Institute of Mathematics, Physics and Chemistry

Department of Chemistry

Water chemistry laboratory

Laboratory exercise

Determination of chemical oxygen demand (water oxidizability) by the permanganate method (COD-Mn)

Elaborated by:
dr inż. Jan Krupowies
mgr inż. Czesław Wiznerowicz
dr inż. Agnieszka Kalbarczyk-Jedynak
dr inż. Konrad Ćwirko
dr Magdalena Ślączka-Wilk

KIEROWNIK
Zakładu Chemii
dr inż. Agnieszka Kalbarczyk-Jedynak

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EXERCISE SHEET

<table>
<tr><td rowspan="5">1</td><td colspan="3">Relation to subjects: ESO/25, 27 DiRMiUO/25, 27 EOUNiE/25, 27</td></tr>
<tr><td>Specialty/Subject</td><td>Learning outcomes for the subject</td><td>Detailed learning outcomes for the subject</td></tr>
<tr><td>ESO/26 Chemistry of water, fuels and lubricants</td><td>EKP3
K_U014, K_U015, K_U016.</td><td>SEKP6 – Determination of selected indicators of technical water quality;</td></tr>
<tr><td>DiRMiUO/26 Chemistry of water, fuels and lubricants</td><td>EKP3
K_U014, K_U015, K_U016.</td><td>SEKP6 – Determination of selected indicators of technical water quality;</td></tr>
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K_U014, K_U015, K_U016.</td><td>SEKP6 – Determination of selected indicators of technical water quality;</td></tr>
<tr><td>2</td><td colspan="3">Purpose of the exercise:
teaching how to independently perform the determination of water oxidation in an acidic environment (the so-called permanganate index);</td></tr>
<tr><td>3</td><td colspan="3">Prerequisites:
the student is trained in the field of health and safety regulations in a laboratory workplace, which is confirmed by a handwritten signature on the appropriate form, knows – the permanganate method (COD-Mn) for determining the chemical oxygen demand, i.e. water oxidizability and its chemistry, knows the redox reaction mechanism and the functional importance of oxidation for the characteristics of the purity of the tested water;</td></tr>
<tr><td>4</td><td colspan="3">Description of the laboratory workplace:
electric water bath, standard lab kit for titration analysis, 1 : 3 sulphuric acid solution, potassium permanganate standard solution, sodium oxalate standard solution, test water samples;</td></tr>
<tr><td>5</td><td colspan="3">Risk assessment *:
contact with sulphuric acid (IV) (1: 3), - due to the small amount of acid (about 30 cm^3), the probability of chemical burns is low.
Final assessment – SMALL THREAT
Safety measures required:
a. lab coats,
b. acid-resistant gloves,
c. protective glasses,
d. health and safety cleaning products, paper towels;</td></tr>
<tr><td>6</td><td colspan="3">The course of the exercise:
a. Read the workplace manual (appendix 1) and familiarize with the laboratory kit for the exercise,
b. Determination of the tested water oxidizability in acidic environment;</td></tr>
<tr><td>7</td><td colspan="3">Exercise report:
a. Develop an exercise in accordance with the instructions contained in the workplace manual (appendix 1),
b. On the basis of the obtained results of oxidizability determinations, determine the quality and operational suitability of the tested water by comparing the obtained oxidizability results with its acceptable value for a given boiler,
c. If necessary, suggest any corrective action, Solve a task and/or answer the questions included in the set of tasks and questions to be completed by the student;</td></tr>
</table>

8	**Archiving of research results:** Submit a written report on the performed exercise to the teacher.
9	**Assessment method and criteria:** a. EKP1, EKP2 – tasks given for independent solution and development: mark 2.0 – has no basic chemical and operational knowledge concerning the determined utility parameter of the tested water, i.e. oxidizability and the related assessment of water purity; mark 3.0 – has basic chemical and operational knowledge regarding the determined utility parameter of the tested water and the ability to make basic chemical calculations and solve simple tasks in the field of water oxidizability; mark 3.5 – 4.0 – has extended chemical and operational knowledge in the field of the determined utility parameter of the tested water and the ability to solve complex tasks in the field of assessing changes in this parameter and the mechanism of oxidation and reduction processes; 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 oxidizability and the ability to make corrective and remedial decisions on this basis. b. EKP3 – control works: mark 2.0 – does not have the ability to analyze and evaluate the results of the performed determinations and draw conclusions; mark 3.0 – has the ability to analyse the obtained results, interpret the laws and phenomena, transform formulas, and interpret charts and tables; mark 3.5 – 4.0 – has the ability to broaden the analysis of the obtained results and their proper interpretation; 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.
10	**References:** 1. J. Krupowies, C. Wiznerowicz, A. Kalbarczyk-Jedynak, K. Ćwirko, M. Ślaczka-Wilk, Workplace instruction for laboratory exercise: „Oznaczanie chemicznego zapotrzebowania tlenu (utlenialność wody) metodą nadmanganianową (ChZT-Mn)", 2022 (in Polish). 2. https://openstax.org/details/books/chemistry-2e (accessed: 10 July 2023). 3. https://planm8.io/blog/marine-boiler-water-treatment (accessed: 10 July 2023). 4. https://marinersgalaxy.com/boiler-water-test-on-ship-name-of-all-tests/(accessed:10 July 2023). 5. https://www.imo.org/en/MediaCentre/HotTopics/Pages/Implementing-the-BWM-Convention.aspx (accessed: 29 June 2023). 6. https://www.imo.org/en/GoogleSearch/SearchPosts/Default.aspx?q=water%20treatment%20on%20ships (accessed: 29 June 2023). 7. https://www.wilhelmsen.com/product-catalogue/products/marine-chemicals/test-kits-and-reagents/water-test-kits/test-kit-for-cooltreat-al/ (accessed: 29 June 2023).

APPENDIX 1 – MANUAL

1. SCOPE OF THE EXERCISE

- getting acquainted with the workplace instructions for the exercise,
- determination of the oxidizability of boiler or cooling water by the permanganate method in an acidic environment,
- assessment of the quality of the tested water and suitability for operational purposes and its possible treatment.

2. THEORETICAL INTRODUCTION TO THE EXERCISE

2.1. Chemical oxygen demand – Oxidizability of water

Chemical oxygen demand COD is a conventional parameter defining the amount of oxygen in mg/dm^3 needed for the oxidation of organic compounds and some inorganic compounds. This oxidation is not mediated by microorganisms, but by strong oxidants. For example, iron(II) salts are oxidized – 1 mg of Fe(II) consumes 0.14 mg of oxygen, nitrates(III) – 1 mg of nitrites consumes 1.14 mg of oxygen, sulphites, sulphides contained in water and others having a lower oxidation state than their maximum oxidation state. The determination of COD must be carried out under strict conditions, since the type of oxidizing compounds and the degree of oxidation can vary over a wide range. It depends, among other things on the composition of the tested water, the structure of compounds, the type of oxidizing substances, the concentration of reagents, temperature, pH of the solution, reaction time, etc. The highest degree of oxidation is achieved with dichromate, the lowest – with permanganate.

Depending on the oxidizing agent used, the oxygen demand is COD-Cr dichromate and COD-Mn permanganate, which have been assumed to be called water oxidizability. Water oxidizability is therefore considered an indicative and conventional indicator of the degree of water pollution.

Unpolluted natural waters have oxidizability from a fraction to 2 – 3 mgO_2/dm^3. In the case of a large amount of humic substances, the oxidizability can reach a value of up to several hundred mgO_2/dm^3. The oxidation capacity of drinking water should not exceed 3 mgO_2/dm^3.

Oxidization significantly increases the foaming of the boiler water, which in turn affects the purity of the steam produced in the boiler.

3. Performing the exercise

Fig. 1 shows a laboratory workplace for testing water oxidizability.

Fig. 1. Laboratory workplace for determination of oxidizability

3.1. Determination of oxidizability

In order to obtain comparable results, COD-Mn determinations must be performed under strictly defined conditions, because the amount of used oxidant depends on them. The oxidizability in this method is understood as the number of mg of O_2 consumed by the test sample, heated in a boiling water bath with an oxidant in an acidic environment.

The oxidizability of water is considered to be an indicative indicator only giving a general characteristic of the contamination of a water sample.

The results of the determination of the oxidizability of water instead o mg/dm^3 of $KMnO_4$ are given in mg/dm^3 O_2 (for example 3.95 mg of $KMnO_4$ corresponds to 1 mg of oxygen).

For example, the oxidation of potassium nitrite in an acid medium proceeds according to the following redox reaction:

$$5KNO_2 + 2KMnO_4 + 3H_2SO_4 \rightarrow 5KNO_3 + 2MnSO_4 + K_2SO_4 + 3H_2O$$

The unreacted amount of potassium permanganate reacts with the added, strictly defined amount of sodium oxalate (10 cm^3 of 0.00625M solution) according to the following reaction:

$$2KMnO_4 + 5Na_2C_2O_4 + 8H_2SO_4 \rightarrow$$
$$\rightarrow 2MnSO_4 + K_2SO_4 + 5Na_2SO_4 + 10CO_2 + 3H_2O$$

The excess unreacted oxalate is titrated with a potassium permanganate solution until a pink colour appears in accordance with the above-mentioned reaction. The amount of permanganate consumed during this titration is a measure of the oxidizability of the test water sample, calculated from that given in point 4.1.1. of the formula.

3.1.1. Performing the determination

Oxidation in acid environment is carried out in water with a chloride ion content below 300 mg/dm^3 as follows.

For 3 conical flasks with a capacity of 300 cm^3, measure 100 cm^3 of the tested water. Then add 10 cm^3 of sulphuric acid solution (1: 3) to each of them and exactly 10.0 cm^3 of potassium permanganate solution (0.0025M) (fig. 2). After mixing the contents of the flasks, place them in a boiling water bath in such a way that the surface of the water in the bath is slightly above the surface of the solution in the flasks and heat for 30 minutes. After this time, remove one of them from the bath (fig. 3) and immediately add 10.0 cm^3 of sodium oxalate solution (0.00625M) (fig. 4). The contents of this flask should be mixed and, if there is no immediate discolouration, the solution should be reheated until discolouration for a short time. Titrate the hot solution with potassium permanganate (0.0025M) until a faint pink colour appears, persisting for 1 – 2 minutes (fig. 5). Repeat these steps for the remaining flasks.

Usually, the consumption of potassium permanganate for sample titration is 2 – 8 cm^3.

Fig. 2. Sample prepared for analysis

Fig. 3. Sample after thermal treatment

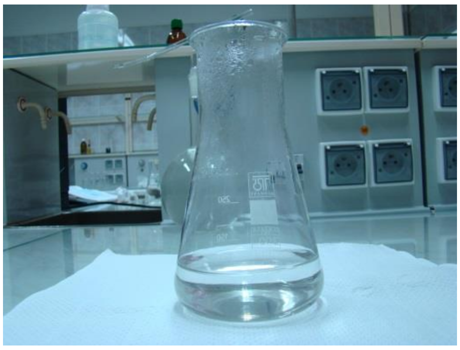

Fig. 4. Sample after adding 10 cm^3 of sodium oxalate

Fig. 5. Final titration effect

Calculation of the results

Calculate the oxidizability – COD-Mn of the tested water according to the formula:

$$\text{COD-Mn} = \frac{0.1 \cdot V_1 \cdot 1000}{V} \, [\text{mg/dm}^3 O_2]$$

where:

- V_1 – the average volume of potassium permanganate solution (0.0025M) used to titrate the sample, cm^3,
- V – volume of the water sample used for the determination, cm^3,
- 0.1 – mg of oxygen corresponding to 1 cm^3 of 0.0025 M potassium permanganate solution.

4. Development of the exercises

1. Present the results of the determination of oxidizability for the tested water sample.
2. On the basis of the obtained results, assess the quality and suitability of the tested water for operation in the selected type of boiler.
3. The auxiliary table 1 gives an example of the technical requirements for drinking water for 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 workplace manual.

3. Final credit for the test at the end of the semester.

Additional tasks

I. Examples of tasks with solutions

1. 0.3210 g of oxalic acid $H_2C_2O_4$ was dissolved in water, the solution was acidified and 31 cm^3 of $KMnO_4$ solution was used for the titration of oxalic acid. Calculate the concentration in moles /dm^3 of potassium permanganate.
   Solution
   The titration of the $KMnO_4$ solution is most often carried out with oxalic acid $H_2C_2O_4$, according to the redox reaction equation below:

$$2MnO_4^- + 5H_2C_2O_4 + 6H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

it follows from the redox reaction equation that 2 moles of $KMnO_4$ react with 5 moles of oxalic acid $H_2C_2O_4$. So, we can write the following proportion:

2 moles of $KMnO_4$ – 5 moles of $H_2C_2O_4$ (stoichiometric ratio)
therefore, $Cm_x \cdot M \cdot V$ – 0.3210 g

and then:

$$\frac{\mathrm{Cm}_x \cdot M \cdot V}{0.3210\mathrm{g}} = \frac{2\ \text{moles}\ \mathrm{KMnO_4}}{5\ \text{moles}\ H_2C_2O_4}$$

after conversion:

$$\mathrm{Cm}_x = \frac{2\ \text{moles}\ \mathrm{KMnO_4} \cdot 0.3210\ g}{M \cdot V \cdot 5\ \text{moles}\ H_2C_2O_4} = \frac{2 \cdot 0.3210\ g}{0.031\ \mathrm{dm^3} \cdot 5 \cdot 90\ \mathrm{g/mol}} = 0.04602\ \mathrm{mol/dm^3}$$

Answer: the concentration of $KMnO_4$ solution is 0.04602 M

2. How many grams of hydrogen peroxide H_2O_2 are contained in the solution for which 14 cm^3 of $KMnO_4$ solution with a concentration of 0.02 mol/dm^3 in an acid medium was used for titration?
   Solution
   We calculate how many grams of $KMnO_4$ are in 14 cm^3 0.02 M of $KMnO_4$ solution. In 1 dm^3 of 0.02 M solution there is: 158 · 0.02 = 3.16 g $KMnO_4$, then in 14 cm^3 we have 3.16 · 0.014 dm^3 = 0.0442 g $KMnO_4$

The redox reaction of $KMnO_4$ with H_2O_2 in an acidic environment proceeds according to the equation on the basis of which we compose the following proportion:

$$2KMnO_4 + 5H_2O_2 + 3H_2SO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 5O_2 + 8H_2O$$

316 – 170
0.0442 – x

$$x = \frac{0.0442 \cdot 170}{316} = 0.0238$$

Answer: there is 0.0238 g of H_2O_2 in the solution.

II. Tasks and questions to be completed by the student

Tasks

1. Calculate the concentration in mol/dm^3 of potassium permanganate $KMnO_4$, if for the titration of 0.1250 g of oxalic acid dihydrate ($H_2C_2O_4 \cdot 2H_2O$) 36.2 cm^3 of $KMnO_4$ solution were used.
   Answer: 0.01096 mol/dm^3 of $KMnO_4$.
2. What is the percentage of hydrogen peroxide H_2O_2 in hydrogen peroxide, if 35 cm^3 of $KMnO_4$ solution with a concentration of 0.02 mol/dm^3 was used for the titration of 5 g of the sample?
   Answer: 1.19 % of H_2O_2.
3. What is the percentage of Fe_2O_3 in the ore, if for the titration of Fe^{2+} ions, after dissolving 0.45 g of the ore sample and reducing Fe^{3+} to Fe^{2+}, 9.00 cm^3 of a 0.1 M $KMnO_4$ solution were used?
   Answer: about 80.00% of Fe_2O_3.
4. During the analysis of iron oxide of unknown composition, a weight of 0.3993 g was dissolved. Iron Fe^{3+} ions contained in the solution were reduced to Fe^{2+} ions and titrated with 0.1250 M of $KMnO_4$ solution, used for 8.00 cm^3. Determine the formula of the analysed iron oxide.
   Answer: Fe_2O_3.

Questions

1. Define the concept of water oxidizability and what it characterizes.
2. Explain what the abbreviations mean: ChZT-Mn and ChZT-Cr?
3. What is the influence of water oxidizability on its tendency to foaming in a steam boiler and on the purity of the generated steam?
4. What is the level of oxidation of natural waters, drinking water and boiler water?
5. What is the determination of the oxidizability of water by the permanganate method in an acidic environment?
6. Write the reaction of oxidation of sodium nitrite in acidic medium with $KMnO_4$.
7. Write the reaction of oxidation of oxalic acid $H_2C_2O_4$ (HOOC–COOH) with $KMnO_4$ in the medium of sulphuric acid H_2SO_4.
8. Name the types of organic pollutants in natural waters and boiler waters.

Auxiliary tables

Table 1

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	
Feed water		average	acceptable	average	acceptable	average	acceptable
General hardness °dH		0.02	0.05	0.015	0.02	0.01	0.015
Content of O_2	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		1
Content of CO_2	ppm	–	–	–	25	–	25
Oxidizability of $KMnO_4$	ppm	–	–	–	–	–	20
Content of NO_2^-	ppm	–	–	–	–	–	0.02
Content of SiO_2	ppm	–	the size is determined according to the manufacturer's instructions				
Proper conductivity	μScm^{-1}	–					
Boiler water							
Alkalinity *p*	ppm	5 – 15	2 – 20	2 – 8	2 – 10	1 – 5	2 –7
Content of SiO_2	ppm	–	60	–	40	–	35
Content of P_2O_5	ppm	–	–	10	20	5 – 10	10 –20
Proper conductivity	μScm^{-1}	7000	9000	4000	6000	2000	3000