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Practical analytical techniques

USED TO DETERMINE SELECTED PHYSICOCHEMICAL INDICATORS OF WATER QUALITY

Bialystok 2021

Bialystok University
of Technology

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FOREWORD

The script "Practical analytical techniques used to determine selected physicochemical indicators of water quality" is dedicated to students of Biotechnology, Environmental Engineering, Environmental Protection and related fields as an aid in performing laboratory exercises on water analysis. The publication includes a set of laboratory instructions along with theoretical material for each of the described exercises. The syllabus covers water quality determination using classical analytical methods (titration methods, gravimetric analysis) and instrumental methods (such as spectroscopy or chromatography). The scope of the presented material includes instructions for determining the most important physicochemical parameters of water affecting its quality (such as water hardness, content of chloride ions, sulfate ions, nitrate ions, cations of various metals, selected organic compounds and many other).

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1. DETERMINATION OF CALCIUM ION CONTENT BY WEIGHT

1.1. INTRODUCTION

Gravimetric analysis is an analytical method that can be used when the component to be determined can be carried off into a hardly soluble precipitate, e.g. $BaSO_4$, $MgNH_4PO_4$, AgCl etc. During the analysis the precipitate is drained, washed, dried and finally weighed. From the weight of the precipitate, the content of the determined component is calculated.

In order to perform the analysis, the precipitate must meet strict conditions. The precipitate should:

- Be as insoluble as possible (the solubility product of the precipitate should be sufficiently small).
- The amount of the determinable component remaining in solution after precipitation must not exceed a fraction of a mg.
- It must be stable and have a well-defined chemical composition.
- It should have as high a molar mass as possible.
- The obtained precipitate must be in a form that enables it to be easily and quickly drained and washed.

The procedure in the gravimetric analysis consists of the following steps:

Precipitation of the component to be determined in the form of a hardly soluble precipitate. The following rules should be observed when precipitating: a) the precipitate should be removed from a sufficiently diluted solution; b) the precipitating reagent should be added slowly, drop by drop; c) the solution should be stirred while precipitating; d) the reagent should be introduced in appropriate excess.

- Ageing of the precipitate – the precipitate is left in the stock solution for some time after the precipitation (several hours). During this time, recrystallization and crystal growth occur.
- Precipitation (Fig. 1.1 and 1.2).

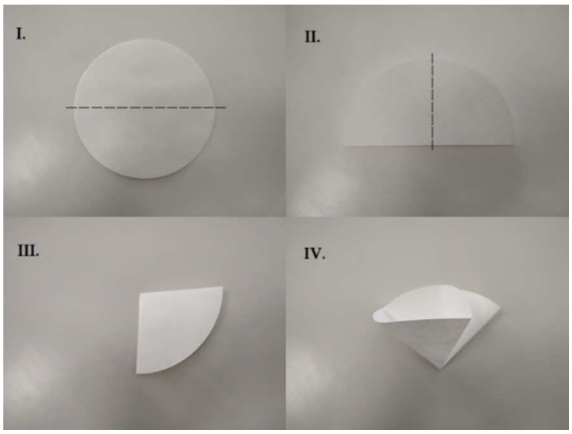

Fig. 1.1. Assembling the filter

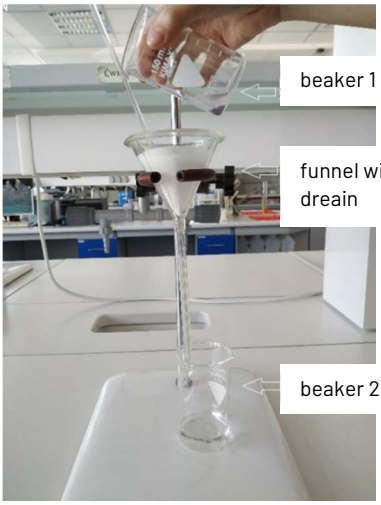

Fig. 1.2. Filtering process

Fig. 1.3. Porcelain crucible

- Washing of the precipitate. Place the washed precipitate in a porcelain crucible (Fig. 1.3).
- Drying of the precipitate, burning the filter, or possibly roasting it.
- Weighing the precipitate to the fourth decimal place.

1.2. PURPOSE AND SCOPE OF THE LABORATORY EXERCISE

The aim of this exercise is to determine the content of calcium ions in a sample.

1.3. TEST METHODOLOGY

Test stand description

Reagents:

substances: Ca^{2+} ion solution, calcium oxalate solution 4% and 0.1%, ammonia solution 10%, methyl orange, hydrochloric acid (1+1), $AgNO_3$ solution acidified with HNO_3 (for the chloride test)

Laboratory equipment:

analytical balance, dryer, hot plate, filter paper, thermometer, beaker 100 cm^3 and 400 cm^3, volumetric flask 100 cm^3, pipette with a capacity of 20 cm^3, multidimensional pipette 5 cm^3, cylinder with a capacity of 10 cm^3 and 25 cm^3, pipette cap, watch glasses, stirring rods, filtering set (tripod, funnel), desiccator.

Running the experiment

Experiment 1. **Determination of Ca^{2+} as $CaC_2O_4 \cdot H_2O$**

Calcium ions are quantified by precipitation as calcium oxalate monohydrate. The determination consists in adding ammonium oxalate to the hydrochloric acid-acidified calcium salt solution, and then neutralizing the obtained solution with ammonia.

$$Ca^{2+} + C_2O_4^{2-} + H_2O \rightarrow CaC_2O_4 \cdot H_2O$$

For calcium oxalate:

$$I_r = 1{,}78 \cdot 10^{-9},\ M = 128{,}1\ g/mol$$

The cold-precipitated oxalate precipitate is fine crystalline and not suitable for filtration. Therefore the precipitation is carried out hot. For quantification, the obtained precipitate should be dried or roasted and then weighed.

Depending on the temperature, the following reactions take place:

$$CaC_2O_4 \cdot H_2O \rightarrow CaC_2O_4\downarrow + H_2O \text{ above } 120°C$$

$$CaC_2O_4 \rightarrow CaCO_3\downarrow + CO\uparrow \text{ above } 350°C$$

$$CaCO_3 \rightarrow CaO\downarrow + CO_2\uparrow \text{ above } 650°C$$

Determination of **Ca^{2+}**

1. Make up the resulting Ca^{2+} in a 100 cm^3 volumetric flask with distilled water to the mark, mix well.
2. Pour 50 cm^3 of 4% ammonium oxalate into a 100 cm^3 beaker and place on a hot plate to heat.
3. Measure 20 cm^3 of the obtained Ca^{2+} analysis (from step 1) into a 400 cm^3 beaker, dilute to 200 cm^3 with distilled water, add 3-4 drops of methyl orange, add 5 cm^3 HCl (1+1), the colour of the orange will change to intense pink pH=3.
4. Cover with a watch glass and heat to temp. 80°C.
5. Slowly, while stirring vigorously with a rod, add dropwise 50 cm^3 of hot 4% ammonium oxalate (from step 2).
6. Stirring slowly, add 10% ammonia (about 1 cm^3) drop by drop, bringing the pH to neutral (change into yellow colour).
7. Cool the beaker with the precipitate, you can put it in cold water and leave for half an hour.
8. Filter the precipitate through a **weighed filter** (with an accuracy of 0.0001 g) – previously dried at 120°C to a solid mass.
9. Wash the precipitate with 0.1% ammonium oxalate solution to elute Cl^- ions (negative test with acidified $AgNO_3$).
10. Dry the precipitate filter in an oven at 120°C to a solid mass. Weigh with an accuracy of 0.0001 g.
11. Calculate the mass of the calcium oxalate precipitate from the difference between the mass of the dried filter and the mass of the precipitate with the filter.

1.4. PRESENTATION AND ANALYSIS OF TEST FINDINGS

Calculation of results

Calculate the calcium content of the sample.

The student report should include

- Purpose and scope of the exercise
- Description of the test stand
- Equations of occurring reactions
- Results of calcium determination

Checklist questions

1. Types of precipitates.
2. What is the ageing process of the precipitate?
3. Co-precipitation, methods to prevent co-precipitation.
4. What conditions should the precipitate meet in gravimetric analysis (precipitate characteristics).
5. Factors affecting the solubility of the precipitate.
6. What is a desiccator and what is it used for? List 5 different drying agents.
7. Analytical multiplier.
8. Describe how to perform the exercise.
9. The principle of calcium determination: reactions, conditions.
10. Calculations from stoichiometry of reactions.
11. Calculations of solubility equilibrium.

Example calculation tasks

1. Calculate the solubility of magnesium hydroxide in water at temp. 25°C.
2. Calculate the solubility of barium sulfate at 25°C in water and 0.1/dm^3 sodium sulfate solution.
3. Will we obtain a calcium fluoride precipitate at 25°C if 50 cm^3 of a 0.0005 mol/dm^3 calcium nitrate(V) solution is mixed with 50 cm^3 of 0.0002 mol/dm^3 sodium fluoride?
4. At 25°C 100 l of saturated aqueous solution of lead carbonate contains 10.35 mg of $PbCO_3$. Calculate the value of the solubility product of this salt.

5. Calculate the solubility in mol/dm^3 and mg/dm^3 of calcium oxalate in water. For calcium oxalate, the solubility product is Ir = $1{,}78 \cdot 10^{-9}$.
6. Calculate the volume of 4% ammonium oxalate solution needed to precipitate 200 mg of Ca^{2+}.
7. Calculate the solubility in mol/dm^3 and mg/dm^3 of calcium oxalate in a 0.1% ammonium oxalate solution.
8. Assuming that the calcium oxalate precipitate was dried at 120°C, calculate the analytical multiplier (F) for Ca^{2+} w CaC_2O_4.

Health and safety requirements

- Only laboratory equipment, a script, and a laboratory notebook may be kept on the table during the exercise.
- Take the solution for analysis with a pipette using a cap.
- Be careful when working with hotplates.
- Concentr. HCl – caustic, irritating to skin, irritating to eyes.

1.5. **Bibliography**

1. Cygański A.: *Chemiczne metody analizy ilościowej*, WNT, Warszawa 2021;
2. Szmal Z. S., Lipiec T.: *Chemia analityczna z elementami chemii instrumentalnej*, PZWL, Warszawa 1997;
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2. DETERMINATION OF SULFATE(VI) ION CONCENTRATION BY WEIGHT

2.1. INTRODUCTION

Sulfates(VI), along with chlorides, are the most common in natural waters. Sulfates enter water through leaching of sedimentary rocks that include gypsum, soil leaching, and sometimes during oxidation of heavy metal sulfides.

In surface waters, sulfates(VI) may also come from urban or industrial wastewater pollution. In addition, mine waters, in which sulfate is present in large quantities, can be a source of sulfate.

Acceptable amounts of sulfates in drinking water should not exceed 150 mg/dm^3 SO_4^{2-}. The presence of calcium or magnesium sulfate(VI) in water for industrial purposes is undesirable, especially in water used to power steam boilers, because they cause hard scale formation. Also, waters used in the construction industry for mortar and concrete should not contain excessive amounts of sulfate(VI), because larger amounts of sulfate (more than 250 mg/dm^3) cause sulfate corrosion of concrete and reinforced concrete structures. Sulfates(VI) in water can be determined by weight or titration methods. The gravimetric analysis is the basic and most accurate method, but it is more time-consuming than the titration method.

The weight determination of sulfate(VI) ions consists in the precipitation of SO_4^{2-} ions with Ba^{2+} ions in the form of a hardly soluble precipitate $BaSO_4$ ($BaSO_4$ Ir=1,1·10^{-10}):

$$SO_4^{2-} + Ba^{2+} \rightleftharpoons BaSO_4$$

The obtained precipitate is drained, washed and roasted in order to completely remove moisture. The sulfate content of the sample to be analysed is calculated by multiplying the weight of the precipitate obtained by the analytical multiplier. The $BaSO_4$ precipitate is extracted in an environment of dilute hydrochloric acid. Too much acidity of the solution

increases the solubility of the precipitate due to a shift in the equilibrium of the reaction

$$SO_4^{2-} + H^+ \rightleftharpoons HSO_4^-$$

to the right, which reduces the concentration of sulfate(VI) ions in the solution and in turn shifts the reaction equilibrium for the formation of $BaSO_4$ to the left. Cold $BaSO_4$ precipitate is formed as a fine crystalline precipitate, passing through a filter. This is due to its low solubility in water and therefore rapid precipitate formation. In order to obtain a coarse crystalline precipitate, it is advisable to introduce barium salts into the hot test solution. In the determination of sulfate, the most serious source of error is the particular susceptibility of the $BaSO_4$ precipitate to contamination by co-precipitation of other ions. The manner in which the precipitate is extracted is therefore of great importance: if it is precipitated by adding a $BaCl_2$ solution to a hot sulfate solution, only small amounts of Cl^- ions in the form of $BaCl_2$ occlude, whereas if the reverse is done, the $BaCl_2$ occlusion is significant. If ions that readily co-precipitate with the $BaSO_4$ precipitate are present in solution, such as cations: K^+, Na^+, Ca^{2+}, Sr^{2+}, Al^{3+}, Fe^{3+} and anions: NO_3^-, ClO_3^-, ClO_4^-, PO_4^{3-}, CrO_4^{2-}, then these should be removed from the solution or removed before sulfate precipitation.

The pure $BaSO_4$ precipitate decomposes at 1400°C. In the presence of impurities this process occurs at much lower temperatures, e.g. in the presence of coal at 600°C, the reduction of sulfate to sulfide can occur:

$$BaSO_4+4C \rightleftharpoons BaS+4CO$$

To avoid decomposition, the $BaSO_4$ precipitate filter is burned slowly at as low a temperature as possible and with good access to air. In this procedure, if sulfide is formed, it is oxidized back to sulfate by oxygen from the air:

$$BaS+2O_2 \rightleftharpoons BaSO_4$$

Alternatively, the resulting sulfide can be oxidized by adding a small amount of concentrated sulfuric acid to the roasted $BaSO_4$ precipitate and roasted again:

$$BaS+ H_2SO_4 \rightleftharpoons BaSO_4+H_2S$$

Before roasting the $BaSO_4$ precipitate, the chloride ions must be removed because $BaCl_2$ is volatile and can cause precipitate loss.

2.2. PURPOSE AND SCOPE OF THE LABORATORY EXERCISE

The objective of this exercise is the determination of sulfate(VI) content by weight.

2.3. TEST METHODOLOGY

Test stand description

Reagents:

Sample to be analysed, 5% barium chloride solution, 10% ammonia solution, methyl orange, concentrated hydrochloric acid, $AgNO_3$ solution

Laboratory equipment:

analytical balance, stirring rods, beaker 250 cm^3, pipette 100 cm^3, dryer

Running the experiment

Experiment 1. **Determination of SO_4^{2-} as $BaSO_4$**

a) **Precipitating $BaSO_4$**

Precipitate $BaSO_4$ in a 250 cm^3 beaker. Pipette 100 cm^3 of the solution containing sulfate ions into the beaker (sample as recommended by the instructor), add 2-3 drops of methyl orange. Then add 2 cm^3 of concentrated hydrochloric acid (1+1). The solution becomes intensely pink. Heat the entire sample on a hotplate until boiling and introduce with a pipette, 10 cm^3 of 5% $BaCl_2$ solution, stirring all the time. Add a few more drops of $BaCl_2$ and observe if any turbidity appears, which indicates incomplete precipitation of sulfate ions. Then leave the solution with the precipitate on the turned off hot plate. Allow to cool (until the next lab classes).

b) **Preparation of $BaSO_4$ precipitate to determine SO_4^{2-}**

Filter the precipitate on a hard filter paper and wash with water until the chloride ions are completely washed away (test with $AgNO_3$ solution acidified with nitric acid). Remove the filtrate from the funnel, fold and place in a quartz crucible, previously roasted to a solid mass, burn slowly with a good air supply so that the blotting paper does not ignite with the flame, and roast at about 800°C for 30 minutes. If the precipitate is grey, indicating partial reduction of $BaSO_4$ to BaS, add 1 drop of concentrated sulfuric(VI) acid, carefully drive off the excess acid, and roast the precipitate again until a solid mass is obtained.

The sulfate concentration is calculated by multiplying the mass of the precipitate (the difference in weights of the crucible with precipitate and the empty crucible) by the analytical multiplication factor *F*:

$$m\ SO_4^{2-} = m_{BaSO_4} \cdot F\ \text{[g]}$$

where:

$$F = \frac{m\ SO_4^{2-}}{m\ BaSO_4} = 0{,}4115$$

2.4. PRESENTATION AND ANALYSIS OF TEST FINDINGS

Calculate the sulfide concentration of the sample.

The student report should include

- Purpose and scope of the exercise
- Description of the test stand
- Equations of occurring reactions
- Results of sulfide determination

Checklist questions

1. Types of precipitates.
2. Co-precipitation, methods to prevent co-precipitation.
3. Describe how to perform the exercise.
4. The principle of sulfide determination: reactions, conditions.
5. Calculations.
7. Calculations of solubility equilibrium.

Example calculation tasks

1. Calculate the solubility in mol/dm^3 and mg/dm^3 of calcium oxalate in water. For calcium oxalate, the solubility product is Ir= 1,78·10^{-9}, Mm = 128,1 g/mol
2. Calculate the volume of 4% ammonium oxalate solution needed to precipitate 200 mg of Ca^{2+}.

Health and safety requirements

- Only laboratory equipment, a script, and a laboratory notebook may be kept on the table during the exercise.
- Take the solution for analysis with a pipette using a cap.
- $BaCl_2$ – toxic if swallowed. Harmful if inhaled.
- Concentr. HCl – may cause corrosion of metals. Causes severe skin burns and eye damage. May irritate the respiratory system.
- Concentr. H_2SO_4 – causes severe skin burns and eye damage. Ensure effective air exchange (ventilation). Follow good industrial practice and general rules of safety and hygiene at work with chemical substances. When using, do not eat or drink anything, avoid contact with the substance; avoid inhaling vapours, use personal protective equipment; work in well-ventilated areas. Dilute by slowly adding acid to water and stirring carefully. Hygroscopic substance – avoid contact with water!

2.5. **Bibliography**

1. Cygański A., *Chemiczne metody analizy ilościowej*, WNT, Warszawa 2021.
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3. DETERMINATION OF SODIUM HYDROXIDE AND SODIUM CARBONATE

3.1. **INTRODUCTION**

Alkalinity of water means its ability to neutralize strong mineral acids against alkacimetric indicators. In waters with pH below 8.3 there exist mostly calcium, magnesium and iron bicarbonates, less often sodium bicarbonates (alkalinity). These are the salts of carbonic acid, e.g.: $Ca(HCO_3)_2$, $Mg(HCO_3)_2$, $NaHCO_3$. In waters contaminated with alkaline industrial wastewater (pH above 8.3), in addition to weak acid anions such as HCO_3^-, CO_3^{2-}, $H_2PO_4^-$, SiO_3^{2-}, OH^- ions may be present from strong bases (NaOH, KOH). Mineral alkalinity (Zp) is a quantitative indicator of the content of hydroxide and carbonate ions, and total alkalinity (Zm) is an indicator of the content of carbonate, bicarbonate, hydroxide and other anions derived from the dissociation of salts of weak acids and strong bases. The principle of determining alkalinity is based on the determination of the content of alkaline reactive compounds in water in the presence of an appropriate indicator. Alkalinity is determined by titrating the test water with a standard solution of strong acid (HCl), first in the presence of phenolphthalein and then in the presence of methyl orange.

The Warder method consists in the titration of a mixture of Na_2CO_3 and NaOH against two indicators: phenolphthalein and methyl orange. The method takes advantage of the fact that the colour changes of the used indicators occur at different pH values. Initially, the mixtures Na_2CO_3 and NaOH are titrated with a standard solution of hydrochloric acid in the presence of phenolphthalein until the solution is completely discoloured. The entire amount of NaOH and a half amount of Na_2CO_3 are titrated. The sodium carbonate changes to bicarbonate during the reaction.

The following chemical reactions take place during the first titration step:

$$NaOH + HCl \rightarrow NaCl + H_2O$$

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

At the equivalent point of the first step of the reaction, the pH of the solution reaches a value of about 8.3. At this pH value, phenolphthalein is completely decolorized. A second indicator, methyl orange, is added to the decolorized solution and titrated with HCl acid until the first colour change of the indicator. During the second stage of titration, the following chemical reaction takes place:

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

At the second equivalence point, the pH of the solution is about 4.0. This titration (the sample includes NaOH, Na_2CO_3, $NaHCO_3$) is practically used to determine the alkalinity of water.

3.2. PURPOSE AND SCOPE OF THE EXERCISE

The aim of the exercise is to determine the NaOH and Na_2CO_3 concentration in a mixture using the Warder method.

3.3. TEST METHODOLOGY

Test stand description

Reagents:

HCl – concentrated solution, sodium carbonate – substance, methyl orange, phenolphthalein

Laboratory equipment:

50 cm^3 burette, 10 and 20 cm^3 pipettes, conical flasks, pipette cap

Running the experiment

Experiment 1. **Preparation and determination of HCl solution**

A titrated HCl solution in the laboratory is obtained by diluting concentrated hydrochloric acid to an appropriate volume with distilled water, and then determining the exact titre of the resulting solution by titration of aliquots of dried sodium carbonate (standard substance).

Measure the density of hydrochloric acid with an areometer and read its percentage concentration from Table 3.1. Knowing the percentage concentration, calculate how many cm^3 of concentrated HCl solution should be taken to prepare 500 cm^3 of acid with a concentration of 0.1 mol/dm^3.

Table 3.1. HCl content in its aqueous solutions of different densities (20°C)

Density at 20°C	HCl % concentration [m/m]	Density at 20°C	HCl % concentration below [m/m]
1.000	0.360	1.125	25.22
1.010	2.364	1.130	26.20
1.025	5.408	1.140	28.18
1.050	10.52	1.150	30.14
1.075	15.485	1.160	32.14
1.090	18.43	1.170	34.18
1.095	19.41	1.175	35.20
1.100	20.39	1.180	36.23
1.105	21.36	1.185	37.27
1.110	22.33	1.190	38.32
1.115	23.29	1.195	39.37
1.120	24.25	1.198	40.00

Measure the calculated volume of concentrated HCl with a measuring cylinder (under the fume hood) and transfer it into a 500 cm^3 volumetric flask (partially filled with distilled water), then fill the flask to the mark with distilled water. Stir the solution by turning the flask upside down several times and transfer it to a signed bottle. Fill the burette with the prepared solution.

To standardize the prepared solution, weigh out about 0.1 g of Na_2CO_3 (o the fourth decimal place). **Transfer quantitatively** the weighed amount to a conical flask, add 1-2 drops of methyl orange and titrate with the prepared HCl solution until the colour changes from yellow to orange (transitional colour between yellow and red). The titration should be performed at least 2-3 times.

Calculate the acid concentration based on the stoichiometry of the reaction.

$$C_{HCl} = \frac{2 \cdot m_{Na_2CO_3}}{V_{HCl} \cdot W \cdot M_{Na_2CO_3}}$$

where:
m – mass of weighed amount
V_{HCl} – volume of hydrochloric acid [dm^3]
W – proportionality of flask and pipette
$M_{Na_2CO_3}$ – molar mass (105.98 g/mol)

Experiment 2. **Determination of NaOH and Na_2CO_3 solutions**

1. Take 20 cm^3 of the solution prepared for the analysis.
2. Add 2-3 drops of phenolphthalein and slowly titrate with standardized HCl solution until the solution is discoloured.
3. Read from the burette the volume of hydrochloric acid that was used for the titration against phenolphthalein (a cm^3).
4. Then add 2-3 drops of methyl orange and continue titrating the sample with hydrochloric acid until the first colour change (from yellow to orange). The volume of HCl used for the titration against the orange is b cm^3.
5. The titration scheme for a mixture of sodium carbonate and sodium hydroxide is shown in Fig. 3.1.

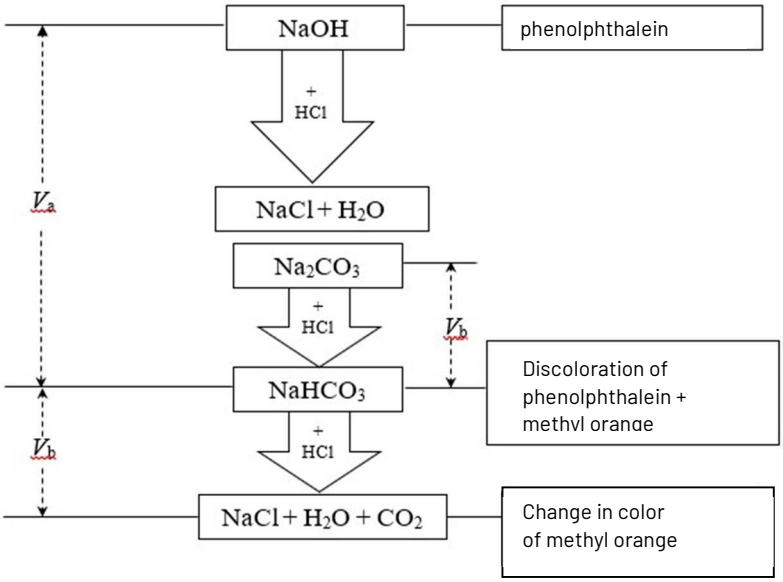

Fig. 3.1. Titration scheme of the mixtures Na_2CO_3 and NaOH

NOTE: In order not to lose carbon(IV) oxide during the titration in the presence of phenolphthalein, the solution to be titrated should be cooled to the lowest possible temperature, and the solution should be titrated slowly, stirring it calmly.

3.4. PRESENTATION AND ANALYSIS OF TEST FINDINGS

Calculation of results. In the first titration, titrate the whole amount of NaOH and $\frac{1}{2}Na_2CO_3$.

1. Calculate the NaOH content (in grams) in the sample using the formula:

$$m_{NaOH} = (a-b) \cdot C_{HCl} \cdot M_{NaOH} \cdot W \text{ [g]}$$

2. Calculate Na_2CO_3 content in the sample:

$$m_{Na_2CO_3} = \frac{2 \cdot b \cdot c_{HCl} \cdot M_{Na_2CO_3} \cdot W}{2} \text{ [g]}$$

where:

a – volume of HCl used for titration in the presence phenolphthalein [dm^3],

b – volume of HCl used in the presence of methyl orange [dm^3],

c_{HCl} – concentration of hydrochloric acid [mol /dm^3],

M_{NaOH} – molar mass NaOH (40 g /mol),

$M_{Na_2CO_3}$ – molar mass Na_2CO_3 (106 g /mol),

W – proportionality of flask and pipette.

Derive the formulas that were used for the calculations.

The student report should include

- Purpose and scope of the exercise
- Description of the test stand
- Equations of occurring reactions
- Results of subsequent titrations
- Calculation of hydrochloric acid concentration
- Calculation of NaOH and Na_2CO_3 content in the mixture (g per sample)

Checklist questions

1. Standard solutions: methods of preparation and titre setting. Standard substances.
2. Principle of alcacimetric determination.
3. Describe how to perform the exercise.
4. Alcacimetric titration curves.
5. Selection of the indicator for a specific titration system.
6. Calculations based on the stoichiometry of the neutralization reaction.
7. Calculations for converting concentrations of solutions.

Example calculation tasks

1. Calculate how many cm^3 of hydrochloric acid with a concentration of 38.32% and a density of 1.19 g/cm^3 should be used to prepare 250 cm^3 HCl with a concentration of 0.1 mol/dm^3.
2. How many cm^3 of concentrated sodium base with a density of 1.52 g/cm^3 should be used to obtain 500 cm^3 of NaOH solution with a concentration of 0.1 mol/dm^3.
3. To neutralize 20 cm^3 of acetic acid sample, 14.2 cm^3 of NaOH solution with a concentration of 0.1031 mol/dm^3 was used. Calculate CH_3COOH content of the sample analysed in milligrams.
4. How many grams of formic acid (HCOOH) are in the analysed sample if 20.5 cm^3 of 0.106 mol/dm^3 of sodium base is neutralized with phenolphthalein?
5. Three weights of Na_2CO_3 were prepared: 0.1249 g; 0.1297 g and 0.1334 g. For their titration against methyl orange, respectively: 25.3 cm^3, 24.6 cm^3 and 23.7 cm^3 of hydrochloric acid. Calculate the molar concentration of HCl.
6. Calculate the percentages of Na_2CO_3 and NaOH in a sample of mass $m = 0.2$ g if 30 cm^3 of 0.35% (*m/m*) was used when titrating against phenolphthalein, followed by 4 cm^3 of the same acid when further titrating against methyl orange.
7. A weight of 247.8 mg Na_2CO_3 was dissolved in water and the resulting solution was titrated against methyl orange with hydrochloric acid, 39 cm^3 of which was used. Calculate the molar concentration of hydrochloric acid.

8. Calculate how many milligrams of NaOH the solution contains if 23.7 cm^3 of hydrochloric acid of concentration C = 0.1374 mol/dm^3 was used for titration.

Health and safety requirements

- Only laboratory equipment, a script, and a laboratory notebook may be kept on the table during the exercise.
- Take the solution for analysis with a pipette using a cap.
- Concentr. HCl – may cause corrosion of metals. Causes severe skin burns and eye damage. May irritate the respiratory system.

3.5. **Bibliography**

1. Cygański A., *Chemiczne metody analizy ilościowej*, WNT, Warszawa 2021.
2. Szmal Z. S., Lipiec T., *Chemia analityczna z elementami chemii instrumentalnej*, PZWL, Warszawa 1997.
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4. IODOMETRIC DETERMINATION OF SULFIDE IONS H

4.1. **INTRODUCTION**

Iodometry is a branch of volumetric analysis that includes titrations involving iodine ($E^0_{I2/I-}$ = 0.535V). It is possible to determine oxidizing and reducing substances:

- Direct determination – by titration with a standard iodine solution. Determination involves substances with oxidation potentials lower than the chemical potential $I_2/2I^-$, e.g.: $S_2O_3^{2-}$, SO_3^{2-}, H_2S, hydroquinone, acetone.
- Indirect determination involves the indirect titration of the substance being analysed by adding a known amount of a standard solution of iodine, the excess of which is then determined. The most commonly used indicator in iodometry is starch. The excess of iodine is usually determined by titrating it with a solution of thiosulfate (e.g. $Na_2S_2O_3$).

As a result, the following reaction takes place:

$$I_2 + 2\ S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2\ I^-$$

The calculated excess of iodine added to the original substance is subtracted from the total iodine used to obtain the amount that reacted with the substance.

Substances with oxidation potentials higher than the chemical potential $I_2/2I^-$ can be determined, e.g.: BrO_3^-, IO_3^-, MnO_4^-, H_2O_2, Cu(II), Fe(III).

At the end of the titration, when the solution becomes transparent (in high concentration iodine colours it yellow), starch is added, which in combination with iodine forms an intense dark blue complex. Titrant is added until the starch becomes discoloured, which indicates the end of the titration.

4.2. PURPOSE AND SCOPE OF THE EXERCISE

The aim of this exercise is to determine the content of sulfide ions.

4.3. TEST METHODOLOGY

Test stand description

Reagents:

substances: $Na_2S_2O_3$ for analysis, I_2, KI for analysis; 2% starch solution, standard $K_2Cr_2O_7$ solution, chloroform, water for analysis containing sulfides

Laboratory equipment:

50 cm^3 burette, 10 and 20 cm^3 pipettes, conical flasks, pipette cap, weighing bottles

Running the experiment

Experiment 1. **Preparation and standardization of $Na_2S_2O_3$ solution**

Sodium thiosulfate can be obtained in a very pure state, but the crystallization water content of the molecule can change. Thus, a standard solution cannot be prepared from a weight of thiosulfate. A solution of approximate concentration is prepared, the standard of which is then determined on the appropriate basic substance (e.g. dichromate).

To prepare 1 litre of sodium thiosulfate solution of about 0.1 mol/dm^3, weigh (on the analytical balance) about 25 g of crystalline $Na_2S_2O_3 \cdot 5H_2O$ (or about 16 g of anhydrous salt) and dissolve in 1 litter of distilled water. The stability of the solution can be increased by adding 0.1 g of sodium carbonate to it. The standard is determined a few days after the preparation of the solution.

Standardization

Measure 20 cm^3 of standard $K_2Cr_2O_7$ solution into a ground glass conical flask. Add 2 g of potassium iodide and 20 cm^3 of 1 mol/dm^3 HCl solution. Seal and stir the solution in the flasks and set aside in a dark place for about 10 minutes. Then titrate the separated iodine with thiosulfate solution, adding about 2 cm^3 of starch solution at the end of the titration. The colour of the solution changes from blue to light green at the end of the titration.

In acidic media, dichromate ions react with iodide ions:

$$Cr_2O_7^{2-} + 6I^- + 14H^+ = 2Cr^{3+} + 3I_2 + 7H_2O$$

releasing an equivalent amount of iodine, which is then titrated with sodium thiosulfate solution:

$$I_2 + S_2O_3^{2-} = 2I^- + S_4O_6^{2-}$$

On the basis of both reactions it is possible to make an equation, on the basis of which the concentration of the standard thiosulfate solution can be calculated. It follows that 1 mole of $K_2Cr_2O_7$ reacts with 6 moles of $Na_2S_2O_3$

$$\frac{n_{K_2Cr_2O_7}}{n_{Na_2S_2O_3}} = \frac{1}{6}$$

$$C_{Na_2S_2O_3} = \frac{6 \cdot V_{K_2Cr_2O_7} \cdot C_{K_2Cr_2O_7}}{V_{Na_2S_2O_3}}$$

If the relative error between successive results does not exceed 0.5%, calculate the arithmetic mean of all three results, thus obtaining the final concentration of the solution to be standardized. If one of the results differs significantly from the others, discard it and calculate the average thiosulfate concentration from the others. If all the results differ significantly from each other (relative error between the results is greater than 0.5%), repeat the titration.

Experiment 2. **Preparation and titration of I_2 solution**

The iodine solution is prepared by dissolving crystalline iodine in an aqueous solution of potassium iodide (the solubility of iodine in pure water is very limited). Prepare a solution of approximate concentration (0.05 mol/dm^3) and then determine its standard.

To obtain 0.5 litres of iodine solution with a concentration of about C = 0.05 mol/dm^3, dissolve 20 g of potassium iodide in 5 cm^3 of water in a beaker. Then weigh out 6.4 g of crystalline iodine (on the analytical balance) and add to the prepared potassium iodide solution while stirring the solution. After the temperature has stabilized, make up to the mark with water. Store the iodine solution thus prepared in a dark glass bottle. The standard of the iodine solution is usually set to a standard $Na_2S_2O_3$ solution.

Standardization

Measure 20 cm^3 of iodine into the conical flask. Titrate the iodine with a standard solution of sodium thiosulfate. Before the end of the titration (when there is little iodine in the solution and the solution becomes visibly lighter), add about 2 cm^3 of the starch solution and titrate until the solution becomes discoloured.

$$I_2 + S_2O_3^{2-} = 2I^- + S_4O_6^{2-}$$

The reaction shows that 1 mole of iodine reacts with 2 moles of thiosulfate. Calculate the concentration of the iodine solution from the formula:

$$C_{I_2} = \frac{V_{Na_2S_2O_3} \cdot C_{Na_2S_2O_3}}{2 \cdot V_{I_2}}$$

Experiment 3. **Determination of sulfide ions**

1. Pipette 20 cm^3 of iodine solution into the conical flask, add 2 cm^3 of 1 mol/dm^3 hydrochloric acid.
2. Pipette 10 of sulfide solution, mix well.
3. Titrate the portion of iodine that has not reacted with a standard solution of sodium thiosulfate, adding the indicator (starch solution) at the end of the titration.
4. The determination should be performed at least three times (the arithmetic mean of at least two determinations with the difference not exceeding 0.2 cm^3).

4.4. PRESENTATION AND ANALYSIS OF TEST FINDINGS

Calculation of results

Calculate the sulfide content of the sample:

$$m_{S2-} = (V_{I_2} \cdot C_{I_2} - \frac{C_{Na_2S_2O_3} \cdot V_{Na_2S_2O_3}}{2}) \cdot \frac{M_S}{1000} [g\ w\ próbie]$$

where:
M_S – molar mass of sulfur 32.07 g/mol

Derive the formulas that were used for the calculations.

The student report should include

- Purpose and scope of the exercise
- Description of the test stand
- Equations of the occurring reactions
- Results of subsequent titrations
- Calculation of sulfide content (g per sample)

Checklist questions

1. Standard solutions: methods of preparation and standardization. Standard substances.
2. Principle of iodometric determination.
3. Describe how to perform the exercise.
4. Principle of sulfide determination: reactions, conditions.
5. What is iodometric determination and what condition must be met by the substance to be determined?
6. Selection of the indicator for a specific titration system.
7. What is reverse titration? When is this method of determination used?
8. Present the redox titration curve. Mark the position of the equivalence point.
9. Calculations based on the stoichiometry of the reaction.
10. Calculations for converting concentrations of solutions.

Example calculation tasks

1. What percentage concentration should the $Na_2S_2O_3$ solution have so that 1 cm^3 of it reacts with 1 mg of $K_2Cr_2O_7$?
2. How many percent of $Na_2S_2O_3$ is included in 25.0 cm^3 of the solution with d=1.144g/cm^3 if 29.48 cm^3 of 0.1mol/dm^3 iodine solution was used for its titration?
3. Potassium iodide was added to 10 g of chlorinated water and the separated iodine was titrated with 14.1 cm^3 of 0.1002 mol/dm^3 $Na_2S_2O_3$. How much chlorine % was contained in the chlorinated water?
4. How many g of $Cr_2O_7^{2-}$ are included in the solution if respectively: 20.2; 20.2 and 20.1 cm^3 of $Na_2S_2O_3$ solution of 0.1008 mol/dm^3 was used for its titration?

Health and safety requirements

- Only laboratory equipment, a script, and a laboratory notebook may be kept on the table during the exercise.
- Take the solution for analysis with a pipette using a cap.
- KI (solid) – harmful if swallowed. Irritating to skin. Irritating to eyes.
- I_2 – harmful in contact with skin. Harmful if inhaled. Very toxic to aquatic organisms.

4.5. **Bibliography**

1. Cygański A., *Chemiczne metody analizy ilościowej*, WNT, Warszawa 2005.
2. Szmal Z. S., Lipiec T., *Chemia analityczna z elementami chemii instrumentalnej*, PZWL, Warszawa 1997.
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5 DETERMINATION OF ZINC IONS BY COMPLEXOMETRIC TITRATION

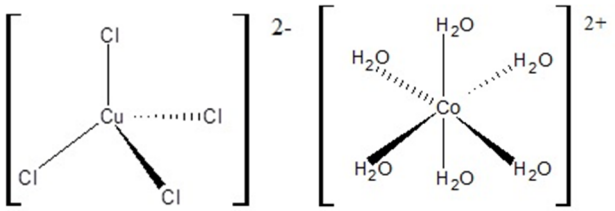
5.1. INTRODUCTION

Coordination complexes (are an assembly of one or more central atoms surrounded by directly related atoms or groups of atoms called ligands. Ligands bond to the central atom with an electron pair of so-called donor atoms, i.e. atoms that have a free electron pair (Fig. 1). In such complexes, donor-acceptor bonds are formed. **Ligands can be neutral molecules (e.g. H_2O, NH_3, CO) or anions (e.g. Cl^-, CN^-, NCS^-, OH^-).** A common feature of ligands is the presence of at least one donor atom. In most coordination complexes, the donor atoms of the ligands are atoms N, S, O, F.

In the molecule of the coordination complex the following can be distinguished.

a) the internal coordination sphere, which is the central ion called the coordination centre,
b) external coordination sphere, i.e. ligands.

Central ions are usually ions of elements of peripheral groups. Their characteristic feature is incomplete filling of the p and d subshells. Examples are copper and zinc ions, as well as iron, cobalt, nickel and manganese ions (Fig. 5.1.).



a) b)

Fig. 5.1. Examples of coordination complexes: **a)** $[Cu(Cl)_4]^{2-}$ and **b)** $[Co(H_2O)_6]^{2+}$

NOTE: the formation of covalent bonds (e.g. in CH_4 molecule) is a result of sharing electrons (each atom gives one electron); the formation of ionic bonds (e.g. in NaCl) is based on transferring an electron towards one of the atoms forming the bond; (b) the formation of coordination bond is based on sharing a pair of electrons that comes from only one atom.

Complexometry is a branch of titration analysis that determines substances in a sample by forming soluble and stable complexes. The used titrants are solutions of ligands that form chelate complexes with metals. These ligands, called **chelate ligands, or complexones**, bind to the central atom with more than one donor atoms, with the formation of at least one chelate ring. Depending on the number of coordination sites occupied at the central atom, one distinguishes between didentate, tridentate, tetradentate, etc. One example of a chelate ligand is ethylenediaminetetraacetic acid (EDTA, H_4Y; complexone II; Fig. 5.2.). In H_4Y determination, four hydrogen atoms are derived from the carboxyl group (-COOH), while the symbol Y denotes the rest of the molecule. During the formation of a coordination complex, the carboxyl group dissociates.

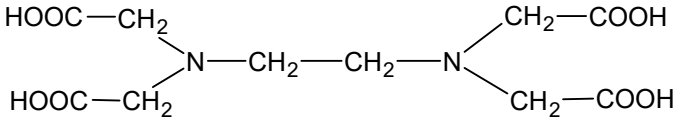


Fig. 5.2. Formula of ethylenediaminetetraacetic acid (H_4Y)

EDTA forms stable complexes with metal ions. **An important feature of EDTA is that, regardless of the valence of the metal ion, it always reacts with them in a molar ratio of 1:1.** The six donor atoms of one EDTA molecule (2 nitrogen atoms and 4 oxygen atoms) saturate only one metal ion with coordination. Depending on the pH value of the solution, EDTA forms chelate complexes with almost all multivalent metal ions. These complexes can be colourless or coloured in cases where the metal ion in the complex has chromophoric properties, such as iron, copper, nickel, chromium.

The equations of complexation with metal ions at different oxidation levels follow the below reactions:

$$M^{2+} + H_2Y^{2-} \rightarrow MY^{2-} + 2H^+$$

$$M^{3+} + H_2Y^{2-} \rightarrow MY^{-} + 2H^+$$

$$M^{4+} + H_2Y^{2-} \rightarrow MY + 2H^+$$

A measure of the stability of the complex formed is the so-called **stability constant of complexes**. For the MY complex it is expressed with the formula:

$$K_{MY} = \frac{[MY]}{[M]\cdot[Y]}$$

where:
[MY] – concentration of complex in solution
[M] – concentration of free metal ion in solution
[Y] – concentration of free ligand in solution

Often, the dissociation constants of the complexes are given as $-\log K_{MY} = pK_{MY}$. The bigger the pK_{MY} value, the more stable the complex.

Table 5.1. Examples of constants of stability of metal complexes with EDTA (T=20°C; I=0,1)

Cation	K_{MY}	pK_{MY}
Mg^{2+}	$4.9\cdot10^{8}$	8.69
Ca^{2+}	$5.0\cdot10^{10}$	10.70
Fe^{2+}	$2.1\cdot10^{14}$	14.33
Zn^{2+}	$3.2\cdot10^{16}$	16.50
Ni^{2+}	$4.2\cdot10^{18}$	18.60
Cu^{2+}	$6.3\cdot10^{18}$	18.80
Fe^{3+}	$1.3\cdot10^{25}$	25.10

Chelate complexes with EDTA have a much higher stability than complexes with simple ligands (including eriochrome black T and murexide; $pK_{MY}<7$), therefore, EDTA displaces the weaker ligand from the complex.

Indicators used in complexometric titration

The end point of the titration is determined using special complexometric indicators (*metal indicators)*. These include coloured organic compounds, which at the appropriate pH form complexes with metal ions of a different colour than that of the indicator itself. In the complexometric determination the stability of the metal-EDTA complex should always be much higher than the stability of the metal-indicator complex. The most commonly used indicators are: murexide for copper determination, calces for calcium, eriochrome black T for zinc.

The indicator used in the standardization of EDTA solution is **murexide**. In acidic or neutral media, murexide turns the solution red; in strongly alkaline media, i.e. at pH >9, the solution has a characteristic violet-pink colour as a result of the murexide anion. EDTA standardization is performed in an environment with a pH of about 12 using $CaCO_3$ (standard substance). In alkaline medium, murexide reacts with Ca^{2+} ions, forming a pink complex. It is less stable than the complex of EDTA with Ca^{2+}. Therefore, when added to the EDTA solution, the Ca^{2+}-murexide breaks down and Ca^{2+} ions move to EDTA. However, the colour of the solution gradually changes from pink to violet-pink.

$$\mathbf{CaH_2Ind^- + H_2Y^{2-} + 2OH^- \rightarrow H_2Ind^{3-} + CaY^{2-} + 2\ H_2O}$$

The indicator used for the determination of zinc ions is eriochrome black T. It is used for the determination of cations, e.g. Mg^{2+}, Zn^{2+}, Cd^{2+}, Ba^{2+}, Pb^{2+}. The colour of eriochrome black T (H_3Ind) depends on the pH of the solution:

$$\mathbf{H_2Ind^-} \leftrightarrow \mathbf{HInd^{2-}} \leftrightarrow \mathbf{Ind^{3-}}$$
pH~6,3 pH~11,5

In alkaline medium at pH~10, $HInd^{2-}$ indicator anions form with ions, e.g. Zn^{2+}, Mg^{2+}, colourful and well water-soluble complexes:

$$Zn^{2+} + \mathbf{HInd^{2-} \rightarrow ZnInd^- + H^+}$$

Zinc coordination complex with the indicator is less stable than zinc complex with EDTA (H_2Y^{2-}). Therefore, when EDTA is added to the solution, Zn^{2+} ions move from bonds $ZnInd^-$ to EDTA. At the same time, the colour of the solution changes from violet to blue:

$$\mathbf{ZnInd^- + H_2Y^{2-} \rightarrow ZnY^{2-} + HInd^{2-} + H^+}$$

5.2. PURPOSE AND SCOPE OF THE EXERCISE

The objective of this exercise is to prepare an EDTA solution, standardize it and determine zinc ions by complexometric titration.

5.3. TEST METHODOLOGY

Test stand description

Reagents:

EDTA substance, $CaCO_3$ standard solution 0.01 mol/dm^3, NaOH 1 mol/dm^3, ammonium buffer pH=10, murexide (1g/100g NaCl – grind in mortar), eriochrome black T (1 g/100 g NaCl – grind in mortar)

Laboratory equipment:

analytical balance, 1 dm^3 volumetric flask, 50 cm^3 burette, 250 cm^3 conical flask, 10 and 20 cm^3 pipettes, 5 cm^3 multidimensional pipette, 50 cm^3 cylinder

Running the experiment

a) **Preparation of EDTA with concentration 0.01 mol/dm^3**

- Prepare an EDTA solution of 0.05 mol/dm^3 (1 litre for 3 persons): weigh 18.6050 g of ethylenedimethyl tetraacetic acid disodium salt $Na_2HY \cdot 2\,H_2O$, dissolve in distilled water and make up to 1 dm^3 in a volumetric flask.
- To prepare an EDTA solution of 0.01 mol/dm^3 (individually for each student): take 100 cm^3 of the 0.05/dm^3, solution, transfer to a dark glass bottle, add 400 cm^3 of distilled water. Mix the prepared EDTA solution and standardize it into $CaCO_3$ standard solution. It will be used to perform complexometric titration in exercises 6 and 7.

b) **Standardization of EDTA solution**

Measure 10 cm^3 of a 0.01 mol/dm^3 $CaCO_3$ standard solution into a 250 cm^3 conical flask, add 5 cm^3 of 1 mol NaOH, a “pinch” of murexide, and titrate with the prepared EDTA solution until the colour changes from pink to purple. Calculate the amount of EDTA used for titration as the arithmetic mean volume based on three independent titrations.

c) **Complexometric determination of Zn^{2+}**

Dilute the resulting Zn^{2+} sample for analysis in a 100 cm^3 volumetric flask to the mark with distilled water. Measure 20 cm^3 of this test solution into a 250 cm^3 conical flask. Then, add 5 cm^3 of ammonium buffer (pH = 10), a "pinch" of eriochrome black T and a 50 cm^3 of a cylinder of distilled water. While stirring well, titrate with the standard EDTA solution until the colour changes from violet to blue.

Perform 3 titration trials. Calculate the average volume of EDTA used to titrate 20 cm^3 of the sample containing Zn^{2+} ions.

5.4. PRESENTATION AND ANALYSIS OF TEST FINDINGS

1. Calculate the concentration of the standard EDTA solution using the formula:

$$C_{EDTA} = \frac{C_{CaCO_3} \cdot V_{CaCO_3}}{V_{EDTA}} \left[\frac{mol}{dm^3}\right]$$

where:

C_{CaCO_3} – concentration of calcium carbonate standard solution, under experimental conditions (0.01 mol/dm^3)

V_{CaCO_3} – volume of calcium carbonate standard solution [cm^3]

V_{EDTA} – volume of used EDTA during the titration [cm^3]

2. Calculate the zinc content in a 20 cm^3 sample based on the formula:

$$m_{Zn^{2+}} = \frac{C_{EDTA} \cdot V_{EDTA} \cdot M_{Zn}}{1000} \ [g]$$

where:

C_{EDTA} – concentration of standard EDTA [mol/dm^3]

V_{EDTA} – volume of used EDTA during the titration [cm^3]

M_{Zn} – molar mass of zinc (65.39 g/mol)

3. Convert the obtained Zn^{2+} content to the content of zinc ions in the initial sample, i.e. in 100 cm^3, and refer to the standards defining parameters for evaluation of drinking water quality (permissible amount of Zn: 5 mg/ dm^3).

The student report should include

- Purpose and scope of the exercise
- Description of the test stand
- Equations of occurring reactions
- Results of subsequent titrations

Checklist questions

1. Describe the process of EDTA titration and complexometric determination of zinc ions.
2. Explain the terms: complex compound, complexone III, titration indicator, titration end point, complexometric titration curves, stability constant of the complex.
3. Discuss in detail the reactions occurring during the determinations.
4. Example calculation tasks in complexometry (literature item 3).

Health and safety requirements

- Only laboratory equipment, a script, and a laboratory notebook may be kept on the table during the exercise.
- Take the solution for analysis with a pipette using a cap.
- $BaCl_2$ – toxic if swallowed. Harmful if inhaled.
- Concentr. HCl – may cause corrosion of metals. Causes severe skin burns and eye damage. May irritate the respiratory system.

5.5. **Bibliography**

1. Cygański A., *Chemiczne metody analizy ilościowej*, WNT, Warszawa 2005.
2. Szmal Z.S., Lipiec T., *Chemia analityczna z elementami chemii instrumentalnej*, PZWL, Warszawa 1997.
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6. DETERMINATION OF CALCIUM AND MAGNESIUM IONS BY COMPLEXOMETRIC TITRATION

6.1. **INTRODUCTION**

Many samples of natural origin, including water, wastewater, soils, and rocks contain calcium and magnesium ions. Therefore, there is often a need for simultaneous determination of both ions in a single sample. One of the methods for the combined determination of calcium and magnesium is complexometric titration of the sample with a standard EDTA solution in the presence of two indicators: murexide and eriochrome black T. First, calcium is determined by titrating the sample with EDTA solution in the presence of murexide. The murexide is then decomposed with hydrochloric acid and magnesium is determined in the presence of eriochrome black T.

Murexide – is the ammonium salt of purple acid (abbreviated H_4Ind^-; Ind^- – murexide anion). The colour depends on the pH of the solution. In alkaline environments pH>12, murexide forms pink complexes with calcium ions. At this high pH, magnesium precipitates in the form of hydroxide and does not hinder the determination (up to a content in the sample of 50-70 mg/dm^3).

$$\mathbf{H_4Ind^-} \leftrightarrow \mathbf{H_3Ind^{2-}} \leftrightarrow \mathbf{H_2Ind^{3-}}$$
pH~9 pH~11

Eriochrome black T – a tri-basic organic acid that changes colour depending on pH. It forms red complexes with some metal cations (Mg^{2+}, Zn^{2+}, Cd^{2+}, Al^{3+}). Determination of metals is usually carried out in solutions of pH 10, at which there is a clear change in the colour of the indicator.

$$\mathbf{H_2Ind^-} \leftrightarrow \mathbf{HInd^{2-}} \leftrightarrow \mathbf{Ind^{3-}}$$
pH 6,3 pH 11,5

6.2. **PURPOSE AND SCOPE OF THE EXERCISE**

The aim of this exercise is to determine the content of calcium and magnesium in a water sample received for analysis.

6.3. **TEST METHODOLOGY**

Test stand description

Reagents:

NaOH 1 mol/dm^3, EDTA standard solution, C=0.01 mol/dm^3 (exact concentration to be determined in the course of titration), HCl (1:1), ammonia solution (1:1), murexide (1 g / 100 g NaCl – grind in mortar), eriochrome black T (1 g / 100 g NaCl – grind in mortar)

Laboratory equipment:

50 cm^3 burette, 250 cm^3 volumetric flask, 25 cm^3 pipette, 5 cm^3 and 10 cm^3 multidimensional pipettes

Running the experiment

a) Prepare and standardize the EDTA solution of 0.01 mol/dm^3 or use the EDTA solution prepared in the previous class.

b) Determine the calcium and magnesium in the sample as follows:

Dilute the resulting sample in a 100 cm^3 volumetric flask to the mark with distilled water. Measure 25 cm^3 of this solution (test sample) into a 250 cm^3 conical flask. Then add 5 cm^3 of NaOH 1 mol/dm^3 and a "pinch" of murexide. While stirring well, titrate with the standard EDTA solution until the colour changes from pink to a permanent dark purple. Read the volume of used EDTA, which should be converted to calcium content.

Next, to the above solution (without putting aside the burette) add 4 cm^3 HCl (1:1) to decompose the murexide. Decolorize the solution after a few seconds by adding 7 cm^3 of ammonia (1:1), add a "pinch" of eriochrome black T and titrate with the EDTA solution while stirring vigorously until the colour changes from violet to blue. The volume of EDTA used in the titration against eriochrome black T must be converted to magnesium content.

Perform each titration three times.

6.4. PRESENTATION AND ANALYSIS OF TEST FINDINGS

1. **Give the reactions that occur during the determination of Ca^{2+} and Mg^{2+} ions**

$$Ca^{2+} + H_2Y^{2-} \rightarrow CaY^{2-} + 2H^+$$

$$Mg^{2+} + H_2Y^{2-} \rightarrow MgY^{2-} + 2H^+$$

2. **Indicate the amount of used EDTA per sample titration**

Volumes of used EDTA in the presence of murexide (titration of Ca^{2+} ions):

- Titration I V_1 = …….. cm^3
- Titration II V_1 = …….. cm^3
- Titration III V_1 = …….. cm^3
- Mean volume of EDTA $\mathbf{V1_{av}}$ **= ……. cm^3**

Volumes of used EDTA in the presence of eriochrome black T:

- Titration I V_2 = …….. cm^3
- Titration II V_2 = …….. cm^3
- Titration III V_2 = …….. cm^3
- Mean volume of EDTA $\mathbf{V2_{av}}$ **= ……. cm^3**

3. **Calculate the quantities of ions to be determined from the formulas:**

$$X_{Ca^{2+}} = V_{1av} \cdot C_{EDTA} \cdot 0{,}04008$$

$$X_{Mg^{2+}} = V_{2av} \cdot C_{EDTA} \cdot 0{,}02432$$

where:
v_{1av} – volume of used EDTA during titration against murexide [cm^3]
v_{2av} – volume of used EDTA during titration against eriochrome black T [cm^3]
CEDTA – EDTA concentration [mmol/cm^3]
0,04008 – Ca^{2+} minimole mass [g/mmol];
0,02432 – Mg^{2+} minimole mass [g/mmol]

Recalculate the content of determined Ca^{2+} and Mg^{2+} ions in the sample obtained for analysis (i.e. in 100 cm^3). Refer to the standards defining the parameters for assessing the quality of drinking water (permissible amount of Mg: 7-125 mg/dm^3).

The student report should include

- Purpose and scope of the exercise
- Description of the test stand
- Equations of occurring reactions
- Results of calcium and magnesium determination

Checklist questions

1. Procedure of EDTA titration and complexometric determination of zinc ions.
2. Explain the terms: complex compound, complexone III, titration indicator, titration end point.
3. Discuss in detail the reactions occurring during determinations.
4. Examples of complexometry calculations carried out during the classes in Analytical Chemistry.

Health and safety requirements

- Only laboratory equipment, a script, and a laboratory notebook may be kept on the table during the exercise.
- Take the solution for analysis with a pipette using a cap.
- Concentr. HCl – may cause corrosion of metals. Causes severe skin burns and eye damage. May irritate the respiratory system.

6.5. **Bibliography**

1. Cygański A., *Chemiczne metody analizy ilościowej*, WNT, Warszawa 2005.
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7. DETERMINATION OF CHLORIDE IONS IN WATER

7.1. INTRODUCTION

Good solubility of chloride and its widespread occurrence in the earth's crust in the form of natural salt deposits (NaCl and $MgCl_2$) means that chloride ions are found in all natural waters. The content of chloride ions in natural waters can range from a few tenths of a milligram up to several hundred grams in 1 dm^3 of water.

When assessing the chloride content in water, special attention should be paid to the source of its origin. According to the sanitary-hygienic requirements, the content of chloride ions of geological origin should not exceed 250 mg/dm^3 (Regulation of the Polish Minister of Health). Chlorides of other origin, e.g. from sewage, make water unfit for drinking. The permissible concentration of chlorides in surface water is: Class I – 250 mg/dm^3, Class II – 300 mg/dm^3, Class III – 400 mg/dm^3.

The determination of chloride ion content in water is carried out by titration methods using silver(V) nitrate(I) as titrant. These include the Mohr method (PN-ISO 9297:1994) or the Volhard method. The Mohr method (direct method) is used for the determination of chloride in a neutral or weakly basic solution (at pH = 6.5 to 10). The Volhard method (indirect method) is used for the determination of chloride in an acidic solution.

Argentometry is one of the methods of precipitation titration analysis, which encompasses methods of titration analysis based on the formation reactions of sparingly soluble silver compounds of well-defined composition. The precipitate is formed when titrant is added to a solution of the substance to be determined. The precipitate must form rapidly and settle readily at the bottom of the vessel.

The precipitation titration analysis uses some of the reactions also used in the gravimetric analysis. The fundamental difference between the two methods is that in precipitation analysis the amount of titrant added must

be strictly equivalent to the amount of the component being determined (the stoichiometric ratios of the reactions must be maintained), whereas in the gravimetric analysis an excess of precipitating reagent is added to reduce the solubility of the precipitate.

Argentometric determination of chlorides

The Mohr method is based on direct titration of a neutral solution containing Cl^- ions with a standard solution of silver nitrate(V) $AgNO_3$ in the presence of potassium chromate(VI) K_2CrO_4 as indicator. Silver ions Ag^+ with chloride ions Cl^- form insoluble precipitate AgCl.

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow$$

After complete precipitation of Cl^- ions, Ag^+ ions react with chromate(VI), then the colour of the solution changes from yellow to red-brown, which indicates the end point of titration

$$2Ag^+ + CrO_4^{2-} \rightarrow Ag_2CrO_4\downarrow$$

The Mohr method can be used to determine chloride in solutions of pH 6.5-10.5. If the starting solution is acidic, it is first neutralized with sodium hydroxide in the presence of phenolphthalein, then a dilute solution of acetic acid is added to discolor the indicator. The determination of chloride ions is hindered by: carbonates, phosphates(V) and other anions, which form soluble compounds with Ag(I) ions in neutral medium.

Chloride determination in the presence of hydrolysing metals, e.g. iron(III), aluminium(III), and in the presence of carbonates, phosphates or oxalates is not possible at pH 6.5-10.5. In such cases, chloride can be determined in an acidic medium by the Volhard method.

The Volhard method is the precipitation of chloride in water by the introduction of an excess of a standard solution of silver nitrate. Unbound silver ions are titrated with a standard solution of ammonium thiocyanate (ammonium rhodanide). The indicator is iron(III) ions from an acidified solution of ammonium-iron(III) sulfate (with the traditional name of iron-ammonium alum – $FeNH_4(SO_4)_2 \cdot nH_2O$). After precipitation of the entire amount of Ag(I) ions, the first drop of excess added thiocyanate solution forms a red complex with iron(III) ions $Fe(SCN)^{2+}$.

$$Ag^+ + Cl^- \rightarrow AgCl$$

$$Ag^{+} + SCN^{-} \rightarrow AgSCN$$

$$Fe^{3+} + SCN^{-} \rightarrow Fe(SCN)^{2+}$$

7.2. PURPOSE AND SCOPE OF THE EXERCISE

The aim of this exercise is to determine the chloride content of water.

7.3. TEST METHODOLOGY

Test stand description

Reagents:

$AgNO_3$ – standard solution of 0.1 mol/dm^3, K_2CrO_4 – 5% solution, NH4SCN – standard solution of 0.02 mol/dm^3, HNO_3 – standard solution of 1 mol/dm^3, alum (sulphate(VI)) of iron (III) and ammonium ($Fe(NH_4)(SO_4)^2 \cdot n\,H_2O$) – 10% solution, chloroform

Laboratory equipment:

50 cm^3 burette, 5 and 10 cm^3 pipettes, pipette cap, conical flasks with stopper, 10 cm^3 cylinder

Running the experiment

Experiment 1. **Determination of chlorides by the Mohr method**

Pipette 10 cm^3 of the test sample, transfer to the conical flask, add 1 cm^3 of potassium chromate and titrate with standard silver nitrate solution until the colour changes from yellow to red-brown. Repeat the determination at least twice. When calculating the arithmetic mean, take results that differ by no more than 0.2 cm^3.

Experiment 2. **Determination of chlorides by the Volhard method**

Pipette 10 cm^3 of the test sample, transfer to the conical flask with a glass stopper, add 5 cm^3 of HNO_3 and 40 cm^3 of standard $AgNO_3$ solution from a burette. Then add 3 cm^3 of chloroform and 1 cm^3 of iron-ammonium alum. Close the flask with a stopper and shake the contents for one minute. The coagulated chloride precipitate should sink to the bottom, leaving a clear solution. Titrate the prepared sample with standard NH_4SCN solution until a slight red coloration appears, which does not disappear in spite of one minute of strong stirring. Repeat the determination at least twice.

When calculating the arithmetic mean, take results that differ by no more than 0.2 cm^3.

7.4. PRESENTATION AND ANALYSIS OF TEST FINDINGS

Determination of chlorides by the Mohr method

From the reaction equation $Ag^+ + Cl^- \rightarrow AgCl\downarrow$ it follows that 1 mole of Ag^+ ions reacts with 1 mole of Cl^- ions.

and so:

$$n_{AgNO_3} = n_{Cl^-}$$

$$c_{AgNO_3} \cdot v_{AgNO_3} = \frac{m_{Cl^-}}{M_{Cl^-}}$$

$$m_{Cl^-} = C_{AgNO_3} \cdot v_{AgNO_3} \cdot M_{Cl^-} \text{ [g w próbie]}$$

where:

M_{Cl^-} = 35.45 [g/mol]

C_{AgNO_3}– concentration of $AgNO_3$ solution [mol/dm^3]

v_{AgNO_3}– volume of $AgNO_3$ solution used for titration [dm^3]

Determination of chlorides by the Volhard method

The chloride content is calculated from the difference between the initial volume of $AgNO_3$ solution and the volume corresponding to the used NH_4SCN solution.

$$m_{Cl^-} = (v_{AgNO_3} \cdot c_{AgNO_3} - v_{NH_4SCN} \cdot c_{NH_4SCN}) \cdot M_{Cl^-} \text{ [g]}$$

where:

v_{AgNO_3} – volume of $AgNO_3$ solution added in excess [dm^3]

c_{AgNO_3} – concentration of $AgNO_3$ solution [mol/dm^3]

v_{NH_4SCN} – concentration of NH_4SCN solution used for titration [dm^3]

c_{NH_4SCN} – concentration of NH_4SCN solution [mol/dm^3]

The student report should include

- Purpose and scope of the exercise
- Description of the test stand
- Equations of occurring reactions

- Results of subsequent titrations
- Calculate the chloride ion content of the sample

Checklist questions

1. Principle of determining chloride ions in water.
2. What properties should precipitates show in a precipitation titration analysis?
3. Preparation and titration of standard solutions used in argentometry.
4. Why is chloroform added in the Volhard method?
5. State in what pH range the Mohr and Volhard method can be used and why.
6. Calculations from stoichiometry of reactions.

Example calculation tasks

1. Calculate the molar concentration of sodium chloride solution obtained by dissolving 200 mg of this salt and making up to 0.25 dm^3 with water.
2. Calculate the molar concentration of ammonium thiocyanate solution if 23.4 cm^3 of 0.0103 mol/dm^3 $AgNO_3$ solution was used to titrate 20 cm^3 of this solution.
3. Calculate molar concentration of $AgNO_3$ solution, if 26.5 cm^3 of this solution was used to titrate 0.1630 g of NaCl.
4. Calculate the molar concentration of $AgNO_3$ solution if 23.8 cm^3 of $AgNO_3$ solution was used for a 0.1815 g weight of salt containing 90% NaCl.
5. What is the molar concentration of NaCl solution, if 28.4 cm^3 of $AgNO_3$ with concentration 0.1052 mol/dm^3 was used to titrate a sample of a volume of 5.0 cm^3 used?
6. 0.1 gram of sodium chloride was dissolved in water and 40 cm^3 of $AgNO_3$ was added at a concentration of 0.0098 mol/dm^3. Excess silver ions were titrated with ammonium rhodanide using 24.3 cm^3 of this solution. Calculate the molar concentration of NH_4SCN solution.
7. How many mg of chloride are in the water sample if 35.2 cm^3 of 0.0111 mol/ dm^3 $AgNO_3$ solution was used to titrate it?
8. Calculate the molar concentration of a solution of calcium chloride if 23.5 cm^3 of 0.0546 mol/dm^3 $AgNO_3$ solution was used to titrate 50 cm^3 of this solution. What is its percent concentration if the density is 0.994 g/cm^3.

Health and safety requirements

- Only laboratory equipment, a script, and a laboratory notebook may be kept on the table during the exercise.
- Take the solution for analysis with a pipette using a cap.
- Make sure that you pour the reagents into the correct burettes, which are labelled accordingly: $AgNO_3$ or NH_4SCN.
- Silver nitrate(V) and its solutions are very dirty. Glassware should be washed immediately after the titration is complete. May cause skin burns and eye damage. Very toxic to aquatic life with long lasting effects.

7.5. **Bibliography**

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8. DETERMINATION OF WATER HARDNESS

8.1. INTRODUCTION

Water hardness is a conventional term for the content of divalent cations in water, mainly calcium and magnesium, which occur in water in significant quantities. Other ions, such as Fe^{2+}, Mn^{2+}, Ba^{2+}, Sr^{2+}, may also cause water hardness, but they occur in water in much smaller concentrations than Ca^{2+}, Mg^{2+} ions and therefore only the hardness caused by calcium and magnesium compounds is determined. Table 8.1 lists types of water hardness.

Table 8.1. Types of water hardness

Total hardness T_0					
Breakdown by cations		Breakdown by anions			
		carbonate hardness T_w		non-carbonate hardness T_n	
T_{Ca}	calcium hardness	T_{wCa}	$Ca(HCO_3)_2$ $Ca(OH)_2$	T_{nCa}	$CaSO_4$ $CaCl_2$ $Ca(NO_3)_2$
T_{Mg}	magnesium hardness	T_{wMg}	$Mg(HCO_3)_2$	T_{nMg}	$MgSO_4$ $MgCl_2$ $Mg(NO_3)_2$

The hardness of water caused by bicarbonates, carbonates and hydroxides of calcium and magnesium present in water is referred to as carbonate hardness (T_w). Hardness caused by other calcium and magnesium compounds is referred to as non-carbonate hardness (T_{nw}). Total hardness (T_o) is the sum of carbonate and non-carbonate hardness.

Water hardness can be expressed in different units. The basic ones are mmol/dm^3 and mval/dm^3 (milligram-equivalent of compounds that cause hardness in 1 dm^3 of water). In practice, most often water hardness is expressed by degrees of hardness (German ^{o}n, French ^{o}f and English ^{o}a). Table 8.2. shows conversion values of water hardness expressed in different units.

Table 8.2. Water hardness conversion units

	French degree [°f]	German degree [°n]	[mg $CaCO_3$] /dm^3	English degree [°e]	[mval/ dm^3]	[mmol/ dm^3]
French degree [°f]	1.00	0.56	10.00	0.70	0.20	0.10
German degree [°n]	1.79	1.00	17.86	1.25	0.36	0.18
[mg $CaCO_3$] /dm^3	0.10	0.056	1.00	0.07	0.02	0.01
English degree [°e]	1.43	0.80	14.30	1.00	0.29	0.14
[mval/dm^3]	5.00	2.80	50.00	3.50	1.00	0.50
[mmol/dm^3]	10.0	5.60	100.00	7.00	2.00	1.00

Natural waters are characterized by varying hardness. Precipitation waters are very soft and have a hardness close to zero. In freshwater, calcium hardness predominates. Surface waters, especially mountain streams, are generally soft. Groundwater exhibits greater hardness. Very soft waters have a bland or tasteless aftertaste. Water hardness is important in assessing its suitability for industrial purposes. Many industries require soft water, such as steam boiler feed water, equipment cooling water and district heating water. Soft water is required by the textile industry, electroplating plants and the food industry.

Table 8.3. Water hardness scale

Water hardness scale	Water hardness unit			
	[mval/dm^3]	[mg $CaCO_3$/dm^3]	[°n]	[mmol/dm^3]
Very soft water	< 2	< 100	< 5,6	< 1
Soft water	2 – 4	100 – 200	5.6 – 11.2	1 – 2
Moderately hard water	4 – 7	200 – 350	11.2 – 19.6	2 – 3.5
Hard water	7 – 11	350 – 550	19.6 – 30.8	3.5 – 5.5
Very hard water	> 11	> 550	> 30.8	> 5.5

Calcium and magnesium salts present in hard water can cause the inclusion of difficult to dissolve deposits called scale and can increase the corrosive properties of water. Hard water causes deterioration of the

quality of fabrics washed in such water, as well as higher consumption of soap and washing agents. The water hardness scale is shown in Table 8.3.

Removing water hardness

Among water softening methods, the following types are distinguished: distillation, thermal methods, chemical methods.

1. **Distillation** gives ideal softening effect, as it deprives water of all salts. However, it is not used in industry because of the high cost of thermal energy. Only thermal engineering uses condensates, i.e. the condensate from heating equipment.
2. **Thermal method.** Thermal decomposition of calcium and magnesium bicarbonates occurs at elevated temperatures above 40°C.
3. **Chemical method.** Chemical methods involve chemically precipitating insoluble precipitates or binding calcium and magnesium ions into complex compounds using various reactants, such as lime hydroxide (lime), sodium bicarbonate (soda), sodium hydroxide (caustic soda), phosphates, and other compounds.

Ionite methods

Depending on the required degree of water hardness to be reduced and the type of hardness to be removed, ion exchange is used:

- hydrogen cycle on weakly acidic cation exchangers – removal of carbonate hardness;
- in the sodium or hydrogen cycle on strongly acidic cation exchangers – removal of carbonate and non-carbonate hardness;
- in hydrogen and sodium cycles – removal of carbonate and non-carbonate hardness;
- in hydrogen cycle (weakly acidic cationite – decarbonation + strongly acidic cationite – removal of carbonate and non-carbonate hardness);
- decarbonation and decation on strongly acidic cationite in the sodium cycle and basic anionite in the chloride cycle.

Determination of water hardness

In the practice of water hardness determination, two analytical methods are used: acidimetry and complexometry.

Acidimetry

Acidimetry is a method for determining the amount of alkali (or alkaline substances) in a solution by titration with a standard acid solution. Carbonate hardness can be determined by titrating a water sample with a standard solution of hydrochloric acid in the presence of methyl orange (alkacimetric indicator). During the titration, reactions take place that can be described by the equations:

$$Ca(HCO_3)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O + 2CO_2$$

$$Mg(HCO_3)_2 + 2HCl \rightarrow MgCl_2 + 2H_2O + 2CO_2$$

Complexometry

The total hardness of water is determined by the complexometric method, titrating a water sample with EDTA solution in the presence of the indicator eriochrome black T. EDTA is the disodium salt of ethylenediaminetetraacetic acid (other names – disodium edetate, complexone III). It is the basic reagent in complexometry.

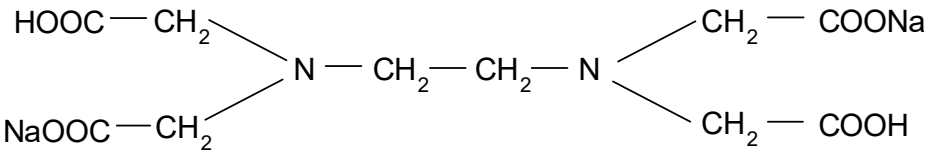

Fig. 8.1. EDTA formula

The basics of complexometry are discussed in chapters 5 and 6. Disodium edetate forms colourless complexes with calcium and magnesium ions. The titration is carried out in the presence of the indicator eriochrome black T, which at pH 10 forms red, weakly dissociated chelate bonds with calcium and magnesium ions. During the titration with EDTA solution the complexes of Ca^{2+} and Mg^{2+} ions with the indicator are replaced by more stable complexes of these ions with vermate and the solution takes on the blue colour of the free salt of the indicator. The titration is performed at pH 10-10.5, because then the difference between the colour of the indicator itself and the colour of its complex with calcium or magnesium ions is the greatest. The following is a schematic representation of the reactions (for example, for Mg^{2+}) occurring during titration:

$$Mg^{2+} + HInd^{2-} \rightarrow HInd^{-} + H^{+}$$

$$\mathbf{MgInd^{2-}} + H_2Y^{2-} \rightarrow MgY^{2-} + \mathbf{HInd^{2-}} + H^{+}$$

where:
$HInd^{2-}$ – indicator anion
H_2Y^{2-} – anion of sodium salt of edetic acid.

In the determination of calcium hardness, murexide –ammonium salt of purple acid – is used as an indicator. In an alkaline medium (pH>12), it forms a pink complex with calcium ions.

$$Ca^{2+} + \mathbf{H_2Ind^{3-}} \rightarrow \mathbf{CaH_2Ind^{-}}$$

$$\mathbf{CaH_2Ind^{-}} + H_2Y^{2-} + 2OH^{-} \rightarrow CaY^{2-} + \mathbf{H_2Ind^{3-}} + 2H_2O$$

At this high pH, magnesium ions precipitate as hydroxide and do not hinder determination.

8.2. PURPOSE AND SCOPE OF THE EXERCISE

The purpose of this exercise is to determine the hardness of tap water. Water hardness can be determined by the complexometric and acidimetric method. Complexometric determination is used for total hardness and calcium hardness, acidimetric determination – for non-carbonate hardness.

8.3. TEST METHODOLOGY

8.3.1. Determination of carbonate hardness

Test stand description

Reagents:

hydrochloric acid 0.01 mol /dm^3, methyl orange

Laboratory equipment:

Titration equipment kit

Running the experiment

1. Measure 100 cm^3 of the test water into a conical flask, then add 2-3 drops of methyl orange.

2. Titrate the water sample with 0.01 mol/dm^3 hydrochloric acid until the colour changes from yellow to orange. Carry out the measurement 2-3 times.

Elaboration of results

1. Calculate the carbonate hardness of water from the formula:

$$T_w = 28 \cdot v_{HCl} \cdot c_{HCl} \quad [°n]$$

where:

v_{HCl} – volume (average of at least three titrations) of HCl solution HCl [cm^3]
c_{HCl} – molar concentration of HCl solution [mol/dm^3].
28 – 1/2 millimolar mass of CaO [mg].

2. Discuss the results.

8.3.2. Determination of calcium hardness

Test stand description

Reagents:

NaOH at 2 mol/dm^3, murexide, EDTA solution at 0.01 mol/dm^3

Laboratory equipment:

Titration equipment kit

The calcium hardness of water is determined by the complexometric method, titrating the water sample with disodium edetate (EDTA) in the presence of murexide indicator.

Running the experiment

1. To a 100 cm^3 sample of test water add 5 cm^3 of 2 mol/dm^3 NaOH solution and a pinch of murexide.
2. Immediately titrate with 0.01 mol/dm^3 disodium edetate (EDTA) solution until the solution turns dark violet (titrate twicenie).

Elaboration of results

1. Calculate the carbonate hardness of water from the formula:

$$T_{Ca} = v_{\mathrm{EDTA}} \cdot c_{\mathrm{EDTA}} \cdot 56{,}08\ [°\mathrm{n}]$$

where:
v_{EDTA} – EDTA volume (mean of at least three titrations) [cm^3]
c_{EDTA} – molar concentration of EDTA solution [mol/dm^3]
56,08 – millimolar mass of CaO [mg].

2. Discuss the results

8.3.3. Determination of total hardness

Test stand description

Reagents:

ammonium buffer pH=10, eriochrome black, EDTA solution 0.01 mol/dm^3

Laboratory equipment:

Titration equipment kit

The total hardness of water is determined by the complexometric method, titrating a water sample with disodium edetate (EDTA) in the presence of the indicator – eriochrome black T.

Running the experiment

1. Measure 100 cm^3 of the test water into a conical flask.
2. Add about 2 cm^3 of ammonium buffer (pH = 10) and a pinch of eriochrome black.
3. Titrate the water sample with 0.01 mol/dm^3 disodium edetate (EDTA) solution until the colour of the solution changes from violet to blue.

Elaboration of results

1. Calculate the total hardness of the water from the formula:

$$T_o = c_{\mathrm{EDTA}} \cdot v_{\mathrm{EDTA}} \cdot 56{,}08\ [°\mathrm{n}]$$

where:
v_{EDTA} – EDTA volume (mean of at least three titrations) [cm^3]
c_{EDTA} – molar concentration of EDTA [mol/dm^3]
56,08 – millimolar mass of CaO [mg].

2. Discuss the results.

8.4. PRESENTATION AND ANALYSIS OF TEST FINDINGS

Calculate the hardness of total, calcium and carbonate and non-carbonate water.

The student report should include

- Purpose and scope of the exercise
- Description of the test stand and test methodology
- Calculations of water hardness
- Discussion and conclusions

Checklist questions

1. Hardness of water, types of water hardness.
2. Compounds that cause water hardness.
3. Methods of removing water hardness.
4. Describe how to perform the exercise.
5. Methodology of determining the calcium, carbonate and total hardness.

Health and safety requirements

- Only laboratory equipment, a script, and a laboratory notebook may be kept on the table during the exercise.
- Take the solution for analysis with a pipette using a cap.
- Be careful when working with hotplates.
- Follow the general rules used in an Analytical Chemistry laboratory

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9. SPECTROPHOTOMETRIC DETERMINATION OF NICKEL IONS

9.1. INTRODUCTION

In exercises 5 and 6, the ion content was determined by classical complexometric titration (indicator: eriochrome black T or murexide; titrant: EDTA). The end point of the titration was assessed visually when the colour of the solution changed. Visual methods are not accurate, so spectrophotometers (Fig. 9.1), colorimeters, or photocolorimeters are used to measure the colour of the solution.

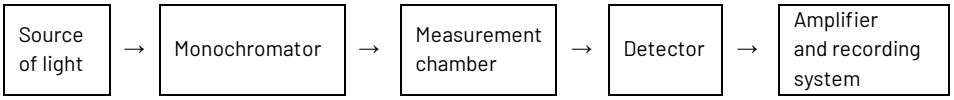

Fig. 9.1. Structure of a spectrophotometer

Sources of radiation are lamps that provide a continuous spectrum over a range of wavelengths:

- tungsten (420-750 nm) or mercury lamps (365-750 nm),
- deuterium lamps emitting a spectrum of molecular hydrogen in the range 200-350 nm,
- xenon lamps in the range UV-Vis (200-750 nm).

Monochromators are used to adjust the wavelength to obtain monochromatic light (of equal wavelength). The monochromator can be a prism or a diffraction grating and a slit that transmits radiation of the appropriate wavelength.

Cuvettes with the test solution are placed **in the measurement chamber.** The cuvettes can be made of glass, plastic masses or quartz (Fig. 9.2). Radiation passes through the two opposite, transparent walls of the cuvette. The cuvette is placed in the measurement chamber by holding it by its frosted walls. The most commonly used cuvettes have layer thicknesses of 1, 2 and 5 cm.

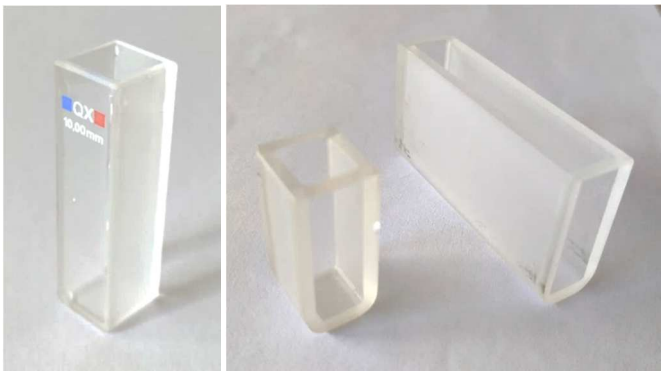

Fig. 9.2. Measurement cuvettes

During the measurement, the SPECTROPHOTOMETER measures a change in intensity of light coming from and passing through the analysed solution, which is placed in the measuring cuvette (Fig. 9.3). Measurement results are expressed in units of transmittance (T) or absorbance (A).

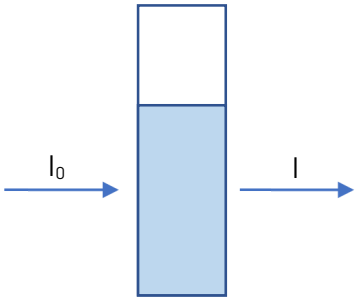

Fig. 9.3. Absorption of light by the sample (radiation incident on the sample I_0, radiation passing through the sample I)

- **Transmittance (T)** is the ratio of the radiation passing through the sample I to the radiation incident on the sample I_0. Transmittance is usually expressed as a percentage. It takes values from 0 to 100%.

$$T = \frac{I}{I_0} \cdot 100\%$$

- **Absorbance (A)** is equal to the logarithm of the ratio of the radiation incident on sample I_0 to the radiation passing through sample I. It takes values from 0 to infinity.

$$A = \log\frac{I_0}{I} = \log\frac{1}{T}$$

Absorbance is directly proportional to the concentration of the solution C and the optical path length l, which is the thickness of the layer of solution through which the light passes, and is expressed by the formula:

$$A = \varepsilon \cdot l \cdot C$$

where:

ε – molar absorption coefficient, which characterizes the intensity of absorption of electromagnetic radiation by a given substance at a given wavelength [dm^3/(mol·cm)]. The coefficient ε is a constant quantity, depending on the wavelength of incident light, the nature of the solute, temperature and pressure.

l – optical path length (cuvette width) [cm].

C – molar concentration of the substance [mol/dm^3].

This equation expresses the fundamental law of absorption spectrophotometry called **the Lambert-Beer law**.

Spectrophotometric titration is a type of titration in which changes in the absorbance of the test solution are recorded as a result of the addition of successive portions of titrant. The end point (EP) of a spectrophotometric titration is determined from the graph of the dependence of absorbance on the volume of added titrant A=f(V) (Fig. 9.4). During the measurement at least one substance: titrated (sample), titrant, or product of the reaction, must absorb radiation at the selected **analytical wavelength**.

The analytical wavelength is the wavelength corresponding to the absorbance maximum (i.e., at this wavelength the analysed solution absorbs incident radiation most strongly). An example UV-Vis spectrum for an organic compound is shown in Fig. 9.5. This spectrum shows two absorbance maxima, at about 213 and 307 nm, which may constitute the analytical wavelength.

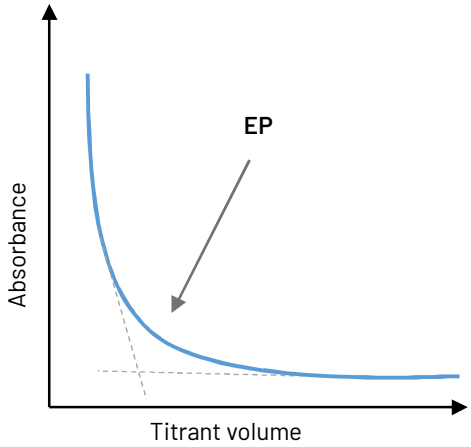

Fig. 9.4. Example of a spectrophotometric titration curve

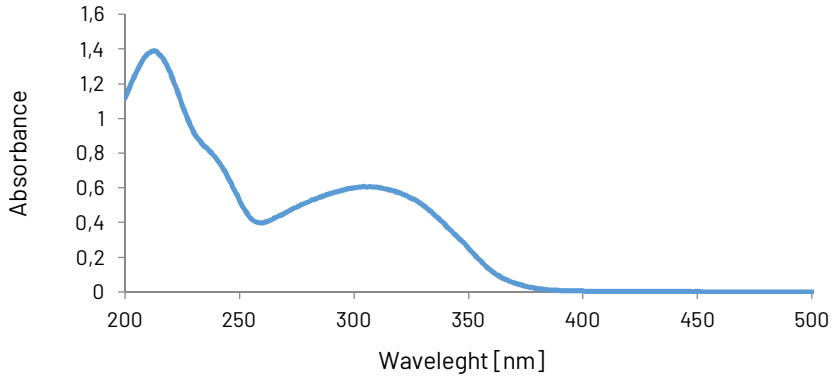

Fig. 9.5. UV-Vis spectrum of tannic acid ($C = 10^{-5}$ mol/dm^3) registered in the range of 200-500 nm

Spectra recorded for the same compound but with increasing concentrations have absorption maxima at the same wavelengths, but they differ in intensity (height) or absorbance (Fig. 9.6). It is important to remember that absorbance is closely dependent on concentration (reaction product, titrant, or sample component). Therefore, during a spectrophotometric titration, spectra are not recorded for a wide spectral range, but absorbance is measured for one selected analytical wavelength.

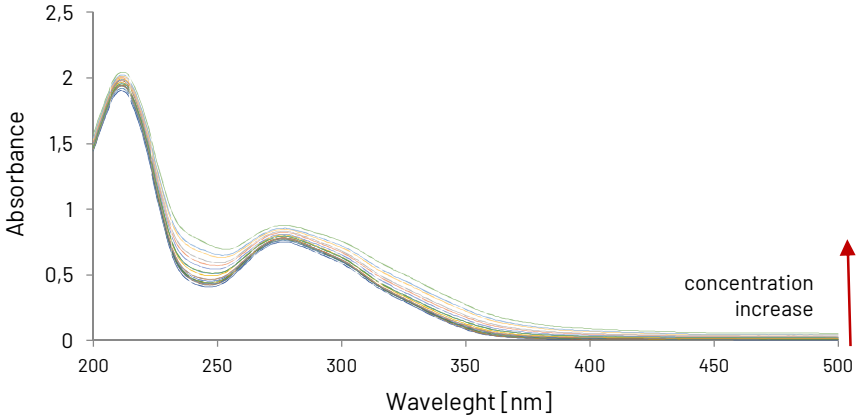

Fig. 9.6. UV-VIS spectra of tannic acid ($C=7\cdot10^{-5}$–$3\cdot10^{-5}$ mol/dm^3)registered in the range of 200-500 nm

9.2. **PURPOSE AND SCOPE OF THE EXERCISE**

The objective of this exercise is to determine nickel ions in a water sample by spectrophotometric titration.

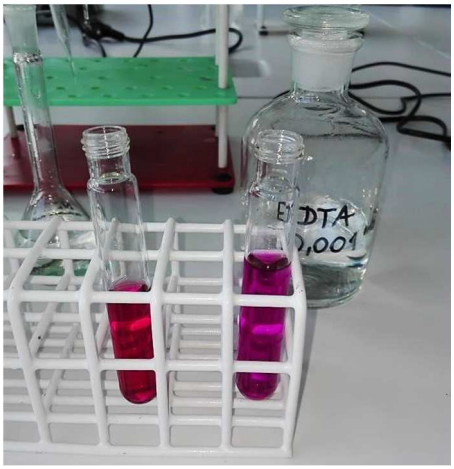

Fig. 9.7. Sample containing Ni^{2+} ions and indicator (murexide) in red and the same sample after adding the titrant (EDTA)

During titration of the sample with EDTA solution, Ni^{2+} ions are displaced from the Ni Ni^{2+}- indicator (Ni-Ind) combinations and move into

much more stable complex combinations with EDTA (Ni-EDTA). During the titration, the indicator is murexide (Fig. 9.7).

$$\text{Ni-Ind} + \text{EDTA} \rightarrow \text{Ni-EDTA} + \text{Ind}$$

9.3. **TEST METHODOLOGY**

Test stand description

Reagents:

0.001 mol/dm^3 EDTA, 0.02% aqueous solution of murexide **(Fig. 9.8)**

Laboratory equipment:

HACH 4000 U or NANOCOLOR VIS spectrophotometer with tube attachment, 50 cm^3 volumetric flask, 12 cm^3 glass test tubes, 5 cm^3 pipette, 200 µl micropipette

Fig. 9.8. Laboratory set and reagents needed to perform the experiment

Running the experiment

a) **Prepare an EDTA solution of 0.001 mol/dm^3**

Prepare an EDTA solution of 0.001mol/dm^3 by diluting an EDTA solution of 0.01 mol/dm^3 (prepared and standardized in Exercise 5).

b) **Determine the Ni^{2+} ion content by spectrophotometric titration. For this purpose:**

- Start the spectrophotometer according to the instrument's manual. Set the ABSORBANCE measurement mode and select an analytical wavelength of 450 nm (this is the wavelength at which the sample shows maximum absorbance).
- Dilute the Ni^{2+} sample obtained for analysis in a 50 cm^3 volumetric flask to the mark with distilled water. Take 5 cm^3 of the prepared solution and transfer it to the test tube (measuring cuvette) and place the test tube in the measurement chamber. Zero the instrument (by pressing BLANC).
- Remove the tube from the spectrophotometer, add a few drops of murexide solution, mix on a VORTEX stirrer (add enough murexide so that the absorbance does not exceed 0.8) and titrate the solution with EDTA solution, adding 200 µl portions of titrant. After each addition of titrant, mix the solution on the VORTEX stirrer. After mixing, place the tube into the spectrophotometer and read the absorbance of the solution. Record the results in the table.
- Run the titration until five consecutive readings are in close agreement.

Each student performs the determination for a 5 cm^3 sample taken from the test solution.

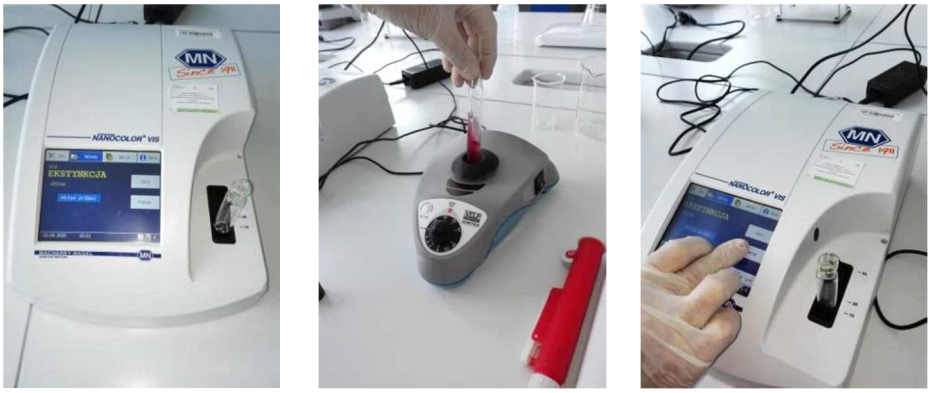

Fig. 9.9. Subsequent activities while performing the exercise (from the left: placing the sample in the measurement chamber; mixing the solution on the stirrer type VORTEX; reading the absorbance of the sample)

9.4. PRESENTATION AND ANALYSIS OF TEST FINDINGS

1. Present the results in a table.

VEDTA [µl]	Absorbance at λ = 450nm
0	
200	
400	
600	
800	
1000	
.....	

2. On MILLIMETER PAPER, plot for each determination a titration curve showing the relationship A=f(V_{EDTA}). Under the drawing (on the millimetre paper!) write the title of the graph and your name.
3. Determine the end point of the titration graphically on the titration curves. To determine the end point of the titration, plot two tangents to the graph (as in Fig. 9.4). The intersection point of the tangents determines the volume of EDTA used to titrate the sample (we use this volume to count the mass of nickel(II) in the sample) on the x-axis. Calculate the average volume of EDTA used to titrate the sample containing Ni^{2+} ions.
4. Calculate the Ni^{2+} ion content of the titrated sample (in 5 cm^3) from the formula below and then convert to the volume of the initial sample, i.e. 50 cm^3.

$$m_{Ni^{2+}} = C_{EDTA} \cdot E_{EDTA} \cdot M_{Ni} \text{ [g]}$$

where:

C_{EDTA} – concentration of standard EDTA [mol/dm^3]

V_{EDTA} – mean volume of EDTA determined from a minimum of two titration curves [dm^3]

M_{Ni} – molar mass of nickel (58,7 g/mol)

Refer to the standards for drinking water quality assessment parameters (acceptable amount of Ni: 20 µg/dm^3).

The student report should include

- Purpose and scope of the exercise
- Description of the test stand and test methodology
- Equations of the occurring reaction
- Results, graphs on millimetre paper, calculations of nickel(II) content in sample

Checklist questions

1. Describe the course of the exercise.
2. Discuss the structure of the spectrophotometer.
3. Explain the terms: absorbance and transmittance.
4. What is spectrophotometric titration?
5. Explain how to determine the end point of titration based on titration curves.

Health and safety requirements

- Only laboratory equipment, a script, and a laboratory notebook may be kept on the table during the exercise.
- Take the solution for analysis with a pipette using a cap.

9.5. **Bibliography**

1. Cygański A., *Chemiczne metody analizy ilościowej*, WNT, Warszawa 2005.
2. Szmal Z. S., Lipiec T., *Chemia analityczna z elementami chemii instrumentalnej*, PZWL, Warszawa 1997.
3. Świsłocka R., Więckowska E., Bryłka J., Lewandowski W., Z*adania rachunkowe oraz przykładowe pytania kolokwialne i egzaminacyjne*, Politechnika Białostocka, Białystok 2004.
4. Minczewski J., Marczenko Z., *Chemia analityczna, Podstawy teoretyczne i analiza jakościowa*, wydanie siódme poprawione, PWN, Warszawa 2011.
5. http://isap.sejm.gov.pl/isap.nsf/download.xsp/WDU20170002294/O/D20172294.pdf

10. SPECTROPHOTOMETRIC DETERMINATION OF IRON(III) IONS

10.1. **INTRODUCTION**

Quantitative spectrophotometric determination

The standard curve method, or the calibration curve method, is the most commonly used method in quantitative spectrophotometric determination. A calibration curve is a plot of the absorbance of a solution of a standard substance against its concentration (Fig. 10.1). After measuring absorbance of a sample of unknown concentration of the determined component, its concentration can be calculated on the basis of the curve equation.

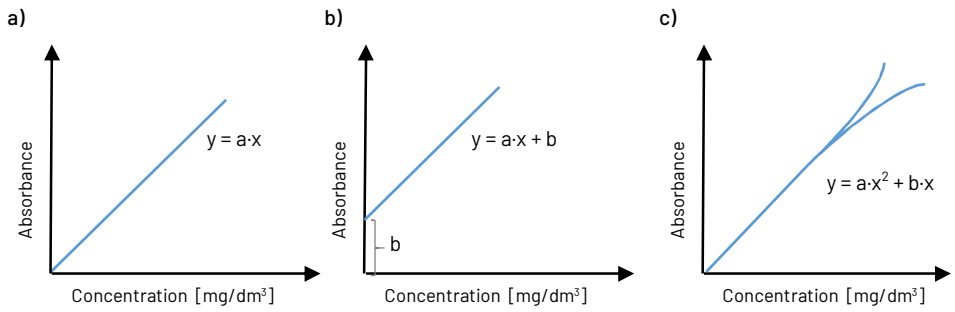

Fig. 10.1. Types of standard curves for single-component systems

a) the system satisfying the Lambert-Beer law, **b)** the system satisfying the Lambert-Beer law containing, besides the determined component, other absorbing substances (substrate, background); if the absorbance of the substrate does not depend on the determined component, its influence is eliminated by subtraction of the determined value a_0 or introduction of a blank as a reference. c) the system not satisfying the Lambert-Beer law

In order to draw a standard curve, 5 to 6 (or more) standard solutions of known concentrations of the test compound are prepared so that:

- they cover the range of concentrations of the determined compounds in the tested samples,

- the maximum absorbance of the standard solution of the highest concentration does not exceed 1.

Since the type of apparatus, temperature, batch of reagents or other factors may influence the standard curve, a new standard curve should be prepared before each experiment or a single curve derived from several series of measurements should be used.

A rectilinear course of the dependence of absorbance on the concentration of a chemical compound proves that **the Lambert-Beer law** is fulfilled, which states that the intensity of absorbed radiation depends on the concentration of solution and on the thickness of absorbing layer:

$$A = \log\frac{I_0}{I} = \log\frac{1}{T} = \varepsilon \cdot l \cdot C$$

where:
A – absorbance,
I_0 – intensity of the radiation incident on the sample,
I_t – intensity of the radiation passing through the analysed sample,
C – concentration of the solution [mol/dm^3],
l – layer thickness [cm],
ε – molar absorption coefficient [dm^3/(mol·cm)], when the concentration of the solution is expressed in mol/dm^3, and the thickness of the layer is expressed in cm.

10.2. PURPOSE AND SCOPE OF THE EXERCISE

The purpose of this exercise is to determine the content of Fe^{3+} ions by spectrophotometric method.

During the experiment, Fe^{3+} ions are converted into blood-red ferric rhodanide (thiocyanate):

$$Fe^{3+} + 3\ SCN^- \rightarrow Fe(SCN)_3$$

The reaction is carried out in a weakly acidic medium. Under these conditions, in addition to iron rhodanide, Fe^{3+} complexes ranging in composition from $[Fe(SCN)]^{2+}$ to $[Fe(SCN)_6]^{3-}$ are formed. For the determination use the standard curve method.

10.3. **TEST METHODOLOGY**

Test stand description

Reagents:

stock Fe^{3+} salt solution of 0.1 mg Fe^{3+}/cm^3, 0.1 mol/dm^3 HCl, 20% KSCN (potassium rhodanide)

Laboratory equipment:

VIS spectrophotometer and glass cuvettes, 50 cm^3 volumetric flasks, 1000 μl, 5000 μl automatic pipettes

Running the experiment

a) **Preparation of standard solutions**

- Prepare 7 50 cm^3 volumetric flasks, numbered 0 to 6. In flasks 1-6 prepare standard solutions of specific Fe^{3+} concentrations to determine the standard curve. The solution in flask 0 will have an Fe^{3+} concentration of 0 (this is the legitimate point of the standard curve); this solution will be used as a blank (reference solution).
- Into flasks 1-6, measure 0.3; 0.6; 0.9; 1.2; 1.5 and 2 cm^3 of the Fe^{3+} stock solution successively with automatic pipettes. Since the stock solution contains 0.10 mg Fe^{3+}/cm^3, diluting the measured volumes to 50 cm^3 will give the following Fe^{3+} concentrations: 0.03; 0.06; 0.09; 0.12; 0.15 and 0.20 [mg/50cm^3].
- Add 2 cm^3 of 0.1-mol HCl and 1 cm^3 KSCN to each of flasks 0-6 using automatic pipettes. **Take care** when pipetting not to transfer solutions from flask to flask (even very small amounts), especially to flask 0, which should be free of Fe^{3+} (it must not take on a pink colour). Make up to the mark with distilled water. Stopper the flasks and mix the solutions thoroughly.

b) **Measurement of the absorption spectrum for the Fe-SCN complex and determination of λ_{max}**

- For solution 3, plot a VIS spectrophotometric spectrum, i.e. measure absorbance in the λ wavelength range of 400 to 600 nm using a blank solution as a reference.
- From the obtained relation A in λ function, read λ_{max}, i.e. the wavelength at which the maximum absorbance occurs for Fe-SCN complexes.

c) **Determination of the standard curve**

Measure the absorbances of standard solutions 1-6 for λ_{max} wavelength against the "blank" (solution 0). Record the results in the table:

Sample no.:	0	1	2	3	4	5	6
Fe^{3+} concentration in the sample [mg/50 cm^3]	0.00	0.03	0.06	0.09	0.12	0.15	0.20
Absorbance in λ_{max}							

d) **Sample preparation and absorbance measurements for the Fe^{3+} sample obtained for analysis**

1. In the flasks labelled 1x, 2x, 3x, prepare three identical samples from the solution for the analysis of Fe^{3+} ions obtained for the determination of iron content. In each of the above-mentioned flasks, take an equal volume (given by the instructor), add 2 cm^3 of 0.1 mol HCl and 1 cm^3 of 20% KSCN with automatic pipettes, and make up to the mark with distilled water.
2. Measure the absorbance of the samples at λ_{max}, wavelength, using a "blank" as reference, in the same way as for the standard solutions.

NOTE: The ferric thiocyanate complex is labile, so add thiocyanate to all samples (both standard and analysis) immediately before measuring absorbance.

10.4. PRESENTATION AND ANALYSIS OF TEST FINDINGS

1. Present the results of measurements to determine the standard curve in the table as above.
2. Plot A = f(C) for the standard solutions and determine the equation of the standard curve (in Excel file).
3. From the resulting standard curve equation, calculate the Fe^{3+} ion content of the three samples 1x, 2x, 3x. Average the result.
4. Calculate the Fe^{3+} content in the solution obtained for analysis (in the flask) in [mg/cm^3] and refer to the standards defining the parameters for assessing the quality of drinking water (permissible amount of Fe: 200 µg/dm^3).

The student report should include

- Purpose and scope of the exercise
- Description of the test stand and test methodology
- Equations of the occurring reactions
- Calculations and results

Checklist questions

1. Structure of a spectrophotometer.
2. Explain terms: absorbance and transmittance.
3. Explain what a standard curve is and what it is used for.
4. Discuss the Lambert-Beer law.
5. What is an analytical wavelength?
6. Discuss the course of the experiment.

Health and safety requirements

- Only laboratory equipment, a script, and a laboratory notebook may be kept on the table during the exercise.
- Take the solution for analysis with a pipette using a cap.
- Waste treatment: dispose of all waste in waste containers.

10.5. **Bibliography**

1. Cygański A., *Chemiczne metody analizy ilościowej*, WNT, Warszawa 2005.
2. Szmal Z.S., Lipiec T., *Chemia analityczna z elementami chemii instrumentalnej*, PZWL, Warszawa 1997.
3. Minczewski J., Marczenko Z.: *Chemia analityczna, Podstawy teoretyczne i analiza jakościowa*, PWN, wydanie siódme poprawione, Warszawa 2011.
4. http://isap.sejm.gov.pl/isap.nsf/download.xsp/WDU20170002294/O/D20172294.pdf.

11. SPECTROPHOTOMETRIC DETERMINATION OF NITRATE(III) AND NITRATE(V)

11.1. INTRODUCTION

Nitrogen in water can occur as a variety of compounds. The main forms of nitrogen that are subject to determination are ammonia nitrogen, nitrate nitrogen(V) and nitrate nitrogen(III) formerly referred to as nitrite nitrogen. In the Regulation of the Polish Minister of Health of 7 December 2017 on the quality of water intended for human consumption (Polish Journal of Laws of 2017, item 318, 1566 and 2180) gives the permissible values of nitrogen compounds in water intended for consumption.

Table 11.1. Limit values for nitrogen compounds in drinking water

Ammonia nitrogen	0,5 mg/dm^3
Nitrate(III)	0,5 mg/dm^3
Nitrate(V)	50 mg/dm^3

Nitrates(V)

Nitrates in waters come mainly from anthropogenic sources. They enter waters with industrial and municipal wastewater, and to a large extent as surface runoff from fields fertilized with nitrogen fertilizers. High levels of nitrates(V) are found in biologically treated wastewater and in water treated in wastewater treatment plants (but the levels must be within acceptable concentrations). Nitrates(V) adversely affect surface waters (lakes) causing their eutrophication (water bloom).

Determination of nitrates(V)

Nitrates(V) in water are determined according to the Polish PN-82/ C-04576/08 standard. The measurement consists in spectrophotometric determination of the product of the reaction of nitrates(V) with sodium salicylate in the environment of concentrated sulfuric acid(VI). As a result of the reaction nitrosalicylic acid is obtained, whose dissociated form (after alkalizing the environment) takes on an intense yellow colour. The concentration of nitrate(V) is determined spectrophotometrically at 410 nm wavelength. The reactions of salicylic acid with nitrates(V) are shown in Figure 11.1.

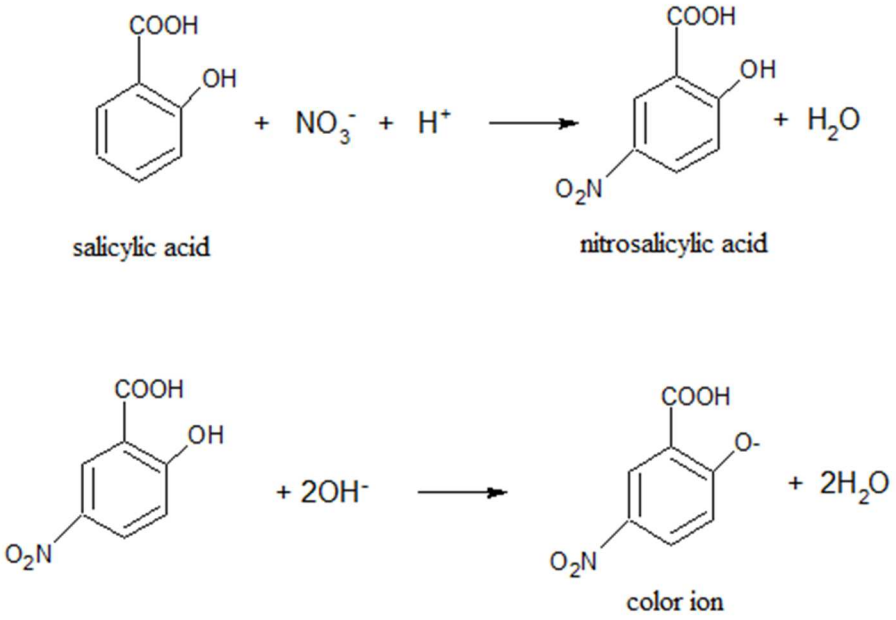

Fig. 11.1. Reaction scheme used in the determination of nitrate(V) in water

Nitrates(III)

Nitrates(III), formerly known as nitrites (a term still used today in non-chemical literature) are formed in the aquatic environment from the oxidation of ammonia or the reduction of nitrates(V). The presence of this form of nitrogen in water indicates the oxidation and reduction processes taking place, which usually accompany the presence of various pollutants.

When ammonium ions are present in the water and no nitrate(III) is observed, it means that the contamination occurred not long ago. On the

other hand, when both forms of nitrogen are present, it may mean that water contamination occurred some time ago and the oxidation of ammonium ions to nitrate(III) took place. After a fairly long period of time since the source of water pollution by nitrogen compounds occurred, one may observe the absence of ammonium and nitrate(III) ions, and the only form of nitrogen present will be nitrate(V). This may also mean that the source of water pollution is surface runoff from fertilized fields.

Determination of nitrates(III)

The concentration of nitrates(III) in water is determined spectrophotometrically after reaction with sulfanilamide and naphthylamine (PN-73/C-04576/06) or N-(1-naphthyl-1,2-diaminoethane) hydrochloride. When reacted with sulfanilamide in the presence of phosphoric acid(V), nitrates(III) form a diazonium salt, which then reacts with N-(1-naphthyl-1,2-diaminoethane) hydrochloride to form a pink azo dye. This compound is determined spectrophotometrically at 540 nm wavelength. The occurring reactions of salicylic acid with nitrates(III) are shown in Figure 11.2.

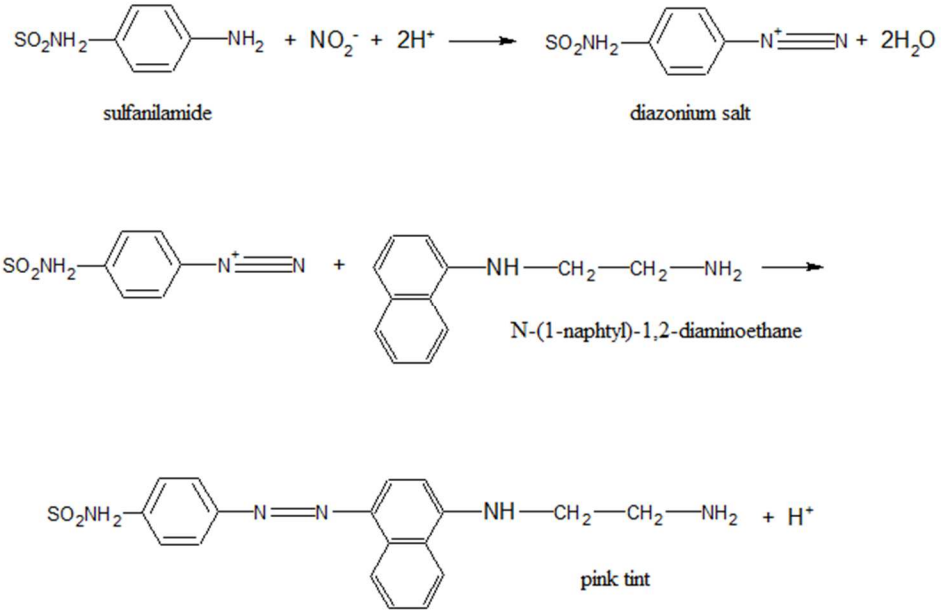

Fig. 11.2. Reaction scheme used in the determination of nitrates(III) in water

11.2. PURPOSE AND SCOPE OF THE EXERCISE

The objective of this exercise is to determine the concentration of nitrate(III) and nitrate(V) in water by spectrophotometric method. The method consists in examining the absorbance of coloured complexes formed in the reaction of added reagents with the determined nitrates, using a UV-Vis spectrophotometer. Nitrate concentrations are determined by comparison with a prepared standard curve.

11.3. TEST METHODOLOGY

11.3.1. Determination of nitrates(V)

Test stand description

Reagents:

0.5% NaOH solution, 0.5% sodium salicylate solution, concentrated sulfuric acid, 1.0 mol/dm^3 alkaline solution of sodium and potassium tartrate, potassium nitrate for analysis

Laboratory equipment:

UV-Vis spectrophotometer, heated bath, analytical balance

Running the experiment

1. **Prepare a stock standard solution of nitrate(V)**
   a) Weigh 0.8155 g of potassium nitrate(V) KNO3 dried to constant weight (at 105^{o}C), dissolve in distilled water and make up to 1 dm^3 with distilled water in a volumetric flask. The stock solution thus prepared contains 0.5 mg of nitrate(V) in 1 cm^3.
   b) Measure 10 cm3 of the stock KNO3 solution into an evaporating dish, add 2-3 drops of 0.5% NaOH solution and then add 20 cm^3 of 0.5% sodium salicylate solution. Evaporate the contents of the evaporating dish to dryness on a heated bath.
   c) Add 1 cm^3 of concentrated sulfuric acid(VI) to the evaporated contents of the evaporator dish.
   d) After 10 minutes, add 30 cm^3 of distilled water and let it stand on a heated bath until the precipitate dissolves.
   e) Quantitatively transfer the total to a 100 cm^3 flask and make up with distilled water.

The solution thus prepared contains 0.05 mg of nitrate(V) in 1 cm^3.

2. **Plot a standard curve of nitrates(V)**
   a) To 7 volumetric flasks (50 cm^3 volumes) add successively 0; 0.5; 1.0; 1.5; 2.0; 3.0 and 5.0 cm^3 of KNO_3 standard solution.
   b) Add 7 cm^3 of alkaline sodium and potassium tartrate solution to each flask and make up to the mark with distilled water. The subsequent standard solutions contain the following amounts of nitrate(V): 0.0; 0.025; 0.05; 0.075; 0.10; 0.15; and 0.25 mg in 50 cm^3.
   c) Measure the absorbance at 410 nm wavelength as a reference using the prepared first standard solution.
   d) Plot a standard curve with the nitrate(V) content in mg on the x-axis and the absorbance values on the y-axis.
3. **Analysis of the sample**
   a) Take 10 cm^3 of test water into an evaporating dish, add 2-3 drops of 0.5% NaOH solution and then add 20 cm^3 of 0.5% sodium salicylate solution. Evaporate the contents of the evaporating dish to dryness on a heated bath.
   b) Add 1 cm^3 of concentrated sulphuric acid (VI) to the evaporated contents of the evaporating dish.
   c) After 10 minutes add cm^3 of distilled water and 7 cm^3 of alkaline sodium and potassium tartrate solution.
   d) Quantitatively transfer the whole into a 50 cm^3 and make up with distilled water.
   e) Measure the absorbance at 410 nm wavelength as a reference using the prepared first standard.

Elaboration of results

1. Plot a standard curve, determining the nitrate(V) content in mg on the x-axis and the absorbance values on the y-axis.
2. Read the nitrate content of the test sample from the standard curve and calculate according to the formula:

$$x = \frac{m \cdot 1000}{V} mg\ NO_3^- / dm^3$$

where:
m – nitrate content read from the standard curve,
V – volume of water sample used for testing

3. Discuss the obtained results, refer to the standards for nitrate in drinking water.

11.3.2. Determination of nitrates (III)

Test stand description

Reagents:

sodium nitrate for analysis, 0.002 mol/dm^3 standard solution of $KMnO_4$ 1:3 sulphuric acid, 10% solution of potassium iodide KI, 0.01 mol/dm^3 sodium thiosulphate, starch solution, colouring reagent (sulfanilamide, phosphoric acid, N-(1-naphthyl-1,2-diaminoethane) hydrochloride

Laboratory equipment:

UV-Vis spectrophotometer, heated bath, titration kit, analytical balance

Running the experiment

1. **Prepare a stock standard solution of sodium nitrate(III)**
   a) Weigh 0.7499 sodium nitrate(III) $NaNO_2$, dissolve in distilled water (free of nitrate(III) and make up to 1 dm^3 with distilled water in a volumetric flask. The stock solution thus prepared contains about 0.5 mg of nitrate(III) in 1 cm^3.
   b) In the solution thus prepared, accurately determine the concentration of nitrate(III). In a conical flask with a ground stopper, measure 20 cm^3 a 0.002 mol/dm^3 standard solution of $KMnO_4$, next add 5 cm^3 of the stock standard solution of $NaNO_2$ and add 5 cm^3 of 1:3 sulfuric acid(VI). Stir the flask and leave it for 15 minutes. Then add 10 cm^3 of a 10% solution of potassium iodide KI.
   c) After 5 minutes, titrate the solution with 0.01 mol/dm^3 sodium thiosulfate in the presence of starch.

Calculate the concentration of the stock solution in mg of nitrate(III) per 1 cm^3 using the formula:

$$x = \frac{(20-V)\cdot 0{,}23}{5} mg\ NO_2^-/cm^3$$

2. **Plot a standard curve**
   a) Dilute the standard solution of approximately 0,5 mg of nitrate per 1 cm^3 to obtain a working standard solution of approximately 0.005 mg of nitrate per 1 cm^3.
   b) To 6 volumetric flasks (50 cm^3 volumes) add successively 0.0; 0.2; 0.5; 1.0; 1.5 and 2.0 cm^3 of the working standard solution. Calculate the exact concentrations of the standard solutions based on the concentration of the stock solution determined in 1.

c) Make up to the mark with distilled water.
d) Add 1 cm^3 of colouring reagent (sulfanilamide, phosphoric acid(V), N-(1-naphthyl-1,2-diaminoethane) hydrochloride to each flask and mix.
e) After 20 minutes, measure the absorbance of the solutions at 540 nm wavelength using the sample prepared as the first standard as reference.
f) Plot a standard curve with nitrate(III) content in mg on the x-axis and absorbance values on the y-axis.

3. **Analysis of the sample**

a) Fill a 50 cm^3 flask to the mark with distilled water.
b) Add 1 cm^3 of staining reagent (sulfanilamide, phosphoric acid(V), N-(1-naphthyl)-1,2-diaminoethane)hydrochloride and mix.
c) After 20 minutes, measure the absorbances of the solutions at 540 nm wavelength using as a reference the sample prepared as first standard.

Elaboration of results

1. Plot a standard curve, determining the nitrate(III) content in mg on the x-axis and the absorbance values on the y-axis.
2. Read the nitrate(III) content of the test sample from the standard curve and calculate according to the formula:

$$x = \frac{m \cdot 1000}{V} mg\ NO_2^- / dm^3$$

where:
m – nitrate content read from the standard curve,
V – nitrate content read from the standard curve

3. Discuss the obtained results, refer to the standards for nitrate in drinking water.

11.4. PRESENTATION AND ANALYSIS OF TEST FINDINGS

Calculate the nitrate(V) and nitrate(III) content based on the reading from the standard curves.

The student report should include

- Description of the test stand and test methodology
- Plots of standard curves
- Calculation of the nitrate(V) and nitrate(III) content
- Discussion and results

Checklist questions

1. Forms of nitrogen found in water.
2. Sources of nitrates(V) and nitrates(III) in water.
3. Describe how to perform the exercise.
4. Principles of nitrate(V) and nitrate(III) determination.

Health and safety requirements

- Only laboratory equipment, a script, and a laboratory notebook may be kept on the table during the exercise.
- Take the solution for analysis with a pipette using a cap.
- Before starting the heated bath, check that the electrical cables are in good working order.
- Start the spectrophotometer and the heated bath according to the instructions provided with the instruments.
- Do not lean over the steaming heated bath.
- Heat the heated bath under the hood.
- Concentr. H_2SO_4 – causes severe skin burns and eye damage. Ensure effective air exchange (ventilation). Follow good industrial practice and general rules of safety and hygiene at work with chemical substances. When using do not eat or drink anything, avoid contact with the substance; avoid inhaling vapours, use personal protective equipment; work in well-ventilated areas. Dilute by slowly adding acid to water and stirring carefully. Hygroscopic substance – avoid contact with water!

11.5. **Bibliography**

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12. DETERMINATION OF FLUORIDE ION CONCENTRATION IN WATER BY POTENTIOMETRIC METHOD

12.1. **INTRODUCTION**

Fluorine is an element necessary for the proper functioning of the body. However, its excess (above 2.5 mg F^- per day) is dangerous to health. Fluorine is the only micronutrient with the smallest range between the dose necessary for the human body and the dose above which symptoms of harmful effects occur. Fluorine compounds enter the environment from natural and anthropogenic sources. The concentration of fluorides in water is an important parameter determining its quality. The content of fluoride ions in natural waters ranges from trace amounts to several milligrams per dm3 depending on the mineral deposits they flow through. The source of fluorides in water may also be the fertilizer industry, chemical industry, aluminium metallurgy, but also agriculture. The maximum permissible concentration of fluoride anions in drinking water (1.5 mg/dm^3) is strictly defined in the Regulation of the Polish Minister of Health.

Commonly known and used methods for the determination of fluoride include:

1. alizarin-zirconium reagent method (visual),
2. spectrophotometric method,
3. ion chromatography,
4. potentiometric method using an ion selective electrode.

Potentiometric methods consist in measuring the electromotive force (EMF) of a cell made up of an indicator electrode (Ei) and a reference electrode (Er), which are immersed in the same test solution. The electrodes are chosen in such a way that the potential of the indicator electrode depends on the concentration (activity) of a particular component in the test sample, while the potential of the reference electrode is constant under measurement conditions. Changes in the EMF of the cell containing the ion-

selective electrode (indicator electrode) can therefore be attributed to changes in the potential of this electrode. The dependence of this potential (E) on ion concentration is defined by the Nikolsky equation:

$$E = E^o + \frac{RT}{nF}\ln(a_i + \sum_{j=1}^{n} K_{ij} \cdot a_j^{n/z}) \quad (12.1)$$

where:

E – electrode potential
E^o – standard electrode potential– constant value;
R – gas constant;
F – Faraday constant;
T – absolute temperature [K];
n, z – respectively: charge of the ion labelled i, charge of the interfering ion j;
K_{ij} – selectivity coefficient of the i ion-sensitive electrode in the presence of ion j;
a_i, a_j – respectively: activity of the determined ion i, activity of the interfering ion j;

Ion-selective fluoride electrode

Ion-selective electrodes react selectively to a specific ion in the presence of other ions. An important part of their construction is the membrane (solid or liquid) containing the electroactive substance. The membrane is the most important part of the ion-selective electrode. It is responsible for the selectivity and sensitivity of the electrode. The ion-selective fluoride electrode has a solid membrane, which is a monocrystalline LaF_3.

When the fluoride electrode is immersed in a solution containing F^- ions, a potential difference is created along the membrane, and its magnitude depends on the ratio of the activity of these ions in the internal and external solution. The measure of the fluoride ion concentration is the potential generated between the ion-selective fluoride electrode immersed in the analysed sample and the reference electrode, usually a calomel (Hg | Hg_2Cl_2 | Cl^-) or chlorosilver (Ag | AgCl | Cl^-) electrode (Fig. 12.1).

The dependence of the electrode potential on the activity of F^- ions is described by the Nernst equation:

$$E = E^o - \frac{RT}{F} ln \frac{(a_{F^-})_{wewn}}{(a_{F^-})_{zewn}} \quad (12.2)$$

where:

E – electrode potential;
E^o – standard electrode potential;
R – gas constant;
F – Faraday constant;

(a_{F^-}) – fluoride ion activity;
T – absolute temperature [K];

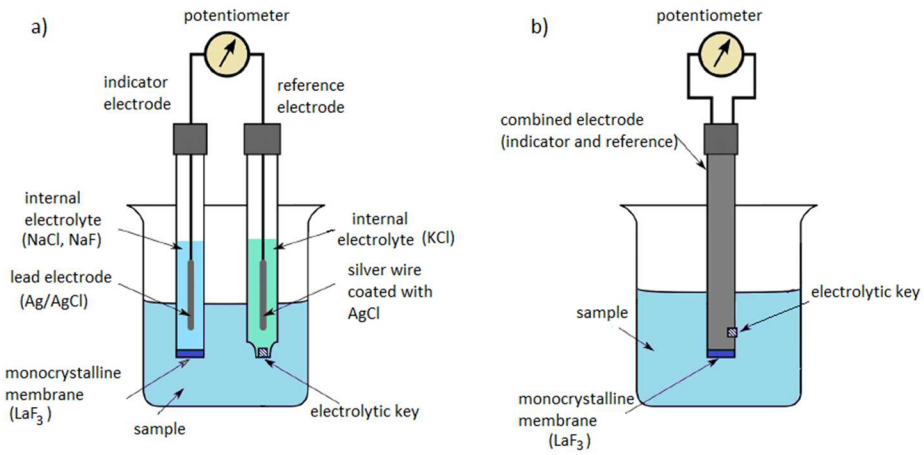

Fig. 12.1. Measuring set for determination of F^- ions using a) two separate electrodes: ion-selective fluoride electrode and chlorosilver electrode; b) combined electrode

This electrode has the ability to determine the concentration of F^- ions over a wide range, and the ions interfering with its determination are only OH^- ions. The optimum pH value of the solution for which proper electrode performance is observed and a constant ionic strength are maintained by using buffers. Often a buffer called TISAB (Total Ionic Strength Adjustment Buffer) is used, which provides both constant ionic strength and constant pH of the solution, and also contains substances that mask cations forming complexes with F^- ions.

12.2. PURPOSE AND SCOPE OF THE EXERCISE

The objective of this exercise is to determine the concentration of fluoride ions in water by direct potentiometry. The determination consists in measuring the potential using a combined ion-selective fluoride electrode (the electrode contains both an indicator and a reference electrode in one housing). The measured potential differences between the electrodes are a measure of the fluoride ion concentration.

12.3. **TEST METHODOLOGY**

Test stand description

Reagents:

1.0 mol/dm^3 NaF solution, TISAB buffer (pH=5) consisting of sodium citrate (0.001 mol/dm^3), acetic acid (0.25/dm^3), sodium acetate (0.75 mol/dm^3), sodium chloride (1.0 mol/dm^3),

Laboratory equipment:

combined ion-selective fluoride electrode, potentiometer, magnetic stirrer

Running the experiment

1. Prepare standard solutions of sodium fluoride (NaF) at concentrations of: 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5}, 10^{-6}, 10^{-7} mol/dm^3. Measure 5 cm^3 of sodium fluoride solution (1.0 mol/dm^3) and 25 cm^3 of TISAB buffer into a 50 cm^3 volumetric flask, then dilute to the mark with distilled water. Obtain solutions of different concentrations by successive tenfold dilutions of the solution (5 cm^3 of the higher concentration solution, 25 cm^3 of the buffer and 20 cm^3 of distilled water). Transfer the solutions into prepared, labelled beakers.
2. Samples for analysis should be prepared as follows: add 25 cm^3 of TISAB solution to the obtained samples and make up to 50 cm^3 with water (to the mark).
3. Submerge the fluoride combined ion-selective fluoride electrode into prepared standard solutions and prepared samples one by one, turn on the magnetic stirrer and read the potential after stabilization.

NOTE. After each measurement, remove both the electrode and stirrer from the beaker, rinse with distilled water and dry carefully with a paper towel. Do not allow any substance (water, other calibration solution, etc.) into the calibration solutions!

12.4. **PRESENTATION AND ANALYSIS OF TEST FINDINGS**

1. Plot a standard curve E = $f(\log C_{F^-})$ (CF^- – F^- ion concentration in mg/dm^3). Give the equation of the standard curve.
2. Determine the concentration of fluoride ions (F^-) in the samples obtained for analysis (from the standard curve or from the standard curve equation).

3. Discuss the results, calculate: $\overline{x}$, S, $S_{\overline{x}}$, give a confidence interval $x = \overline{x} \pm tS_{\overline{x}}$ for α=0.05; List the results in a table.

The student report should include

- Purpose and scope of the exercise
- Description of the test stand and test methodology
- Plots of the standard curve, calculations and table filled with test results.

Checklist questions

1. Presence of fluoride ions in water.
2. Describe the principle of potentiometric measurements.
3. The Nikolsky and the Nernst equation.
4. Structure of a fluoride ion exchange electrode.
5. Methodology for determination of fluoride ions by the potentiometric method. Calculations.

12.5. **Bibliography**

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13. DETERMINATION OF SODIUM IN WATER BY FLAME PHOTOMETRY

13.1. INTRODUCTION

Flame photometry belongs to emission spectrometry methods. It is a method of measuring the intensity of characteristic electromagnetic radiation emitted by atoms or molecules in a burner flame. This technique is used for the analysis of elements with low excitation potentials (1.4-3.0 V), emitting radiation in the visible range.

In this method the sample, in the form of atomized solution, is introduced into a flame, where the solution is evaporated, followed by thermal dissociation of compounds of the elements into atoms and thermal excitation (thermal activation) of free atoms as a result of collisions with molecules and atoms with high kinetic gas energies obtained at high flame temperature. When an atom is excited, one or more valence electrons move from the ground state, or initial energy (Ei) (having the lowest energy) to higher energy levels, i.e. final energy (Ei) (characterized by higher energy). The excited states are unstable (approx. 10^{-10} sec.) and the electrons return to lower energy levels (more stable), and the resulting energy difference $\Delta E = E_f - E$ is emitted by an atom in the form of monochromatic light of a precisely defined wavelength (λ), depending on the energy difference between the energy levels.

The lowest level to which an electron can be transferred from **the ground state level** is called **the resonant level**, and an excitation involving a transition between them is called **resonant excitation.** There are many transitions allowed in each atom. However, the most common are low-energy transitions, which give a linear spectrum in the visible range characteristic of the element, the so-called resonance line (emission radiation with energy and wavelength corresponding to the transition of a valence electron from a lower level of excitation (resonance level) to the basic level). Resonance line is characterized by the highest intensity.

The total intensity of the emitted radiation, at a given wavelength, is proportional to the concentration of atoms of the element in question released in the flame during thermal dissociation. The relationship between the concentration of the element being determined (c) (at low concentrations) and the intensity of the emitted radiation (I) is expressed by the equation:

$$I = a \cdot c, \tag{13.1}$$

where:

a – empirical constant dependent on experimental conditions.

For low concentrations of the component to be determined, the standard curve is a straight line and the concentration of the unknown component can be read off this curve as long as it is within the calibration range and the intensity of the emitted beam is known.

The phenomenon of the formation of this spectral line is the basis of analytical emission methods.

Quantitative determinations are carried out by comparative methods:

a) Standard curve method,
b) Standard addition method,
c) Limiting solutions method.

In flame photometry, the excitation source is a gas flame (at 1500-3000°C), into which the test substance is introduced, usually in the form of a spray solution. The burner is usually supplied with a mixture of propane and air, in which case the atoms with low transition energies are excited.

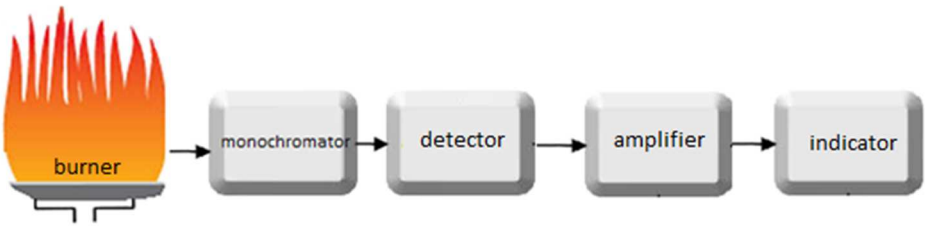

Fig. 13.1. Scheme of apparatus for flame photometry

The test solution is nebulized and then introduced into a burner flame where the sample is atomized. The resulting free atoms are excited and, returning to their ground state, emit radiation of a wavelength characteristic of the element. Next, the radiation passes through a monochromator,

whose task is to “cut out” a fragment corresponding to the resonance line of the element being determined. Then the radiation falls on the detector (photomultiplier, photodiode, photocell), where it is converted into an electrical signal proportional to the intensity of radiation. This signal after amplification is transmitted to the recorder.

The following processes take place in the flame region: aerosol formation from solution (nebulization), solvent removal, sample evaporation, atomization (thermal dissociation of chemical compounds into atoms), valence electron excitation, emission. Each of these steps depends on the experimental parameters used in the apparatus, e.g.: solvent viscosity affects aerosol formation; the type of solvent affects evaporation process; fuel jet velocity and residence time of atoms in the flame affect nebulization process; flame temperature controls evaporation, atomization and ionization degree.

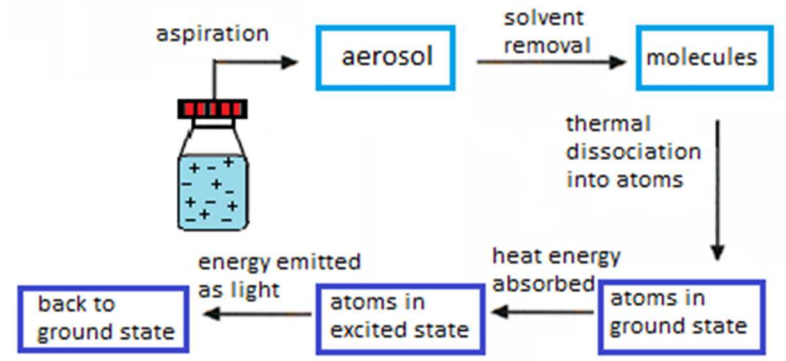

Fig. 13.2. Diagram of the processes occurring in the flame

In natural waters, sodium occurs most frequently in the form of ionized sodium bicarbonate ($NaHCO_3$), chloride (NaCl) and sodium nitrate(V) ($NaNO_3$). The content of this element in natural waters ranges from several to several dozen mg/dm^3, while in mineral waters, the concentration of sodium ions may be as high as several grams per dm^3.

Water consumed by humans must meet specific quality and technological requirements set out in the Regulation of the Polish Minister of Health on natural mineral waters, spring waters and table waters. Among other things, the chemical (ionic) composition of these waters, including

the sodium content, is subject to analysis. One of the commonly used methods for the determination of these elements is **flame photometry**, which can be used to determine sodium in concentrations of 1-50 mg/dm^3. However, potassium (up to 10 mg/dm^3), magnesium (up to 100 mg/dm^3) and calcium (up to 100 mg/dm^3) ions as well as suspended solids and organic matter hinder the determination. Suspensions are removed by draining, organic substances are removed by evaporating the water sample and then roasting the dry residue at 550°C.

13.2. PURPOSE AND SCOPE OF THE EXERCISE

The objective of this exercise is to determine the sodium content of water of different origin (e.g., mineral water, spring water, tap water).

13.3. TEST METHODOLOGY

Test stand description

Reagents:

stock solutions of sodium, potassium, calcium and magnesium at 1000 mg/dm^3, hydrochloric acid (d=1.19 g/cm^3) solution for analysis (1+1), nitric acid (d=1.39 g/cm^3) solution for analysis (1+15)

Laboratory equipment:

flame photometer, pipettes and volumetric flasks for preparing solutions, plastic containers for measurements

Running the experiment

a) **Plot the standard curve**

1. Prepare working solutions from stock solutions of Na^+, K^+, Ca^{2+}, Mg^{2+}:
   a) sodium at a concentration of 0.1 mg Na^+/cm^3 in a 1000 cm^3 conical flask PP.
   b) potassium with a concentration of 0.1 mg K^+/cm^3 in a 1000 cm^3 conical flask PP.
   c) calcium with a concentration of 0.1 mg Ca^{2+}/cm^3 in a 1000 cm^3 conical flask PP.

d) magnesium with a concentration of 0.1 mg Mg^{2+}/cm^3 in a 1000 cm^3 conical flask PP.

2. Prepare 9 100 cm^3 conical flasks PP and measure into them successively 0.0; 1.0; 2.0; 5.0; 10.0; 20.0; 30.0; 40.0; and 50.0 cm^3 of Na+ working solution. Add to each flask successively 0.5 cm^3 of potassium working solution, 5 cm^3 of calcium and magnesium working solutions, and 2 cm^3 of HCl solution (1+1). Fill the flasks with redistilled water to 100 cm^3 (to the mark). The solutions thus prepared contain successively: 0.0; 0.1; 0.2; 0.5; 1.0; 2.0; 3.0; 4.0 and 5.0 Na/100 cm^3.
3. Take three measurements for each standard and calculate the arithmetic means. Present the results in the table below.

Flask no.	Volume of Na^+ working solution [cm^3]	Na^+ concentration in standard solutions	RAW photometer signal	Arithmetic mean
0	0	BLANK		
1	1	0.1 mg/dm^3		
2	2	0.2 mg/dm^3		
3	5	0.5 mg/dm^3		
4	10	1.0 mg/dm^3		
5	20	2.0 mg/dm^3		
6	30	3.0 mg/dm^3		
7	40	4.0 mg/dm^3		
8	50	5.0 mg/dm^3		

4. From the obtained results, plot in Excel or on millimetre paper the standard curve in the system: emission of RAW radiation – sodium concentration in mg per 100 cm^3. Make the equation of the straight line and value R^2.

b) **Determination**

1. Evaporate a 100 cm^3 test sample of water to dryness in a quartz evaporator, then roast at 550°C for 1 hour. After cooling, dissolve the resulting precipitate in 2 cm^3 of hydrochloric acid solution and then add 25 cm^3 of distilled water. Strain the obtained solution through a medium filter into a 100 cm^3 volumetric flask PP and make up to the mark with distilled water.

2. Introduce the prepared sample 3 times into the flame photometer, read the RAW signal for Na once and 3 times from the standard curve, or calculate the sodium concentrations from its equation.

13.4. PRESENTATION AND ANALYSIS OF TEST RESULTS

1. Recalculate the Na content of the test water as read from the standard curve from [mg /100cm^3] per [mg/dm^3].
2. Discuss the obtained results for: $\bar{x}, S, S_{\bar{x}}$, give a confidence interval $x = \bar{x} \pm t \cdot S_{\bar{x}}$ $[units]$ for a probability level 95% (α = 0.05). Present the results in the table below.

No.	Determined element	RAW photometer signal	Concentration read off the standard curve [mg/100 cm^3]	Sodium content [mg/dm^3]	$\overline{x}$	$x = \overline{x} \pm t \cdot S_{\overline{x}}$
1	Na					
2						
3						

The student report should include

- Purpose and scope of the exercise
- Description of the test stand
- Summary of the obtained results in Tables 13.1. and 13.2.
- Plot of a standard curve and all calculations, including error estimates and conclusions

Checklist questions

1. Knowledge of the basic concepts of atomic emission spectrometry. What is flame photometry analysis?
2. Block diagram of a flame photometer including description of the role of all components.
3. Method of determining sodium in a water sample by flame photometry (preparation of solutions, subsequent measurements, graph, method of determination, conversion of concentration determined from standard curve into concentration in the test sample).

4. Describe the processes that occur in a sample placed in the flame of a burner. What kind of spectrum occurs?
5. The standard curve method in flame photometry (preparation of standard series and application to determination, tasks).
6. What is the concentration of the Na^+ working solution if 200 cm^3 of the standard solution was used to make 25 mg/dm^3 of the 15 cm^3 working solution.
7. Calculate the sodium content of water in mg/dm^3, knowing that 100 cm^3 of the water sample showed an emission intensity of 4000, while 100 cm^3 of the solution with a concentration of 30 mg/dm^3 showed 7000.

13.5. **Bibliography**

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14. DETERMINATION OF THMS IN WATER BY GAS CHROMATOGRAPHY

14.1. **INTRODUCTION**

The use of strong oxidants in water disinfection processes can lead to the formation of by-products, a group of undesirable substances formed by the reaction of disinfectants with admixtures and organic contaminants in water. The main by-products of water chlorination are mainly trihalogenomethanes, halogenoacetic acids, halogenoacetonitriles, halogenoketones, chloral hydrate and chloropicrin. The concentration of these compounds in water after the chlorination process depends on many factors, including pH, temperature, chlorine dose, bromide content, and the amount and quality of organic matter.

In chemical terms, trihalogenomethanes (THMs) are derivatives of methane in which three hydrogen atoms have been replaced by halogen atoms: chlorine, fluorine, bromine or iodine. Theoretically, it is possible to have more than twenty of these types of compounds, but in water, mainly four compounds are formed, whose presence can be detected at concentrations μg/dm^3. These compounds include:

- trichloromethane (TCM) (chloroform) – $CHCl_3$;
- bromodichloromethane (BDCM) – $CHCl_2Br$;
- dibromochloromethane (DBCM) – $CHClBr_2$;
- tribromomethane (TBM) (bromoform) – $CHBr_3$.

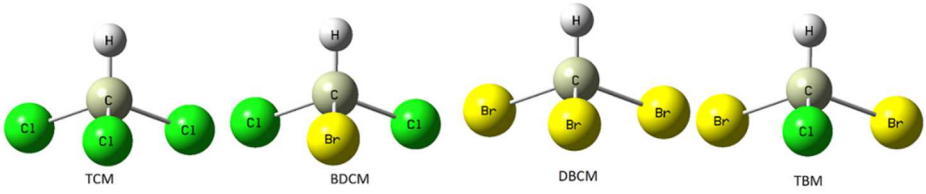

Fig. 14.1. Formulas of selected trihalomethanes

They are present in water in small quantities, however, they are toxic compounds and show mutagenic and carcinogenic properties, which should be taken into account in the final quality assessment of treated water.

Table 14.1 shows the maximum permissible concentrations of THMs in water according to the regulation of the Polish Minister of Health and the World Health Organization (WHO).

Table 14.1. Maximum concentration limits for THMs in drinking water

Name of the compound	Maximum permissible concentrations of halogen disinfection by-products [μg/dm³]	
	Regulation of the Polish Minister of Health	WHO recommendations
Trichlorometan	30	300
Bromodichlorometan	15	60
Dibromochlorometan	-	100
Tribromometan	-	100
Σ THM	100	

Two chromatographic methods are most commonly used for the determination of trihalomethanes in water: gas chromatography with electron capture detector (GC-ECD) and gas chromatography with mass spectrometry detector (GC-MS). The method using the ECD detector is more sensitive and allows the determination of trihalomethanes at the μg/dm³ level. Various methods are also used for isolation and enrichment as well as for dosing of samples to the chromatographic column.

Gas chromatography

Chromatography is a physicochemical method of separating homogeneous mixtures into their components by differential partitioning between two immiscible phases of a chromatographic system:

- Stationary phase,
- Mobile phase that moves along the stationary phase.

This separation occurs due to the different mass exchange dynamics between these phases. The stationary phase constitutes the filling of the column and can also be deposited on the inner walls of the column. The mobile phase moves within the column. Substances that have a greater affinity with the stationary phase move more slowly along the chromato-

graphic column; components with the greatest affinity with the mobile phase leave the chromatographic column most quickly. In gas chromatography, the mobile phase is a gas, which is called **a carrier gas**. It is usually hydrogen, nitrogen, argon, or helium.

The result of a chromatographic separation is **a chromatogram** – this is a graph showing the change in analyte concentration in the mobile phase leaving the column, usually as a function of time (or mobile phase volume). The signals recorded by the detector as a function of time are proportional to the concentration of the substance in the mixture under study.

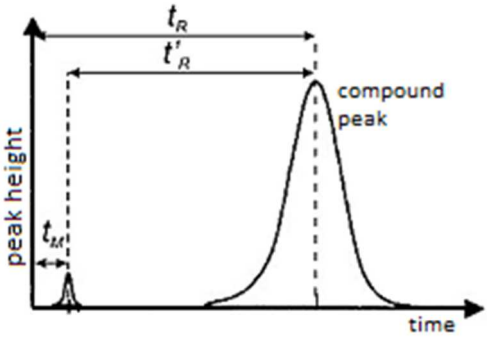

Fig. 14.2. Chromatogram and basic retention parameters

Retention parameters describe the behaviour of the components being separated and can be determined by measuring distances on the chromatogram. The following can be determined on the chromatogram:

- t_R – total retention time: time calculated from the moment the test substance is introduced into the column until the peak maximum appears on the chromatogram,
- t'_R – reduced retention time: the difference between the total retention time of a test substance and the retention time of an unretained substance. t'_R is specific to a substance (characterizes its retention on the stationary phase) and can be used to identify it,
- t_M – retention time of an unretained substance; the time of presence of a substance that does not interact with the stationary phase (e.g. helium).

The chromatogram is a source of both qualitative and quantitative information. The basis for qualitative analysis (identification of substances present in a mixture) is the retention values. Based on the position of the peak on the chromatogram (retention time), it is possible to deduce the

nature of the components of the mixture to be separated. The peak retention time of the identified substance is compared with that of the standard peak (analysed under the same conditions). The number of peaks, on the other hand, indicates the number of components (provided, however, that the used chromatographic system ensures the separation of all components of the mixture and that an appropriately sensitive detector is applied). The peak size (height, area) is a function of the concentration or mass of the component in the sample injected into the chromatographic column.

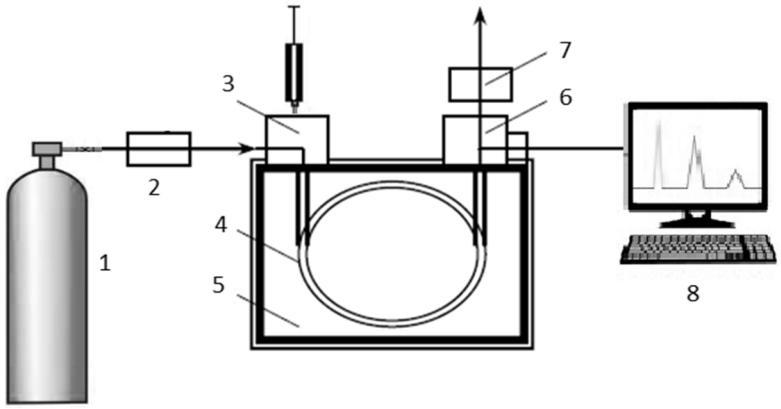

Fig. 14.3. Scheme of a gas chromatograph (1 – carrier gas bottle, 2 – carrier gas flow controller, 3 – dispenser, 4 – column, 5 – thermostat, 6 – detector, 7 – flow meter, 8 – recorder/computer)

An inert carrier gas supplied from a bottle (1), flows into a dispenser (3), where the sample is injected into a stream of carrier gas, which then carries it to a chromatographic column (4) placed in a thermostat (5). The temperature of the column should be regulated so that the mixture being separated is stable in the gaseous state. In the column, the chromatographic separation of the components of the test sample takes place: the individual components of the mixture adsorb on an active adsorbent (column fill) or dissolve in a deposited organic solvent, so that they move through the column at different speeds and successively reach the detector (6). Those substances that do not adsorb or dissolve will come out of the column first. The components of the sample generate electrical signals in the detector, which are automatically recorded as chromatograms after amplification in an amplifier. If the separation of the analysed mixture is quantitative, each peak on the curve corresponds to one substance.

14.2. PURPOSE AND SCOPE OF THE EXERCISE

The aim of the exercise is to quantify the concentration of trihalomethanes (THMs): chloroform, bromodichloromethane, chlorodibromomethane and bromoform in tap water samples.

14.3. TEST METHODOLOGY

Test stand description

Reagents:

Pentane (or hexane) for gas chromatography

Laboratory equipment:

gas chromatograph suitably equipped with: dispenser, HP-1 capillary column (Methyl Siloxane 30 m × 0.53 × 2.65 m), ECD ^{63}Ni electron capture detector, computer with appropriate software; 1 µl Hamilton microsyringe; 15 cm^3 ground glass test tubes with stoppers; 10 cm^3 and 1 cm^3 Mohr pipettes

Running the experiment

a) **Water sampling from water mains**

Fill three 0.5 dm^3 bottles with tap water immediately before the exercise so that there is no air in them and close them tightly. Before filling the bottles, turn off the tap for a few minutes so that the water in the water pipes drains away.

b) **Preparation of samples for analysis**

From each bottle, pipette 10 cm^3 of tap water and transfer to test tubes, then add 1 cm^3 of pentane to each and cap tightly with a stopper.

c) **Extraction with pentane**

Intensively shake the tube for about one minute and then leave it in the rack to separate the layers. The extraction is performed for each sample immediately before entering the chromatograph dispenser.

d) **Injecting the sample and recording the chromatogram**

Using a micropipette, after separating the organic layer, take 1 µl from the pentane layer (top layer), insert the needle of the syringe into the dispenser chamber, and then inject while pressing the Start key on the chromatograph control panel. Leave the syringe for approximately 3 minutes in

the dispenser chamber. Record the chromatogram. When the analysis is complete, the procedure is automatically invoked to prepare the chromatograph for the next analysis.

14.4. PRESENTATION AND ANALYSIS OF TEST RESULTS

1. Using a standard chromatogram (to be provided by the instructor) and the retention times read from the obtained chromatograms, identify the individual trihalomethanes present in the water sample.
2. Read the concentrations of the determined compounds from the obtained chromatograms and convert into μg/dm^3.
3. Discuss the results. Calculate the mean value of the obtained results for each compound and determine the confidence interval of the mean values for a probability level of 95%. Present the obtained results in the table below.

Table 14.2. Analysis of individual chromatograms

Chromatogram no.	Retention time	Identified compound	Peak area	Concentration [μg/dm^3]	$x = \bar{x} \pm t_{0.05} \cdot S_x$

4. Does the tested water meet the conditions specified in the current Regulation of the Polish Minister of Health (dated 7 December 2017, Polish Journal of Laws of 2017, item 2294) as to the permissible content of these compounds in drinking water?

The student report should include

- Purpose and scope of the exercise
- Description of the test stand
- Summary of the obtained results in Table 14.2.
- All calculations, including error estimates and conclusions

Checklist questions

1. What are THMs? Give their names and formulas. In what process are these compounds formed, what effect drinking water with THM content has on human health?

2. Permissible concentrations of THMs in drinking water.
3. Basic chromatography terms (retention time, retention factor, resolution, definition of chromatography).
4. A block diagram of a gas chromatograph with an explanation of the role of each element.
5. Chromatogram and its parameters.
6. What data can be read from a chromatogram and what information do they provide?
7. What are the functions of the carrier gas?
8. Describe how to perform the exercise and discuss the purpose of the subsequent steps.

14.5. **Bibliography**

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15. DETERMINATION OF BENZENE AND ITS DERIVATIVES IN A MIXTURE USING HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

15.1. **INTRODUCTION**

Benzene (C_6H_6) and its derivatives: toluene (C_7H_8), ethylbenzene (C_8H_{10}) and isomers of xylene ($C8H_{10}$) belong to monoaromatic hydrocarbons. In short, they are called BTEX. They play an important role in the assessment of environmental contamination.

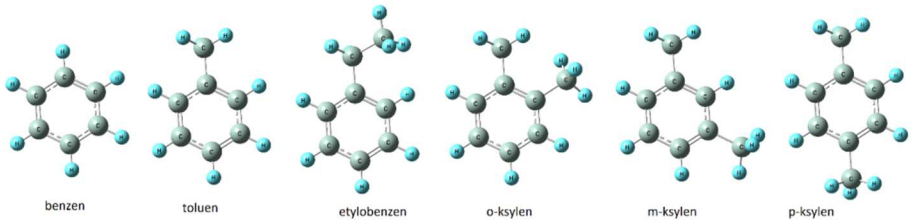

Fig. 15.1. BTEX formulae

The presence of hydrocarbons from this group in the environment results mainly from their use in industry as solvents and in the processes of obtaining various organic industry products, such as lubricants, paints, varnishes, plastics, rubbers, resins, dyes and adhesives. BTEX compounds are also present in fuels: gasoline (where they can be present in high concentrations) and in derivatives, such as diesel fuel, lubricating oil and heating oil. The presence of monoaromatic hydrocarbons in the environment may also be related to the activities of the mining industry, particularly oil extraction in a given area. This poses a serious threat to the environment as well as to public health. All the above considerations have led to the recognition of BTEX as indicators of environmental contamination (water, air, soil) with petroleum products. Due to toxicity of benzene,

and harmfulness of toluene, ethylbenzene and xylenes, most countries introduce strict regulations limiting their presence both in drinking water and industrial wastewater.

Table 15.1. Permissible concentrations of BTEX hydrocarbons in drinking water

Institution	Compound	NDS [μg/dm^3]	Document
European Union	Benzene	1	Directive 98/83/EC 03.11.98, Off.J.Eur. Commun. 330, 05.12.1998
US Environmental Protection Agency	Benzene toluene etylobenzene xylenes	5 1000 700 10000	40 CFR Part 141, National Primary Drinking Water Regulations, 17.04.2002
Polish Minster of Health	Benzene	1	Polish Dz.U.2017 item 2294

Liquid chromatography

Chromatography is a physicochemical method of separating homogeneous mixtures into their components by differential partitioning between two immiscible phases of a chromatographic system:

- Stationary phase,
- Mobile phase that moves along the stationary phase.

This separation occurs due to the different mass exchange dynamics between the phases. In liquid chromatography, the mobile phase is a liquid (single solvents or their two or more component mixtures), while the stationary phase can be either a solid (adsorption chromatography) or a liquid deposited on a carrier (partition chromatography). The mobile phase that is introduced into the column is called the eluent. The mobile phase may also consist of components of the mixture to be separated. After separation, these components are present in the column effluent – the eluate. The composition of the mobile phase, i.e. the type and amount of solvents, has a significant effect on the chromatography process. When selecting the eluent for analysis, it is necessary to take into account such characteristics as: its elution force, polarity, viscosity, refractive index (when using a refractometric detector). The elution force can be characterized by the magnitude of the interaction strength of its molecules with the adsorbent surface. In order to facilitate the selection of an appropriate solvent as an eluent,

the solvents are arranged in the so-called elutropic series (ranking according to increasing eluting power).

In order to separate the components of a mixture, liquid chromatography uses the differences in the interaction of the analysed compounds with the stationary phase. Different groups of compounds have different affinities for the column filling and therefore adsorb on it with different strength. The components that are less strongly adsorbed in the stationary phase will be eluted faster by the mobile phase (eluent), those adsorbed more strongly will be eluted slower.

When selecting the appropriate mobile phase for a particular analysis, the composition of the mixture to be analysed, the type of column filling and the type of detector must also be considered.

Nowadays, mainly High Performance Liquid Chromatography (HPLC) is used in practice).

The result of a chromatographic separation is a **chromatogram** (Fig. 15.2). This is a graph showing the changes of analyte concentration in the mobile phase leaving the column, usually as a function of time (or mobile phase volume). The signals recorded by the detector as a function of time are proportional to the concentration of the substance in the mixture under study.

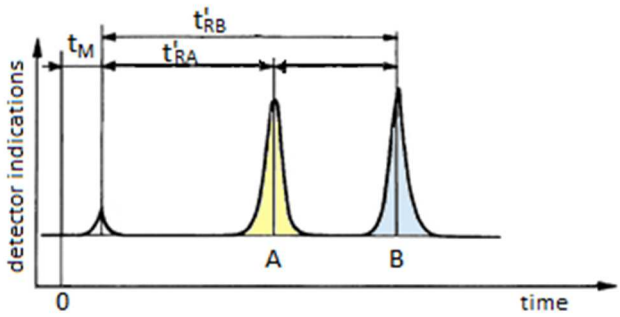

Fig. 15.2. Example chromatogram of a binary mixture: t_M – dead retention time, t'_{RA} –reduced retention time of component A, t'_{RB} – reduced retention time of component B

From the retention volumes (discussed in Chapter 14) read from (or counted from) the chromatogram, peaks corresponding to individual sample components can be identified (qualitative analysis) by comparing the retention time of a given peak with that of a standard peak obtained under identical conditions.

The quantitative content of the components in a sample is calculated based on the fact that their quantity is proportional to the area or height of the peaks corresponding to them. It is recommended that the peak heights be used for the calculation provided that they are symmetrical.

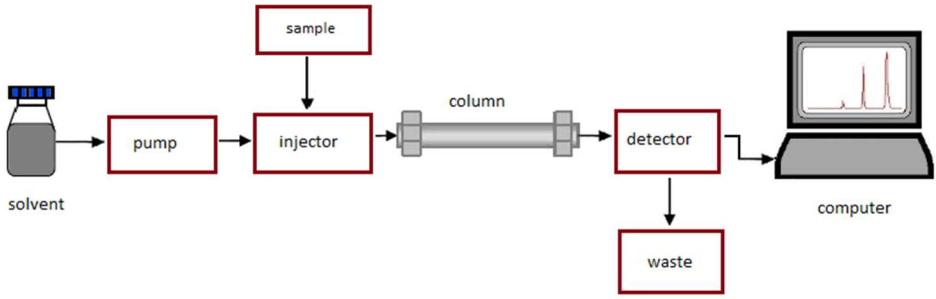

Fig. 15.3. Liquid chromatograph diagram

Figure 15.3 shows a block diagram of a liquid chromatograph. From a tank or tanks, a pump is used to start the mobile phase, which flows through a dispenser and is pumped to a chromatographic column placed in a thermostat. The sample to be analysed is injected by means of a dispenser into the liquid stream, which flows into the chromatographic column, where the components separate and are detected at the exit of the column by a detector. The most commonly used detectors include spectrophotometric detectors, which operate on the principle of absorption of light from the ultraviolet range (UV: 200-400 nm) or ultraviolet and visible light (UV-VIS: 200-900 nm). Absorption of radiation in the UV range is associated with the transition of valence electrons and electron pairs from a lower energy orbital to a higher energy orbital. The electrical signal from the detector after amplification is recorded with a computer as chromatographic peaks. The fluid flow is regulated and controlled electronically.

15.2. PURPOSE AND SCOPE OF THE EXERCISE

The aim of this exercise is qualitative and quantitative determination of the components of a mixture containing benzene and its derivatives (toluene, chlorobenzene, iodobenzene, nitrobenzene and o-xylene) after extraction from the aqueous phase.

15.3. TEST METHODOLOGY

Test stand description

Reagents:

solutions of benzene and its derivatives in methyl alcohol, methanol, water for HPLC

Laboratory equipment:

liquid chromatograph Agilent 1260: ODS Hypersil column, DAD spectrophotometric detector, mobile phase: 75% methanol and 25% water; computer with appropriate software; microsyringe; volumetric flasks, pipettes

Running the experiment

a) **Determination of retention time of individual compounds**

Prepare working solutions of the compounds to be analysed by taking the number of cubic centimetres of standard solution given by the instructor into a 10 cm^3 volumetric flask and making up to the mark with a solution of mobile phase composition. Then record the chromatograms under the supervision of the instructor.

b) **Determination of benzene and its derivatives**

Prepare at least three samples of the water received for analysis and dilute them with the mobile-phase composition solution as instructed by the instructor, then record the chromatograms for the tested samples.

15.4. PRESENTATION AND ANALYSIS OF TEST RESULTS

1. Using the chromatograms obtained for the working solutions (point a) read the retention times of the individual compounds and the peak areas for the known contents of the compounds in the samples.
2. Based on the retention times, identify the individual compounds present in the sample of the analysed water.
3. Using the model chromatograms and the peak areas read from the chromatograms obtained for the test water sample, calculate the concentrations of the determined compounds in the mixture (unless the concentrations were given in the analysis report).
4. Discuss the results. Calculate the mean value of the obtained results for each compound and determine the confidence interval of the mean values for a probability level of 95%. Present the obtained results in the table below.

Table 15.2. Analysis of individual chromatograms

Chromatogram no.	Retention time	Identified compound	Peak area	Concentration [μg/dm^3]	$x = \bar{x} \pm t_{0.05} \cdot S_x$

The student report should include

- Purpose and scope of the exercise
- Description of the test stand
- Summary of the obtained results in Table 15.2.
- All calculations, including error estimates and conclusions

Checklist questions

1. BTEX: compound formulas, origin, harmfulness.
2. Basic chromatographic concepts (retention time, retention factor, resolution, definition of chromatography).
3. A block diagram of a gas chromatograph with an explanation of the role of each component.
4. Chromatogram and its parameters.
5. What data can be read from a chromatogram and what information does it carry?
3. Discuss the implementation of the exercise and the purpose of the next steps.

15.5. **Bibliography**

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