Experimental Researches on Measuring the Concentration of Dissolved Oxygen in Water

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ABSTRACT

The paper presents three successive methods for measuring the concentration of dissolved oxygen in water, namely:
- chemical method;
- electric method;
- optical method.

The electrical method is detailed and the measurement methodology and the experimental researches obtained results are presented.

The devices used and energy consuming that appear in performing these measurements are presented.

Keywords: Dissolved oxygen in water, Oxygenometer.

1. Introduction

Dissolved oxygen in water can come from the following sources [1] [2]:

- by aeration, oxygen is introduced from the atmospheric air (21% O₂; 79% N₂);
- by oxygenation, oxygen is introduced from the following sources [3] [4]:
  - atmospheric air + O₂ from a cylinder;
  - atmospheric air + O₂ delivered by oxygen concentrators (95% O₂; 5% N₂);
  - atmospheric air + ozone (O₃) delivered by ozone generators.

Oxygenation processes are found in the following areas:

- in wastewater treatment and purification plants;
- in stations for disinfection (by ozonation) of raw water taken from a source in order to make it drinkable;
- in the chemical industry;

Fig.1. View of Molecular Structure: Dissolved Oxygen

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in the food, fish industry, etc.;

- in water treatment and purification processes, oxygenation is a basic process in ensuring water quality.

The most common method of removing organic impurities under the action of an aerobic bacterial biomass is the introduction of gaseous oxygen into the wastewater.

Dissolved oxygen in water is known as dissolved oxygen (figure 1) and is measured in mg O$_2$/dm$^3$.

From Figure 1 one can see that each molecule of water consists of one molecule of oxygen connected to two molecules of hydrogen (the purple sphere coupled to two green spheres). The oxygen molecules (purple spheres) that create dissolved oxygen can be found among water molecules. The maximum amount of oxygen that can be dissolved in water depends on a number of physical and chemical parameters, such as: atmospheric pressure, water temperature, water salinity, degree of water turbulence [6].

Water temperature is an important factor, so the warmer the water, the lower the dissolved oxygen concentration. So [4]: at t = 10ºC, in clean, fresh water, an amount of 11.3 mgO$_2$/dm$^3$ can be absorbed; at t = 25ºC, in clean water, only 8.3 mgO$_2$/dm$^3$ can be absorbed.

The following are the three methods for determining the dissolved oxygen content of water.

2. Methods for Measuring the Concentration of Dissolved Oxygen in Water

2.1 Chemical Method

For the three methods, it is important how the water sample is collected and analyzed. The water sample must not be aerated during collection and there must be no air bubbles in the container containing the sample. Some of the above methods must be used to calibrate the measuring instruments.

The following is the IODOMETRIC method for determining the content of DO (dissolved oxygen) in drinking water based on the Winkler process [7] [8].

In short, the essence of this method is:

a) $V_1$ [ml] of water is placed in a glass container;

b) The dissolved oxygen in $V_1$ [ml] of water is fixed by introducing into the container under the water surface:

- potassium iodide solution (KI);
- sodium hydroxide solution (NaOH);
- manganese chloride solution (MnCl$_2$);

The sum of the volumes of these solutions is denoted $V'$ [ml].

Following the addition of the reagents, a white manganese hydroxide precipitate appears from the reaction.

$$MnCl_2 + 2NaOH \rightarrow Mn(OH)_2 + 2NaCl \quad (1)$$
a) The formed manganese hydroxide combines with the oxygen dissolved in water and is transformed into manganese hydroxide Mn(OH)$_3$ which is a brown precipitate by the reaction:

$$2Mn(OH)_2 + \frac{1}{2}O_2 + H_2O \rightarrow 2Mn(OH)_3$$ \hspace{1cm} (2)

b) Wait for the precipitate to settle, add concentrated hydrochloric acid solution and shake the contents of the container until the precipitate dissolves, the reaction taking place:

$$4Mn(OH)_2 + 12HCl + 4KI \rightarrow 4MnCl_2 + 4KCl + 12H_2O + I_2$$ \hspace{1cm} (3)

In this reaction potassium iodide (KI) comes from the solution of KI in NaOH which was initially added to the vessel. The volume of HCl solution added to the precipitate dissolving container is not taken into account because this reagent replaces water that no longer contains dissolved oxygen.

c) After dissolving the precipitate in the vessel, a solution of sodium thiosulphate of volume $V_2$ [ml] of concentration $c$ [mmol / l] is introduced for the treatment of the released iodine (I).

During titration, the solution in the container reaches a light-yellow color; at this point, a few drops of a solution of starch glue are added to the container, which will react with the iodine to give it a blue color.

d) Continue the titration until the liquid in the container has discolored and note the total amount of sodium thiosulphate ($V_2$) used in the titration. During the titration sodium thiosulphate is combined with iodine to form sodium tetrathionate according to the reaction:

$$4Na_2S_2O_3 + I_2 \rightarrow 2Na_2S_4O_6 + 2NaI$$ \hspace{1cm} (4)

e) The dissolved oxygen content is:

$$DO = \frac{M_r \cdot V_2 \cdot c \cdot f_1}{4 \cdot V_1}$$ \hspace{1cm} (5)

Where:

- $M_r$ - relative mass of oxygen, $M_r = 31.998$ [g / mol];
- $V_2$ - volume of sodium thiosulphate solution used in the titration of the entire contents of the container [ml];
- $c$ - concentration of sodium thiosulfate solution [mmol / l];
- $V_1$ - sample volume in [ml];
- $f_1$ - solution factor $f_1 = \frac{V_0}{V_0 - V'}$,

- $V_0$ - volume of the container in milliliters [ml];
- $V'$- sum of the volumes of manganese sulphate solution and alkaline reagent [ml]

Note $V_0 = V_1$ if the entire container content is titrated and the dissolved oxygen content is:
The main disadvantages of chemical methods are:

- the presence of catalysts used for deoxygenation;
- the presence of oxygen in the reagents;
- occurrence of errors in the titration process;
- DO cannot be monitored instantly or continuously;
- consumes more time than electrical or optical methods.

### 2.2 Electrical Methods

The electrical methods named, in some papers, electrochemical methods are based on two techniques for measuring the dissolved oxygen concentration in water [9] [10]:

a) the technique of the galvanic process, in which there is a very low electrical voltage between the electrodes, it is not necessary to apply an external electrical voltage;

b) the technique of the polarographic process, in which an electric voltage (direct current) is applied between the two electrodes (cathode and anode).

In the following, only the polarographic procedure is analyzed. The devices used to measure DO in water are called oxygen meters. As a whole, an oxygenometer consists (figure 2) of a microprocessor (1) connected to a probe (3) which is introduced into the water whose DO content is to be measured. This oxygen meter is used to perform experimental measurements. In the laboratory of the Department of Thermotechnics, Engines, Thermal and Refrigeration Equipment’s there is such an oxygenometer which is used in experimental researches on water oxygenation.

![Oxygenometer Used in the Measurements](image)

**Fig.2. Oxygenometer Used in the Measurements [5]**

1 - MICROPROCESSOR; 2 - CONNECTING CABLE; 3 - PROBE BODY; 4 - SMALL CYLINDER CONTAINING AN ELECTROLYTE SOLUTION; 5 - OXYGEN PERMEABLE TEFLON MEMBRANE
The oxygen passing through the oxygen-permeable Teflon membrane (5) causes a change in the electric current between the cathode and the anode, in a small cylinder containing an electrolyte solution (4); this change is proportional to the amount of oxygen that has penetrated the membrane and is displayed on the microprocessor screen in [mg / dm\(^3\)].

Disadvantages of electrical methods:

1. Difficulties regarding the calibration and maintenance of the devices (cleaning the electrodes and replacing the membranes);
2. Consumption of electrolyte while using the device;
3. The devices are relatively expensive between 600 ÷ 1500 €;
4. The disappearance of oxygen molecules in the vicinity of the sensor can only be prevented by keeping the water sample or probe moving.

Points 1 and 2 can only be solved by regular calibrations and electrolyte changes.

Advantages of electrical methods:

1. The device is portable, measurements can be performed in the laboratory, swimming pools, lakes, ponds;
2. The device instantly or continuously monitors the DO concentration;
3. No equipment for sampling, etc. is required.

The experimental installation for measuring the dissolved oxygen concentration in water (figure 3) consists of:

- Electro compressor with air tank (1), for the production of compressed air with the following functional parameters: maximum discharge pressure \( p = 8 \) bar, suction flow rate \( \dot{V} = 600 \, \text{dm}^3/\text{h} \), operating temperature \( t = -10 \, ^\circ\text{C} \div 100 \, ^\circ\text{C} \), electric motor power \( P = 1,1 \, \text{kW} \), speed \( n = 2850 \, \text{rpm} \), tank volume \( V = 24 \, \text{dm}^3 \). The electric compressor is equipped with a differential pressure manometer in the range 0 ÷ 16 bar for displaying the air pressure in the compressor tank and a pressure reducer (2), for setting the pressure in the installation pipes.

- Compressed air pipes for the delivery of compressed air made of plastic, with inside diameter \( \phi 15 \, \text{mm} \) and a wall thickness of 2 mm; they supply the microbubble generator with air and ensure the evacuation of the surplus air delivered by the compressor to the atmosphere.

- Aeration tank made of plexiglass plates with a thickness of 5 mm, measuring 0.5 x 0.5 x 1.6.

- The microbubble generator. This type of microbubble generator was subjected to tests in an experimental installation built in the laboratories of the University POLITEHNICA of Bucharest. Plate orifices with \( d_0 = 0.1 \, \text{mm} \) were made using a C.N.C. (Computer Numerical Control) which has a special machine for micro processing type KERN Micro [11].

- Oxygenometer probe actuation mechanism.

The scheme of the installation used to carry out the experimental researches is presented in figure 3.
Fig. 3. Scheme of the Experimental Installation for Researches on Water Oxygenation

1 - ELECTROCOMPRESSOR WITH AIR TANK; 2 - PRESSURE REDUCER; 3 - MANOMETER; 4 - CONNECTION FOR EVACUATING AIR INTO THE ATMOSPHERE; 5 – T-JOINT; 6 - ROTAMETER; 7 - ELECTRICAL PANEL; 8 - PANEL WITH MEASURING DEVICES; 9 - PIPE FOR TRANSPORTING COMPRESSED AIR TO THE MICROBUBBLE GENERATOR; 10 - WATER TANK; 11 - MECHANISM FOR ACTUATION OF THE PROBE; 12 - OXYGENOMETER PROBE; 13 - MICROBUBBLE GENERATOR; 14 - SUPPORT FOR INSTALLATION; 15 - CONTROL ELECTRONICS: A - POWER SUPPLY, B - SWITCH, C - CONTROL ELEMENT, 16 - DIGITAL MANOMETER; 17 - OXYGENOMETER; 18 - DIGITAL THERMOMETER

Figure 3 shows that, after compressing the air, the air temperature, pressure and flow rate are measured; subsequently is introduced into the generator. With parameters: \( V = 600 \text{ dm}^3/h \), \( p = 573 \text{ mm H}_2 \text{O} \).

Research methodologies

Measurements involve the following steps [12]:

1. Check that the 152 orifices are working, i.e., air is introduced into the microbubble generator (MBG);
2. Fill the tank with water up to \( H = 500 \text{ mm H}_2 \text{O} \);
3. Measure \( t_{\text{H}_2 \text{O}}, t_{\text{air}} \);
4. Insert the MBG and note the time (\( \tau \));
5. Every 15 minutes, remove the microbubble generator outside the tank and measure the dissolved oxygen concentration;
6. When a horizontal level of the function \( C = f(\tau) \) is reached, the measurements stop with the condition: \( C \approx C_s \).
7. From previous researches [13], [14], [15], the concentration of dissolved oxygen in water tends to saturate after two hours. So, the measurement of the oxygen concentration will be performed at the times: 15 minutes; 30 minutes; 45 minutes; 60 minutes; 75 minutes; 90 minutes; 105 minutes; 120 minutes.

8. At the end of the measurements, clean the oxygenometer probe and drain the water from the tank.

Following the measurements, the data in Table 1 were obtained.

Table 1. Concentration Values as a Function of Time

<table>
<thead>
<tr>
<th>( \tau ) [min]</th>
<th>0</th>
<th>15</th>
<th>30</th>
<th>45</th>
<th>60</th>
<th>75</th>
<th>90</th>
<th>105</th>
<th>120</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \dot{V}_{\text{air}} \ [dm^3/h] )</td>
<td>600</td>
<td>600</td>
<td>600</td>
<td>600</td>
<td>600</td>
<td>600</td>
<td>600</td>
<td>600</td>
<td>600</td>
</tr>
<tr>
<td>( \dot{V}_{\text{H}_2\text{O}} ) = 0.21 \cdot 600 = 126 [ dm^3/h ]</td>
<td>126</td>
<td>126</td>
<td>126</td>
<td>126</td>
<td>126</td>
<td>126</td>
<td>126</td>
<td>126</td>
<td>126</td>
</tr>
<tr>
<td>( \dot{V}_{\text{O}_2} ) from other sources</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>( t_{\text{H}_2\text{O}} ) [( ^\circ \text{C} )]</td>
<td>23.7</td>
<td>23.7</td>
<td>23.7</td>
<td>23.7</td>
<td>23.7</td>
<td>23.7</td>
<td>23.7</td>
<td>23.7</td>
<td>23.7</td>
</tr>
<tr>
<td>( t_{\text{air}} ) [( ^\circ \text{C} )]</td>
<td>24.1</td>
<td>24.1</td>
<td>24.1</td>
<td>24.1</td>
<td>24.1</td>
<td>24.1</td>
<td>24.1</td>
<td>24.1</td>
<td>24.1</td>
</tr>
<tr>
<td>( C_o ) [mg/dm$^3$]</td>
<td>5.84</td>
<td>5.84</td>
<td>5.84</td>
<td>5.84</td>
<td>5.84</td>
<td>5.84</td>
<td>5.84</td>
<td>5.84</td>
<td>5.84</td>
</tr>
<tr>
<td>( C_t ) [mg/dm$^3$]</td>
<td>8.4</td>
<td>8.4</td>
<td>8.4</td>
<td>8.4</td>
<td>8.4</td>
<td>8.4</td>
<td>8.4</td>
<td>8.4</td>
<td>8.4</td>
</tr>
<tr>
<td>( C ) [mg/dm$^3$]</td>
<td>5.84</td>
<td>6.89</td>
<td>7.65</td>
<td>8.01</td>
<td>8.10</td>
<td>8.26</td>
<td>8.31</td>
<td>8.35</td>
<td>8.39</td>
</tr>
</tbody>
</table>

Based on the data in table 1, the graph in figure 4 was drawn.

Fig.4. Variation in the Dissolved Oxygen Concentration in the Water in Time
These results are in good agreement with those obtained theoretically [5], as well as with those contained in similar papers [16], [17].

2.3 Optical Method

Optical methods include reflection spectroscopy, analysis of light transmitted by transparent electrodes and ellipsometry. In 2003, HACH LANGE became the first manufacturer of measuring instruments to launch the L.D.O. (Luminescent Dissolved Oxygen) for the determination of dissolved oxygen in water. The devices consist of a microprocessor (1), a connecting cable (2) and a probe that is inserted into the water (3) (figure 5).

![Fig.5. DO Meter Based on the L.D.O.](image)

1 - MICROPROCESSOR; 2 - CONNECTING CABLE; 3 - PROBE THAT IS INSERTED INTO THE WATER

Technical data on the measuring device based on the L.D.O. are presented in table 2:

<table>
<thead>
<tr>
<th>Measurement method</th>
<th>Luminescence, optical</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excitement</td>
<td>Pulses of blue light</td>
</tr>
<tr>
<td>Calibration</td>
<td>It's not necessary</td>
</tr>
<tr>
<td>Measuring range</td>
<td>0.1–20 mg / dm$^3$ (ppm) O$_2$; 1 - 200% O$_2$ saturation; 0.1 - 50 °C</td>
</tr>
<tr>
<td>Accuracy</td>
<td>± 0.1 mg / dm$^3$ O$_2$ &lt;1 mg / dm$^3$; ± 0.2 mg / dm$^3$ O$_2$ &gt; 1 mg / dm$^3$</td>
</tr>
<tr>
<td>Reproducibility</td>
<td>± 0.5% of the final value of the measuring range</td>
</tr>
<tr>
<td>Response time</td>
<td>T90 &lt;40 sec (20 °C), T95 &lt;60 sec (20 °C)</td>
</tr>
<tr>
<td>Temperature range</td>
<td>0 - 50 °C</td>
</tr>
</tbody>
</table>
The operating principle of the L.D.O. is based on the physical phenomenon of luminescence; it is defined as the property of materials to emit light when excited.

For a suitable combination between a phosphor and an excitation light of a certain wave, the luminescence intensity and the time until its disappearance are dependent on the oxygen concentration around the phosphor.

Hach Lange Probe - L.D.O. is composed of two elements (figure 6):

a) the head of the probe, on which there is a layer of phosphor deposited on a transparent transfer material; during measurements the head is screwed into the body of the probe which is immersed in water (figure 6);

b) the body of the probe, which includes:

- a blue LED that emits light necessary to create luminescence;
- a red LED as a reference element;
- a photodiode.

In operation, the blue LED emits pulses of blue light (excitation light) that reaches the phosphor, to which it transfers some of its radiant energy. As a result, some of the electrons in the phosphor layer jump from their initial level to a higher energy level.
After a very short time they return to their original level, emitting energy that they lose in the form of red light (figure 7).

Oxygen molecules are able to absorb the energy of high-level electrons and allow them to return to their normal level without emitting red light.

The higher the oxygen concentration, the greater the intensity of the red light emitted.

As the electrons return to lower energy levels faster, the life of the emitted red light is thus shortened.

To determine the oxygen concentration, the lifetime of the red light is evaluated. So, DO measurement is based on the simple physical measurement of time.

Advantages of the L.D.O method:

1) The L.D.O. measures the dissolved oxygen concentration in water based on measuring an exact period of time.
2) The method only requires the oxygen molecules to be in contact with the phosphor.
3) Any cleaning of the phosphor in the probe head does not affect the lifetime of the emitted red light which depends only on the oxygen concentration in the sample.
4) All optical components of the probe are adjusted before each measurement using the red reference LED.

Before each measurement it transmits a ray of light that is reflected in the phosphor and passes through the entire optical system in the same way as light from luminescence.

Disadvantages of the L.D.O method:

1) Cleaning the probe head;
2) Changing the probe head every 2 years.

3. Conclusion

Of the three methods, chemical, electrical, optical, the electrical method was chosen because it is reliable, and the indication of the measurement performed is digitally presented on the microcomputer screen [18].

Optical methods based on reflection spectroscopy, analysis of light transmitted by transparent electrodes and ellipsometry are also mentioned; the devices for determining the dissolved oxygen in water by the method of measuring the luminescence of dissolved oxygen is described.

Disadvantage: The electrical method has the disadvantage that the HI 7041S electrolyte solution must be purchased and inserted into the oxygenometer probe. The conclusions highlight the differences between the three methods of measuring the concentration of dissolved oxygen in water, specifying the advantages and disadvantages.

The advantages of opting for the oxygenometer provided with a polarographic probe for the experimental determination of dissolved oxygen in water are emphasized [19] [20].
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Competing Interests Statement

The authors declare no competing financial, professional and personal interests.

Consent for publication

We declare that we consented for the publication of this research work.

Code availability

The programming code that we have used for this research is available and authors are willing to share when it is required.

References


