

Determination of some components in mineral water

There are numerous mineral water springs in Slovakia. The effect of mineral water on human health depends on the composition of salts (ions) dissolved in water. Quantitative determination of some components in mineral water is aimed like a task of this analytical work.

I. Determination of calcium and magnesium concentration in a sample of mineral water

I.1. Task

The determination of content of Ca^{2+} and Mg^{2+} by chelatometry in two fractions of mineral water sample.

I.2. Principle

Bivalent ions like calcium and magnesium form complexes with disodium salt of ethylene-diamintetraacetic acid (EDTA)- Complexone III. Stability of the complexes is depending on the pH value of solution, what can be used in the determination of ions by complexometric titration.

I.3. Reagents

Reagent	R codes	S codes	Notes
0.02 mol.dm ⁻³ solution of Complexone III	22-36/37/38	26-36	Ready for use
CaCO ₃ (analytical grade)			Standard specimen
4 mol.dm ⁻³ HCl solution	34-37	26-45	Ready for use
ammonium buffer	36/37/38	26	Ready for use
Murexide			Powder indicator
Eriochrome black T		22-24/25	Powder indicator
2 mol.dm ⁻³ NaOH solution	34	26-37/39-45	Ready for use
distilled water			

I.4. Some notes to units

In this text the solution with the concentration of 1mol.dm⁻³ is called 1 molar solution and denoted 1 M (this does not correspond to the SI unit system and IUPAC recommendations).

I.5. Safety, danger and hazardous recommendations

Some of chemical substances and used solutions are highly dangerous. Read the appropriate R/S codes of used chemicals before working with them. Use eye protecting glass, if necessary. The pipette filler is ready for use on the table.

I.6. PROCEDURE

I.6.1. Determination of exact concentration of approximately 0.02 M Complexone III solution.

Weigh ca 0.2 g CaCO_3 standard specimen. Put the shot in a 250 cm^3 conical (Erlenmeyer) flask. Add 40 cm^3 of distilled water. Under shaking add step – by – step 4 M HCl solution until whole dissolving of CaCO_3 . Bring the solution to boiling and continue boiling 5 min. to remove CO_2 . Cool down the solution with tap water and prepare 100 cm^3 of stock solution from it.

Pipette 10.0 cm^3 of stock solution into three titration flasks, add 40 cm^3 of distilled water and then 25 drops of 2 M NaOH solution to adjust the pH value of solution to 12 (Check with indicator paper.). Then add the small amount of Murexide powder indicator.

Fill the burette with Complexone III solution of unknown exact concentration. Carry out the titration of 10.0 cm^3 of standard solution using Murexide powder indicator from rose to blue – violet colour.

Stock solution for the blank test:

Put ca 20 cm^3 distilled water into 100 cm^3 volumetric flask. Add 2 cm^3 of 4 M HCl solution, fill the volumetric flask to 100 cm^3 and shake well. Carry out the above described titration with 10.0 cm^3 of blank sample solution.

Calculate the exact concentration of volumetric solution in mol dm^3 .

I.6.2. Determination of total content of Calcium Ca^{2+} and Magnesium Mg^{2+} ions.

Put quantitatively 50 cm^3 of sample (ready for use in volumetric flask on the table) into 250 cm^3 volumetric flask, add the distilled water to declared volume and shake well. Measure 25.0 cm^3 of sample stock solution into 3 pcs titration flasks, add 10 cm^3 ammonium buffer and Eriochrome black T powder indicator. Titrate by Complexone III volumetric solution from wine-red to blue colour. The consumption of Complexone (III) solution for this titration represents the total content of Ca^{2+} and Mg^{2+} salts in titrated solution.

The solution for the blank test contains 25.0 cm^3 distilled water, 10 cm^3 of ammonium buffer and indicator.

Calculate the summary concentration of Ca^{2+} and Mg^{2+} ions in mol dm^3

I.6.3. Determination of Ca^{2+} ions content

Pipette 25.0 cm^3 of sample stock solution into 3 flasks, add the 2 mol.dm^{-3} NaOH solution to change the pH value of solution to 12. Then add the Murexide powder indicator. Titrate the sample by Complexone III volumetric solution from rose to violet colour. Consumption of volumetric solution for this titration represents the content of Ca^{2+} in titrated solution.

The sample for the blank test contains 25.0 cm^3 of distilled water, volume of 2 M NaOH solution necessary for pH regulation and Murexide powder indicator.

Calculate the mass concentration of Ca^{2+} in the sample [$\text{mg} \cdot \text{dm}^{-3}$].

The difference between total content and calcium content in the sample represents the content of magnesium in the sample.

Calculate the mass concentration of Mg^{2+} in the sample [$\text{mg} \cdot \text{dm}^{-3}$].

II. Photometrical determination of half-time for oxidative hydrolysis reaction of Fe²⁺ ions

II.1. Task:

The aim is to follow dependence of ferrous Fe²⁺ ions concentration in mineral water on time and determine the half-time of an oxidative hydrolysis reaction taking place at 25°C.

II.2. Principle:

Ferrous Fe²⁺ ions in mineral water are oxidised under aerobic conditions to ferric Fe³⁺ ions and as a result, a precipitate of hydrated Fe(III) oxide is formed. After its separation the concentration of Fe²⁺ can be determined so that Fe²⁺ is oxidized to Fe³⁺ which is then bounded in a complex Fe[SCN]₆³⁻ and determined by photometric analysis.

II.3. Reagents

Reagent	R codes	S codes	Notes
FeSO ₄ ·7H ₂ O (analytical grade)	22-36/37/38	26-36	Standard specimen
Fe ₂ (SO ₄) ₃ ·9 H ₂ O, (analytical grade)	22-36/37/38	26-36	Standard specimen
Hydrogen peroxide H ₂ O ₂ , concentrated solution	34	3-28-36/39-45	Ready for use
Nitric acid, HNO ₃ , concentrated solution	8-35	23-26-36-45	Ready for use
10% KSCN solution	20/21/22-32	13	Ready for use
3 % citric acid solution	37/38-41	26-36/37/39	Ready for use
Model solution of mineral water			Ready for use
distilled water			

All chemicals and solutions are ready for use on the laboratory bench

II.4. Some notes to units

In this text the solution with the concentration of 1mol.dm⁻³ is called 1 molar solution and is denoted 1 M (this does not correspond to the SI unit system and IUPAC recommendations).

II.5. Safety, danger and hazardous recommendations

Some of chemical substances and used solutions are highly dangerous. Read R/S codes of used chemicals before working with them. Use eye protecting glass, if necessary. The pipette filler is ready for use on the table.

II.6. PROCEDURE

II.6.1. Determination of molar absorption coefficient ϵ of $\text{Fe}[\text{SCN}]_6^{3-}$ complex in aqueous solution

Calculate the mass of $\text{Fe}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$ needed for preparation of 500 cm^3 of standard solution with a mass concentration of Fe^{3+} exactly $0,1 \text{ mg} \cdot \text{cm}^{-3}$. Weigh the calculated amount. Put some distilled water in a 250 cm^3 conical (Erlenmeyer) flask. Add 2 cm^3 of concentrated nitric acid and weighed amount (shot) of $\text{Fe}_2(\text{SO}_4)_3 \cdot 9 \text{H}_2\text{O}$. Dissolving of sulphate can be supported by carefully heating of solution. Cool the solution with the tap water, transfer the solution quantitatively into 500 cm^3 volumetric flask and add the distilled water to declared volume. Shake the stock solution well.

Prepare the reference test for the photometric analysis: put some distilled water in a in a 100 cm^3 volumetric flask, add 10 cm^3 of 10 % KSCN solution, $0,4 \text{ cm}^3$ of concentrated nitric acid and $0,5 \text{ cm}^3$ of 3% citric acid solution. Fill up to declared volume with distilled water and shake the reference solution properly.

Pipette $5,0 \text{ cm}^3$ of standard solution in three 100 cm^3 volumetric flasks, add 10 cm^3 of 10% KSCN solution, $0,5 \text{ cm}^3$ of 3% citric acid solution and fill to declared volume with distilled water. Shake the standard solution well.

Note: Note, that the hydrated ferric ions show relatively good stability under conditions of oxidative solution.

In contrast, the $\text{Fe}[\text{SCN}]_6^{3-}$ complex can be easily decomposed on the daily light.

Fill the cuvette with the solution and measure the absorbance A at wave length $\lambda = 480 \text{ nm}$ in comparison with the reference test solution.

The instruction for this measuring are described in chapter II.6.5. and attached to each apparatus.

Calculate the molar absorption coefficient ϵ of $\text{Fe}[\text{SCN}]_6^{3-}$ complex.

II.6.2. Preparation of a reference solution for measuring of kinetics

Prepare 50 cm^3 of reference solution containing:

$0,5 \text{ cm}^3$ of concentrated nitric acid

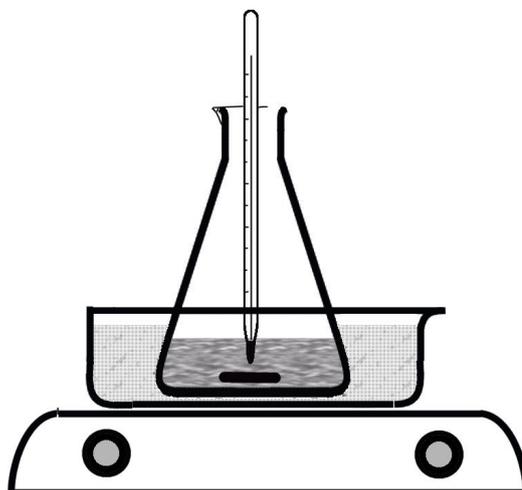
$0,2 \text{ cm}^3$ of concentrated hydrogen peroxide

$0,5 \text{ cm}^3$ of 3 % citric acid solution

5 cm^3 of 10 % KSCN solution and distilled water.

II.6.3. Oxidative decomposition of FeSO_4 in mineral water

Assemble apparatus according scheme:



Calculate the mass of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, (analytical grade) that is necessary for preparation of exactly 500 cm^3 of solution with mass concentration of Fe^{2+} $42 \text{ mg} \cdot \text{dm}^{-3}$. Weigh out the calculated amount of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$. Pour exactly 500 cm^3 of model solution of mineral water (ready for use in bottle remarked KORYTNICA) into a dry 1000 cm^3 conical (Erlenmeyer) flask and temper the solution to 25°C under gentle stirring (150 min^{-1}) by magnetic stirrer. Add the $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ shot to the mineral water in starting time 0. Regulate the stirring of solution to constant gentle speed and sample always 10.0 cm^3 of solution after certain time periods.

Following time periods are recommended:

5 min.	45 min.
15 min.	60 min.
30 min.	90 min.

Modify the sample according the procedure described in chapter II. 6.4.

II.6.4. Sample treatment:

Pour small amount distilled water in a 50 cm^3 volumetric flask. Using pipette or 2 cm^3 syringe measure the following solutions to prepare oxidative mixture:

0.5 cm^3 of concentrated nitric acid

0.2 cm^3 of concentrated hydrogen peroxide

0.5 cm^3 of 3 % citric acid solution

Carry out filtration of the sample trough the paper filter directly into volumetric flask. Wash the filter with small amount of distilled water and close the flask carefully with plug. Add 5 cm^3 of 10 % KSCN solution after min.10 minutes waiting. Fill the measuring flask to declared volume with distilled water, shake well and measure immediately (within one minute after mixing) the absorbance A (at $\lambda = 480 \text{ nm}$) of solution in comparison with the reference solution.

Note: Note, that the hydrated ferric ions show relatively good stability under conditions of oxidative solution.

In contrast, the $\text{Fe}[\text{SCN}]_6^{3-}$ complex can be easily decomposed on the daily light.

II.6.5. Measuring of absorbance A of samples

Carry out the measurements using following instructions:

Turn on the photometer. The turned – on state is indicated by the illuminating digits on digital display. Press button E from the blinking push buttons. Set the wave length of apparatus to 480 nm , insert the kuvette with reference solution into apparatus. Press button R. The apparatus must signalise zero value on the display. Insert the kuvette with sample into apparatus. Read the value of absorbance A on the display. Take the kuvettes with sample and with reference solution out from the apparatus.

II.6.6. Calculation of Fe²⁺ concentration

The concentration of Fe²⁺ in each sample can be calculated using Lambert – Beer relation or use the calibration curve if necessary (Ask for the graph the referees.) Take into consideration that from one mole of Fe²⁺ is formed one mole of Fe[SCN]₆³⁻.

Calculate the concentration of Fe²⁺ using the molar absorption coefficient and thickness of cuvette.

Compare the calculated concentration with those estimated from an appropriate calibration curve (available on each bench).

II.6.7. Determination of starting concentration of Fe²⁺

Weigh the in chapter II.6.3.calculated mass of homogenous crystalline FeSO₄.7H₂O and prepare 500 cm³ of solution by dissolving of shot in distilled water. Measure 10.0 cm³ of the solution and perform with it the sample treatment according procedure described in II.6.4. Measure the absorbance A and calculate the real starting concentration Fe²⁺ using the molar absorption coefficient, calculated for Fe[SCN]₆³⁻ and the thickness of the cuvette. Repeat the determination.

II.6.8. Determination of half-time for oxidative hydrolysis reaction of Fe²⁺ ions

Calculate the concentration of Fe²⁺ ions in each particular sample from the results of photometric analysis and arrange the values into table.

Plot the concentration of Fe²⁺ against time period (in minutes) on the graph. Determine the time period necessary for the decreasing of Fe²⁺ ions to the half value of real starting concentration.

Complete the attached protocol

Repeat the kinetic measuring, if necessary

Reagent	M [g.mol ⁻¹]
CaCO ₃	100.09
Ca	40.08
Mg	24.30
FeSO ₄ .7H ₂ O	278.01
Fe ₂ (SO ₄) ₃ .9 H ₂ O	562.01
Fe	55.85