Institute of Mathematics, Physics and Chemistry

Department of Chemistry

Water chemistry laboratory

Laboratory exercise

Determination of corrosion inhibitors: phosphates, sulphites and hydrazine

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EXERCISE SHEET

1	**Relation to subjects:** 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 – Determination of selected indicators of technical water quality;
	DiRMiUO/26 Chemistry of water, fuels and lubricants	EKP3 K_U014, K_U015, K_U016.	SEKP6 – Determination of selected indicators of technical water quality;
	EOUNiE/26 Chemistry of water, fuels and lubricants	EKP3 K_U014, K_U015, K_U016.	SEKP6 – Determination of selected indicators of technical water quality;
2	**Purpose of the exercise:** teaching the student how to independently perform determinations in boiler or cooling water of corrosion inhibitors and assess the corrosive hazards of technical water on ships;		
3	**Prerequisites:** the student is trained in the occupational health and safety regulations on a laboratory workplace, which he states with his own signature on the appropriate form, knows – quantitative methods for the determination of phosphates, sulphites and hydrazine in water, knows the types and mechanisms of corrosion, the most important factors of intra-boiler corrosion and methods their elimination, types and mechanisms of action of corrosion inhibitors suitable for water systems in ships;		
4	**Description of the laboratory workplace:** KH_2PO_4 standard solution, a set of Nessler cylinders for the preparation of color standards with different content of PO_4^{3-} ions, reaction indicators, a typical laboratory kit for iodometric analysis, buffering solution, hydrazine hydrate standard solution, a set of Nessler cylinders for the preparation of colour standards with different hydrazine content, reaction indicator for the determination of hydrazine, a sample of tested water;		
5	**Risk assessment *:** contact with a diluted solution of hydrazine hydrate – very low probability of harmful effects of hydrazine. Final assessment – **VERY SMALL THREAT** **Safety measures required:** a. lab coats, b. health and safety cleaning products, paper towels;		
6	**The course of the exercise:** a. Read the workplace manual (appendix 1) and familiarize with the laboratory kit for the exercise, b. Determine the content of PO_4^{3-} phosphate ions, sulphates (IV) and hydrazine in the tested water;		
7	**Exercise report:** a. Develop the exercise in accordance with the instructions contained in the workplace manual (appendix 1),		

	b. On the basis of the obtained results of the determination of the content of phosphate ions PO_4^{3-}, sulphates (IV) and hydrazine, determine the quality and operational suitability of the tested water by comparing the determined parameters with their permissible values, c. If necessary, suggest any corrective action, d. Solve the given task and/or answer the questions included in the set of tasks and questions to be completed by the student;
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 determined operational parameters of the tested boiler or cooling water, i.e. the content and dosage of corrosion inhibitors to water systems on ships, the chemistry of their operation, does not know the effects of an overdose of inhibitors; mark 3.0 – has basic chemical and operational knowledge concerning the determined functional parameters of the tested boiler or cooling water and the ability to make basic chemical calculations and solve simple tasks in the field of application, dosage and mechanism of action of corrosion inhibitors; mark 3.5 – 4.0 – has extended chemical and operational knowledge in the field of the determined functional 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 corrosion inhibitors; mark 4.5 – 5.0 – has the ability to apply complex chemical and operational knowledge to partial assessment of the quality and operational suitability of the tested water due to the content and type of corrosion inhibitors and the ability to make corrective and repair decisions on this basis. b. EKP3 – control works: mark 2.0 – does not have the ability to analyse 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 inhibitorów korozji: fosforanów(V), siarczanów(IV) i hydrazyny”, 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 content of phosphates (V), sulphates (IV) and hydrazine in the boiler or cooling water.

2. THEORETICAL INTRODUCTION TO THE EXERCISE

The most popular method of protecting metals and structural alloys against corrosion is the use of substances that inhibit or completely stop this process. Such substances are called corrosion inhibitors. The mechanism of the protective effect of inhibitors is varied and is not fully understood due to the lack of a uniform view explaining their action. They are generally divided into: cathode, anode and mixed. Cathode inhibitors inhibit the cathode reaction (oxygen or hydrogen depolarization), and anodic inhibitors inhibit the transfer of metal from the crystal lattice to the electrolyte into the ionic state, while mixed inhibitors inhibit simultaneously cathode and anode reactions.

Due to the conditions and mechanism of action, corrosion inhibitors can also be divided into those acting on the metal surface or reducing the aggressiveness of the corrosive environment. These properties often occur together with the advantage of one of them. The first group includes, for example, chromates that passivate the metal surface by creating a protective film. The second group includes, for example, sulphites or hydrazine, which bind chemically dissolved oxygen in water.

Passivating inhibitors are widely used in the protection of metals working in conditions of permanent immersion in water. They create a protective layer on the metal that prevents further corrosion. Its composition varies depending on the inhibitor used (it may contain metal oxides or derivatives of the inhibitor used). The chemistry of these inhibitors is based on the redox reaction between strong oxidizing agents (nitrites, nitrates, chromates, dichromates) and reducing agents, i.e. metal atoms contained in the structure of the water system. Metals oxidize to oxides, hydroxides, often hydrated, reach electrode potentials shifted towards positive values.

Anodic passivating inhibitors are then effective if they are used in a quantity that ensures that the entire surface of the metal is covered with a passive protective film.

Also, the presence of depassivators (especially chlorides) counteracts the protective ability of the above-mentioned layers.

Inhibitors can also be divided into inorganic and organic inhibitors. In neutral and alkaline environments, inorganic compounds are inhibitors of both cathodic and anodic corrosion. However, they do not show any protective effect in an acidic environment during corrosion with hydrogen depolarization. Organic inhibitors are used in an acidic environment. The mechanism of their action is adsorptive. They are adsorbed on the cathode points of the metal undergoing corrosion in the corrosive cell, inhibiting the hydrogen ion discharge process, and thus stop the metal dissolution process. The oxidized surface of the metal or the corrosion product does not adsorb the colloidal particles of the organic inhibitor and therefore they are not protected against digestion in an acidic environment. Therefore, organic inhibitors are commonly used, for example, in acid cleaning of metal covered with rust, scale or limescale. Scale or rust dissolve in the acid without damaging the clean metal surfaces, which are protected by adsorbed organic inhibitor molecules (e.g. urotropine, gelatine, benzoic acid, quinoline and others).

The effectiveness of corrosion inhibitors used in water systems depends mainly on:

- the type and dose of inhibitor;
- pH, composition, temperature and water aggressiveness;
- the presence of corrosion stimulants (e.g. Cl^-);
- operating temperature and pressure of the steam boiler and its design;
- the presence of metal contact with the phase separation boundary and corrosive micro-cells.

The conditions and scope of application of corrosion inhibitors are provided by the manufacturers of these substances.

Figure 1 below shows a diagram of the classification of corrosion inhibitors used in water systems:

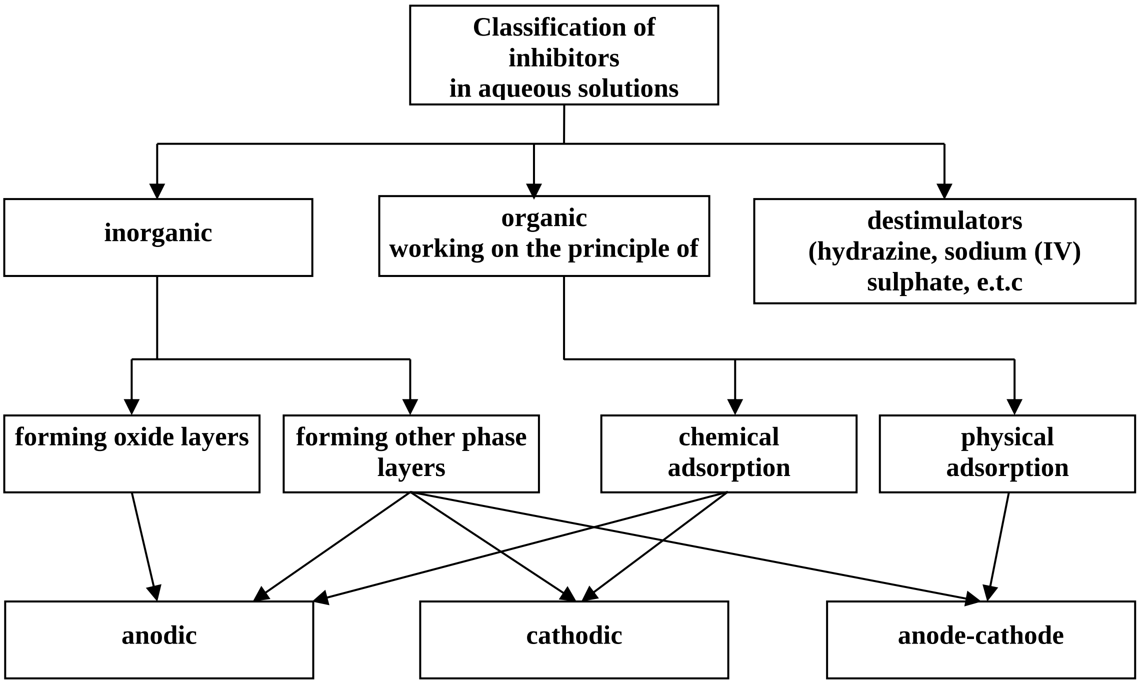


Fig. 1. Classification of corrosion inhibitors to water systems

2.1. Phosphates

Phosphates are often components of the proprietary preparations used to soften water in ships by chemical precipitation of calcium and magnesium ions, giving the water hardness, on sparingly soluble calcium and magnesium orthophosphate deposits ($Ca_3(PO_4)_2$ and $Mg_3(PO_4)_2$). They also act as coating corrosion inhibitors, classified as anodic inhibitors with oxidizing properties (e.g. Na_3PO_4, Na_2HPO_4). Their operation is mainly based on passivation of the surface of the protected metal, sealing this surface and preventing, in particular, corrosion cracking of the metal and the formation of limescale. These inhibitors work most effectively in neutral and alkaline environments, producing sparingly soluble oxide coatings.

2.2. Sulphites

Oxygen dissolved in water is a dangerous factor of internal boiler corrosion due to the role of a depolarizer in the electrochemical corrosion process. The effect of this gas is manifested by the formation of local corrosion micro-cells on the metal surface, as a result of which voids are formed under the local iron oxide (rust) clusters, which, deepening, may cause perforation of the metal wall. Even a small amount of oxygen in the water can cause this dangerous process, the intensity of which increases with increasing temperature and pressure in the boiler. A prerequisite for preventing this corrosion is the removal of dissolved oxygen from the feed water.

For the chemical deoxidation of water in low-pressure boilers, an inhibitor is used, among others, sodium sulphiteNa_2SO_3. It chemically binds dissolved oxygen in water according to the following reaction:

$$2Na_2SO_3 + O_2 \rightarrow 2Na_2SO_4$$

Overdosing of sodium sulphite under conditions of elevated pressure and intense heat load may lead to its decomposition according to the following reactions:

$$4Na_2SO_3 \rightarrow Na_2S + 3Na_2SO_4$$
$$Na_2SO_3 + H_2O \rightarrow 2NaOH + SO_2$$

According to some authors, the product of this decomposition may also be hydrogen sulphide H_2S with poisonous and highly corrosive properties.

2.3. Hydrazine

For the chemical deoxidation of the feed water to modern diesel boilers, N_2H_4 hydrazine is used, which binds dissolved oxygen in the water according to the following reaction:

$$N_2H_4 + O_2 \rightarrow N_2 + 2H_2O$$

The formed nitrogen evaporates with the water vapour 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 $N_2H_4 \cdot H_2O$ 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 it is recommended for chemical deoxidation also hydrazine sulphate $N_2H_4 \cdot H_2SO_4$.

Hydrazine chemically binds oxygen the fastest at temperatures higher than 80ºC. 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. With a large excess, hydrazine breaks down, resulting in one of the products being NH_3 ammonia, which is formed according to the following reactions:

$$2N_2H_4 \rightarrow 2NH_3 + N_2 + H_2$$
$$3N_2H_4 \rightarrow 4NH_3 + N_2$$

The ammonia formed by the above reactions alkalizes the circulating water to give NH_4OH and binds CO_2 if present in the water, according to the equations:

$$NH_3 + H_2O \rightarrow NH_4OH$$
$$NH_4OH + CO_2 \rightarrow NH_4HCO_3$$
$$2NH_4OH + CO_2 \rightarrow (NH_4)_2CO_3 + H_2O$$

Neutral ammonium carbonate $(NH_4)_2CO_3$ is formed at a water pH above 9.5.

The use of hydrazine as an inhibitor of internal boiler oxygen corrosion is beneficial for this reason, because water deoxidation in optimal conditions is very quick and effective, without additional increase in water salinity. With the use of hydrazine, it is possible to reduce the oxygen content in water within the range of 0.01 – 0.005 mg O_2/dm^3. However, the excess of hydrazine used should not be greater than it is necessary, for example, to remove CO_2 dissolved in water, because the excess ammonia formed then in the presence of oxygen may cause corrosion of copper or copper alloys (brass, bronze). For this reason, the excess hydrazine in the boiler water should be in the range 0.1 – 0.2 ppm.

3. PERFORMING THE EXERCISE

Fig. 2 shows a laboratory workplace for testing the phosphate content in boiler water.

Fig. 2. Laboratory workplace for phosphate determination

3.1. Determination of phosphates

Phosphates are used in water to removal of corrosion and to prevent precipitation of certain compounds, e.g. iron or calcium, in the form of complex compounds. The amounts of phosphates added for this purpose range from 0.25 – 1.0 mg/dm^3 PO_4^{3-}. Their protective effect is to seal the metal surface from the water side. Phosphates and polyphosphates show good corrosion inhibiting properties also in the presence of chloride ions, however, they show slightly worse protective properties at elevated temperatures.

All forms of phosphorus present in water are determined in the form of orthophosphates.

For the determination of phosphates in water, the colorimetric method with ammonium molybdate and tin (II) chloride as a reducing agent is most often used.

The principle of determination is based on the formation of yellow-coloured phosphoromolybdic acid $H_7(P)MoO_2(O_4)_6$ in an acid solution, which is reduced by tin (II) chloride, forming a complex compound (molybdenum blue) with an intense blue colour. The colour intensity is proportional to the phosphate content. It is defined visually or spectrophotometrically. The minimum determined concentration is about 0.01 mg/dm^3 PO_4^{3-} .

3.1.1. Performing the determination

Preparation of the scale of unstable reference samples

To 11 Nessler cylinders with a capacity of 100 cm^3 measure in each successively: 0; 0.5; 1.0; 1.5; 2.0; 2.5; 3.0; 4.0; 5.0; 6.0 and 7.0 cm^3 of potassium dihydrogen phosphate KH_2PO_4 solution (1 cm^3 of this solution contains 0.01 mg of PO_4^{3-}), which corresponds to the following contents: 0; 0.005; 0.01; 0.015; 0.02; 0.025; 0.03; 0.04; 0.05; 0.06; 0.07 mg of PO_4^{3-} in the individual prepared samples (see table 1). Then fill the cylinders with distilled water up to the mark. Add successively, stirring thoroughly each time – 2 cm^3 of ammonium molybdate solution and 0.5 cm^3 (8 drops) of tin (II) chloride solution (ready set of standards is shown in Fig. 3). The rate of formation of the blue complex and the intensity of its colour also depend on the temperature of the solution. An increase in temperature by 1°C causes an increase in colour intensity by 1%. Therefore, the temperature of the sample, reagents and standards should not differ by more than 2°C.

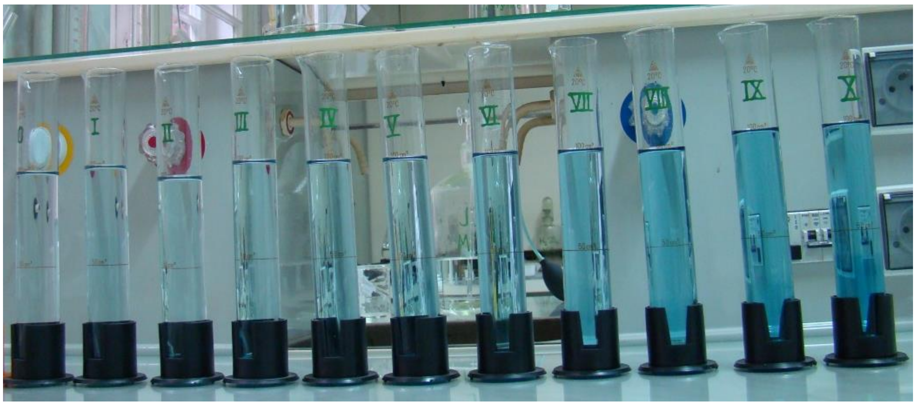


Fig. 3. Set of unstable reference samples

Performing the analysis

Measure 100 cm^3 of a clear, non-coloured sample of the water under test into the Nessler cylinder. Then add – while mixing thoroughly each time – 2 cm^3 of ammonium molybdate solution and 0.5 cm^3 (8 drops) of tin (II) chloride solution.

After 10 minutes, visually compare the colour of the test sample with the scale of the prepared samples (Fig. 4), which scale is presented in Table 1.

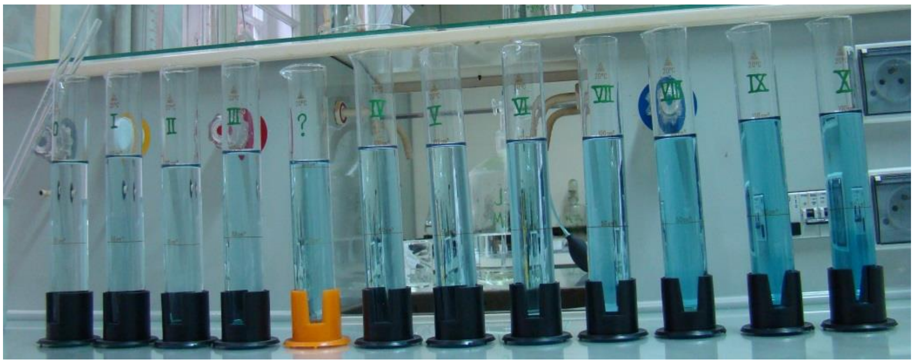


Fig. 4. Comparison of the tested water sample with the scale of unstable reference samples

Note:

If the colour of the tested sample is more intense than the sample with the highest concentration of PO_4^{3-} ions, then a smaller volume of the tested water should be taken for the determination, the sample should be supplemented with distillate to 100 cm^3 and then the solutions of ammonium molybdate and tin (II) chloride should be added as above.

Table 1

Scale of unstable standards for the determination of ions PO_4^{3-} ions

Nessler cylinder number with sample	**I**	**II**	**III**	**IV**	**V**	**VI**
Amount of working solution KH_2PO_4 [cm^3]	**0.0**	**0.5**	**1.0**	**1.5**	**2.0**	**2.5**
Content of PO_4^{3-} in the sample [mg]	**0.000**	**0.005**	**0.010**	**0.015**	**0.020**	**0.025**
Nessler cylinder number with sample	**VII**	**VIII**	**IX**	**X**	**XI**	
Amount of working solution KH_2PO4 [cm^3]	**3.0**	**4.0**	**5.0**	**6.0**	**7.0**	
Content of PO_4^{3-} in the sample [mg]	**0.030**	**0.040**	**0.050**	**0.060**	**0.070**	

Calculation of the results

Calculate the phosphate content according to the formula:

$$C_{PO_4^{3-}} = \frac{a \cdot 1000}{V} [\mathrm{mg\ PO_4^{3-}/dm^3}]$$

where:

a – the amount of phosphate read from the samples scale,
V – the volume of the water sample taken for the test, cm^3.

The determined PO_4^{3-} content should also be given in terms of P_2O_5.

Determine the phosphorus pentoxide C_{P2O5} content from the proportion:

PO_4^{3-}		P_2O_5
95	–	142
C_{PO43-}	–	C_{P2O5}

$$C_{P_2O_5} = \frac{Z_{PO_4^{3-}} \cdot 142}{95} [\mathrm{mg\ P_2}O_5\mathrm{/dm^3}]$$

which consequently comes down to the multiplication of the calculated content of phosphate ions PO_4^{3-} by the conversion factor 1.495.

Fig. 5 shows a laboratory stand workplace for testing the content of sulphites in water.

Fig. 5. Laboratory workplace for determination of sulphates (IV)

3.2. Determination of sulphites

Determination of sulphites consists in their oxidation in an acidic environment with a solution of iodine with a known concentration.

$$Na_2SO_3 + I_2 + H_2O \rightarrow H_2SO_4 + 2NaI$$

The excess iodine (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:

$$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$$

3.2.1. Performing the determination

Measure exactly 10.0 cm^3 of iodine solution and 5 cm^3 of acetic acid into the conical flask. Then pour 100 cm^3 of the tested water (Fig. 6) and quickly titrate with sodium thiosulphate solution until it turns straw-coloured (Fig. 7). Then add 1 cm^3 of the starch solution (Fig. 8) and titrate until the blue colour disappears (Fig. 9). Repeat the test three times.

Fig. 6. Sample after adding the tested water, ready for titration

Fig. 7. End of pre-titration – straw colour

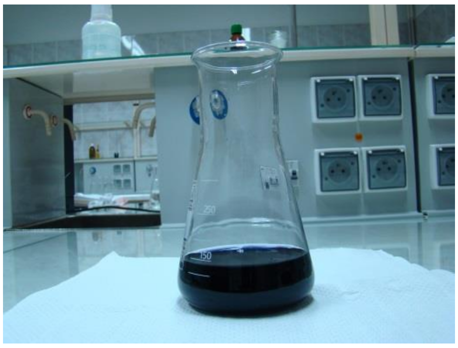


Fig. 8. Sample after adding starch solution

Fig. 9. Final titration effect

Calculation of the results

Calculate the sulphite content according to the formula:

$$C_{\mathrm{Na_2SO_3}} = \frac{(a-b)\cdot 1.575 \cdot 1000}{V}\ [\mathrm{mg\ Na_2SO_3/dm^3}]$$

where:

a – volume of 0.025 M iodine solution added, cm^3,

b – the average volume of 0.025 M sodium thiosulfate solution used for the titration of the samples, cm^3,

1.575 – conversion factor, sodium sulphate (IV) content corresponding to 1 cm^3 of 0.025 M thiosulphate solution, mg,

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

3.3. Determination of hydrazine

Determination is performed using the colorimetric method, in which hydrazine and its derivatives in an aqueous solution react in a slightly acidic environment (pH approx. 5) with phosphoromolybdic acid ($H_3PO_4 \cdot 12MoO_3 \cdot 24H_2O$). The reaction product is a heteroacid complex which is blue in colour. The intensity of this colour is proportional to the hydrazine content in a sample of the tested water.

3.3.1. Performing the determination

Preparation of the scale of unstable reference samples

Measure 10 cm^3 of the buffer solution into 8 Nessler cylinders with a capacity of 100 cm^3 and add successively: 0; 2.5; 5; 10; 20; 30; 40 and 50 cm^3 of the hydrazine hydrate working standard solution. Then add 5 cm^3 of phosphoromolybdic acid solution to each cylinder, fill with distilled water to 100 cm^3, mix and immerse the cylinders in a boiling water bath for 5 minutes. After cooling down, the samples are ready for use. They correspond to the following contents: 0; 0.025; 0.05; 0.10; 0.20; 0.30; 0.40; 0.50 mg of hydrazine hydrate in each standard (see table 2).

Performing the determination

Measure 50 cm^3 of the tested water into the Nessler cylinder. Then add 10 cm^3 of the buffer solution to it and continue in the same way as for the preparation of the samples. It is best to prepare a water sample for the determination simultaneously with the preparation of the samples scale. Compare the colour of the water sample with the samples scale in Table 2 and read the result.

Table 2

Scale of unstable samples for the determination of hydrazine

Nessler cylinder number with the sample	**0**	**I**	**II**	**III**	**IV**	**V**	**VI**	**VII**
Amount of working solution $N_2H_4 \cdot H_2O$ [cm^3]	**0.0**	**2.5**	**5.0**	**10**	**20**	**30**	**40**	**50**
Hydrazine content in the sample [mg]	**0.00**	**0.025**	**0.05**	**0.10**	**0.20**	**0.30**	**0.40**	**0.50**

Calculation of the results

Calculate the hydrazine $C_{N_2H_4}$ content in the tested water according to the formula:

$$C_{N_2H_4} = \frac{a \cdot 1000}{V} \, [\mathrm{mg\ N_2}H_4/\mathrm{dm}^3]$$

where:

a – the amount of hydrazine in the tested water sample determined by comparison with the samples scale, mg,

V – volume of the water sample used for the determination, cm^3.

4. DEVELOPMENT OF THE EXERCISE

1. Present the results of determinations in the tested water:
   a) of phosphate ions,
   b) of sulphites,
   c) of hydrazine;
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 3 shows the technical requirements of utility water in selected examples of steam boilers, and Annexes 2 and 3 of the analytical control form for boiler and cooling water along with their permissible operating parameters recommended by Unitor.

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. The oxygen content in the steam boiler feed water after its thermal degassing is 0.025 ppm. Calculate how much hydrazine should be used to chemically deoxygenate 10^3 kg of this water. Use the water density d = 1 g/cm^3 for calculations.
   Solution:

Hydrazine chemically binds oxygen according to the following reaction:

$$N_2H_4 \quad + \quad O_2 \quad \rightarrow \quad N_2 \quad + \quad 2H_2O$$

this reaction shows that 1 mole of hydrazine binds 1 mole of dissolved oxygen in water. The molar mass of hydrazine is the same as the molar mass of oxygen, 32 g/mol. If 1 kg of deoxidized water contains 0.025 mg of dissolved oxygen, then 10^3 kg of water contains 0.025 mg 1000 kg = 25 mg of oxygen.

In order to calculate the amount of hydrazine needed to bind 25 mg of oxygen, we compose the following proportion:

$$N_2H_4 \quad + \quad O_2 \quad \rightarrow \quad N_2 \quad + \quad 2H_2O$$

$$32 \quad - \quad 32$$

$$x \quad - \quad 25\ \text{mg}$$

$$x = \frac{32 \cdot 25}{32} = 25\ \text{mg}\ N_2H_4$$

Answer: to bind the oxygen contained in 10^3 kg of water, use 25 mg of hydrazine.

2. The sodium sulphite content in the boiler water should be kept at 50 ppm. Calculate how much this inhibitor needs to be added to $2 \cdot 10^3$ kg of water containing 0.05 ppm of dissolved oxygen to meet this condition. Use the water density d = 1 g/cm^3 for calculations.
   Solution:
   Sodium sulphite chemically binds oxygen according to the following reaction:

$$2Na_2SO_3 \quad + \quad O_2 \quad \rightarrow \quad 2Na_2SO_4$$

In order to calculate the amount of sodium sulphite needed to deoxygenate 1 kg of water, we use the following proportion:

$$2Na_2SO_3 \quad + \quad O_2 \quad \rightarrow \quad 2Na_2SO_4$$

$$252 \quad .....- \quad 32$$

$$x \quad - \quad 0.05\ \text{mg}$$

$$x = \frac{252 \cdot 0.05}{32} = 0.3938\ \text{mg}\ Na_2SO_3$$

for deoxidation of $2 \cdot 10^3$ kg of water you need to use $0.3938 \cdot 2\,000 = 787.5$ mg of Na_2SO_3.

In order to obtain the required excess of 50 ppm of Na_2SO_3 in water,

50 mg $\cdot$ 2 000 kg = 100 000 mg of this inhibitor should be added, so the total dose of Na_2SO_3 is 787.5 + 100 000 = 100 785.5 mg, i.e. 100.7855 g Na_2SO_3.

II. Tasks and questions to be completed by the student

Tasks

1. The oxygen content in the steam boiler feed water after its thermal degassing is 0.025 ppm. Calculate how much sodium sulphite should be used to chemically deoxygenate 10^3 kg of this water. Use the water density d = 1 g/cm^3 for calculations.
   Answer: 196.9 mg of Na_2SO_3.
2. The oxygen content in the steam boiler feed water after its thermal degassing is 0.05 ppm. Calculate how much $N_2H_4 \cdot H_2O$ hydrazine hydrate in grams should be used to chemically deoxygenate 10^3 kg of this water. Use the water density d = 1 g/cm^3 for calculations.
   Answer: 0.078 g of hydrazine hydrate.
3. The oxygen content in the steam boiler feed water after its thermal degassing is 0.05 ppm. Calculate how much hydrazine hydrate $N_2H_4 \cdot H_2O$ should be used so that after chemical deoxidation of 10^3 kg of this water, the excess of hydrazine would be 0.2 ppm. Use the water density d = 1 g/cm^3 for calculations.
   Answer: We should use 278.125 mg of hydrazine hydrate.

Questions

1. What are corrosion inhibitors and what is their division?
2. What factors influence the protective effect of corrosion inhibitors?
3. What is the action of anode, cathode and mixed inhibitors? Give examples.
4. What is the mechanism of action of metal passivators as corrosion inhibitors? When are they most effective?
5. What is the principle of the determination of phosphates and hydrazine in water by the comparative colorimetric method?
6. What can cause a large excess of phosphate, sulphite and hydrazine in the boiler water? Justify your answer with appropriate chemical reactions.
7. What is the effect of nitrites as corrosion inhibitors? Under what conditions does their operation give the best results, and when cannot they be used?
8. What is the optimal content of phosphates and hydrazine in the boiler water?
9. Why are sodium sulphite and hydrazine used as inhibitors of intra-boiler oxygen corrosion? Justify your answer with the appropriate equations of chemical reactions.

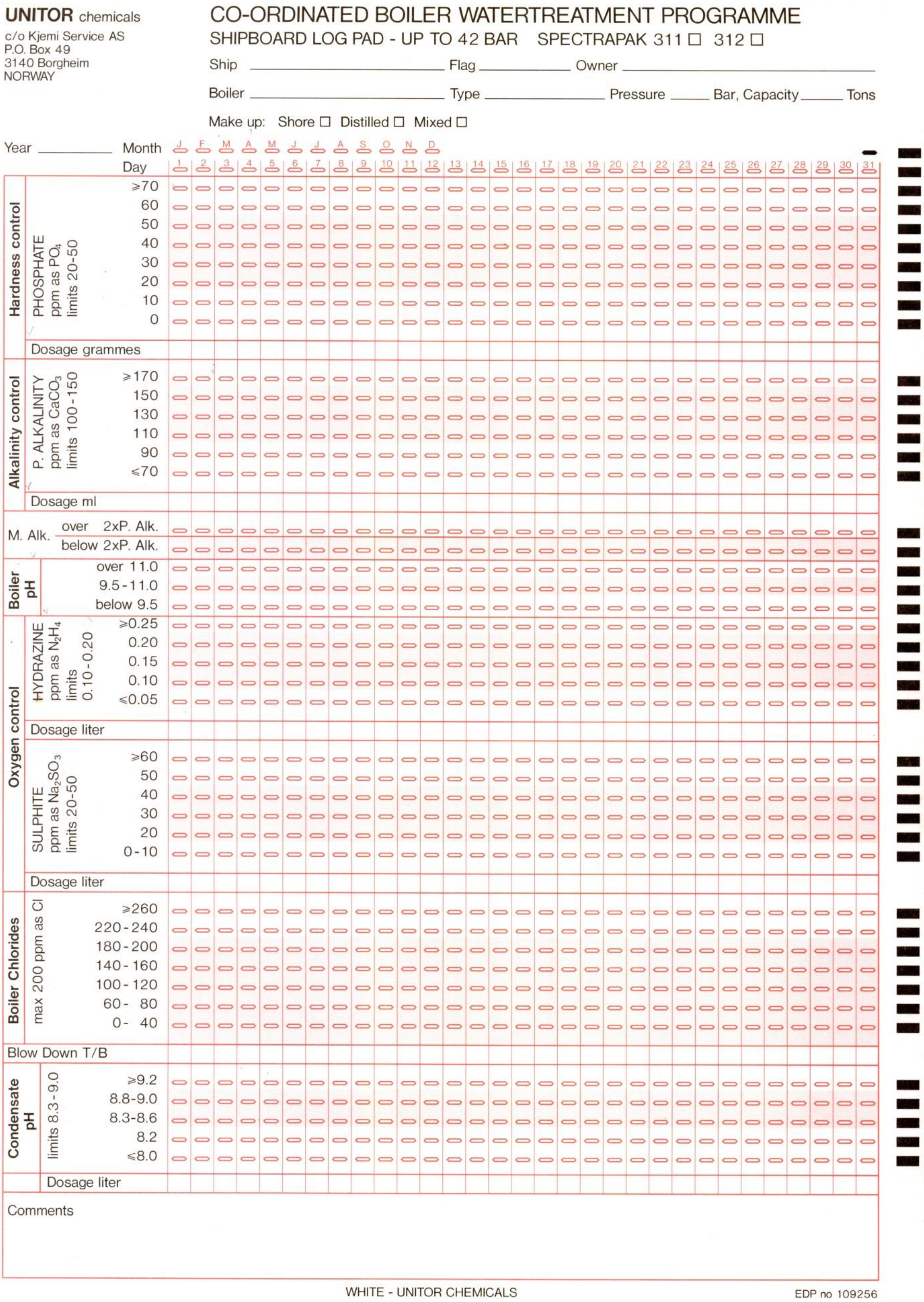
Auxiliary tables

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	
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	µS/cm	–					
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
Conductivity	µS/cm	7000	9000	4000	6000	2000	3000

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	

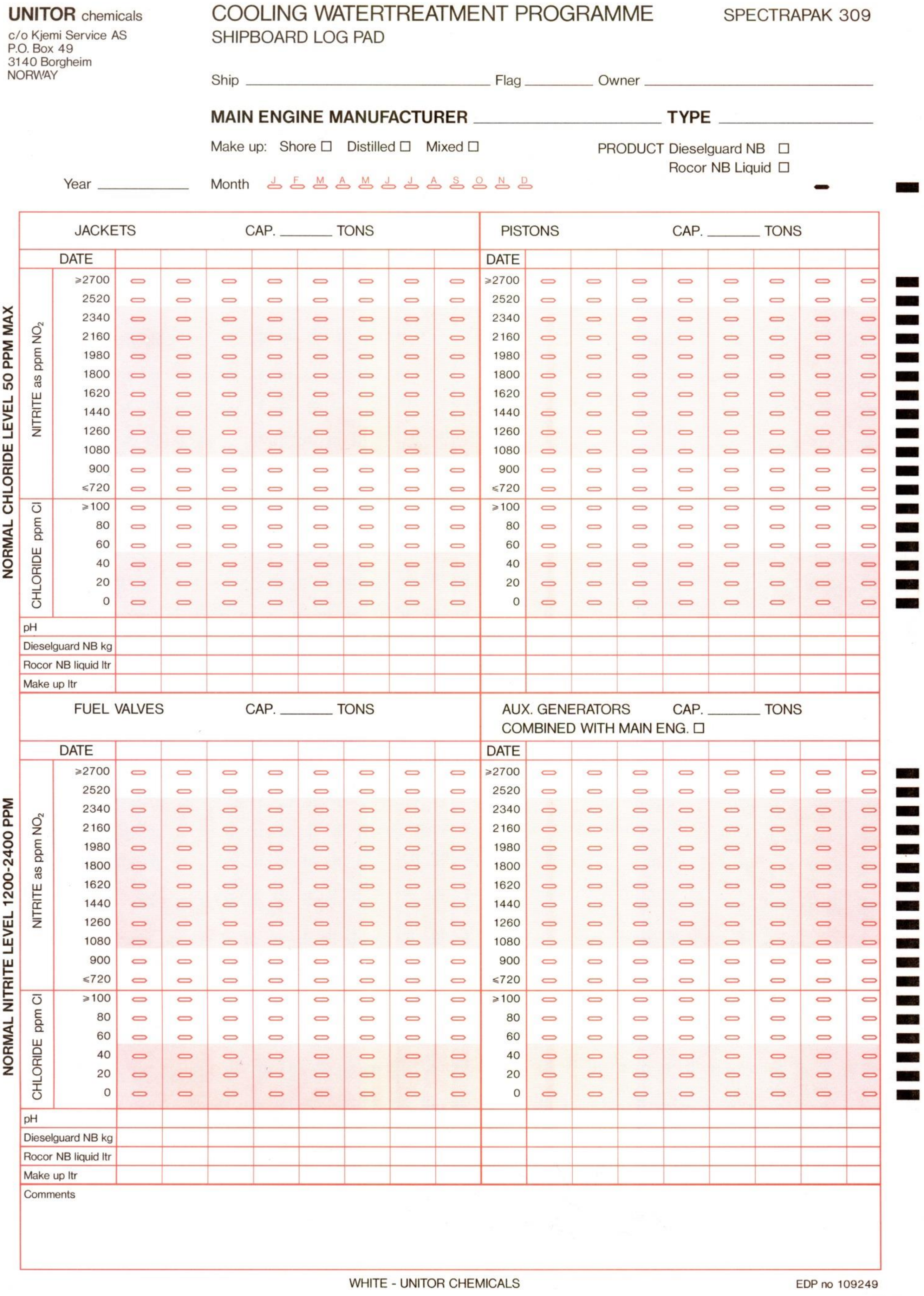
Comments

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