined cases). The main application field of these sensors is DO concentration monitoring in nitrification zones in aeration tanks. The sensors used by the respondents are manufactured nearly exclusively by either Hach-Lange or Endress+Hauser. In two facilities (out of twelve) the electrochemical sensors are applied for continuous DO concentration monitoring or in laboratories (manufacturers: Hach Lange or WTW). Only in two facilities Winkler titration analyses are carried out periodically (every month) to verify instrumental measurements. The wastewater treatment plants operators point out that optical sensors in comparison to electrochemical ones are more reliable and sensitive to DO concentration changes, exhibit shorter response time, can be cleaned less often and keep calibration settings for a significantly longer period of time.

CONLCUSIONS

One may presume that in near future optical DO sensors will completely supplant electrochemical probes at wastewater treatments plants, at least in online DO monitoring. The standard issued by ISO in 2014 will accelerate this process as the optical probe method has become a legitimised method for DO concentration measurements. Although the standard has not been implemented to Polish Standards yet, one may presume that it is only a matter of short time (a couple of months). The process of installing optical DO sensors at Polish wastewater treatment facilities instead of electrochemical ones is already advanced and will continue as optical sensors become cheaper and more available.

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