MARITIME UNIVERSITY OF SZCZECIN
MUS
POLAND

Institute of Mathematics, Physics and Chemistry

Department of Chemistry

Water chemistry laboratory

Laboratory exercise

Measurement of pH and determination of water alkalinity

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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
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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 the student how to independently perform pH measurements and determination of alkalinity of boiler and cooling water for marine engines;</td></tr>
<tr><td>3</td><td colspan="3">**Prerequisites:**
the student is trained in the occupational health and safety regulations in a laboratory workplace, which he confirms with his signature on the appropriate form, knows the methods of measuring pH and its ranges, indicators and their mechanism of action, and determines the alkalinity p and m of water by titration method, knows the technical requirements and operational meaning of these parameters;</td></tr>
<tr><td>4</td><td colspan="3">**Description of the laboratory workplace:**
typical laboratory kit for titration analysis, pH-meter, indicator papers, indicators, samples of tested water;</td></tr>
<tr><td>5</td><td colspan="3">**Risk assessment:**
contact with 0.1M hydrochloric acid – probability of chemical burn – very small, effects – minor.
Final assessment – **VERY SMALL THREAT**
Safety measures required:
a. lab coats,
b. 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. Measure the pH and determine the alkalinity p and m of the tested water;</td></tr>
<tr><td>7</td><td colspan="3">**Exercise report:**
a. Develop the exercise in accordance with the instructions contained in the workplace manual,
b. Determine the relationship between the determined alkalinity *p* and *m* and on this basis calculate the content in water of basic compounds causing this alkalinity,
c. On the basis of the obtained results of measurements and determinations, determine the quality and operational suitability of the tested water,
d. If necessary, suggest possible water treatment or appropriate corrective action,
e. Solve the given 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 academic teacher.
9	**Assessment method and criteria:** a. EKP1, EKP2 – tasks given for independent solution and development: mark 2.0 – the student has no basic chemical and operational knowledge concerning the pH and alkalinity p and m of boiler and cooling water; mark 3.0 – has basic chemical and operational knowledge regarding the pH and alkalinity of the tested boiler and cooling water as well as the ability to basic chemical calculations and solve simple tasks in the field of these performance parameters; mark 3.5 – 4.0 – has extensive chemical and operational knowledge in the field of the determined usable parameters of the tested water and the ability to solve complex tasks in the scope of assessing changes in these parameters; 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 determined operational parameters and the ability to make diagnostic decisions as well as corrective and remedial actions on this basis. b. EKP3 – control works: mark 2.0 – does not have the ability to analyse and evaluate the results of the performed analyses and determinations, and to 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 results, apply laws, construct monograms and charts; mark 4.5 – 5.0 – has the ability to comprehensively analyse the obtained results, make generalizations, detect cause-effect relationships and make the right operational decisions.
10	**References:** 1. J. Krupowies, C. Wiznerowicz, A. Kalbarczyk-Jedynak, K. Ćwirko, M. Ślaczka-Wilk, Workplace instruction for laboratory exercise: „Pomiar pH oraz oznaczanie alkaliczności wody”, 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,
- pH measurement of boiler or cooling water samples using indicator papers and a pH meter,
- determination of the *p* and *m* alkalinity of water,
- 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. Exponent of the concentration of hydronium ions – pH

The chemical reaction of aqueous solutions depends on the concentration of H_3O^+ hydronium ions. It has been assumed to define this reaction by means of the pH value, which symbol means the negative decimal logarithm of the concentration of hydronium ions:

$$pH = -\log [H_3O^+]$$

where:

$[H_3O^+]$ – concentration of hydronium ions expressed in moles/dm^3, which is symbolized by square brackets.

Water is a very weak electrolyte and only 1 part per million self-ionizes to form hydronium and hydroxide ions according to the following scheme:

$$2H_2O \rightleftarrows H_3O^+ + OH^-$$

For the sake of simplification, the dissociation of water was adopted in the instruction to be written in accordance with the following equation:

$$H_2O \rightleftarrows H^+ + OH^-$$

bearing in mind, however, the conventional meaning of this provision, because in fact in water solutions there are not hydrogen ions H^+, but hydronium ions H_3O^+.
The equilibrium constant of this reaction, called the dissociation constant, can be written as:

$$K_{H_2O} = \frac{[H^+] \cdot [OH^-]}{[H_2O]}$$

The value of this constant depends on the temperature. Due to the negligible dissociation of water into ions, it can be assumed that the concentration $[H_2O]$ is constant and equal to 55.6 moles/dm^3. After the transformation, we get:

$$K_W = K_{H_2O} \cdot [H_2O] = [H^+] \cdot [OH^-]$$

K_W was assumed to be the ionic product of water, which is a constant value at a given temperature and at 25ºC K_W is $1.008 \cdot 10^{-14}$.

The changes of the ionic product of water K_W depending on the temperature and the corresponding pH values of the water are given in Table 1

Table 1

Values of the ionic product of water K_W at different temperatures

Temperature [ºC]	K_W [mol^2/(dm^3)^2]	pH
0	$0.1139 \cdot 10^{-14}$	7.47
18	$0.5702 \cdot 10^{-14}$	7.12
25	$1.0080 \cdot 10^{-14}$	6.99
50	$5.4740 \cdot 10^{-14}$	6.63
100	$5.9000 \cdot 10^{-14}$	6.11

Pure water (distillate) is a neutral compound; therefore the concentrations of hydrogen (hydronium) and hydroxide ions are equal to:

$$[H^+] = [OH^-] = 1.004 \cdot 10^{-7} \text{ mol/dm}^3 \text{ at } 25ºC$$

Therefore, it can be assumed that at the concentration of hydrogen ions $[H^+] = 10^{-7}$ mol/dm^3 water is neutral, i.e. its pH is 7. From a practical point of view, the pH scale ranges from 0 to 14. If the pH is 7, the solution is neutral when the pH is less than 7 the solution is acidic and the lower the pH is, the more acidic it is, and when the pH is greater from 7 the solution is alkaline, and the more alkaline the higher the pH of the solution.

The ionic product of water at constant temperature is constant not only for pure water, but also for dilute aqueous solutions of various substances. Thus, knowing the concentration of hydrogen ions, one can calculate the concentration of hydroxide ions from the ionic product of water. By denoting the negative decimal logarithm of the concentration of hydroxide ions as pOH, that is:

$$pOH = -\log [OH^-]$$

it can be easily proven that:

$$pH + pOH = 14$$

For example, the pH of natural waters ranges from 4 – 9, but most of these waters have a pH of 6.5 – 8.5. Drinking water should have a pH of 6.5 – 9.0. Low pH waters have corrosive properties and bring large economic losses, e.g. corrosion of water supply and heating networks, corrosion of ship boilers, etc.

For boiler water, the pH value at 20°C should be within the range of 8.5 – 10.5, depending on the type of boiler and its operating parameters.

The pure distillate obtained on the ship in the evaporator is chemically neutral and its pH at ambient temperature is 7. However, ship boilers cannot be fed with such untreated distillate, because at the boiler operating temperature of e.g. 200°C, the pH of the distillate drops to 5.4, which poses a risk of corrosion of the boiler. Therefore, the distillate should be treated with a package of alkaline compounds in such a way that it shows the pH at the boiler operating temperature within the limits of 8.4 – 9.0 (Fig. 1). In this range, the treated boiler water no longer has corrosive properties. At ambient temperature in the range of pH 9 – 11, water also has no corrosive properties (Fig. 2).

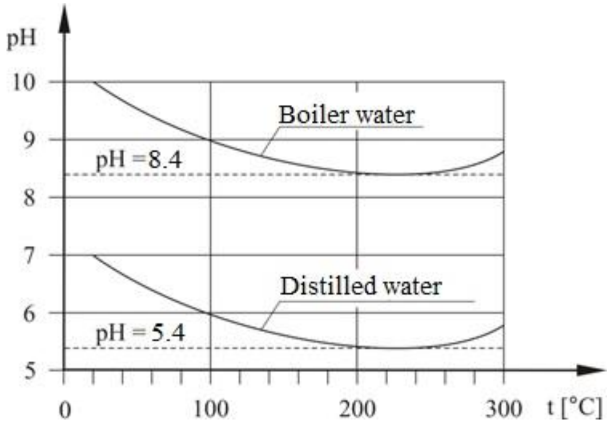


Fig. 1. Influence of temperature on the pH value of pure water (distillate) and boiler water

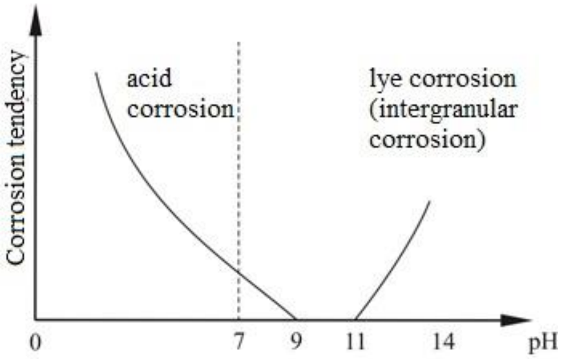


Fig. 2. Influence of pH on the aggressiveness of aqueous solutions

2.2. Alkalinity *p* and *m* of boiler and cooling water for marine engines

A property of water that is referred to as alkalinity is its ability to neutralize mineral acids under certain conditions. This property is given by the water present in the bicarbonates and hydroxides of calcium, magnesium and sodium, and additionally phosphates, silicates – in the case of boiler water.

The deliberate use of alkaline watering agents is to prevent corrosion. The alkalinity of feed and boiler water is a very important utility parameter that must be monitored on an ongoing basis and maintained within the limits set for a given boiler. The results of measurements of boiler water alkalinity constitute the basis for the intensity of desalination (desludging) of water in the steam boiler and for the assessment of water tendency to foaming. Excessive alkalinity of water can cause lye corrosion, the so-called intergranular. This phenomenon occurs in places where there is no water circulation and where there are high mechanical stresses in the metal.

The basis for determining the basic (alkaline) properties of water in ships are two quantities, the so-called *p* mineral alkalinity (determined against phenolphthalein) and total alkalinity, also determined as total *m* (determined against methyl orange).

The principle of determining *p* and *m* alkalinity is to titrate the tested water sample with a standard hydrochloric acid solution to a pH of 8.3 against phenolphthalein (until the raspberry colour disappears) and to a pH of 4.5 against methyl orange (until the colour changes from yellow to yellow-red) for this the water sample itself.

The course of titration of a water sample with standard HCl solution is illustrated in Table 2, in which for each group of compounds causing alkalinity, the course of chemical reactions is given on the example of sodium salts in the same order as the amount of added hydrochloric acid increases. As can be seen from this table, the alkalinity *p* denotes the total hydroxide content, half the carbonate content and 1/3 the phosphate content. On the other hand, total (total) alkalinity – *m* determines the total content of hydroxides and carbonates and 2/3 of the content of phosphates.

Table 2

The course of the reaction during the titration
of boiler water with standard HCl solution

Alkalinity	**Hydroxides**	**Carbonates**	**Phosphates**
m ↑ *p* ↓	$NaOH + HCl \rightarrow$ $\rightarrow NaCl + H_2O$	$Na_2CO_3 + HCl \rightarrow$ $\rightarrow NaH CO_3 + NaCl$	$Na_3PO_4 + HCl \rightarrow$ $\rightarrow Na_2HPO_4 + NaCl$
pH=8.3 ↓		$NaH CO_3 + HCl \rightarrow$ $\rightarrow NaCl + CO_2 + H_2O$	$Na_2HPO_4 + HCl \rightarrow$ $\rightarrow NaH_2PO_4 + NaCl$
pH=4.5			$2NaH_2PO_4 + 2HCl \rightarrow$ $\rightarrow P_2O_5 + 2NaCl + 3H_2O$

Natural waters contain the highest amounts of calcium and magnesium bicarbonates. In addition, there are: magnesium carbonate and low concentrations of calcium carbonate. In addition to calcium and magnesium bicarbonates and carbonates, some waters contain sodium and potassium carbonates and bicarbonates. In such cases, water is more alkaline than general hardness. The difference between basicity and total hardness is referred to as alkaline alkalinity. This type of alkalinity is caused precisely by the potassium and sodium bicarbonates or carbonates in the water.

The alkalinity of the water is of secondary importance from a sanitary point of view. However, it is of great importance in the assessment of water for economic and technical purposes. For example, the total alkalinity, which corresponds to the carbonate hardness, is relevant for the boiler feedwater. Likewise, excessive alkaline alkalinity for water for technical purposes is undesirable as it causes high foaming of the water in the boiler.

Total alkalinity is defined as the sum of all chemicals in water which are alkaline react with methyl orange (pH 4.5). Alkalinity to phenolphthalein means the sum of all alkaline reacting compounds above pH 8.3.

Fig. 3 shows a general view of the laboratory stand for testing the pH and alkalinity of water.

3. PERFORMING THE EXERCISE

Fig. 3 shows a general view of the laboratory workplace for testing the pH and alkalinity of water.

Fig. 3. Laboratory workplace for determination of pH and alkalinity *p* and *m* of water

3.1. Measurement of the pH of the boiler or cooling water

3.1.1. Measurement of the pH with indicator papers

In laboratory practice and on a ship for quick pH measurements, the so-called indicator papers are used. Indicator papers are tissue strips saturated with an appropriate indicator and dried. The most commonly used are universal papers that have different pH ranges (with a wide range, e.g. 1 – 12 and various narrowed ranges - i.e. more accurate, e.g. with an accuracy of 0.1 pH).

Performing the pH measurement with indicator papers

Pour the tested water sample to 1/2 of its volume into a 100 cm^3 beaker. Then choose a paper with the widest pH range and immerse it for 2 – 3 seconds in the tested water, then compare the colour of the paper with the colour scale of the standard and read the pH value corresponding to this colour.

After the initial measurement, select a suitable paper with an exact, narrowed range and make another three pH measurements.

List the measurement results in the table.

3.1.2. Measurement of the pH with a pH meter

The determination of pH consists in measuring the electromotive force of the cell in the system: reference electrode (calomel electrode), test solution, measuring electrode (glass electrode). Before the measurement, start the pH meter in accordance with the operating manual. Rinse the electrode with distilled water and gently dry its lower part with a filter paper.

Before the measurement, mix the tested water sample well so that the composition of the liquid on the surface corresponds to its general composition. Then measure the pH according to the pH meter operating instructions (perform the measurement three times). After the measurement, remove the electrode and rinse it with distilled water.

Calculation of the results

Take as the final result the arithmetic mean of 3 measurements not differing by more than 0.1 pH.

3.2. Determination of *p* and *m* alkalinity of boiler water or cooling water

3.2.1. Determination of *p*-alkalinity by titration against phenolphthalein

The basic compounds in the water are neutralized with a standard solution of a strong mineral acid to a pH of 8.3 using a phenolphthalein solution as an indicator. Titration continues until the raspberry colour of the sample disappears.

Determination is disturbed by: turbidity over 30 mg/dm^3 and color over 50 mg/dm^3 Pt. If the turbidity of the tested water exceeds 30 mg/dm^3, the water sample should be filtered before the determination. If the water shows a color greater than 50 mg/dm^3 Pt, the alkalinity is determined using the potentiometric method.

Performing the determination

For a conical flask with a capacity of 250 cm^3 measure 100 cm^3 of the tested water and add 4 drops of 1% alcoholic phenolphthalein solution (Fig. 4.) If the water turns raspberry colour, it should be titrated with 0.1 M hydrochloric acid solution until the color disappears (Fig. 5.).

Fig. 4. Sample prepared for titration

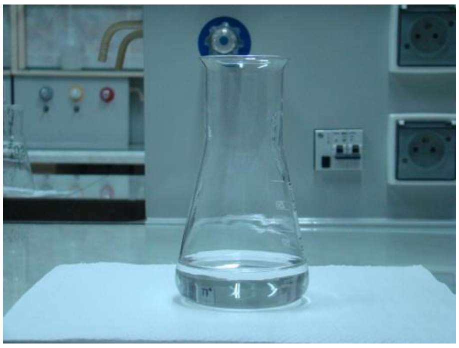


Fig. 5. Final effect of titration
(determination of *p* alkalinity)

If the water does not turn raspberry after adding phenolphthalein solution to it, it means that the tested water does not show this type of alkalinity (alkalinity $p = 0$).

Note - after titration, keep the sample for the determination of *m* alkalinity, without adding the spent acid in the burette. Then proceed with the determination of *m* alkalinity of the tested sample according to point 4.2.2.

Carry out the titration against phenolphthalein for 3 parallel determinations.

Calculation of the results

Calculate the alkalinity of water in relation to phenolphthalein p according to the formula:

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

where:

a – the average volume of 0.1 M hydrochloric acid solution used to titrate the test water to pH 8.3, in cm^3,

V – the volume of the water sample taken for the test, cm^3.

3.2.2. Determination of total alkalinity *m* by titration against methyl orange

The total alkalinity m of tested water is determined by titration with 0.1 M hydrochloric acid to pH 4.5, against methyl orange as an indicator. Titration changes the colour of the sample from yellow to yellow-pink. Determination is disturbed, as in the determination of alkalinity towards phenolphthalein, the turbidity and colour of water.

Performing the determination

For the determination, use the same sample of the tested water that was previously titrated against phenolphthalein.

Add 2-3 drops of a 0.1% aqueous solution of methyl orange (Fig. 6) and continue the titration with 0.1 M hydrochloric acid until the colour changes from yellow to yellow-pink (Fig. 7), which persists for one minute.

Fig. 6. Sample prepared for titration

Fig. 7. Final titration effect (determination of m alkalinity)

Read from the burette the total amount of cm^3 of 0.1 M HCl used for the titration.

Carry out the titration against methyl orange for 3 parallel determinations.

Calculation of the results

Total alkalinity m of water is calculated according to the formula:

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

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.

4. DEVELOPMENT OF THE EXERCISE

1. Present the results of pH measurements using indicator papers and a pH meter and compare them with the required parameters for boiler or cooling water.
2. After determining the p and m alkalinity and determining the appropriate relationship between these parameters from Table 4, then calculate the content of ions or alkali compounds in mg/dm^3, which give the water this alkalinity. A calculation example is shown on page 13.
3. Compare the obtained contents of specific ions or salts with their permissible concentrations for the boiler water of the selected type of ship's boiler or for cooling water.
4. On the basis of the obtained results, assess the quality and suitability of the tested water for exploitation.
5. In auxiliary tables 3 – 7 at the end of the manual some data on the technical requirements for boiler water are given, and in table 8 and appendices 2 and 3 constituting the forms of analytical control of Unitor boiler and cooling water, technical data recommended by this company.

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. To 50 cm^3 of hydrochloric acid HCl with the density d = 1.1 g/cm^3, containing 20% by mass of HCl, 14 g of potassium hydroxide KOH was added. What will be the chemical reaction of the obtained solution? How much KOH should be added to make this solution neutral?

   Solution

   The equation for the neutralization reaction has the form:

$$HCl + KOH \longrightarrow KCl + H_2O$$

   We calculate the mass of the HCl solution from the following density formula:

$$d = \frac{m}{V} \quad \text{hence:} \quad m = d \cdot V\text{, therefore } m_{HCl} = 1.1\ g/cm^3 \cdot 50\ cm^3 = 55\ g\ HCl$$

Then we calculate the mass of hydrogen chloride in the amount of hydrochloric acid calculated above, knowing that HCl is 20%:

100 g of acid – 20 g of pure HCl
55 g of acid – x

$$x = \frac{55 \cdot 20}{100} = 11\,g \text{ of pure HCl}$$

The molar masses of the reactants are as follows: M_{HCl} = 36.5 g/mol; M_{KOH} = 56.1 g/mol
Based on the neutralization reaction given above, we compose the following proportion:

36.5 g HCl – 56.1 g KOH
11.0 g HCl – x g KOH

$$x = \frac{11 \cdot 56.1}{36.5} = 16.92 \text{ g KOH}$$

Answer:
In order to completely neutralize 50 cm^3 of HCl with the above composition, 16.92 g of KOH should be used. After adding only 14 g of KOH the solution will be acidic, so you need to add 16.92 g KOH – 14 g KOH = 2.92 g KOH to keep it neutral.

2. Calculate the pH of a saturated $Fe(OH)_2$, solution if its solubility product (K_{sp} solubility product constant) is at room temperature $Ksp_{Fe(OH)_2} = 4 \cdot 10^{-14}$. What is the chemical reaction of this solution?

   Solution

   The equation for the electrolytic dissociation reaction of $Fe(OH)_2$ is as follows:

$$Fe(OH)_2 \overset{H_2O}{\rightleftarrows} Fe^{2+} + 2OH^-$$

On the other hand, the solubility product of $Ksp_{\mathrm{Fe(OH)_2}}$ has the form: $Ksp_{\mathrm{Fe(OH)_2}} = [\mathrm{Fe^{2+}}] \cdot [\mathrm{OH^-}]^2$

The molar concentrations of ions in the solution are as follows: $\left[\mathrm{Fe^{2+}}\right] = x$ $\left[\mathrm{OH^-}\right] = 2x$ (OH^- ions are 2 times more than Fe^{2+} ions)

So the expression for $\mathrm{L_{Fe(OH)_2}}$ can be written as:

$$Ksp_{\mathrm{Fe(OH)_2}} = x \cdot (2x)^2 = 4x^3 = 4 \cdot 10^{-14}$$

$$x = \sqrt[3]{\frac{4 \cdot 10^{-14}}{4}} = 2.14 \cdot 10^{-5}$$

So, the concentration of $[OH^-]$ ions is:

$$[\mathrm{OH^-}] = 2x = 2 \cdot 2.14 \cdot 10^{-5} = 4.28 \cdot 10^{-5} \text{ mol/dm}^3$$

$$\mathrm{pOH} = -\log [\mathrm{OH^-}] = -\log [4.28 \cdot 10^{-5}] = -(0.6314 - 5) \quad \mathrm{pOH} = 4.37$$

Knowing that pH + pOH = 14, we calculate the value of pH

$$\mathrm{pH} = 14 - \mathrm{pOH} = 14 - 4.37 = 9.63$$

pH = 9.63, thus, a saturated solution of $Fe(OH)_2$ at room temperature is alkaline.

3. Calculate the alkalinity of water in mval/dm^3, if it contains 324 mg/dm^3 of calcium bicarbonate $Ca(HCO_3)_2$.

Solution

In order to calculate the alkalinity of water in mval/dm^3, the amount of calcium bicarbonate $Ca(HCO_3)_2$ (expressed in mg/dm^3), should be divided by the milligramequivalent value of calcium bicarbonate (R), which is:

$$\mathrm{R_{Ca(HCO_3)_2}} = \frac{\mathrm{M}}{2} = \frac{162}{2} = 81\,\mathrm{mg}$$

Thus, the alkalinity of the water $m = \frac{324}{81} = 4.0 \text{ mval/dm}^3$.

Answer: Alkalinity *m* = 4 mval/dm^3.

4. Calculate the content of NaOH and Na_2CO_3 in mg/dm^3, if the alkalinity of water is p = 6 mval/dm^3, and the alkalinity m = 6.5 mval/dm^3.

Solution

Since $p > \frac{m}{2}$, so, we use the formulas (table 4 of the instructions) to calculate the concentration of the appropriate ions: $[OH^-] = 2p - m$ and $[CO_3^{2-}] = 2(m - p)$ after substituting the values, we get: $[OH^-] = 2 \cdot 6 - 6.5 = 5.5$ mval/dm^3. So the amount of NaOH is: $R_{NaOH} \cdot 5.5 = 40 \cdot 5.5 = 220$ mg/dm^3

We calculate the amount of Na_2CO_3 in the water analogously:

$[CO_3^{2-}] = 2(6.5 - 6.0) = 1$ mval/dm^3.

The amount of Na_2CO_3 is $\mathrm{R_{Na_2CO_3}} \cdot 1 = 53 \cdot 1 = 53\,\mathrm{mg/dm^3}$.

Answer: The content of NaOH = 220 mg/dm^3, and Na_2CO_3 is 53 mg/dm^3.

II. Tasks and questions to be completed by the student

Tasks

1. The concentration of H_3O^+ ions in the boiler water at the boiler operating temperature is 10^{-9} mol/dm^3. Calculate the pH and pOH of this water, the content of hydroxide ions OH^- and determine the chemical reaction of the water. Is this water a corrosive hazard at the boiler operating temperature?
2. The concentration of hydroxide ions OH^- in water is 10^{-5} mol/dm^3. Calculate the pOH and pH of this water, the content of H_3O^+ oxonium ions and determine the chemical reaction of this water.
3. In 200 cm^3 of an aqueous solution there are 0.0034 g of hydroxide ions OH^-. Calculate the pH of this solution and determine its chemical reaction.
   Answer: pH = 11, the solution is strongly alkaline.
4. Calculate the content of sodium hydroxide, NaOH and sodium carbonate Na_2CO_3 in mg/dm^3, if alkalinity $p = 4.0$ mval/dm^3, and alkalinity $m = 7.5$ mval/dm^3.
   Answer: the content of NaOH is 20.0 mg/dm^3, Na_2CO_3 = 371.0 mg/dm^3.
5. Calculate the content of sodium bicarbonate $NaHCO_3$ and sodium carbonate Na_2CO_3 in the water in mg/dm^3, if the alkalinity of the water is $p = 2.0$ mval/dm^3, and the alkalinity $m = 6.0$ mval/dm^3.
   Answer: $NaHCO_3$ = 168 mg/dm^3, and Na_2CO_3 = 212 mg/dm^3.
6. The water alkalinity is $m = 400$ mg/dm^3 $CaCO_3$, and the total hardness is 11.2 °dH. Calculate the content of $NaHCO_3$ in mg/dm^3.
   Answer: 336 mg/dm^3 $NaHCO_3$.

Questions

1. Define the concept of pH and state its ranges.
2. What are the methods of measuring pH and which of these methods are used on board ships.
3. Why is the pure (untreated) distillate not fed to steam boilers?
4. What should be the pH of the boiler water at the boiler operating temperature and at room temperature?
5. What is the influence of water pH on its corrosive aggressiveness and tendency to foaming?
6. Explain why sodium carbonate Na_2CO_3 and sodium phosphate Na_3PO_4 make water alkaline? Justify your answer on the basis of appropriate chemical reactions.
7. Can the *p* alkalinity be greater than the *m* water alkalinity? Justify your answer.
8. Write the equations of chemical reactions occurring during the determination of water alkalinity, when alkalinity $p = 0$ and alkalinity $m > 0$.
9. What remedial action should be taken if the alkalinity of the boiler water exceeds the permissible values for the steam boiler concerned?

Auxiliary tables

Table 3

Quantities of basic compounds in mg/dm^3 equivalent to alkalinity units

Salt name	Chemical formula	Alkalinity to phenolphthalein		Alkalinity to methyl orange	
		p = 1	°dH = 1	m = 1	°dH = 1
Sodium hydroxide	NaOH	40	14.3	40	14.30
Sodium carbonate	Na_2CO_3	106	37.8	53	18.90
Calcium carbonate	$CaCO_3$	100	35.7	50	18.85
Calcium bicarbonate	$Ca(HCO_3)_2$	162	57.8	81	28.90
Magnesium bicarbonate	$Mg(HCO_3)_2$	146	52.2	73	26.10
Trisodium phosphate anhydrous	Na_3PO_4	164	58.6	82	29.30
Hydrated trisodium phosphate	$Na_3PO_4 \cdot 12H_2O$	380	135.8	190	67.90
Phosphoric acid anhydride	P_2O_5	71	25.4	35.5	12.70
Phosphate ion	PO_4^{3-}	95	34.0	49.5	17.00

Calculation example:

As a result of titration of 100 cm^3 of water with 0.10M hydrochloric acid solution, the values $\boldsymbol{p = 3}$ i $\boldsymbol{m = 4.5}$ were obtained.

Assuming that the tested water is free of phosphates, calculate the equivalent levels of sodium hydroxide and sodium carbonate to this alkalinity.

Since the value $p > \frac{m}{2}$ the alkalinity caused by the presence of hydroxides will be as shown in Table 4 (overleaf) $2p - m = 2 \cdot 3 - 4.5 = 1.5$, which corresponds to the content $1.5 \cdot 40 = 60$ mg NaOH/dm^3, the alkalinity caused by the presence of carbonates will be: $2(m - p) = 2(4.5 - 3) = 3$, what the content corresponds to $3 \cdot 53 = 159$ mg Na_2CO_3/dm^3. The correctness of the obtained result can be easily checked using table 4.

The content of 60 mg NaOH/dm^3 corresponds to the values	$p = 1.5\ i\ m = 1.5$
The content of 159 mg Na_2CO_3/dm^3 corresponds to the values	$p = 1.5\ i\ m = 3.0$
so, in total:	$p = 3.0\ i\ m = 4.5$

Table 4

Approximate contents of hydroxides, carbonates and bicarbonates for different values of p and m alkalinity

Group of chemical compounds	The name of the chemical or ion	Chemical formula	Content equivalent to the unit of alkalinity p or m [mg/dm^3]	Alkalinity value p and m				
				For $p = 0$	For $p < \frac{m}{2}$	For $p = \frac{m}{2}$	For $p > \frac{m}{2}$	For $p = m$
Hydroxides	Hydroxide ion	OH^-	17	0	0	0	$2p - m$	m
	Calcium hydroxide	$Ca(OH)_2$	37					
	Magnesium hydroxide	$Mg(OH)_2$	29					
	Sodium hydroxide	NaOH	40					
Carbonates	Carbonate ion	CO_3^{2-}	30	0	$2p$	m	$2(m - p)$	0
	Calcium carbonate	$CaCO_3$	50					
	Magnesium carbonate	$MgCO_3$	42					
	Sodium carbonate	Na_2CO_3	53					
Bicarbonate	Bicarbonate ion	HCO_3^-	61	m^*	$m - 2p$	0	0	0
	Calcium bicarbonate	$Ca(HCO_3)_2$	81					
	Magnesium bicarbonate	$Mg(HCO_3)_2$	73					
	Sodium bicarbonate	$NaHCO_3$	84					

[*] If m <0.05 the water is devoid of bicarbonate (distilled water).

Table 5

Physicochemical values of water for VL 512 / 10-01
boilers recommended by the manufacturer

Physicochemical quantities	Type of water			
	Condensate	Distillate	Feed water	Boiler water
Content of Cl^- in ppm	≤	12 + 24	x	≤ 1200
General hardness in °dH	x	≤ 0.084	≤ 0.84	< 0.56
Alkalinity p in ppm	x	x	x	150 + 200
Content of PO_4^{3-} in ppm	x	x	x	2 + 5
Exponent of the concentration of oxonium ions pH	x	x	6.5 + 9.5[xx]	x
Oil content in ppm	x	0	< 3	traces
Total salt content in ppm	x	x	x	≤ 3000

[x] Not included in the standard.

[xx] At a temperature of approx 20°C.

Table 6

Acceptable ranges of physicochemical values for
"Unitor" boilers operating at various pressures

Vapour pressure in the boiler	Alkalinity		Ions			$N_2H_4 \cdot 10^{-1}$	pH
	p	m	Cl^-	PO_4^{3-}	SO_4^{2-}		
MPa	ppm	ppm	ppm	ppm	ppm	ppm	
0 – 1.75	100 – 150	2p	200	20 – 50	20 – 50	1 – 2	8.3 – 9
1.75 – 3.1	100 – 150	2p	200	20 – 50	20 – 50	1 – 2	8.3 – 9
3.1 – 4.2	100 – 150	2p	200	20 – 50	20 – 50	1 – 2	8.3 – 9
4.2 – 6.0	100 – 120	2p	50	15 – 30	x	1 – 1.5	8.3 – 9
6.0 – 8.0	–	–	30	10 – 25	x	0.5 – 1	8.3 – 9

[x] Not included in the standard.

Table 7

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	aver.	accep.	aver.	accep.	aver.	accep.
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				
Conductivity μScm^{-1}	–					
Boiler water						
Alkalinity of *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
Conductivity μScm^{-1}	7000	9000	4000	6000	2000	3000

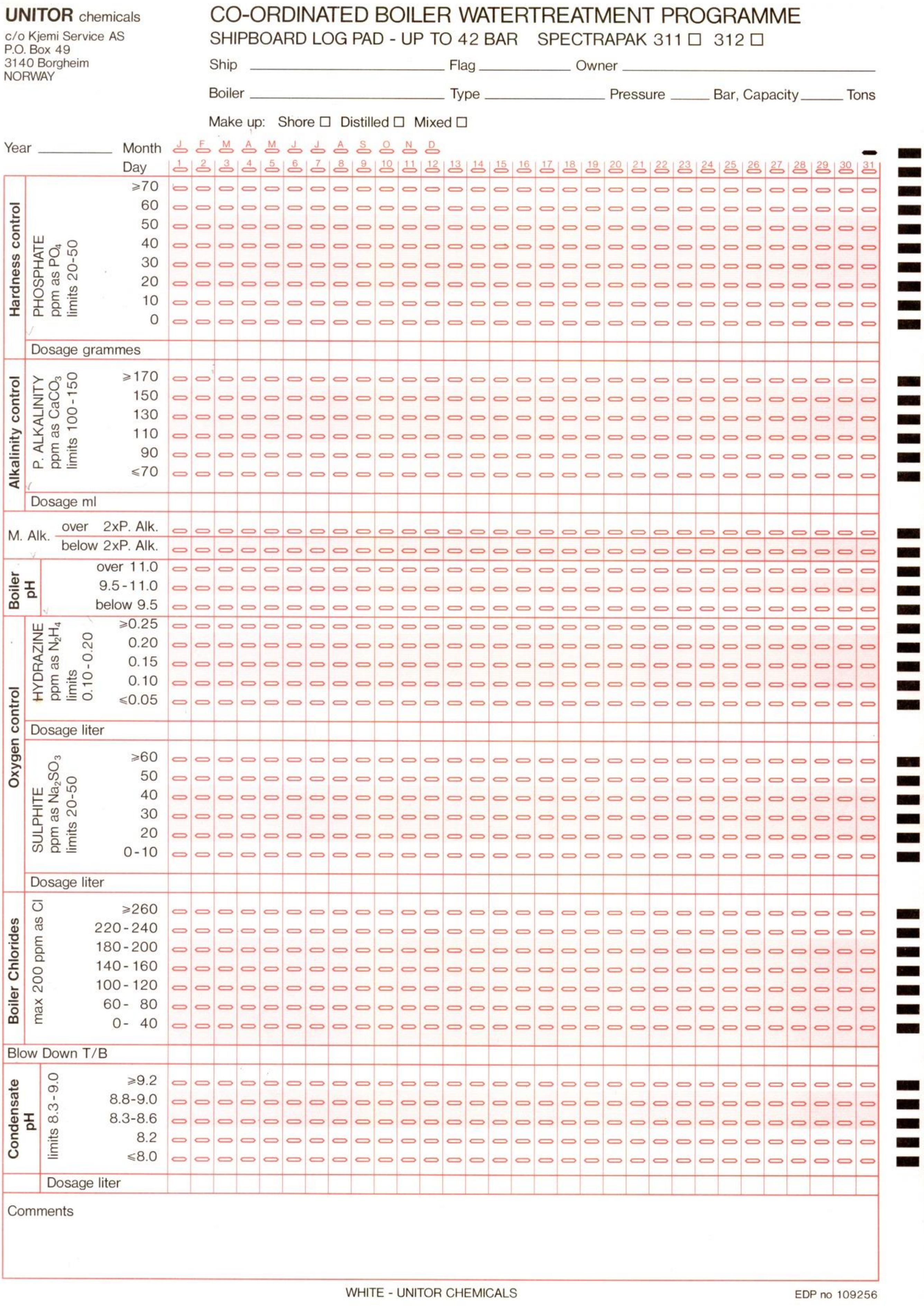
Table 8

The amounts of boiler water preparations used, recommended by Unitor

Name of the preparation	Alkalinity *p* ppm $CaCO_3$						
	0	50	100	150	200	225	300
Combitreat kg/1000 dm^3	0.4	0.3	0.2	0.1	0	0	0
Liquitreat kg/1000 dm^3	2.4	1.8	1.2	0.6	0	0	0

Appendix 2

Unitor boiler water analytical control report form



UNITOR chemicals
c/o Kjemi Service AS
P.O. Box 49
3140 Borgheim
NORWAY

CO-ORDINATED BOILER WATERTREATMENT PROGRAMME

SHIPBOARD LOG PAD - UP TO 42 BAR SPECTRAPAK 311 ☐ 312 ☐

Ship ____________ Flag ____________ Owner ____________

Boiler ____________ Type ____________ Pressure ______ Bar, Capacity ______ Tons

Make up: Shore ☐ Distilled ☐ Mixed ☐

Year ____________ Month J F M A M J J A S O N D

		Day	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31
Hardness control	PHOSPHATE ppm as PO_4 limits 20-50	≥70																															
		60																															
		50																															
		40																															
		30																															
		20																															
		10																															
		0																															
	Dosage grammes																																
Alkalinity control	P. ALKALINITY ppm as $CaCO_3$ limits 100-150	≥170																															
		150																															
		130																															
		110																															
		90																															
		≤70																															
	Dosage ml																																
M. Alk.		over 2xP. Alk.																															
		below 2xP. Alk.																															
Boiler pH		over 11.0																															
		9.5-11.0																															
		below 9.5																															
Oxygen control	HYDRAZINE ppm as N_2H_4 limits 0.10-0.20	≥0.25																															
		0.20																															
		0.15																															
		0.10																															
		≤0.05																															
	Dosage liter																																
	SULPHITE ppm as Na_2SO_3 limits 20-50	≥60																															
		50																															
		40																															
		30																															
		20																															
		0-10																															
	Dosage liter																																
Boiler Chlorides	max 200 ppm as Cl	≥260																															
		220-240																															
		180-200																															
		140-160																															
		100-120																															
		60- 80																															
		0- 40																															
Blow Down T/B																																	
Condensate pH	limits 8.3-9.0	≥9.2																															
		8.8-9.0																															
		8.3-8.6																															
		8.2																															
		≤8.0																															
	Dosage liter																																

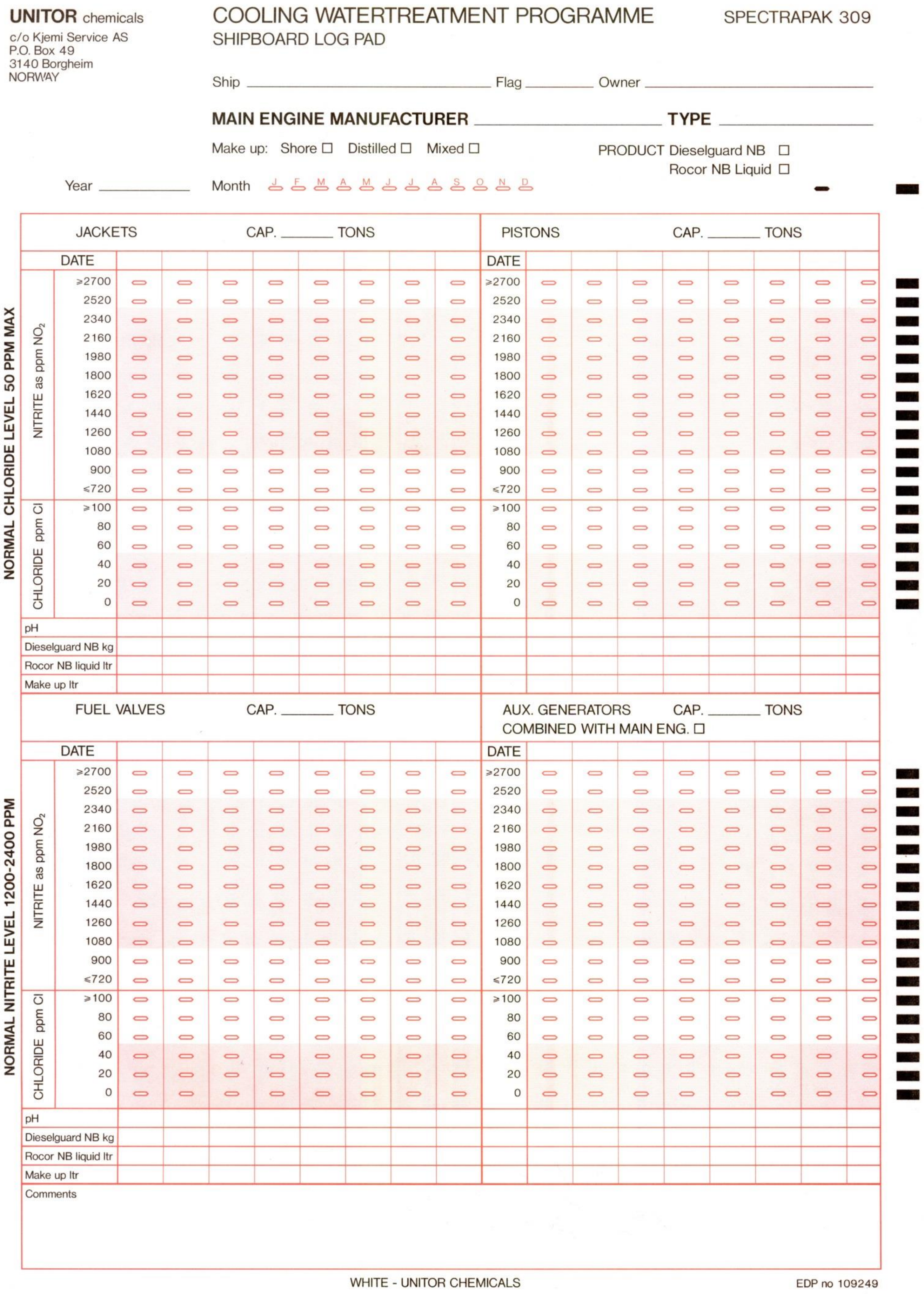
Comments

WHITE - UNITOR CHEMICALS

EDP no 109256

Appendix 3

Unitor cooling water analytical control report form



UNITOR chemicals
c/o Kjemi Service AS
P.O. Box 49
3140 Borgheim
NORWAY

COOLING WATERTREATMENT PROGRAMME

SHIPBOARD LOG PAD

SPECTRAPAK 309

Ship ______________________ Flag ________ Owner ______________________

MAIN ENGINE MANUFACTURER ______________________ **TYPE** ______________

Make up: Shore ☐ Distilled ☐ Mixed ☐

PRODUCT Dieselguard NB ☐
Rocor NB Liquid ☐

Year __________ Month J ○ F ○ M ○ A ○ M ○ J ○ J ○ A ○ S ○ O ○ N ○ D ○

NORMAL CHLORIDE LEVEL 50 PPM MAX

JACKETS CAP. _______ TONS

DATE									
NITRITE as ppm NO_2	≥2700	○	○	○	○	○	○	○	○
	2520	○	○	○	○	○	○	○	○
	2340	○	○	○	○	○	○	○	○
	2160	○	○	○	○	○	○	○	○
	1980	○	○	○	○	○	○	○	○
	1800	○	○	○	○	○	○	○	○
	1620	○	○	○	○	○	○	○	○
	1440	○	○	○	○	○	○	○	○
	1260	○	○	○	○	○	○	○	○
	1080	○	○	○	○	○	○	○	○
	900	○	○	○	○	○	○	○	○
	≤720	○	○	○	○	○	○	○	○
CHLORIDE ppm Cl	≥100	○	○	○	○	○	○	○	○
	80	○	○	○	○	○	○	○	○
	60	○	○	○	○	○	○	○	○
	40	○	○	○	○	○	○	○	○
	20	○	○	○	○	○	○	○	○
	0	○	○	○	○	○	○	○	○
pH									
Dieselguard NB kg									
Rocor NB liquid ltr									
Make up ltr									

PISTONS CAP. _______ TONS

DATE								
≥2700	○	○	○	○	○	○	○	○
2520	○	○	○	○	○	○	○	○
2340	○	○	○	○	○	○	○	○
2160	○	○	○	○	○	○	○	○
1980	○	○	○	○	○	○	○	○
1800	○	○	○	○	○	○	○	○
1620	○	○	○	○	○	○	○	○
1440	○	○	○	○	○	○	○	○
1260	○	○	○	○	○	○	○	○
1080	○	○	○	○	○	○	○	○
900	○	○	○	○	○	○	○	○
≤720	○	○	○	○	○	○	○	○
≥100	○	○	○	○	○	○	○	○
80	○	○	○	○	○	○	○	○
60	○	○	○	○	○	○	○	○
40	○	○	○	○	○	○	○	○
20	○	○	○	○	○	○	○	○
0	○	○	○	○	○	○	○	○

NORMAL NITRITE LEVEL 1200-2400 PPM

FUEL VALVES CAP. _______ TONS

DATE									
NITRITE as ppm NO_2	≥2700	○	○	○	○	○	○	○	○
	2520	○	○	○	○	○	○	○	○
	2340	○	○	○	○	○	○	○	○
	2160	○	○	○	○	○	○	○	○
	1980	○	○	○	○	○	○	○	○
	1800	○	○	○	○	○	○	○	○
	1620	○	○	○	○	○	○	○	○
	1440	○	○	○	○	○	○	○	○
	1260	○	○	○	○	○	○	○	○
	1080	○	○	○	○	○	○	○	○
	900	○	○	○	○	○	○	○	○
	≤720	○	○	○	○	○	○	○	○
CHLORIDE ppm Cl	≥100	○	○	○	○	○	○	○	○
	80	○	○	○	○	○	○	○	○
	60	○	○	○	○	○	○	○	○
	40	○	○	○	○	○	○	○	○
	20	○	○	○	○	○	○	○	○
	0	○	○	○	○	○	○	○	○
pH									
Dieselguard NB kg									
Rocor NB liquid ltr									
Make up ltr									

AUX. GENERATORS CAP. _______ TONS
COMBINED WITH MAIN ENG. ☐

DATE								
≥2700	○	○	○	○	○	○	○	○
2520	○	○	○	○	○	○	○	○
2340	○	○	○	○	○	○	○	○
2160	○	○	○	○	○	○	○	○
1980	○	○	○	○	○	○	○	○
1800	○	○	○	○	○	○	○	○
1620	○	○	○	○	○	○	○	○
1440	○	○	○	○	○	○	○	○
1260	○	○	○	○	○	○	○	○
1080	○	○	○	○	○	○	○	○
900	○	○	○	○	○	○	○	○
≤720	○	○	○	○	○	○	○	○
≥100	○	○	○	○	○	○	○	○
80	○	○	○	○	○	○	○	○
60	○	○	○	○	○	○	○	○
40	○	○	○	○	○	○	○	○
20	○	○	○	○	○	○	○	○
0	○	○	○	○	○	○	○	○

Comments

WHITE - UNITOR CHEMICALS

EDP no 109249