Institute of Mathematics, Physics and Chemistry

Department of Chemistry

Water chemistry laboratory

Laboratory exercise

Determination of total and calcium hardness

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

Szczecin 2023

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>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>
<tr><td>EOUNiE/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>2</td><td colspan="3">Purpose of the exercise:
teaching the student to independently perform the determination of the total, calcium and magnesium hardness of boiler or cooling water using the edetate method, learning the technical requirements for these parameters, operational significance;</td></tr>
<tr><td>3</td><td colspan="3">Prerequisites:
the student is trained in the occupational health and safety regulations on a laboratory stand, which he confirms with his signature on the appropriate form, knows – the edetate method for water hardness determination, types and units of hardness, methods and preparations for water treatment and softening on ships, as well as technical requirements and operational meaning marked parameters;</td></tr>
<tr><td>4</td><td colspan="3">Description of the laboratory workplace:
a typical laboratory kit for the analysis of titratable hardness by the edetate method, reaction indicators, pH buffering compounds, water samples;</td></tr>
<tr><td>5</td><td colspan="3">Risk assessment *:
contact with KOH tablets (1 – 3) – very low probability of chemical burn.
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. Determine the total and calcium hardness and calculate the magnesium hardness 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 (appendix 1),
b. Based on the results of determinations and calculations, determine the quality and operational suitability of the tested water by comparing the determined hardness parameters with their acceptable values for the selected type of boiler,
c. If necessary, suggest possible water treatment or appropriate 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;</td></tr>
<tr><td>8</td><td colspan="3">Archiving of research results:
Submit a written report on the performed exercise to the academic teacher.</td></tr>
</table>

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 regarding the determined operational parameters of the tested boiler or cooling water, i.e., hardness and types of hardness, softening methods and preparations used for this purpose on ships and the chemistry of their operation, does not know the harmful effects of sediments and limescale; mark 3.0 – has basic chemical and operational knowledge regarding 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 water hardness and softening; mark 3.5 – 4.0 – has extended chemical and operational knowledge in the field of determined utility parameters of the tested water and the ability to solve complex tasks in the field 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 its hardness and the ability to make diagnostic decisions on this basis, as well as corrective and remedial actions. 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 twardości ogolnej i wapniowej", 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. THE SCOPE OF THE EXERCISE

- getting acquainted with the workplace instructions for the exercise,
- determining the total and calcium hardness of the tested water using the edetate method and calculating the magnesium hardness on this basis,
- 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. Types and units of water hardness

Water hardness – it is a property caused by the presence of calcium, magnesium, iron, aluminium, manganese and heavy metal cations in the water. Since calcium and magnesium salts are present in the highest concentrations in natural waters, it is assumed that the hardness of the water comes mainly from them. Hence, magnesium calcium hardness is distinguished.

The hardness of natural water caused by calcium and magnesium carbonates, bicarbonates and hydroxides is referred to as carbonate hardness. There is also a difference between the so-called temporary hardness, which is caused by calcium and magnesium bicarbonates. On the other hand, chlorides, sulphates, nitrates, calcium and magnesium silicates are responsible for the non-carbonate hardness of water (the so-called constant). The sum of calcium and magnesium hardness, as well as the sum of carbonate and non-carbonate hardness is the total hardness of water, which is expressed by the following formulas:

$$H_{total} = H_{Ca} + H_{Mg}$$

where:

H_{Ca} – calcium hardness (caused by salts Ca^{2+}),
H_{Mg} – magnesium hardness (caused by salts Mg^{2+}),
H_{total} – total or general hardness,

and:

$$H_{total} = H_t + H_p$$

H_t – carbonate hardness (temporary hardness),
H_p – non-carbonate hardness (permanent hardness).

Water hardness can be expressed in different units. The basic ones are mmol/dm^3 and mval/dm^3 (milligramequivalent of hardness compounds in 1 dm^3 of water). However, in the literature on water treatment technology for industrial purposes, water hardness is most often expressed in terms of degrees of hardness (ºdH, German °n, French° F and English °A). In America, the hardness of water is given in ppm. In Poland, in addition to the basic units of water hardness compliant with the SI system, German degrees are used. The relationship between the units of water hardness mentioned is given in Table 1.

Table 1

Converting different units of water hardness

The unit of water hardness and its designation	ppm [mg $CaCO_3$ /dm^3]	[mmol /dm^3]	degree of hardness [ºdH]	German degree [ºn]	French degree [ºF]	English degree [ºA]	[mval/dm^3]
ppm [mg $CaCO_3$/dm^3]	1	0.01	0.056	0.056	0.1	0.07	0.02
[mmol/dm^3]	100	1	5.6	5.6	10	7.0	2.0
degree of hardness [ºdH]	17.86	0.18	1	1	1.79	1.25	0.36
German degree [ºn]	17.86	0.18	1	1	1.79	1.25	0.36
French degree [ºF]	10	0.10	0.56	0.56	1	0.70	0.20
English degree [ºA]	14.3	0.14	0.8	0.8	1.43	1	0.29
[mval/dm^3]	50	0.5	2.8	2.8	5	3.5	1

Instructions for using the conversion table of different units of water hardness

1. In the first column of the table, we are looking for the initial unit of water hardness (from which we convert), e.g. [mval/dm^3].
2. In the first row of the table, we are looking for the target water hardness unit (to which we want to convert), e.g. [mg $CaCO_3$/ dm^3].
3. The value of water hardness in units that we have at our disposal is multiplied by the coefficient in the table at the intersection of the row with the column for the converted hardness units, e.g., 50 when converting from [mval/dm^3] to [mg $CaCO_3$/dm^3].
4. The calculated value of the water hardness will be expressed in the units we require.
5. From table 2 – Scale of water hardness – we can read the degree of water hardness.

Example No. 1:

Initial water hardness H_{total} = 5.0 [mval/dm^3].
Target water hardness unit [mg $CaCO_3$/dm^3].
Convertor read from the table P = 50.
Calculated water hardness H_{total} = 250 [mg $CaCO_3$/dm^3].
Medium-hard water (according to table 2).

$$H_{total} = 5.0\ [mval/dm^3] \cdot 50 = 250\ [mg\ CaCO_3/dm^3]$$

Example No. 2:

Initial water hardness H_{total} = 2.5 [mmol/dm^3].
Target water hardness unit – German degree [ºn].
Convertor read from the table P = 5.6.
Calculated water hardness H_{total} = 14 [ºn].
Medium-hard water (according to table 2).

$$Ht_{otal} = 2.5\ [mmol/dm^3] \cdot 5.6 = 14\ [^{o}n]$$

The hardness of general-purpose water on a descriptive scale is given in Table 2.

Table 2

Water hardness scale

No.	Degree of hardness	Hardness unit			
		mg $CaCO_3/dm^3$; ppm	mmol/dm^3	dH; °n	mval/dm^3
1.	Very soft water	< 100	< 1	< 5.6	< 2
2.	Soft water	100 – 200	1 – 2	5.6 – 11.2	2 – 4
3.	Medium-hard water	200 – 350	2 – 3.5	11.2 – 19.6	4 – 7
4.	Hard water	350 – 550	3.5 – 5.5	19.6 – 30.8	7 – 11
5.	Very hard water	> 550	> 5.5	> 30.8	> 11

2.2. Methods of removing water hardness used in ships

The water for supplying marine boilers must be softened, i.e., free from some or all of the chemicals that cause hardness, i.e., mainly magnesium calcium salts. Boiler water softening methods used in ships can be broadly divided into the following types:

- physical methods,
- chemical methods,
- physico-chemical methods.

Physical methods – these include distillation and magnetic method. Distillation allows for very good softening, but it is an expensive method due to the high cost of thermal energy necessary to conduct the distillation process.

However, there are specific conditions on ships and the situation is much more favourable than on land, because the distillation uses the heat removed during the cooling of the main engine, thanks to which there is no energy loss, and the efficiency of the ship's engine room increases. Seawater heated while cooling freshwater from the engine's closed cooling circuit is distilled. Due to the low distillation temperature of water (on the order of 30° to 50 °C), the process must be carried out under reduced pressure in devices called evaporators. In modern marine power plants, evaporators are installed with the capacity to fully cover the needs for technical water as well as sanitary and consumption water. It is one of the most important water treatment methods used in marine power plant conditions. The quality of the obtained distillate depends on the type of the evaporator, its operating parameters and technical condition. The salt content in the distillate usually does not exceed 120 mg/dm^3. Therefore, despite the supply of distilled water to the circuits, it is necessary to use additional methods of chemical treatment (preparations of different companies). Moreover, equipping the power plant with an evaporator does not preclude the use of freshwater taken from the land. The reason for this can often be insufficient evaporator performance or failure of the evaporator. The ship must therefore also be equipped with means that enable the use of chemical methods of water treatment.

Magnetic water treatment consists in passing the entire amount of water supplied to the boiler through a device generating a constant magnetic field, the so-called magnetizers. The action of this field on water is physical. The magnetic field affects the process of crystallization of salts dissolved in water, i.e., the sludge formed here can be easily removed from the boiler by desludging. However, the method of magnetic water cutting is currently very rarely used on ships.

Chemical methods – they consist in the chemical precipitation of insoluble sediments with the use of various reagents (e.g., calcium hydroxide, sodium hydroxide, sodium carbonate, phosphates) or binding calcium and magnesium ions into complex compounds using e.g., metaphosphates, polyphosphates and others. Chemical treatment of the boiler water causes not only the precipitation of stone-forming components from the water, but also ensures the appropriate alkalinity of the water, which protects the boiler against corrosion.

The softening method of using hydrated sodium orthophosphate $Na_3PO_4 \cdot 12H_2O$ has the greatest advantages of the mentioned reagents. It removes both carbonate and non-carbonate hardness and allows to obtain softened water with an openness of 0.1 ºdH. Moreover, the dosing of this reagent does not have to be very accurate as its presence in a limited excess in the boiler water is desirable. In the presence of sodium orthophosphate, a thin protective layer of iron oxides is more easily formed on the walls of the boiler, which inhibits the progress of corrosion. The chemical reactions that occur during the treatment of water with sodium orthophosphate are as follows:

$$3Ca(HCO_3)_2 + 2Na_3PO_4 \rightarrow \downarrow Ca_3(PO_4)_2 + 6NaHCO_3$$
$$3Mg(HCO_3)_2 + 2Na_3PO_4 \rightarrow \downarrow Mg_3(PO_4)_2 + 6NaHCO_3$$
$$3CaCl_2 + 2Na_3PO_4 \rightarrow \downarrow Ca_3(PO_4)_2 + 6NaCl$$
$$3MgCl_2 + 2Na_3PO_4 \rightarrow \downarrow Mg_3(PO_4)_2 + 6NaCl$$

Thermal decomposition of $NaHCO_3$ at higher temperatures leads to the formation of sodium carbonate Na_2CO_3 which removes the non-carbonate hardness, thus reducing the consumption of Na_3PO_4. Thermal decomposition of $NaHCO_3$ takes place according to the following reaction:

$$6NaHCO_3 \xrightarrow{(60^{\circ} - 70^{\circ}C)} 3Na_2CO_3 + \uparrow 3CO_2 + 3H_2O$$

In shipbuilding practice, almost exclusively chemical treatment is currently used with the intra-boiler method by adding ready-made preparations of various companies. Often these preparations contain sodium phosphate as a precipitating agent. Regardless of the manufacturer of these softeners, they contain such solid components as: descaling agents (precipitating calcium and magnesium ions), pH buffering agents at a specific level for a given type of boiler, corrosion inhibitors and agents facilitating the precipitation of sparingly soluble deposits.

Chemical water treatment can also be carried out with complex active phosphorus compounds. The most common complexing compounds are metaphosphates and polyphosphates. The action of these compounds is that they do not deposit with calcium and magnesium salts, but form water-soluble complex salts. Ca^{2+} and Mg^{2+} ions pass into the complex anion and cease to be a stone-forming factor.

Physico-chemical methods – ion exchange methods are among the physico-chemical methods of water softening. Ion exchangers are solid substances, most often amorphous, porous, insoluble in water, which have the ability to exchange their own ions with the ions of the electrolyte solution surrounding them. The cation exchanging ion exchangers are called cation exchangers, and the anion exchanging ion exchangers are the anion exchangers. In water technology, synthetic organic ion exchangers are used almost exclusively. Water treatment with ion exchangers is now widespread. It consists in removing unwanted ions from water by replacing them with ions such as: Na^+, H^+, OH^-.

In marine practice, water softening is most often carried out on sodium cation exchanger placed in an ion exchange column through which treated water is passed, so it takes place in the so-called the soda cycle. The exchange in the sodium cycle can be represented by the following reactions:

$$2KtNa + Ca(HCO_3)_2 \longrightarrow Kt_2Ca + 2NaHCO_3$$

$$2KtNa + Mg(HCO_3)_2 \longrightarrow Kt_2Mg + 2NaHCO_3$$

$$2KtNa + CaCl_2 \longrightarrow Kt_2Ca + 2NaCl$$

$$2KtNa + MgCl_2 \longrightarrow Kt_2Mg + 2NaCl$$

The sodium cation exchanger (designated here conventionally as KtNa, where: Kt – is the organic invariant part of the cation exchanger) gives off sodium ions, and instead binds calcium and magnesium ions with the water, which leads to the removal of hardness. This cation exchanger must be regenerated after some time, because sodium ions are depleted. Regeneration is carried out by passing an appropriate excess of NaCl solution (5 – 15%) through the ion exchange column. The following reactions then occur:

$$Kt_2Ca + 2NaCl \longrightarrow 2KtNa + CaCl_2$$

$$Kt_2Mg + 2NaCl \longrightarrow 2KtNa + MgCl_2$$

As a result of the above reactions, the ion exchanger is restored to its sodium form, and Ca^{2+} and Mg^{2+} ions pass from the ion exchanger phase to the solution. The regeneration solution is then slowly displaced from the column with the wash water. Rinsing is continued until the rinsing water has a hardness of 0.1 – 0.5 °dH. Periodicity results from the cycle of work presented above. In practice, therefore, two ion exchange columns are most often used, one of which is in operation and the other is regenerated, and vice versa. The ion-exchange method has a limited use on ships due to the need to install large-size devices in the ship's engine room, the operation of which is quite time-consuming and troublesome. The ion exchange method is used, inter alia, on passenger ferries for the treatment of hot water intended for sanitary purposes.

In addition, modern membrane water treatment methods such as reverse osmosis and ultrafiltration can be found on ships. They can be used to desalinate water or purify oily waters.

3. PERFORMING THE EXERCISE

Fig. 1 shows a laboratory stand for testing water hardness.

Fig. 1. Laboratory stand for determination of total hardness and calcium hardness

3.1. Determination of boiler water or cooling water hardness using the edetate method

3.1.1. Determination of general hardness

A solution of disodium edetate, which has the properties of complex binding of various metal ions (cations), is introduced into the sample of the tested water. Among other things, edetate forms complex compounds with calcium and magnesium cations. Complexometric titration of the water sample is carried out in the presence of the indicator, which is the Eriochrome black dye T. This dye forms with calcium and magnesium cations also a complex compound with a red colour at pH approx. 10.0. However, the complex compounds of calcium and magnesium with eriochrome black T are less stable than with the edetate and during water titration, the calcium and magnesium cations combine complexes with the edetate. At the end point of the titration, the eriochrome black T is completely freed from its previously formed complex compounds, which leads to a color change of the solution from red to blue. The colour change of the titration solution is noticeable when there is a sufficient amount of magnesium ions in it. The sharpness of the end point of the titration is influenced by the pH of the sample, the distinctiveness of the colour of the solution increases with the increase of its pH. However, the pH of the sample should not be too high as precipitation of calcium carbonate or magnesium hydroxide may then occur. Moreover, the dye used as an indicator in a very alkaline solution changes its colour. The assumed pH value of approx. 10.0 ensures a sufficiently good course of the determination. The titration itself should not take longer than 5 minutes due to the possibility of precipitation of calcium carbonate.

Performing the determination

Measure 50 cm^3 of the water under test into three conical flasks. To all flasks add 3 cm^3 of ammonium buffer solution and a pinch (about 0.1 g) of a titration indicator – Eriochrome black T (Fig. 2). Then titrate immediately with 0.01 M disodium edetate until the colour changes from violet to blue (Fig. 3). Titration should take no more than 5 minutes from the addition of the indicator. If the colour of the sample does not change after 2 – 3 minutes, the titration is complete.

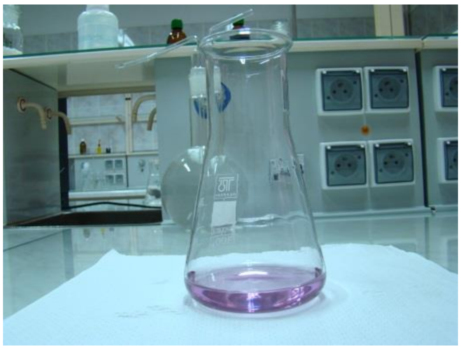

Fig. 2. Prepared sample for titration

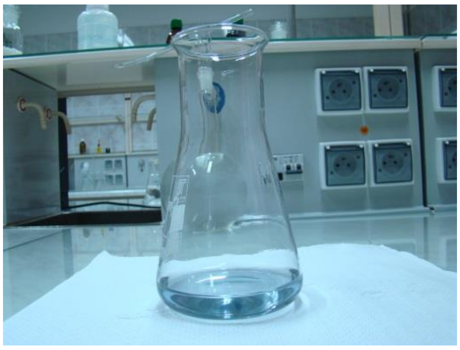

Fig. 3. Final titration effect

Calculation of the results

The total hardness (H_{total}) of the tested water sample is to be calculated according to the formula:

$$\boldsymbol{H_{total} = \frac{V \cdot M \cdot 1000}{V_{pr}}} \left[\frac{\text{mmol}}{\text{dm}^3}\right]$$

where:

- *V* – mean value of the volume of disodium edetate solution from three titrations, cm^3,
- *M* – the titre of the disodium edetate solution, M = 0.01 mol/dm^3,
- V_{pr} – volume of the water sample used for the analysis, 50 cm^3.

3.1.2. Determination of the calcium hardness

Performing the determination

Measure 50 cm^3 of the water under test into three conical flasks. To all flasks add 3 – 4 tablets of solid KOH and a pinch (about 0.2 g) of the titration indicator - murexide (fig. 4). After adding the indicator, mix the sample thoroughly and immediately titrate with 0.01 M disodium edetate until the solution turns pink to purple (Fig. 5). Titration should take no more than 5 minutes from the addition of the indicator. If the colour of the titrated sample does not change after 2 – 3 minutes, the titration is complete.

Fig. 4. Prepared sample for titration

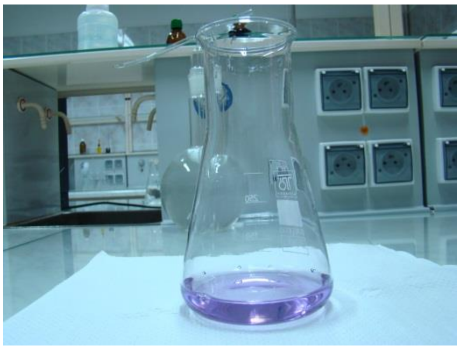

Fig. 5. Final titration effect

Calculation of the results

Calculate the calcium hardness (H_{Ca}) of the tested water sample according to the formula:

$$H_{Ca} = \frac{V \cdot M \cdot 1000}{V_{pr}} \left[\frac{\text{mmol}}{\text{dm}^3}\right]$$

where:

- V – mean value of the volume of disodium edetate solution from three titrations, cm^3,
- M – the titre of the disodium edetate solution, M = 0.01 M,
- V_{pr} – volume of the water sample used for the analysis, 50 cm^3.

4. DEVELOPMENT OF THE EXERCISE

1. Present the results of the general and calcium hardness determination.
2. On the basis of the determined total and calcium hardness, calculate the magnesium hardness.
3. Convert the obtained hardness results to ºdH, ppm, mval/dm^3,
4. On the basis of the obtained results, assess the quality and suitability of the tested water for operation in the selected type of steam boiler.
5. In auxiliary tables 3 and 4 at the end of the manual, technical requirements for utility water in selected steam boilers are given.

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 performed exercise, which should include:
   - 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. Calculate the calcium, magnesium and total hardness of water in degrees ºdH, if 400 mg of calcium sulphate $CaSO_4$, 200 mg of calcium chloride $CaCl_2$, 160 of magnesium chloride $MgCl_2$ and 80 mg of magnesium sulphate $MgSO_4$ are dissolved in 1 dm^3 of distilled water.
   Solution
   We calculate the calcium hardness:

$$\text{H Ca} = \frac{400}{R_{\text{CaSO}_4}} + \frac{200}{R_{\text{CaCl}_2}} = \frac{400}{68.1} + \frac{200}{55.5} = 5.87 + 3.61 = 9.48 \text{ mval/dm}^3$$

where: R - milligram equivalents of the corresponding salts.
Because 1 $mval/dm^3$ = 2.8ºdH, then:

$$H_{\text{Ca}} = 9.48 \cdot 2.8 = 26.6^{\circ}\text{dH}$$

We calculate the magnesium hardness by analogy:

$$\text{H Mg} = \frac{80}{R_{\text{MgSO}_4}} + \frac{160}{R_{\text{MgCl}_2}} = \frac{80}{60.2} + \frac{160}{47.6} = 1.33 + 3.36 = 4.69 \text{ mval/dm}^3$$

Thus, the magnesium hardness in ºdH is:

$$H_{\text{Mg}} = 4.69 \cdot 2.8 = 13.1^{\circ}\text{dH}$$

We calculate the total hardness one by one

$$H_{\text{total}} = H_{\text{Ca}} + H_{\text{Mg}} = 26.6 + 13.1 = 39.7^{\circ}\text{dH}$$

Answer:
The total hardness of water is 39.7ºdH.

2. Calculate the calcium hardness in ºdH and $mval/dm^3$, if 120 mg of calcium oxide CaO are dissolved in 100 cm^3 of distilled water.
   Solution
   If there are 120 mg CaO in 100 cm^3 of water, then in 1000 cm^3 there is 1200 mg CaO.
   As one degree of ºdH corresponds to 10 mg/dm^3 of CaO, the calcium hardness of H_{Ca} the water is:

$$\text{H Ca} = \frac{1200}{10} = 120^{\circ}\text{dH and H Ca} = \frac{120}{2.8} = 43.0 \text{ mval/dm}^3$$

$$CaO + H_2O \rightarrow Ca(OH)_2 \text{ – it is called limestone water}$$

Calcium hardness can also be calculated in another way:

$$\text{H Ca} = \frac{1200}{R_{\text{CaO}}} = \frac{1200}{28} = 43.0 \text{ mval/dm}^3\text{, hence: H Ca} = 43.0 \cdot 2.8 = 120^{\circ}\text{dH}$$

Answer:

The calcium hardness of this water is 43.0 mval/dm^3, which corresponds to the value 120ºdH.

3. Calculate the content in mg/dm^3 of calcium bicarbonate $Ca(HCO_3)_2$ and calcium sulphate $CaSO_4$, if the alkalinity of *m* water is 3.8 mval/dm^3, and total hardness H_{total} = 15.4 ºdH

Solution

The content of calcium bicarbonate $Ca(HCO_3)_2$ in mg/dm^3 is calculated from the alkalinity *m* by multiplying the number of mval/dm^3 by the milligramequivalent (R) of calcium bicarbonate $Ca(HCO_3)_2$, that is:

$$3.8 \cdot 81 = 308 \text{ mg/dm}^3 \text{ Ca(HCO}_3)_2$$

The amount of calcium sulphate $CaSO_4$ in mg/dm^3 is calculated from the non-carbonate hardness by multiplying the non-carbonate hardness by the milligramequivalent (R) of calcium sulphate $CaSO_4$, that is:

$$\left(\frac{15.4}{2.8} - 3.8\right) \cdot 68 = (5.5 - 3.8) \cdot 68 = 116 \text{ mg/dm}^3 \text{ CaSO}_4$$

Answer:

The content of calcium bicarbonate $Ca(HCO_3)_2$ is 308 mg/dm^3 and calcium sulphate $CaSO_4$ 116 mg/dm^3.

II. Tasks and questions to be completed by the student

Tasks

1. How much sodium carbonate Na_2CO_3 should be added to soften 10 m^3 of hard water containing 0.01% calcium sulphate $CaSO_4$ and 0.015% calcium hydrogen carbonate $Ca(HCO_3)_2$? Use water density of 1 g/cm^3 for calculations.
   Answer: 1.76 kg of Na_2CO_3.
2. 2.5 cm^3 of 0.12M hydrochloric acid HCl were used to neutralize 100 cm^3 of water containing calcium hydrogen carbonate. How many moles of calcium hydrogen carbonate $Ca(HCO_3)_2$ were in 1 dm^3 of this water?
   Answer: $1.5 \cdot 10^{-3}$ mol.
3. How much limescale will be produced after the evaporation of 10^3 kg of water containing 0.1% calcium bicarbonate.
   Answer: 0.617 kg of $CaCO_3$.
4. The two water samples were mixed in a 2 : 3 ratio. The calcium hardness of water sample no. 1 is 12ºdH, and the magnesium hardness = 4ºdH. The calcium hardness of water sample 2 = 6.9 mval/dm^3, and the magnesium hardness is 1 mval/dm^3. Calculate the total, calcium and magnesium hardness of the mixture obtained in ºdH.
   Answer: H_{Ca} of the mixture = 16.4ºdH, H_{Mg} of the mixture = 3.28ºdH, H_{total} = 19.68ºdH.
5. 200 cm^3 of water with a total hardness of 12ºdH were mixed with 300 cm^3 of water with a total hardness of 16ºdH. What is the total hardness of the mixture obtained?
   Answer: The total hardness of the mixture obtained is 14.4 °dH.

Questions

1. What causes water hardness? Why is water hardness an important factor in determining its suitability for industrial and economic purposes?
2. What are the types of water hardness and degrees of water hardness? Give the formulas and names of the chemical compounds that produce the appropriate hardness.
3. How and why does the so-called "transient hardness" of water during heating? Justify your answer with the equations of chemical reactions.
4. What is the principle of determining the total hardness of water by titration with standard EDTA solution.
5. What is the principle of determining the carbonate hardness?
6. What is water softening with the phosphate method? Write the reaction equations for hard water containing: calcium and magnesium bicarbonates and calcium chloride.
7. How to demineralise water without distilling it? What is water desalination and demineralization?
8. What is the physicochemical method of water softening?
9. What is the regeneration of the cation exchanger used to soften the water? Give the appropriate reaction equations.
10. What components are included in the proprietary preparations for in-boiler water softening and what tasks do they fulfil?

Auxiliary tables

Table 3

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 w 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 4

Water quality for water-tube boilers operating at a pressure of 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 *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