

# Institute of Mathematics, Physics and Chemistry

## Department of Chemistry

### Water chemistry laboratory

#### Laboratory exercise

#### Determination of oxygen and ammonium nitrogen content

Elaborated by:

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## EXERCISE SHEET

1	<b>Relation to subjects:</b> ESO/25, 27 DiRMiUO/25, 27 EOUnIE/25, 27		
	Specialty/Subject	Learning outcomes for the subject	Detailed learning outcomes for the subject
	ESO/26 Chemistry of water, fuels and lubricants	EKP3 K_U014, K_U015, K_U016.	SEKP6 – Performing determinations of selected indicators of technical water quality;
	DiRMiUO/26 Chemistry of water, fuels and lubricants	EKP3 K_U014, K_U015, K_U016.	SEKP6 – Performing determinations of selected indicators of technical water quality;
	EOUnIE/26 Chemistry of water, fuels and lubricants	EKP3 K_U014, K_U015, K_U016.	SEKP6 – Performing determinations of selected indicators of technical water quality.
2	<b>Purpose of the exercise:</b> teaching students how to independently determine the content of oxygen and ammonium nitrogen in water;		
3	<b>Prerequisites:</b> the student is trained in the field of health and safety regulations on a laboratory workplace, which he states with his own signature on the appropriate form, knows – the Winkler method for determining the oxygen content in water and its chemistry, the Nessler comparative method for the determination of ammonia (ammonium nitrogen) in water and its chemistry, the origin of oxygen and ammonia in boiler water, oxygen corrosion and methods of deoxidation of boiler water on ships, operational importance of the determined parameters;		
4	<b>Description of the laboratory workplace:</b> typical laboratory kit for iodometric analysis, bottle with ground stopper of known capacity, manganese (II) sulphite solution, alkaline KI solution, concentrated sulphuric acid H <sub>2</sub> SO <sub>4</sub> , starch solution, standard sodium thiosulphate solution, set of Nessler cylinders with coloured standard solutions, sodium-potassium tartrate solution, Nessler's reagent, water samples;		
5	<b>Risk assessment*:</b> contact with concentrated sulphuric acid (about 2 cm <sup>3</sup> ), Nessler's reagent (1 cm <sup>3</sup> ) – due to the very small amounts of harmful reagents, the probability of chemical burns and harmful Nessler's reagent is very small. Final assessment – <b>SMALL THREAT</b> <b>Security measures required:</b> a. lab coats, b. acid-resistant gloves, c. protective glasses, d. health and safety cleaning products, paper towels;		
6	<b>The course of the exercise:</b> a. Read the workplace manual (appendix 1) and the laboratory kit for the exercise, b. Determine the dissolved oxygen content in the tested water using the Winkler method and determine the ammonium nitrogen content using the Nessler comparative method;		

7	<p><b>Exercise report:</b></p> <ol style="list-style-type: none"> <li>Develop an exercise in accordance with the instructions contained in the workplace manual (appendix 1),</li> <li>On the basis of the obtained results of determination of oxygen and ammonium nitrogen content, determine the quality and operational suitability of the tested water by comparing the determined parameters with their permissible values,</li> <li>If necessary, suggest possible chemical deoxidation of the tested water and calculate the necessary dose of inhibitor per ton of water used.,</li> <li>On the basis of the determined content of ammonium nitrogen (ammonia), determine whether an overdose of hydrazine as a deoxidizing agent has not been carried out,</li> <li>Solve the given task and/or answer the questions included in the set of tasks and questions to be completed by the student;</li> </ol>
8	<p><b>Archiving of research results:</b> Submit a written report on the performed exercise to the academic teacher.</p>
9	<p><b>Assessment method and criteria:</b></p> <ol style="list-style-type: none"> <li>EKP1, EKP2 – tasks given for independent solution and development: <ul style="list-style-type: none"> <li>mark 2.0 – there is no basic chemical and operational knowledge regarding the functional parameters of the tested water, i.e. the content of oxygen and ammonia and their corrosive effects, as well as the dosage of inhibitors;</li> <li>mark 3.0 – has basic chemical and operational knowledge regarding the determined functional parameters of the tested water and the ability to make basic chemical calculations and solve simple tasks in the field of application, dosage and mechanism of action of deoxidizing agents;</li> <li>mark 3.5 – 4.0 – has extended chemical and operational knowledge in the field of determined utility parameters of the tested water and the ability to solve complex tasks related to the assessment of changes in these parameters as well as the dosage and mechanism of action of deoxidizing agents;</li> <li>mark 4.5 – 5.0 – has the ability to apply complex chemical and operational knowledge to partial evaluation of the quality and operational suitability of the tested water due to the content of both oxygen and ammonia, and the ability to make corrective and remedial decisions on this basis.</li> </ul> </li> <li>EKP3 – control works: <ul style="list-style-type: none"> <li>mark 2.0 – does not have the ability to analyse and evaluate the results of the performed determinations and draw conclusions;</li> <li>mark 3.0 – has the ability to analyse the obtained results, interpret the laws and phenomena, transform formulas, and interpret charts and tables;</li> <li>mark 3.5 – 4.0 – has the ability to broaden the analysis of the obtained results and their proper interpretation;</li> <li>mark 4.5 – 5.0 – has the ability to comprehensively analyse the obtained results of determinations and their proper interpretation, as well as to make generalizations, detect cause-effect relationships, and make appropriate operational decisions on this basis.</li> </ul> </li> </ol>
10	<p><b>References:</b></p> <ol style="list-style-type: none"> <li>J. Krupowies, C. Wiznerowicz, A. Kalbarczyk-Jedynak, K. Ćwirko, M. Ślaczka-Wilk, Workplace instruction for laboratory exercise: „Oznaczenie zawartości tlenu i azotu amonowego”, 2022 (in Polish).</li> <li><a href="https://openstax.org/details/books/chemistry-2e">https://openstax.org/details/books/chemistry-2e</a> (accessed: 10 July 2023).</li> <li><a href="https://planm8.io/blog/marine-boiler-water-treatment">https://planm8.io/blog/marine-boiler-water-treatment</a> (accessed: 10 July 2023).</li> </ol>

4.	<a href="https://marinersgalaxy.com/boiler-water-test-on-ship-name-of-all-tests/">https://marinersgalaxy.com/boiler-water-test-on-ship-name-of-all-tests/</a> (accessed:10 July 2023).
5.	<a href="https://www.imo.org/en/MediaCentre/HotTopics/Pages/Implementing-the-BWM-Convention.aspx">https://www.imo.org/en/MediaCentre/HotTopics/Pages/Implementing-the-BWM-Convention.aspx</a> (accessed: 29 June 2023).
6.	<a href="https://www.imo.org/en/GoogleSearch/SearchPosts/Default.aspx?q=water%20treatment%20on%20ships">https://www.imo.org/en/GoogleSearch/SearchPosts/Default.aspx?q=water%20treatment%20on%20ships</a> (accessed: 29 June 2023).
7.	<a href="https://www.wilhelmsen.com/product-catalogue/products/marine-chemicals/test-kits-and-reagents/water-test-kits/test-kit-for-cooltreat-al/">https://www.wilhelmsen.com/product-catalogue/products/marine-chemicals/test-kits-and-reagents/water-test-kits/test-kit-for-cooltreat-al/</a> (accessed: 29 June 2023).

# APPENDIX 1 – MANUAL

## 1. SCOPE OF THE EXERCISE

- getting acquainted with the workplace instructions for the exercise,
- determination of oxygen using the Winkler method,
- determination of the content of ammonia (ammonium nitrogen) by the Nessler method.

## 2. THEORETICAL INTRODUCTION TO THE EXERCISE

### 2.1. Oxygen dissolved in water

The oxygen dissolved in water comes mainly from air. Apart from the pH value, chloride ions, aggressive CO<sub>2</sub>, H<sub>2</sub>S and NH<sub>3</sub> it is one of the most important factors limiting the rate of electrochemical corrosion. At pH ≥ 4, it is the major acceptor of electrons generated during the oxidation of corroded iron as the main component of structural steels for marine steam boilers. The diagram of operation of a corrosive micro-cell with the participation of dissolved oxygen in water is shown in Fig. 1:

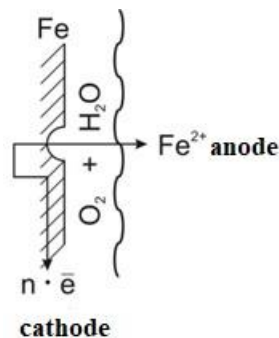


Fig. 1. Diagram of a corrosion micro-cell

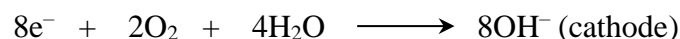
In electrochemical terms, iron corrosion is associated with the formation of many short-circuited galvanic cells on the metal surface, i.e. areas that differ in the oxidation-reduction potential at a given moment.

The process of steel (iron) destruction in saline water can be presented as follows:

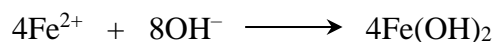
At the metal-solution interface, iron transforms into an ion as a result of oxidation:



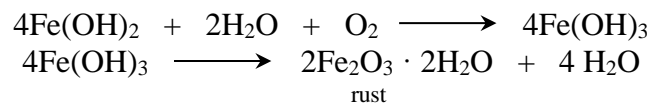
The resulting electrons move and take part in the reaction at the metal-electrolyte interface (oxygen depolarization)



The adjacent ions then react according to the equation:



The iron (II) hydroxide formed is further transformed in accordance with the following reactions:



In general, along with an increase in the concentration of oxygen dissolved in water, the corrosion rate of most metals on the surface of which no protective layer has not formed increases linearly. The presence of the protective layer hinders the diffusion of oxygen to the surface of the corroded metal and inhibits the process of oxygen reduction at the cell cathode. In the course of corrosion, the concentration of dissolved oxygen is very important, because at concentrations higher than the critical concentration, the corrosion rate may be reduced as a result of metal passivation. The critical oxygen concentration depends on the type of metal and increases with increasing temperature, salinity, and decreasing pH. For example, the critical oxygen concentration for slow-flowing distilled water at 25°C is 17 g O<sub>2</sub>/m<sup>3</sup>, and for water with pH = 10, about 8 g O<sub>2</sub>/m<sup>3</sup>. As a result of passivation, the corroded metal is covered with a natural oxide layer that inhibits corrosion.

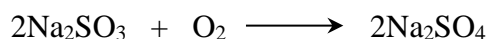
In order to eliminate oxygen as a factor causing intra-boiler corrosion, preliminary thermal deoxidation is used on the ship, and the remaining residual oxygen is chemically removed in the so-called chemical deoxidation process.

Thermal deoxidation takes place in a heat box or in mixed heaters and regenerative condensers, depending on the type of condensate supply system (open or closed), operating pressure and the type of boiler for which the feed water is intended. This process is based on the use of the physical phenomenon of the decrease in the solubility of gases in water with increasing temperature and decreasing pressure.

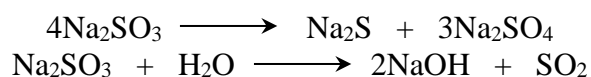
Modern marine diesel boilers require complete oxygen removal from the supply water, which is not ensured by the thermal degassing method. Chemical deoxidation is performed to remove the oxygen completely. The essence of the chemical deoxidation of the feed water consists in dosing it with strong chemically binding oxygen-binding agents. The effectiveness of this deoxidation depends on the type and dose of the reducer, the pH and temperature of the water, the concentration of dissolved oxygen and the presence of other oxidants in the water than dissolved oxygen.

For chemical deoxidation of water, sodium sulfite Na<sub>2</sub>SO<sub>3</sub> or hydrazine N<sub>2</sub>H<sub>4</sub> (often also hydrazine hydrate N<sub>2</sub>H<sub>4</sub> · H<sub>2</sub>O or hydrazine sulphate) N<sub>2</sub>H<sub>4</sub> · H<sub>2</sub>SO<sub>4</sub> is used.

Sodium sulfite is used in heating circuits and for deoxidation of water fed to low-pressure steam boilers with working pressures of 4 to 7 MPa. It chemically binds dissolved oxygen in water according to the reaction:

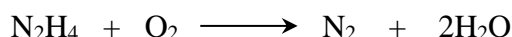


The resulting Na<sub>2</sub>SO<sub>4</sub> causes significant salinity of the water, which is a disadvantage of this method. The reaction is quantitative according to the ratio: O<sub>2</sub> : Na<sub>2</sub>SO<sub>3</sub> = 1 : 7.9, which means that 7.9 mg of Na<sub>2</sub>SO<sub>3</sub> is needed to bind 1 mg of O<sub>2</sub>. The course of the deoxidation reaction depends not only on the excess sodium sulfite (usually 3 – 5 g/m<sup>3</sup>), but also on the temperature. The higher the water temperature, the faster oxygen binding occurs. The most advantageous is deoxidation at a temperature of 80 - 100 °C, because the time of this process is then from several seconds to about 1 minute. The excess of Na<sub>2</sub>SO<sub>3</sub> used for deoxidation under elevated pressure and intense heat load may undergo thermal decomposition or even hydrolysis according to the following reactions:



SO<sub>2</sub> is particularly dangerous here, it acidifies the condensate and causes corrosion of the pipes. For this reason, sodium sulfite is recommended for use in low-pressure steam boilers. The dosing of Na<sub>2</sub>SO<sub>3</sub> must be careful, because its excess, not bound to oxygen, may, at higher temperatures, result in decomposition of hydrogen sulphide H<sub>2</sub>S with toxic and highly corrosive properties.

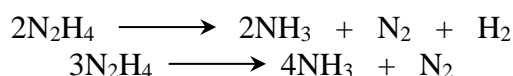
Hydrazine N<sub>2</sub>H<sub>4</sub> is used for chemical deoxidation of the feed water to diesel boilers, which binds dissolved oxygen according to the reaction:



The formed nitrogen evaporates with the water vapor and as a chemically inert gas it does not react in any way under the conditions of the water-steam cycle.

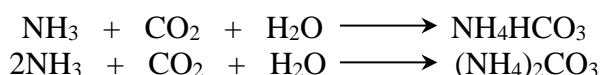
Hydrazine is introduced into the feed water upstream of the boiler feed pump, often as N<sub>2</sub>H<sub>4</sub> · H<sub>2</sub>O, hydrazine hydrate, 0.18g for every 1000kg of water, including copper and manganese salts as catalysts. Hydrazine and hydrazine hydrate are caustic and toxic compounds, therefore hydrazine sulphate N<sub>2</sub>H<sub>4</sub> · H<sub>2</sub>SO<sub>4</sub> is also recommended for deoxidation.

Hydrazine chemically binds oxygen the fastest at temperatures higher than 80°C. For example, with an excess of up to 100%, the reaction time is very short, and with good mixing and at a pH of 9 - 11, the reaction time is 2 - 3 seconds. At large excess and at temperatures above 270 °C, hydrazine decomposes, as a result of which one of the products is NH<sub>3</sub> ammonia, formed according to the following reactions:



The source of NH<sub>3</sub> in the boiler water may also be ammonium salts used as anti-corrosion additives.

The ammonia formed as a result of the above reactions alkalizes the circulating water and binds CO<sub>2</sub> if present in the water, according to the equations:



Neutral ammonium carbonate (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> is formed at a water pH above 9,5.

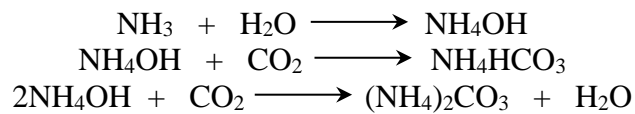
The use of hydrazine as a deoxidizer is beneficial because the removal of oxygen under optimal conditions is very quick and effective, without an additional increase in the salinity of the water. Using hydrazine, it is possible to reduce the oxygen content in the water within the range of 0.01 – 0.005 mg O<sub>2</sub>/dm<sup>3</sup>. However, the excess of hydrazine used should not be greater than it is necessary, for example, to remove CO<sub>2</sub> dissolved in water, because the excess ammonia formed then is dangerous and requires control. It is aggressive towards system components made of non-ferrous metals or their alloys (copper, brass, bronze). Therefore, the excess of hydrazine in the boiler water should be in the range of 0.1 – 0.2 ppm, with the simultaneous lack of dissolved oxygen.

Theoretically, the consumption of hydrazine compounds to bind 1 g of O<sub>2</sub> is correspondingly for:

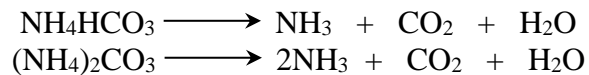
- hydrazine  $N_2H_4$  – 1 g,
- hydrazine hydrate – 1.6 g,
- hydrazine sulphate – 4.1 g.

## 2.2. Ammonium nitrogen - ammonia

The source of ammonia in the boiler water may be ammonium salts used as anti-corrosion additives or the breakdown of excess hydrazine as an inhibitor of oxygen corrosion introduced to this water. The resulting ammonia alkalizes the water in the steam-water circuit, giving it ammonium hydroxide  $NH_4OH$ , which can chemically bind  $CO_2$  according to the following reactions:



The presence of carbon dioxide in water causes its acidity and enhances the corrosive effect of water on iron, and in the case of simultaneous presence of oxygen, it intensifies the course of oxygen corrosion. At elevated temperatures and during the evaporation of water in the boiler, the following opposite reactions may also take place as compared to the above-mentioned reactions, namely:





### 3. PERFORMING THE EXERCISE

Fig. 2 shows a general view of the laboratory stand for testing oxygen content in water.

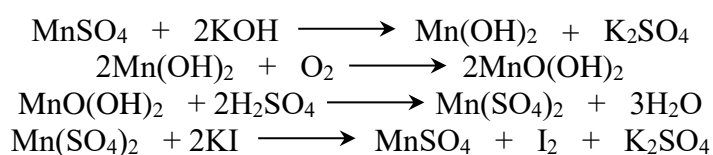


Fig. 2. Laboratory stand for the determination of oxygen in water using the Winkler method

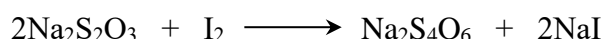
#### 3.1. Determination of oxygen

To determine the content of dissolved oxygen in water, the Winkler titration method and its modifications are used, depending on the presence of interfering substances, and electrochemical methods with the use of membrane sensors.

In the Winkler titration method in an alkaline solution, oxygen dissolved in water oxidizes freshly precipitated manganese (II) hydroxide to  $\text{MnO}(\text{OH})_2$ . After acidifying the sample, the manganese (IV) compound formed oxidizes the added potassium iodide to free iodine, in an amount equivalent to the oxygen content of the water. The diagram of the course of the above reactions is as follows:



The iodine released in the reaction (brown solution) is then titrated with sodium thiosulphate in the presence of starch as an indicator (blue solution) to discolour the sample according to the reaction:



##### 3.1.1. Performing the determination

Place a 300 cm<sup>3</sup> bottle with a ground stopper into the cuvette, then fill it with the tested water up to the overflow. Then introduce 1 cm<sup>3</sup> of manganese (II) sulphate solution and 2 cm<sup>3</sup> of alkaline potassium iodide solution under the water surface. Close the bottle with a stopper, leaving no air bubble behind. Mix the contents of the bottle thoroughly (Fig. 3), turning it upside down several times and allow the brown sediment to settle down (Fig. 4).



Fig. 3. Sample after mixing



Fig. 4. Sample after sedimentation

After the sediment has settled into the bottle, add a pipette slowly under the surface of  $2 \text{ cm}^3$  of sulphuric acid solution, close the stopper and shake until the sediment is completely dissolved (Fig. 5). Next, measure  $50 \text{ cm}^3$  of the obtained clear solution into 3 conical flasks (Fig. 6) and titrate with  $\text{Na}_2\text{S}_2\text{O}_3$  sodium thiosulphate solution until a light yellow colour is obtained (Fig. 7), then add  $1 \text{ cm}^3$  of the starch solution (the solution becomes blue, Fig. 8) and continue titrating until this solution becomes discoloured (Figs. 9 and 10).



Fig. 5. Sample after adding sulphuric acid



Fig. 6. Prepared sample for titration

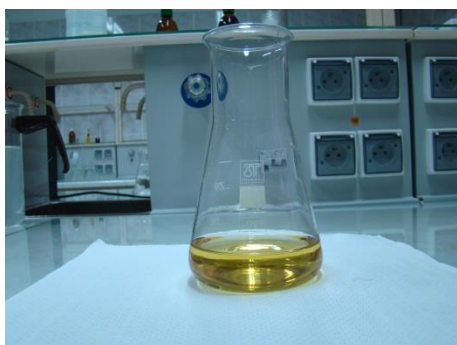


Fig. 7. Sample after pre-titration

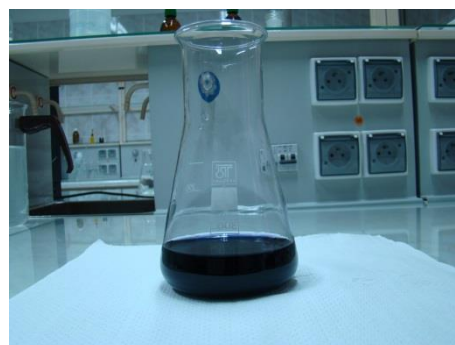


Fig. 8. Sample after adding starch solution



Fig. 9. Sample during titration just before discolouration

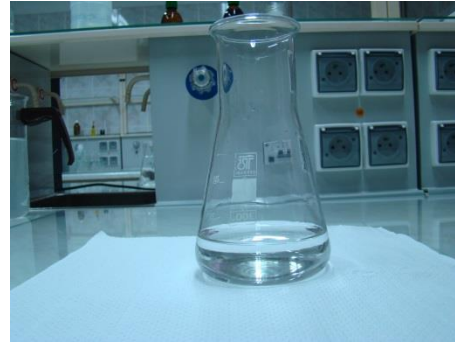


Fig. 10. Final titration effect

### Calculation of the results

Calculate the oxygen  $C_{O_2}$  content in the test sample from the formula:

$$C_{O_2} = \frac{V_2 \cdot M \cdot 32 \cdot V_0 \cdot 1000}{(V_0 - V_3) \cdot 4V_1} \text{ [mgO}_2\text{/dm}^3\text{]}$$

where:

- 32 – the molar mass of oxygen  $O_2$ ,
- $M$  – the titre of the sodium thiosulfate solution,  $M = 0.01 \text{ mol/dm}^3$ ,
- $V_0$  – the capacity of the bottle used for the determination,  $300 \text{ cm}^3$ ,
- $V_1$  – the volume of the test sample measured for the titration,  $50 \text{ cm}^3$ ,
- $V_2$  – average value of the volume of sodium thiosulfate solution used for titrations,  $\text{cm}^3$ ,
- $V_3$  – the sum of the volumes of the added solutions: manganese (II) sulfate, alkaline potassium iodide solution and sulphuric acid,  $\text{cm}^3$ .

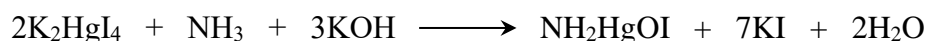
Fig. 11 shows a general view of the laboratory stand for testing the content of ammonium nitrogen in water.



Fig. 11. Laboratory stand for the determination of ammonium nitrogen

### 3.2. Determination of ammonium nitrogen

Ammonia reacts with Nessler's reagent ( $K_2HgI_4$ ), to form a yellow compound, the intensity of which is proportional to the concentration of ammonia. The reaction is according to the scheme:



Calcium, magnesium and iron (II) salts, turbidity and colour interfere with the determination.

The turbidity of the water is removed by filtration. The effect of calcium, magnesium and iron is eliminated by adding a solution of sodium potassium tartrate.

A severe overdose of an oxygen corrosion inhibitor (hydrazine) may lead to the formation of ammonia in the boiler water.

#### 3.2.1. Performing the determination

Measure the amount of a clear sample of the tested water into the Nessler cylinder so that the ammonia content in the sample falls within the scale of the prepared standards (Fig. 12). Then make up to the mark with water free of ammonia, add 1 cm<sup>3</sup> of sodium-potassium tartrate solution and mix, add 1 cm<sup>3</sup> of Nessler's reagent, mix again (Fig. 13) and after 10 minutes compare with prepared permanent standards (Fig. 14).

If the tested water is cloudy, the sample should be filtered through a filter paper.



Fig. 12. Persistent standards



Fig. 13. Sample ready for comparison with standards



Fig. 14. Final effect of the sample comparison

## Calculation of the results

Calculate the ammonium nitrogen  $N_{\text{NH}_4^+}$  content in the test sample from the formula:

$$N_{\text{NH}_4^+} = \frac{a \cdot 1000}{V} [\text{mg } N_{\text{NH}_4^+} / \text{dm}^3]$$

where:

- $a$  – the amount of ammonium nitrogen in the sample, determined by comparison with the standards in mg, (table 1),
- $V$  – volume of the water sample used for the determination,  $\text{cm}^3$ .

Calculate the ammonia  $C_{\text{NH}_3}$  content from the proportion:

$$C_{\text{NH}_3} = \frac{N_{\text{NH}_4^+} \cdot 17.0307}{14.007} [\text{mg } \text{NH}_3 / \text{dm}^3]$$

which consequently comes down to multiplying the calculated content of ammonium nitrogen  $N_{\text{NH}_4^+}$  by 1.216.

Table 1 shows the standards for the determination of ammonium nitrogen in water.

Table 1 Scale of standards for the determination of ammonium nitrogen

Nessler cylinder number with standard	<b>0</b>	<b>I</b>	<b>II</b>	<b>III</b>	<b>IV</b>	<b>V</b>	<b>VI</b>	<b>VII</b>
Ammonium nitrogen content in the sample [mg]	<b>0.000</b>	<b>0.001</b>	<b>0.002</b>	<b>0.004</b>	<b>0.006</b>	<b>0.008</b>	<b>0.010</b>	<b>0.012</b>
Nessler cylinder number with standard	<b>VIII</b>	<b>IX</b>	<b>X</b>	<b>XI</b>	<b>XII</b>	<b>XIII</b>	<b>XIV</b>	<b>XV</b>
Ammonium nitrogen content in the sample [mg]	<b>0.015</b>	<b>0.017</b>	<b>0.020</b>	<b>0.025</b>	<b>0.030</b>	<b>0.035</b>	<b>0.040</b>	<b>0.05</b>

## 4. DEVELOPMENT OF THE EXERCISES

1. Present the results of oxygen determination for the tested water sample.
2. Present the results of the determination of ammonium nitrogen and ammonia for the tested water sample.
3. On the basis of the obtained results, assess the quality and suitability of the tested water for operation in the selected type of boiler.
4. Supplementary table 2 at the end of the manual gives an example of the technical requirements for the water used in the selected type of steam boiler.

## **5. THE FORM AND CONDITIONS FOR PASSING THE LABORATORY EXERCISE**

1. Passing the so-called "entry" before starting the exercise.
2. Submission of a correct written report on the completed exercise, which should contain:
  - short theoretical introduction,
  - operational significance of the measured parameter,
  - processing of the obtained results according to the position manual.
3. Final credit for the test at the end of the semester.

## Additional tasks

### I. Examples of tasks with solutions

1. What is the percentage of water saturation with oxygen, if the oxygen content in water at 18°C is 6.8 mg/dm<sup>3</sup> O<sub>2</sub>? The barometric pressure at the time the water sample was taken was 754 mmHg.

Solution

We use the following formula for the percentage of water oxygenation:

$$\% = \frac{a \cdot 760 \cdot 100}{b \cdot B}$$

where:

- $a$  – determined dissolved oxygen content in the tested water, in mg/dm<sup>3</sup> O<sub>2</sub>,
- $b$  – the maximum amount of oxygen in mg, contained in 1 dm<sup>3</sup> of distilled water at the temperature of the tested water, needed to saturate the water with oxygen after contact with free air at a pressure of 760 mmHg, the numerical value of  $b$  is read from the auxiliary table 2 at the end of this manual,
- $B$  – barometric pressure at the time of taking the water sample, in mmHg.

Using that:  $b = 9.54$  mg/dm<sup>3</sup> O<sub>2</sub> (value read from auxiliary table 2 at the end of this manual) for a temperature of 291 K (18°C) and  $B = 754$  mmHg and  $a = 6.8$  mg/dm<sup>3</sup>

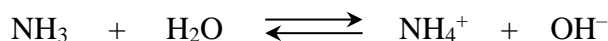
$$\% = \frac{6,8 \cdot 760 \cdot 100}{9.54 \cdot 754} = 71.86\%$$

Answer: The percentage of water oxygenation is 71.86%.

2. Calculate the pH of NH<sub>3</sub>, ammonia solution if its dissociation  $\alpha$  degree is 0.117. Determine also the chemical reaction of this solution.

Solution

Ammonia dissolved in water gives ammonium hydroxide NH<sub>4</sub>OH according to the equation:



The ion concentrations are equal to each other and amount to:

$$[\text{NH}_4^+] = [\text{OH}^-] = C_{\text{initial}} \cdot \alpha = 0.001 \cdot 0.117 = 1.17 \cdot 10^{-4} \text{ mol/dm}^3$$

$$\text{pOH} = -\log[\text{OH}^-] = -\log[1.17 \cdot 10^{-4}] = -(0.0682 - 4) = 3.93$$

because:  $\text{pH} + \text{pOH} = 14$ , hence  $\text{pH} = 14 - \text{pOH} = 14 - 3.93 = 10.07$

$\text{pH} = 10.07$ , so,  $\text{pH} > 7$ , that is, the solution is alkaline.

## II. Tasks and questions to be completed by the student

### Tasks

1. What will be the percentage of water saturation with oxygen, if the determined content of dissolved oxygen in water at 20°C is 5.4 mg/dm<sup>3</sup> O<sub>2</sub>? The barometric pressure at the time of sample collection was 748 mmHg.  
Answer: 59.83%
2. 34 g of NH<sub>3</sub> ammonia were mixed with hydrogen chloride HCl. How much HCl took part in the reaction, what new substance and in what amount was it formed as a result?  
Answer: 73 g HCl which resulted in 107 g of the product.
3. 1200 volumes of NH<sub>3</sub> ammonia were dissolved in one volume of water under standard conditions. Calculate the percentage of ammonia in the formed solution.  
Answer: 47.6% NH<sub>3</sub>.
4. Calculate how many mg of hydrazine should be added to 4000 dm<sup>3</sup> of water to lower the content of dissolved oxygen in water from 0.05 mg/dm<sup>3</sup> to 0.03 mg/dm<sup>3</sup>  
Answer: 80 mg of N<sub>2</sub>H<sub>4</sub> should be added.

### Questions

1. What is the source of oxygen and ammonia in the boiler water?
2. Explain the mechanism of oxygen corrosion on the example of electrochemical corrosion of iron in salted water? Write down the equations of the appropriate reactions until rust is formed.
3. What is thermal deoxidation of boiler water in ships? What physical phenomenon is used for this purpose?
4. What is the chemical deoxidation of boiler water with hydrazine N<sub>2</sub>H<sub>4</sub> and what are the consequences of its severe overdose? Write down the appropriate chemical reactions.
5. Give the chemical reactions occurring when dissolving ammonia NH<sub>3</sub> in the distillate and in water containing aggressive CO<sub>2</sub>.
6. What is the principle of determining oxygen in water by the Winkler titration method?
7. For what purpose the content of hydrazine and ammonia in the boiler water is controlled.
8. What is the principle of determining the ammonia content in boiler water using the Nessler comparative method.



## Supporting tables

Table 2

The amount of oxygen needed to completely saturate 1 dm<sup>3</sup> of distilled water in contact with air with 20.9% oxygen at a pressure of 1013 hPa according to Bogusława and Edward Gomółka "Laboratory exercises in water chemistry"

Temperature K	Oxygen solubility mg/dm <sup>3</sup>	Temperature K	Oxygen solubility mg/dm <sup>3</sup>	Temperature K	Oxygen solubility mg/dm <sup>3</sup>
273	14.62	283	11.33	293	9.17
274	14.23	284	11.08	294	8.99
275	13.84	285	10.83	295	8.83
276	13.48	286	10.60	296	8.68
277	13.13	287	10.37	297	8.53
278	12.80	288	10.15	298	8.38
279	12.48	289	9.95	299	8.22
280	12.17	290	9.75	300	8.07
281	11.87	291	9.54	301	7.92
282	11.59	292	9.35	302	7.77

Table 3

Water quality for water-tube boilers operating under pressure up to 4 MPa according to P. Orłowski "Steam boilers in industrial power engineering"

Physicochemical quantities	Pressure in MPa					
	1.4		2.4		4.0	
	aver.	accep.	aver.	accep.	aver.	accep.
Feed water	aver.	accep.	aver.	accep.	aver.	accep.
General hardness °dH	0.02	0.05	0.015	0.02	0.01	0.015
Content of O <sub>2</sub> ppm	0.03	0.05	0.02	0.05	0.02	0.03
Content of Fe ppm	0.30	–	0.10	0.2	0.05	0.10
Content of Cu ppm	–	–	–	–	–	0.01
pH value at approx. 20°C	8.50	9.50	8.5	9.5	8.5	9.5
Oil content ppm		3.00		2.00		1.00
Content of CO <sub>2</sub> ppm	–	–	–	25	–	25
Oxidizability by KMnO <sub>4</sub> ppm	–	–	–	–	–	20
Content of NO <sub>2</sub> <sup>-</sup> ppm	–	–	–	–	–	0.02
Content of SiO <sub>2</sub> ppm	–	the size is determined according to the manufacturer's instructions				
Proper conductivity μScm <sup>-1</sup>	–					
Boiler water						
Alkalinity <i>p</i> ppm	5 – 15	2 – 20	2 – 8	2 – 10	1 – 5	2 – 7
Content of SiO <sub>2</sub> ppm	–	60	–	40	–	35
Content of P <sub>2</sub> O <sub>5</sub> ppm	–	–	10	20	5 – 10	10 – 20
Proper conductivity μScm <sup>-1</sup>	7000	9000	4000	6000	2000	3000