	Institute of Mathematics, Physics and Chemistry **Department of Chemistry**
	Third Year Full-Time Students – Faculty of Mechanical Engineering, Fifth Semester **Specialisation: Operation of Marine Power**

The example of final laboratory report regarding subject of chemistry of water, fuels and lubricants

Exercise topic:	**Measurement of pH and determination of water alkalinity**		
Date of performance:	**20.10.2023 r.**	Date of submission:	**27.10.2023 r.**
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Model report of the laboratory exercise according to the requirements of the National Qualifications Framework (NQF)

1. PURPOSE OF THE EXERCISE

Understanding the concepts and acquiring knowledge in the field of pH and alkalinity *p* and *m* of technical water on ships, methods of their determination, applicable limits according to shipping companies and manufacturers of ship boilers, the operational significance of these parameters and chemical calculations in the field of pH and alkalinity of water.

2. EXPECTED LEARNING OUTCOMES FOR THE EXERCISE

Acquiring the ability to independently perform pH measurements and determination of the p and m alkalinity of technical water, correct interpretation of the obtained test results and analysis, and on this basis to assess the quality and operational suitability of the tested water, and, in justified cases, to conduct its treatment by the appropriate addition of mining agents or boiler skimming to maintain required in operation limits of pH and alkalinity of the tested water at the appropriate level.

3. BASIC CONCEPTS THAT YOU ARE FAMILIARIZED WITH BEFORE STARTING THE EXERCISE

Ion product of water, pH and its ranges and the dependence of pH on temperature, indicators and their effects (e.g., phenolphthalein, methyl orange, litmus), methods of pH measurement, water alkalinity p and m, condensate, distillate, boiler water, feed and supplementary water, water cooling, internal boiler corrosion (oxygen, acid and lye or the so-called intercrystalline), cavitation, proprietary preparations for the treatment of boiler water and cooling water, corrosion inhibitors, upper skimming and lower skimming of the boiler (so-called boiler desludging or desalination), foaming of water in boiler.

4. DESCRIPTION OF PERFORMED MEASUREMENTS AND MARKINGS

4.1. DETERMINATION OF THE pH OF BOILER WATER USING INDICATOR PAPERS

The pH of the tested boiler water was determined by immersing the test papers with a wide measuring range of pH 1 to 12 in it for a few seconds. The pH readings are presented in the measurement table No. 1. The pH of the tested water was determined in a similar way using indicator papers with narrowed pH ranges, i.e.: 7.0 – 14.0 and 9.4 – 10.3. The pH readings are shown in Table 1.

4.2. BOILER WATER pH MEASUREMENT WITH A pH METER

A pH-meter electrode, previously rinsed with distilled water and dried filter paper, was placed in a 100 cm^3 beaker half filled with the tested water. After stabilization of the instrument readings, the pH values were read. Measurements were made in triplicate and the results are given in Table 1.

4.3. PERFORMING THE DETERMINATION OF BOILER WATER ALKALINITY

4.3.1. DETERMINATION OF BOILER WATER ALKALINITY P

100 cm^3 of the tested boiler water was measured into a 250 cm^3 conical flask with a measuring cylinder. Then 4 drops of phenolphthalein solution were added and titrated with 0.1 M HCl until the colour of the solution changed from raspberry to colourless, i.e., to discolour the solution. The amount of cm^3 HCl used was entered in the measurement table no. 2. This amount was the basis for calculating the alkalinity p of the tested boiler water according to the formula provided in the workplace manual for this exercise [1]. Titration was performed for three parallel determinations.

4.3.2. DETERMINATION OF *M* ALKALINITY IN BOILER WATER

For the determination of m alkalinity, the same sample of the tested water was used, which was previously titrated against phenolphthalein. 4 drops of methyl orange were added to it and the titration with 0.1 M HCl was continued until the colour changed from yellow to yellow-pink. The total amount of cm^3 of hydrochloric acid used for the titration was read from the burette. It was used to calculate boiler water alkalinity m according to the formula provided in the instruction for exercise [1]. Titration was performed for three parallel determinations.

5. RESULTS OF MEASUREMENTS AND DETERMINATIONS

5.1. BOILER WATER pH MEASUREMENT RESULTS

Table 1

PH measurement results

No.	Water sample no.	Marking with indicator papers			Measurement with a pH meter
		pH range 1 – 12	pH range 7,0 – 14,0	pH range 9,4 – 10,3	
1	7	10	9,5	9,8	9,9
2		9	10,0	10,0	10,0
3		10	9,5	9,8	9,9
Average pH value		9,67	9,67	9,87	9,93

The average pH value determined with papers with narrow pH ranges is: 9,87

The average pH value determined with a pH meter is: 9,93

Note: to assess the quality of the tested water, the value of pH = 9.93 was adopted, which was determined using a more precise method, i.e., using a pH-meter.

5.2. BOILER WATER ALKALINITY DETERMINATION RESULTS

5.2.1. THE RESULTS OF THE DETERMINATION OF ALKALINITY *P*

Table 2

The results of the determination of alkalinity *p*

No.	Water sample no.	Sample volume [cm^3]	Volume of 0.1 M HCl consumed in relation to Phenolphthalein [cm^3]	Calculated alkalinity *p*	
				[$mval/dm^3$]	[ppm $CaCO_3$]
1	7	100	2,80	2,75	137,5
2		100	2,70		
3		100	2,75		
Average value from titration (*a*)			2,75		

The alkalinity of water *p* in relation to phenolphthalein was calculated according to the formula [1]:

$$p = \frac{a \cdot 100}{V} \ [\text{mval/dm}^3]$$

where:

- a – average volume of 0.1 M hydrochloric acid solution used to titrate the tested water to pH 8.3, in cm^3,
- V – the volume of the water sample taken for the test, cm^3.

$$p = \frac{2,75 \cdot 100}{100} = 2,75 \text{ mval/dm}^3$$

The conversion of alkalinity *p* in mval/dm^3 to alkalinity in ppm $CaCO_3$, was made on the basis of the following proportion:

1 mval	–	50 mg $CaCO_3$
2,75 mval	–	x

$$x = \frac{2,75 \cdot 50}{1} = 137,5 \text{ ppm } CaCO_3$$

5.2.2. RESULTS OF *M* ALKALINITY DETERMINATION

Table 3

The results of the *m* alkalinity determination

No.	Water sample no.	Sample volume [cm^3]	Volume of 0.1 M HCl consumed in relation to methyl orange [cm^3]	Calculated alkalinity *m*	
				[mval/dm^3]	[ppm $CaCO_3$]
1	7	100	5,20	5,17	258,5
2		100	5,20		
3		100	5,10		
Average value from titration (*b*)			5,17		

The alkalinity of water *m* in relation to methyl orange was calculated according to the formula [1]:

$$m = \frac{b \cdot 100}{V} \ [\text{mval/dm}^3]$$

where:

- *b* – the average volume of 0.1 M hydrochloric acid solution used to titrate the test water to pH 4.5, in cm^3,
- *V* – the volume of the water sample taken for the test, cm^3.

$$m = \frac{5,17 \cdot 100}{100} = 5,17 \text{ mval/dm}^3$$

The conversion of alkalinity *m* in mval/dm^3 to alkalinity in ppm $CaCO_3$, was made on the basis of the following proportion:

1 mval	–	50 mg $CaCO_3$
5,17 mval	–	x

$$x = \frac{5,17 \cdot 50}{1} = 258,5 \text{ ppm } CaCO_3$$

5.3. CALCULATION OF THE CONTENT OF IONS AND CHEMICAL COMPOUNDS IN THE BOILER WATER CAUSING ITS ALKALINITY

Using the data contained in Tables 2 and 3, the relationship between the determined values of alkalinity p and m of the tested water was determined. This relationship applies when $p > \frac{m}{2}$ or otherwise $2p > m$. Assuming that the tested water was free of phosphates, the ion content in the water for this case was calculated on the basis of the data in Table 4 [1–4].

Table 4

The content of alkaline ions in the tested water for the case $2p > m$ [1–4]

Ion content $[OH^-]$ [mval/dm^3]		Ion content $[HCO_3^-]$ [mval/dm^3]		Ion content $[CO_3^{2-}]$ [mval/dm^3]	
Relationship between *p* and *m*	Numerical value	Relationship between *p* and *m*	Numerical value	Relationship between *p* and *m*	Numerical value
$2p - m$	0,33	$2p > m$	0	$2(m - p)$	4,84

The calculations that were used to convert the determined alkalinity of the boiler water into the content in mg/ dm^3 of ions and alkaline compounds of sodium for the considered case of $2p > m$ are presented below. They consisted in multiplying the numerical values of the alkalinity from Table 4 (0.33 and 4.84) by the corresponding milligram equivalents of these ions and compounds.

Calculations:

Content of hydroxide ions:	$[OH^-] = 0,33 \cdot 17 = 5,61$ mg/dm^3
Sodium hydroxide content:	$[NaOH] = 0,33 \cdot 40 = 13,2$ mg/dm^3
Carbonate ion content:	$[CO_3^{2-}] = 4,84 \cdot 30 = 145,2$ mg/dm^3
Sodium carbonate content:	$[Na_2CO_3] = 4,84 \cdot 53 = 256,52$ mg/dm^3

6. METHOD OF PROCESSING THE OBTAINED RESULTS

On the basis of the determined pH and alkalinity *p* and *m* of the tested boiler water, an assessment of its quality and operational suitability for the selected type of ship boilers was made and the possible water treatment on the ship was analysed, resulting from this assessment.

In order to prevent corrosion inside the boiler and the formation of foam in the boiler, the boiler water should have an appropriate pH value and alkalinity, depending on the operating conditions of the boiler. For boilers with a working pressure of steam up to 31 bar, the pH of the boiler water should be in the range 9.5 – 11.0, and the alkalinity *p* in the range of 100 to 150 ppm. $CaCO_3$ (i.e.: 2 – 3 mval/dm^3), while the alkalinity *m* – have a value of about 2*p* [2–4]. Assuming that the tested boiler water is used in boilers of this type, the obtained values of its pH (9.93) and alkalinity *p* (2,75 mval/dm^3, which corresponds to a content of 137.5 ppm $CaCO_3$), with the operational limits of these parameters given above [1–4]. The result of such an assessment of the tested water is given in the conclusions.

7. FINAL CONCLUSIONS

When assessing the quality and operational suitability of the tested water for marine boilers with a pressure of up to 31 bar, due to the determined pH value = 9.93 and alkalinity *p* = 2.75 mval/dm^3 (which corresponds to the content of 137.5 ppm $CaCO_3$), it can be stated that this water meets the requirements for the limits of pH and alkalinity *p* and therefore does not require any corrective measures by adding mining agents.

In order to maintain the alkalinity p of the feed water during operation at the appropriate level (100 – 150 ppm of $CaCO_3$), the addition of the Combitreat conditioning agent in the amount of 0.2 – 0.1 kg per 1000 dm^3 of condensate or Liquitreat should be used according to the recommendations of Unitor. in the amount of 1.2 – 0.6 dm^3 per 1000 dm^3 of condensate [2, 3].

If the analysis showed too low value of boiler water alkalinity, then these conditioning agents should be added. On the other hand, if the water alkalinity is too high, the boiler should be skimmed down [4, 8, 9].

Unitor recommends an initial dose of Combitreat of 300 g per ton of water. A dose of 100 g/tonne of water of this agent increases the level of alkalinity *p* by 50 ppm. The initial dose of Liquitreat is 2 dm^3 per ton of water, and the amount of 0.8 dm^3/tonne of water increases the alkalinity *p* by 50 ppm [2, 3].

8. TASKS AND QUESTIONS GIVEN FOR SELF-COMPLETION

8.1. QUESTION FOR INDIVIDUAL DEVELOPMENT

The tested boiler water discoloured after adding phenolphthalein. Write down what chemical reactions occur during the determination of the alkalinity of this water, if the alkalinity is expressed in the relationship: $m > 2p$ or otherwise $2p < m$. Determine also the content of ions and sodium compounds causing this alkalinity.

Answer: If the tested water does not contain other basic compounds (e.g., phosphates) apart from hydroxides, carbonates and bicarbonates, then on the basis of the above-mentioned interdependence between the values of p and m, which has the form $2p < m$, the following possible variant of the alkalinity of the water should be considered:

– the test water may contain bicarbonates and carbonates, but not hydroxides, since the coexistence of hydroxides and bicarbonates is mutually exclusive, according to the following molecular and ionic reaction:

$$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O$$
$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$$

The reactions occurring during titration with hydrochloric acid, i.e., when determining the alkalinity of the tested water, are as follows:

$$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$$
$$NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$$

or in ionic form:

$$CO_3^{2-} + H^+ \rightarrow HCO_3^-$$
$$HCO_3^- + H^+ \rightarrow H_2CO_3 \rightarrow CO_2 + H_2O$$

We calculate the content of bicarbonates and carbonates from the following system of equations:

$$p = \frac{1}{2}\left[CO_3^{2-}\right], \quad m = \left[HCO_3^-\right] + \left[CO_3^{2-}\right], \quad \left[OH^-\right] = 0$$

The value of 2p corresponds to the content of neutral carbonates, and the excess of *m* in relation to 2*p* means that there are also bicarbonates in the water. Ultimately, therefore, the alkalinity of the tested boiler water consists of the following contents of ions or alkaline compounds converted to sodium compounds, which we calculate by multiplying the alkalinity value by the appropriate equivalents of these ions or compounds.

$$[CO_3^{2-}] = 2p \text{ [mval/dm}^3\text{] and } [HCO_3^-] = (m - 2p) \text{ [mval/dm}^3\text{]}$$

The amount of carbonate ions is then:	$[CO_3^{2-}] = 2p \cdot 30$ [mg/dm^3]
The amount of sodium carbonate:	Na_2CO_3 is: $2p \cdot 53$ [mg/dm^3]
The amount of bicarbonate ions is:	$[HCO_3^-] = (m - 2p) \cdot 61$ [mg/dm^3]
The amount of sodium bicarbonate:	$NaHCO_3$ is: $(m - 2p) \cdot 84$ [mg/dm^3]

8.2. A TASK FOR INDEPENDENT DEVELOPMENT

To 25 cm^3 of 0.1 M HCl solution 24 cm^3 of 0.15 M NaOH solution was added. Consider the excess of NaOH as completely dissociated in solution. Calculate the pH of the obtained solution and determine its chemical reaction.

Solution:
The excess of NaOH in the solution is:

$$24 \text{ cm}^3 \cdot 0{,}15 \text{ M} - 25 \text{ cm}^3 \cdot 0{,}1 \text{ M} = 3{,}6 - 2{,}5 = 1{,}1 \text{ mmol}$$

The total volume of the solution is: $25 \text{ cm}^3 + 24 \text{ cm}^3 = 49 \text{ cm}^3$
The concentration of hydroxide ions OH^- is equal to:

$$\left[OH^-\right] = \frac{1{,}1}{49} = 0{,}0224 \text{ mmol/cm}^3$$

converted to moles/dm^3 it is $\left[OH^-\right] = 2{,}24 \cdot 10^{-2} \text{ mol/dm}^3$

Knowing the concentration of OH^- ions, we calculate the pOH of the solution:

$$pOH = -\log [OH^-],$$
$$pOH = -\log (2{,}24 \cdot 10^{-2})$$

$$pOH = -(\log 2{,}24 + \log 10^{-2}) = -(0{,}35 - 2) = 1{,}65$$

Thus, the pH of the solution is:

$$pH + pOH = 14, \quad pH = 14 - pOH = 14 - 1{,}65 = 12{,}35$$

Answer: the pH of the resulting solution is 12.35 (pH> 7), i.e., the solution is alkaline.

9. REFERENCES:

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10. THE TEACHER'S COMMENTS AND RECOMMENDATIONS AFTER CHECKING THE REPORT

The boiler water quality analysis performed on the basis of only two partial parameters, i.e., pH value and alkalinity of the tested boiler water is in fact incomplete and its other performance parameters important for operation should be determined, such as: chloride ion content and specific conductivity, oxygen content and ammonia, and corrosion inhibitors, as well as oxidisability or the so-called permanganate index. It will be possible after the next program laboratory exercises in water chemistry, and then the analysis will be a full and comprehensive assessment.