

1. ACID-BASE MEASUREMENTS

1.1. MEASUREMENTS IN AQUEOUS SOLUTIONS

Preparation of 0.1 mol/dm³ HCl titrant and determination of its exact concentration

a.) *Preparation of the solution:* Prepare 250 cm³ approximately 0.1 mol/dm³ HCl solution by diluting concentrated (36 %(w/w), d = 1.18 g/cm³) hydrochloric acid solution with distilled water.

b.) *Determination of the exact concentration of the prepared solution:*

The chemical equation of the determination is:



Description: Weigh approximately 0.1 g analytical grade KHCO₃ in a 100 cm³ titration flask on an analytical balance. Dissolve the weighed reagent in 20-30 cm³ distilled water by stirring, and, after the addition of 1-3 drops of methyl red indicator, titrate it by the approximately 0.1 mol/dm³ HCl until a pale orange color is observed. Boil the solution in the titration flask for 2-3 minutes (use boiling stone) to remove CO₂. After cooling down the solution to room temperature, titrate it drop by drop to reach pale orange color again. Repeat this whole procedure 3 times.

Another possible method is to prepare 100.00 cm³, approximately 0.1 mol/dm³ (but exactly known) KHCO₃ stock solution in a volumetric flask, by weighing directly the mass of the required KHCO₃ on an analytical balance, then titrating 10 cm³ of this stock solution by the approximately 0.1 mol/dm³ HCl in the same way as described earlier.

Molar weight of KHCO₃: 100.12 g/mol

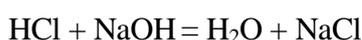
Preparation of 0.1 mol/dm³ NaOH titrant and determination of its exact concentration

a.) *Preparation of the solution:* Solid NaOH is hygroscopic and always coated with sodium carbonate i.e. it contains an unknown quantity of carbonate because of CO₂ absorbed on its surface. Therefore, it is not possible to prepare NaOH solution of exact concentration by weighing the mass of solid NaOH. Carbonate-free titrant can be prepared by weighing twice the mass of NaOH necessary for the solution quickly on a tare balance in a 250 cm³ Erlenmeyer flask, then shaking it with 100 cm³ pre-prepared (boiled up and cooled down) distilled water until approximately one half of NaOH is dissolved, pouring off the solution quickly and instantly dissolving the remaining solid (now carbonate-free) NaOH in another portion of pre-prepared distilled water. The solution so prepared should be stored in a well stoppered flask to avoid carbonate re-formation.

Another method (Sørensen method) to prepare carbonate-free NaOH titrant is preparing a concentrated, 50 %(w/w) NaOH solution by adding a sufficient amount of solid NaOH to distilled water. At this concentration, Na₂CO₃ is no longer soluble and will settle out. The carbonate-free titrant can be prepared by diluting the clear NaOH solution above the precipitate and below the solid film on the surface of the concentrated NaOH solution.

b.) *Determination of the exact concentration of the prepared NaOH solution by titration of HCl:*

The chemical equation of the determination is:



Description: Put 10.00 cm³ of approximately 0.1 mol/dm³ (but exactly known) HCl solution into a 100 cm³ titration flask. Dilute the sample with distilled water to 20-30 cm³ and, after adding 2-3 drops of methyl red indicator, titrate it with the NaOH solution from a buret to the pale orange endpoint.

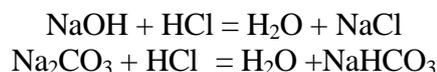
Molar weight of NaOH: 40.00 g/mol

1.2. TITRATION OF STRONG AND WEAK ACIDS, STRONG AND WEAK BASES, ACID MIXTURES AND BASE MIXTURES

Simultaneous determination of NaOH and Na₂CO₃ in a mixture (Warder method)

The chemical equations of the determination are:

When using phenolphthalein indicator:



When using methyl red or methyl orange indicator:



Description: An individual sample of NaOH and Na₂CO₃ mixture of unknown concentrations will be given in a vial. Transfer the sample without loss into a 100.00 cm³ volumetric flask and fill up the flask with distilled water up to the mark. Shake this stock solution well, then put 10.00 cm³ of the stock solution into a 100 cm³ titration flask using a pipette. Dilute all samples to approx. 40 cm³ with distilled water, add approx. 3 g of NaCl and 3-4 drops of phenolphthalein to each sample and titrate them with the HCl titrant of known (earlier determined) concentration without shaking the samples. The endpoint color is pale pink. This is the first volume of titrant you should use for the calculation.

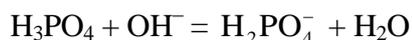
Add 1-3 drops of methyl red indicator to the samples and continue the titration to the pale orange endpoint color of methyl red. Before finishing the titration and reading the second volume of titrant for the calculation, CO₂ has to be removed by boiling the solution for 2-3 minutes and then cooling it down.

Molar weights: NaOH: 40.00 g/mol; Na₂CO₃: 106.00 g/mol

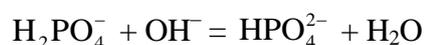
Simultaneous determination of H₃PO₄ and KH₂PO₄ in a mixture

The ionic equations of the determination are:

When using methyl orange indicator:



When using phenolphthalein indicator:



Description: Transfer the sample from the vial without loss into a 100.00 cm³ volumetric flask and fill up the flask with distilled water up to the mark. Shake the stock solution well, then

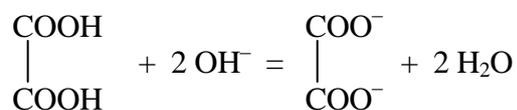
put 10.00 cm³ of the stock solution into a 100 cm³ titration flask using a pipette. Dilute all samples to 20-30 cm³ with distilled water, add 1-3 drops of methyl orange indicator to each sample and titrate them with the NaOH titrant of known (earlier determined) concentration to incipient yellow color. This is the first volume of titrant you should use for the calculation.

Add approx. 1 g of solid NaCl to each sample and, after dissolving the solid, add also 4-5 drops of phenolphthalein indicator. Continue the titration to the permanent pink endpoint color. This is the second volume of titrant you should use for the calculation.

Molar weights: H₃PO₄: 98.00 g/mol; KH₂PO₄: 136.09 g/mol

Determination of oxalic acid

Oxalic acid is a dibasic weak acid, in which the two consecutive deprotonation steps overlap ($K_{a1} = 6.5 \times 10^{-2}$; $K_{a2} = 6.1 \times 10^{-5}$). Therefore, the amount of oxalic acid in a solution can be determined using the first or second deprotonation process only with high error. The determination based on the total deprotonation process is, however, more practicable.



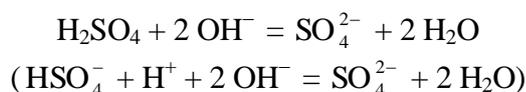
Description: Transfer the solution sample of oxalic acid without loss into a 100.00 cm³ volumetric flask and fill up the flask with distilled water up to the mark. Shake this stock solution well, then put 10.00 cm³ of the stock solution into a 100 cm³ titration flask using a pipette. Add 2-3 drops of phenolphthalein to each sample and titrate them with the NaOH titrant of known (earlier determined) concentration to the appearance of the pale pink endpoint color. Calculate the mass of oxalic acid in your solution sample (mg).

Molar weight of (COOH)₂·2H₂O: 126.07 g/mol

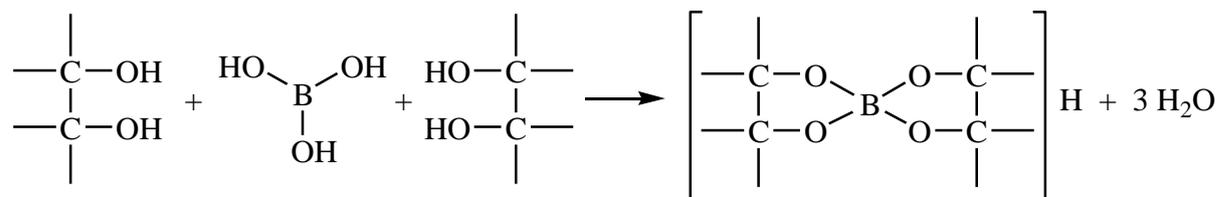
Simultaneous determination of sulfuric acid and boric acid in a mixture

The ionic equations of the determination are:

When using methyl orange indicator:



When adding mannite and using phenolphthalein indicator:



Boric acid is a weak acid with pH > 5.0 at $c_{\text{boric acid}} = 0.1 \text{ mol/dm}^3$. Indicators with lower indicator exponent (methyl red, methyl orange) are practically not affected by boric acid. Using these indicators, acids other than boric acid can be separately titrated in the solution.

After adding an excess of polyalcohol (e.g. mannite) to the solution, the weak boric acid is transformed into a stronger acid and the amount of boric acid can be determined by acid-base titration.

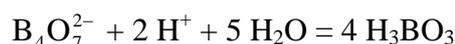
Description: Transfer the sample without loss into a 100.00 cm³ volumetric flask and fill up the flask with distilled water up to the mark. Shake the stock solution well, then put 10.00 cm³ of the stock solution into a titration flask. Add 1 drop of methyl red indicator to each sample and titrate them with the NaOH titrant of known concentration to the pale orange endpoint. Before finishing the titration and reading the volume of titrant for the calculation, CO₂ has to be removed by boiling the solution for 2-3 minutes and then cooling it down.

Add approx. 1.0 g of mannite and 2 drops of phenolphthalein indicator to each sample. After adding mannite to the solution, it turns red first (acidic color of methyl orange), then, during the titration, it turns yellow (basic color of methyl orange). Continue the titration to the appearance of the pink endpoint color of phenolphthalein with the yellow background of methyl orange. This is the second volume of titrant you should use for the calculation. Calculate the mass of sulfuric acid and boric acid in your sample (mg).

Molar weights: H₂SO₄: 98.08 g/mol; H₃BO₃: 61.84 g/mol

Determination of borax (sodium tetraborate) content of a solid sample by acid-base titration

The ionic equation of the determination is:



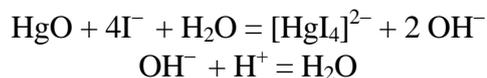
Description: Homogenize the sample containing borax and inert impurity, then weigh approx. 0.4 g (accurately known mass) of sample on an analytical balance into a titration flask. Dissolve the solid samples in 20-30 cm³ of distilled water, add 2 drops of methyl orange indicator to each sample and titrate them with the HCl titrant to the pale orange endpoint. Calculate the mass percentage of borax in your solid sample.

Molar weight of Na₂B₄O₇·10H₂O: 381.37 g/mol

1.3. ACID-BASE TITRATIONS AFTER PREPARATORY CHEMICAL RECTIONS (COMPLEX FORMATION OR REDOX REACTIONS) FORMING HYDROXONIUM OR HYDROXIDE IONS

Determination of HgO

The ionic equations of the determination are:

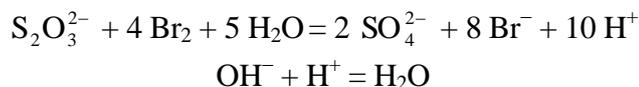


Description: Homogenize the sample containing HgO and an inert impurity in a mortar, then weigh approx. 0.2 g (accurately known mass) of the sample using an analytical balance into a titration flask. Add approx. 2 grams of KI to each and dissolve the mixtures in 20-30 cm³ of distilled water. After dissolving all the HgO, add 1-3 drops of methyl red indicator to each sample and titrate them with the HCl titrant to the pale orange endpoint color. Calculate the mass percentage of HgO in your solid sample.

Molar weight of HgO: 216.62 g/mol

Determination of sodium thiosulfate by measuring the acid formed in the oxidation reaction of Na₂S₂O₃ with bromine

The ionic equations of the determination are:



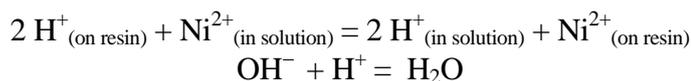
Description: An individual sodium thiosulfate sample of unknown concentration will be given in a vial. Transfer the sample without loss into a 100.00 cm³ volumetric flask and fill up the flask with distilled water up to the mark. Shake this stock solution well, then put 10.00 cm³ of the stock solution into a 100 cm³ Erlenmeyer flask. Dilute the solutions to 50 cm³ with distilled water and then carefully add freshly prepared bromine water* dropwise to each sample until its color becomes stable pale yellow. Remove the excess of bromine by boiling the solution for 10-15 minutes (use boiling stone). The efficiency of bromine removal can be checked by adding one drop of 10-fold diluted methyl red indicator to the solution. If there is still some bromine in the solution, it will destroy the indicator and the solution will be colorless. In this case, boil the solution for another 10-15 minutes. If the removal of bromine was successful, the pale pink color of the indicator remains, and you can stop boiling the solution. Use the hood when working with bromine.

After removing all of the bromine from the solutions, add 1-3 drops of methyl red indicator to each sample and titrate them with the NaOH titrant to the pale orange endpoint. Calculate the mass of sodium thiosulfate in your sample (mg).

Molar weight of Na₂S₂O₃: 158.12 g/mol

Determination of nickel(II) ions by measuring the acid formed in an ionic exchange reaction on a cation exchange resin

The ionic equations of the determination are:



A cation exchange resin in H⁺ form is used to exchange Ni(II) ions in the solution for H⁺ ions. After elution of the released H⁺ ions, its molar amount can be determined by titration with NaOH titrant of known concentration.

Wash the ionic exchange column in H⁺ form with approx. 50 cm³ distilled water until neutral pH is reached. You can check whether or not the resin contains free H⁺ ions by measuring the pH of the eluent with pH test paper.

Description: Transfer the sample from the vial without loss into a 100.00 cm³ volumetric flask and fill up the flask with distilled water up to the mark. Shake the stock solution well, then put 5.00 cm³ of the stock solution onto the column prepared in advance. At 15-20 drops/minute flow rate, 60-70 cm³ distilled water is necessary for the elution. Be careful not to let the column dry. Before finishing the elution, check the pH of the eluent with pH test paper, and if it is not neutral, continue the elution until neutral pH of the eluent drops. Add some solid methyl red/ methylene blue indicator mixture to the eluate and titrate it with the NaOH titrant of known concentration to the endpoint. Calculate the mass of nickel(II) ion in your sample (mg).

* Bromine vapors are severe skin, eye and mucous membrane irritants. Contact with liquid bromine can cause severe burns. The readily identifiable color and pungent odor gives immediate warning of bromine's presence. Use only in well-ventilated areas (hood) and wear chemical splash goggles and gloves to prevent eye and skin protection.

Molar weight of nickel: 58.71 g/mol

1.4. TITRATIONS IN NON- AQUEOUS MEDIUM

Preparation of 0.1 mol/dm³ perchloric acid titrant in glacial acetic acid and determination of its exact concentration

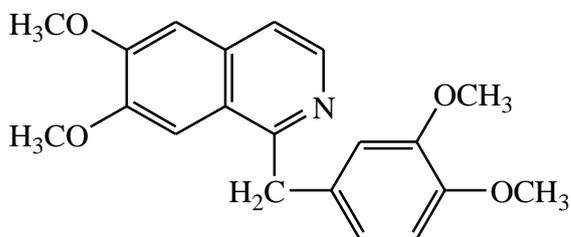
Use analytical grade concentrated (69-71%) perchloric acid and glacial acetic acid[†] to prepare the titrant. Acetic acid may contain a maximum of 0.5% water. If the water content of acetic acid is higher than 0.5%, it should be mixed with acetic acid anhydride in equivalent amount to the water content of acetic acid and left for a day.

Description: When making the titrant, transfer 9 cm³ of concentrated perchloric acid into a 1000 cm³ volumetric flask, add approx. 600 cm³ of glacial acetic acid, 16 cm³ of acetic acid anhydride, shake the solution well and left for a day. Fill up the flask with glacial acetic acid up to the mark and shake it again the next day.

To determine its exact concentration, weigh approx. 0.2 g (accurately known mass) of dry potassium hydrogen phthalate[‡] on an analytical balance and dissolve it in 15 cm³ of glacial acetic acid. Use mild heating if necessary but never direct flame because the solvent is highly flammable. Add 2-3 drops of crystal violet indicator (0.1 mol/dm³ of crystal violet solution in glacial acetic acid as solvent) to the sample and titrate it with the perchloric acid titrant of unknown concentration to the cyan endpoint color at room temperature.

Molar weight of potassium hydrogen phthalate: 204.23 g/mol

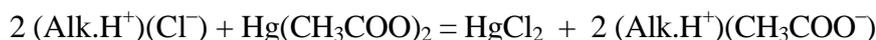
Determination of alkaloids (papaverine) in non-aqueous solution by titration



Papaverine (Alk.)

Weak bases and acids with K_b and $K_a < 10^{-8}$ can be titrated in non-aqueous solution by using acidic or basic solvents, respectively. The most frequently used titrant of the determination of weak bases is perchloric acid in glacial acetic acid. By adding mercury(II) acetate to papaverine hydrochloride salt (Alk.HCl or (Alk.H⁺)(Cl⁻)) in glacial acetic acid medium, the weakly soluble mercury(II) chloride precipitates while changing the chloride counter-ion of papaverine to acetate.

The chemical equation of the determination is:



[†] Glacial acetic acid causes painful, severe eye and tissue damage. Use safety glasses and gloves when working with glacial acetic acid.

[‡] Dry potassium hydrogen phthalate for 2 hours at 120°C.

The weak base (Alk.) content of the solution can be determined by titration with perchloric acid in glacial acetic acid as a solvent. Mercury(II) acetate excess does not disturb the determination because it is a very weak base in glacial acetic acid.

Description: Weigh approx. 0.4 g (accurately known mass) of the sample using an analytical balance into a 100 cm³ stoppered Erlenmeyer flask and dissolve it in 5 cm³ of glacial acetic acid. Add 10 cm³ of mercury(II) acetate in glacial acetic acid and 2-3 drops of crystal violet indicator to the solution and titrate it with the perchloric acid titrant of known concentration to the cyan endpoint color. (The possible precipitation of solid KClO₄ during the titration does not disturb the accuracy of the determination.) Calculate the mass percentage of papaverine hydrochloride in your sample.

Molar weight of papaverine hydrochloride: 375.84 g/mol

2. REDOX MEASUREMENTS

2.1. PERMANGANOMETRIC TITRATIONS

Preparation of 0.02 mol/dm³ KMnO₄ titrant and determination of its exact concentration

a.) *Preparation of the solution:* Weigh the calculated amount of analytical grade KMnO₄ using a tare balance and dissolve it in approx. 250 cm³ of distilled water. Let the freshly prepared solution settle for some hours then filter it using glass filter.

b.) *Determination of the exact concentration of the prepared solution by titration of Na₂(COO)₂ (sodium oxalate):*

The chemical equation of the determination is:



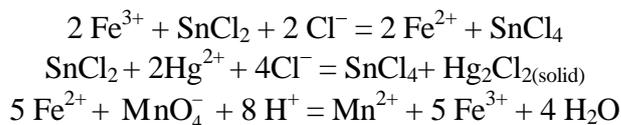
Preparation of 0.05 mol/dm³ Na₂(COO)₂ stock solution: Weigh the calculated amount of analytical grade Na₂(COO)₂ with analytical balance, transfer into a 100.00 cm³ volumetric flask and after dissolving the solid in some water, fill up the flask with distilled water up to the mark and shake it well.

Description: Put 10.00 cm³ of approx. 0.05 mol/dm³ (but exactly known) Na₂(COO)₂ into a titration flask, dilute it to approx. 30 cm³, add 10 cm³ of 10 % (w/w) H₂SO₄ and 0.2-0.3 g of MnSO₄ to the solution, heat it to 60-80 °C and titrate it with the KMnO₄ titrant of unknown concentration to the pale pink endpoint. If the solution cools down during the titration, raise its temperature again to 60-80 °C before finishing the titration.

Molar weights: KMnO₄: 158.04 g/mol; Na₂(COO)₂: 134.00 g/mol

Simultaneous determination of Fe(II) and Fe(III) by permanganometric titration

The ionic equations of the determination are:



Description: Transfer the sample without loss into a 100.00 cm³ volumetric flask and fill up the flask with distilled water up to the mark. Shake this stock solution well, then put 10.00 cm³ of it into a 100 cm³ titration flask using a pipette. Add 15 cm³ of Zimmermann-Reinhardt reagent to the sample and titrate it at room temperature with the KMnO₄ titrant of known concentration to the permanent pale pink endpoint that is stable for at least 30 seconds. This is the first volume of titrant you should use for the calculation.

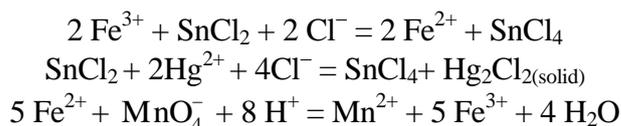
Add 10 cm³ of 20 % (w/w) HCl and boil it up (use boiling stone). Add some freshly prepared 15 % (w/w) SnCl₂ in concentrated HCl dropwise to the hot sample until it becomes colorless. It is practical to add one more drop of the SnCl₂ solution to the sample to make sure that the reaction is complete. Cool the solution to room temperature and add quickly 10 cm³ of 5 % (w/w) HgCl₂. White, silky Hg₂Cl₂ precipitates from the solution.

Put 300 cm³ of distilled water into a 1000 (or 500) cm³ flask, add some drops of KMnO₄ titrant to the water (these drops are included in the total volume of titrant) and transfer the reduced iron(II) solution without loss into the flask. Titrate the solution with the KMnO₄ titrant of to the permanent pale pink endpoint. This is the second volume of titrant you should use for the calculation. Calculate the mass of iron(II) and iron(III) in your sample (mg's).

Molar weight of iron: 55.85 g/mol

Determination of Fe(III) by permanganometric titration

The ionic equations of the determination are:



Description: Transfer the sample without loss into a 100.00 cm³ volumetric flask and fill up the flask with distilled water up to the mark. Shake this stock solution well, then put 10.00 cm³ of it into a 100 cm³ titration flask using a pipette. Add 15 cm³ of Zimmermann-Reinhardt reagent and 10 cm³ of 20 % (w/w) HCl to the sample and boil it up (use boiling stone). Add some freshly prepared 15 % (w/w) SnCl₂ in concentrated HCl dropwise to the hot sample until it becomes colorless. It is practical to add one more drop of the SnCl₂ solution to the sample to make sure that the reaction is complete. Cool the solution to room temperature and add quickly 10 cm³ of 5 % (w/w) HgCl₂. White, silky Hg₂Cl₂ precipitates from the solution.

Put 300 cm³ of distilled water to a 1000 (or 500) cm³ flask, add some drops of KMnO₄ titrant to the water (these drops are included in the total volume of titrant) and transfer the reduced iron(II) solution without loss into the flask. Titrate the solution with the KMnO₄ titrant of to the permanent pale pink endpoint. Calculate the mass of iron(III) in your sample (mg).

Molar weight of iron: 55.85 g/mol

Determination of Mn(II) by Volhard-Wolf method

The ionic equation of the determination is:

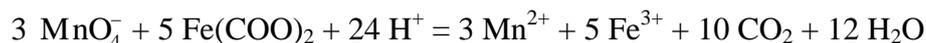


Description: An individual Mn(II) sample of unknown concentration will be given in a vial. Transfer the sample without loss into a 100.00 cm³ volumetric flask and fill up the flask with distilled water up to the mark. Shake this stock solution well, then put 10.00 cm³ of it into a 1000 cm³ Erlenmeyer flask using a pipette and dilute it to approx. 500 cm³ with distilled water. Add 1-2 g of ZnO and approx. 5 g of ZnSO₄·7H₂O to the sample and stir it until dissolve the solids. Boil the solution (use boiling stone) and titrate it with the KMnO₄ titrant to the permanent pale pink endpoint color that is stable for at least 2-3 minutes. If the solution cools down during the titration, boil it again before finishing the titration. Calculate the mass of Mn(II) in your sample (mg).

Molar weight of manganese: 59.94 g/mol

Determination of ferrous oxalate

The chemical equation of the determination is:

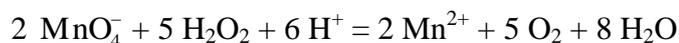


Description: An individual solid ferrous oxalate sample of unknown weight will be given in a vial. Dissolve this sample in 50 cm³ 20% sulfuric acid and set the final volume of the stock solution to 100.00 cm³ in a volumetric flask. Put 10.00 cm³ of this stock solution into a titration flask, add 10 cm³ more 10% sulfuric acid and 20 cm³ 20% phosphoric acid. Heat the solution to 60-80 °C and titrate it with KMnO₄ titrating solution to the permanent pale pink endpoint.

Molar weight of Fe(COO)₂·2H₂O: 179,90 g/mol.

Determination of hydrogen peroxide

The chemical equation of the determination is:



Description: An individual solution sample will be given in a vial. Dilute this sample to 100.00 cm³ in a volumetric flask. Put 10.00 cm³ of this stock solution into a titration flask, and add 10 cm³ 10% sulfuric acid and 10-20 cm³ distilled water. Titrate it with KMnO₄ titrating solution to the permanent pale pink endpoint.

Molar weight of H₂O₂: 34,02 g/mol.

2.2. BROMATOMETRIC TITRATIONS

Preparation of 0.02 mol/dm³ KBrO₃ titrant

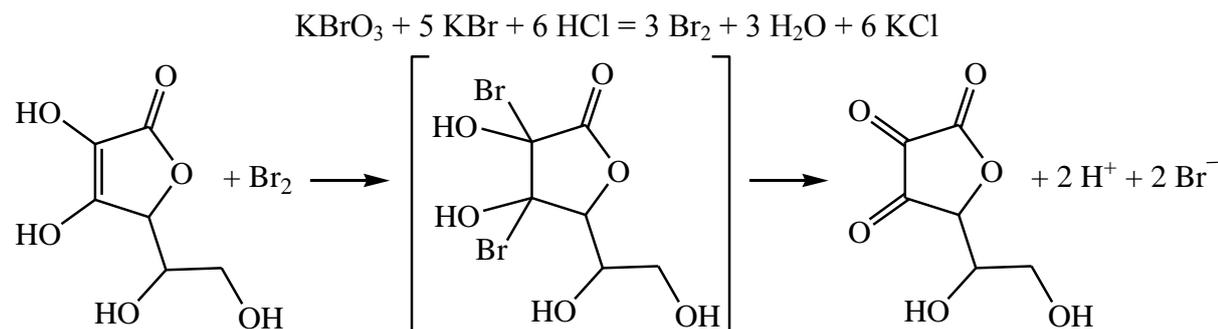
Weigh the calculated amount of analytical grade KBrO₃ with analytical balance, transfer into a

250.00 cm³ volumetric flask and after dissolving the solid in some water, fill up the flask with distilled water up to the mark and shake it well.
Molar weight of KBrO₃: 167.02 g/mol

Determination of ascorbic acid active ingredient content of vitamin C tablet

This is a typical bromine addition determination. In the reaction of KBr and KBrO₃, bromine is released. Ascorbic acid (vitamin C) is oxidized by bromine resulting in the formation of dehydroascorbic acid.

The chemical equations of the determination are:



Description: Homogenize the vitamin C tablet containing ascorbic acid and redox-inert ingredients (carrier substance, usually starch) in a mortar, then weigh approx. 1 g (accurately known mass) of the sample using an analytical balance into a volumetric flask. Fill up the flask with distilled water up to the mark, shake this stock solution well, then put 10.00 cm³ of it into a 100 cm³ titration flask using a pipette. Add 10 cm³ of 10 % (w/w) HCl to the sample and dilute it to 40-50 cm³ with distilled water. Add approx. 0.2 g of KBr and 2 drops of p-ethoxy chrysoidine indicator to the sample and titrate it with the KBrO₃ titrant to the endpoint. Calculate the mass percentage of the active ingredient (ascorbic acid) in the tablet.

Molar weight of ascorbic acid: 176.12 g/mol

2.3. IODOMETRIC TITRATIONS

Preparation of 0.008 mol/dm³ KIO₃ titrant

Weigh the calculated amount of analytical grade KIO₃ using an analytical balance, transfer it into a 100.00 cm³ volumetric flask and after dissolving the solid in some distilled water fill up the flask.

Molar weight of KIO₃: 214.00 g/mol

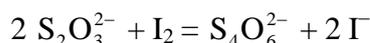
Preparation of 0.05 mol/dm³ Na₂S₂O₃ titrant and determination of its exact concentration

a.) Preparation of the solution: Prepare 250 cm³ approximately 0.05 mol/dm³ Na₂S₂O₃ titrant by weighing the calculated mass of analytical grade Na₂S₂O₃·5H₂O solid and dissolving it in distilled water.

Molar weight of Na₂S₂O₃·5H₂O: 248.19 g/mol

b.) *Determination of the exact concentration of the prepared solution:*

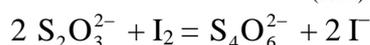
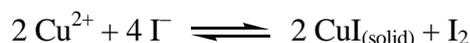
The ionic equations of the determination are:



Description: Put 10.00 cm³ of approx. 0.008 mol/dm³ (but exactly known) KIO₃ into a stoppered Erlenmeyer flask using a pipette. Add approx. 20 cm³ of distilled water and 1-2 cm³ of 20 % (w/w) HCl to the sample, then dissolve 0.5 g of KI in it. Cover the flask immediately with a glass stopper lubricated with distilled water and keep it in the dark (in your laboratory cabinet). After 3-5 minutes, titrate the released iodine[§] with the Na₂S₂O₃ titrant of unknown concentration to the colorless endpoint. Before finishing the titration and reading the volume of titrant for the calculation, add some drops of 1% starch solution to the sample to intensify the color change.**

Determination of Cu(II) by iodometric titration

The ionic equations of the determination are:

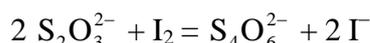


Description: An individual copper(II) sample of unknown concentration will be given in a vial. Transfer the sample without loss into a 100.00 cm³ volumetric flask and fill up the flask with distilled water up to the mark. Shake this stock solution well, then put 10.00 cm³ of the stock solution into a stoppered Erlenmeyer flask using a pipette. Dilute the solution to 50 cm³ with distilled water and add 3 cm³ of 10 % (w/w) acetic acid to it. Dissolve approx. 1 g of KI in the sample, cover the flask immediately with a glass stopper lubricated with distilled water and keep it in the dark (in your laboratory cabinet). After 5 minutes, titrate the released iodine with the Na₂S₂O₃ titrant of known concentration to the colorless endpoint. Before finishing the titration and reading the volume of titrant for the calculation, add some drops of 1% starch solution to the sample to intensify the color change and finish the titration slowly. Calculate the mass of Cu(II) in your sample (mg).

Molar weight of copper: 63.54 g/mol

Determination of I⁻ ions by the Winkler's iodine multiplying method

The ionic equations of the determination are:



Description: Transfer the sample of I⁻ without loss into a 100.00 cm³ volumetric flask and fill up the flask with distilled water up to the mark. Shake this stock solution well, then put 10.00 cm³ of

[§] When elemental iodine (I₂) exists in the presence of excess iodide ion, an acid-base reaction occurs in which elemental iodine acts as a Lewis acid and iodide ion acts as a Lewis base to produce a triiodide (I₃⁻) or polyiodide ion. These ions have dark brown to yellow color in aqueous solution with decreasing concentration.

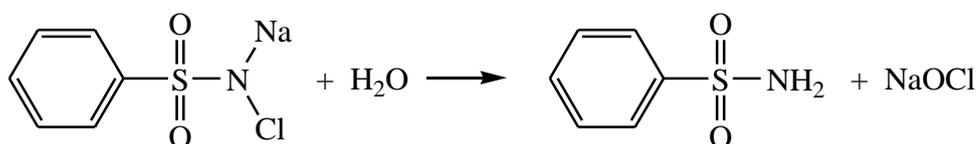
** Adding starch to aqueous iodine solution results in much more intense, black to blue color which is due to the formation of starch-polyiodide complex. Thus, after adding some starch, a very low concentration of iodine can be detected visually.

the stock solution into a stoppered Erlenmeyer flask using a pipette. Dilute the solution to 50 cm³ with distilled water and add 0.5 cm³ of 1 mol/dm³ HCl to it. Add freshly prepared chlorine water dropwise to the sample until its initial yellow color (color of the I₂ formed) becomes colorless. It is practical to add four times the amount of chlorine water necessary for the discoloration to the sample to make sure that the reaction is complete. At this stage, the solution has an intense chlorine smell^{††}. Use the hood when working with chlorine water. Remove the excess of chlorine by intense boiling of the solution for 10-15 minutes (use boiling stone). Add some more distilled water in small portions as needed to keep the volume constant. After removing the chlorine from the solution, cool it down and check the efficiency of chlorine removal by adding 1-2 drops of 10-fold diluted methyl orange indicator to the solution. If there is still some chlorine in the solution, it will destroy the indicator and the solution will be colorless. In this case, boil the solution for another 10-15 minutes. If the removal of chlorine was successful, the pale pink color of the indicator remains, and you can stop boiling the solution. After removing all of the chlorine from the solutions, add approx. 0.5 g of KI and 5 cm³ of 20 % (w/w) phosphoric acid to the solution. Cover the flask immediately with a glass stopper lubricated with distilled water and keep it in the dark (in your laboratory cabinet). After 3-5 minutes, titrate the released iodine with the Na₂S₂O₃ titrant of known concentration to the colorless endpoint. Before finishing the titration and reading the volume of titrant for the calculation, add 5-6 drops of 1% starch solution to the sample. Calculate the mass of iodine in your sample (mg).

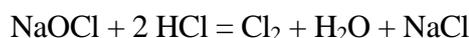
Molar weight of iodine: 126.90 g/mol

Determination of active chlorine content of Neomagnol tablet

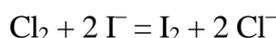
The active ingredient of Neomagnol tablet is the sodium salt of N-chlorobenzenesulfonamide (chlorogen^{‡‡}). In aqueous solution, it hydrolyzes to form sodium hypochlorite and benzene sulfonamide:



Sodium hypochlorite forms chlorine with hydrochloric acid:



The amount of chlorine so formed i.e. the active chlorine content of neomagnol can be measured by iodometric titration. The ionic equation of the determination is:



^{††} Chlorine gas is corrosive and irritating to the eyes, skin and mucous membranes. Chlorine inhalation may cause coughing, nausea, vomiting, headache, dizziness and difficulty breathing. It may also cause pulmonary edema (build-up of fluid in the lungs) which may be delayed by several hours and can be fatal. Use only in well-ventilated areas (hood) and wear chemical splash goggles and gloves to prevent eye and skin protection.

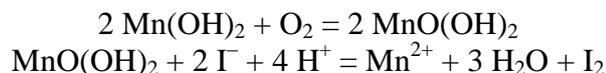
^{‡‡} Other names for neomagnol: annogen, benzene chloramine, benzenesulfo-sodium chloramide, chloramine B, [chloro(phenylsulfonyl)amino]-sodium, monochloramine B, (N-chlorobenzenesulfonamido)-sodium, N-chlorobenzenesulfonamide sodium salt, sodium benzenesulfonchloramine, sodium benzosulfochloramide, sodium benzene sulfochloramide, sodium N-chlorobenzenesulfonamide, sodium benzenesulfonchloramide, sulfenazone

Description: Weigh the mass of three Neomagnol tablets on an analytical balance (use a weighing dish) and calculate the average mass of one tablet. Homogenize the three tablets in a mortar and store this powder in the stoppered weighing dish. For the determination of the active chlorine content, weigh approx. 0.1 g (accurately known mass) of the powder using an analytical balance into a stoppered Erlenmeyer flask, dissolve it in approx. 20 cm³ of distilled water and add 0.5 g of KI and 5 cm³ of 2 mol/dm³ hydrochloric acid to the solution. After keeping the solution in the dark and stoppered for some minutes, titrate the released iodine with the Na₂S₂O₃ titrant of known concentration to the colorless endpoint. Before finishing the titration and reading the volume of titrant for the calculation, add 5 drops of 1% starch solution to the sample to intensify the color change. Calculate the chlorogen content of a Neomagnol tablet of average mass (mg) and mass percentage of active chlorine content in a tablet.

Molar weight of chlorogen: 240.56 g/mol

Determination of dissolved oxygen concentration of water samples (Azide-Winkler Method)

The basic principle of the measurements is that manganese(II) hydroxide precipitated from alkaline solution reacts with the dissolved oxygen content of water instantaneously to form manganese hydroxides of higher (mainly +4) oxidation state. After acidifying the solution, manganese hydroxide in oxidation state higher than two reacts with iodide ion to give iodine and manganese(II) ions. The released iodine can be measured by titration with sodium thiosulfate titrant. The ionic equations of the determination (without giving the detailed mechanisms of the reactions) are as follows:



The most important steps are to collect the water sample properly and to avoid oxygen introducing into the sample with the other chemicals (MnCl₂, KI, NaOH and HCl solutions) necessary for the determination. To avoid this latter error, use concentrated solutions which practically cannot dissolve oxygen. After acidifying your sample, the oxygen content of the air does not disturb the determination any more.

Description: Collect the water sample into a glass stoppered Erlenmeyer flask. Ensure the sample is not aerated during collection and that no bubbles are trapped in the flask.^{§§} Remove the glass stopper and carefully add 1.00 cm³ of approx. 30 % (w/w) MnCl₂ solution to the sample by inserting the 1.00 cm³ calibrated bulb pipette just on the bottom of the flask. (If the reagent is added above the sample surface, you will introduce oxygen into the sample.) The high density MnCl₂ solution will stay on the bottom of the flask. Squeeze the pipette slowly so that no bubbles are introduced via the pipette. Using another 1.00 cm³ calibrated bulb pipette, add 1.00 cm³ of concentrated NaOH solution containing KI to the sample in the same manner. Stopper the bottle with dry glass stopper and make sure no air is introduced.^{***} This act will push out 2 × 1.00 cm² of water sample which has to be taken into account in the calculation. If oxygen is present, a brownish-orange cloud of precipitate or floc will appear.

^{§§} If you are hand dipping the flask, lower it about halfway into the water and let it fill slowly. If you are sampling in a stream, allow the water to overflow for a least 2 minutes or until the water has flushed the entire bottle two or three times. Make sure that no air bubbles are present before you lift the bottle – look closely just below the neck of the bottle, where bubbles often get caught. If you see bubbles, gently tip the bottle to either side to allow them to escape. Carefully stopper the bottle so that no air pockets form below the cap. Do this by tilting the bottle slightly and slowly lowering the cap. You may want to turn the bottle upside down and watch for bubble movement. If you see bubbles, dump the sample and start over.

^{***} Check for air bubbles, discard the sample and start over if any are seen.

Mix the sample by turning the flask upside down several times to ensure the intense contact of the $\text{Mn}(\text{OH})_2$ precipitate and water containing the dissolved oxygen. Finally, let it settle again for 15 minutes.

Remove the stopper of the flask carefully and add 5-10 cm^3 of concentrated HCl with a pipette held just on the bottom of the sample. It will push out water sample again, but its amount has not been taken into account because it is oxygen-free now. Carefully stopper the flask^{†††}, and after keeping the solution in the dark and stoppered for some minutes, transfer the sample into a 300-500 cm^3 flask and titrate the released iodine with the $\text{Na}_2\text{S}_2\text{O}_3$ titrant of known concentration to the colorless endpoint. Before finishing the titration and reading the volume of titrant (at pale straw color), add 5 drops of 1% starch solution to the sample so a blue color forms. Continue slowly titrating until the sample turns clear. Calculate the oxygen content of your water sample (mmol/dm^3 and mg/dm^3).

Determination of the iodine and iodide ion content of alcoholic iodine solution preparation (Solutio iodi alcoholica, Sol. iodi alcohol, Solutio iodi spirituosa)

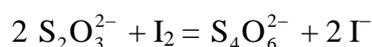
Preparation of the product:

Kalium iodatum (KI)	40.00 g
Iodum (I_2)	50.00 g
Aqua destillata	100.00 g
Alcoholum 96%	810.00 g

Dissolve first the KI, then iodine in 40 g of distilled water. Add an additional 60 g of water to the sample, and finally mix it with the 96% alcohol. This pharmaceutical preparation contains 4.8 – 5.2 % iodine and 3.7 – 4.3 % potassium iodide.

a.) Determination of iodine content:

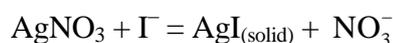
The ionic equation of the determination is:



Description: Dilute approx. 1 g (accurately known mass) of preparation with 10.0 cm^3 of freshly boiled and cooled distilled water. Add 1 drop of 1% starch solution as indicator to the sample and titrate it with the $\text{Na}_2\text{S}_2\text{O}_3$ titrant of known concentration (approx. 0.05 mol/dm^3) until the originally blue color of the sample turns clear. Use this titrated solution for the next determination.

b.) Determination of potassium iodide content:

The ionic equation of the determination is:



Description: Add 5.0 cm^3 of 1 mol/dm^3 sulfuric acid, 50 cm^3 of distilled water and 5 drops of I-metanyl yellow indicator to the previously titrated sample. Titrate the sample immediately with AgNO_3 titrant of known concentration (approx. 0.05 mol/dm^3). When the titration is close to the endpoint, continue titrating the sample by slowly dropping the titrant solution into your sample and continually stirring or swirling the sample until the color of the solution turns from greyish blue to magenta and the precipitate absorbs the dye with blue color.

Calculate the mass of iodine and iodide in your approx. 1 g of preparation (mg's).

Molar weights: I_2 : 253.80 g/mol; KI: 166.00 g/mol

^{†††} At this point, the sample is “fixed” and can be stored for up to 8 hours if kept in a cool, dark place. As an added precaution, squirt distilled water along the stopper, and cap the bottle with aluminum foil and a rubber band during the storage period.

3. PRECIPITATION TITRIMETRY

3.1. ARGENTOMETRIC TITRATIONS

Preparation of 0.05 mol/dm³ AgNO₃ titrant

Weigh the calculated amount of analytical grade AgNO₃ using an analytical balance, transfer it into a 100.00 cm³ volumetric flask and, after dissolving the solid in some distilled water, fill up the flask.

Molar weight of AgNO₃: 169.87 g/mol

Determination of the composition of a KCl-KBr mixture by (Mohr method, indirect method)

The ionic equations of the determination are:

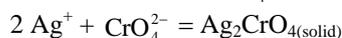


Description: An individual solid sample containing KI and KBr will be given in a covered container. Homogenize your sample in a mortar then “wash” the container two or three times with a small portion of this powder. Between two “washing” always homogenize your sample in the same mortar.

Weigh approx. 0.50 g (accurately known mass) of sample, dissolve it in distilled water, transfer this solution without loss into a 100.00 cm³ volumetric flask and fill up the flask with distilled water up to the mark. Shake this stock solution well, then put 10.00 cm³ of the stock solution into a 100 cm³ titration flask using a pipette. Dilute all samples to approx. 50 cm³ with distilled water, add 1 cm³ of 5 % K₂CrO₄ indicator^{†††} to the sample and titrate it with the AgNO₃ titrant of known concentration. When we add the titrant slowly, a deep brick-red color may appear briefly as silver chromate forms and re-dissolves. Precipitating AgCl and AgBr has white and light yellow color. At some point, all the chloride and bromide will have been precipitated. We can tell that this point has been reached because the red color of Ag₂CrO₄ will stay. At this stage, the sample is already over-titrated. It is not too easy to detect the appearance of the red color in the yellow sample, so, it is practical to quickly over-titrate one sample (visible orange shade of color, Reference 1), then add approx. 0.5 cm³ less titrant to another sample (under-titrated yellow-green sample^{§§§}, Reference 2). Finally, titrate another sample until you can see the appearance of the orange color compared to Reference 2. Subtract the volume of one single drop of titrant (approx. 0.04 cm³) from this last volume of titrant to have the volume of titrant at the endpoint. Calculate the mass percentage composition of your KCl-KBr sample.

Molar weights: KCl: 74.56 g/mol; KBr: 119.01 g/mol

^{†††} Potassium chromate is yellow. Silver and chromate ion (CrO₄²⁻) combine to form brick-red silver chromate:



This compound has a higher solubility product than that of AgCl or AgBr, so, as long as there is chloride present, any silver chromate that forms will disappear as the silver gets taken out of solution by the silver chloride. Once the chloride is gone, the silver chromate persists.

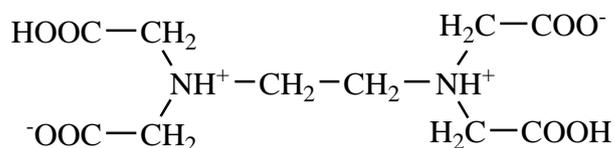
^{§§§} Silver precipitates are light sensitive and black silver is formed when exposed to sunlight which gives the greenish shade of color to the solution.

4. COMPLEXOMETRIC TITRATIONS

Preparation of 0.01 mol/dm³ Na₂EDTA titrant

Weigh the calculated amount of analytical grade Na₂EDTA·2H₂O (Complexone III) using an analytical balance, transfer it into a 250.00 cm³ volumetric flask and after dissolving the solid in some distilled water fill up the flask.

Molar weight of Na₂EDTA·2H₂O: 372.25 g/mol

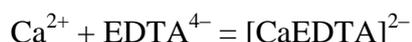


The structure of the ligand (H₄EDTA).

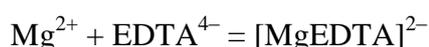
Simultaneous determination of Ca(II) and Mg(II) by complexometric titration

The ionic equations of the determination are:

At pH > 12:



At pH ≈ 10:



Description: An individual sample of Ca(II) and Mg(II) will be given in a vial. Transfer the sample without loss into a 100.00 cm³ volumetric flask and fill up the flask with distilled water up to the mark. Shake this stock solution well, then put 10.00 cm³ of the stock solution into a 100 cm³ titration flask using a pipette. Dilute the sample to approx. 40-50 cm³ with distilled water, add approx. 2 cm³ of 10 % (w/w) NaOH and 0.1-0.2 g of solid Murexide indicator to it and titrate it with the Na₂EDTA titrant of known concentration until its red color becomes violet. This is the first volume of titrant you should use for the calculation.

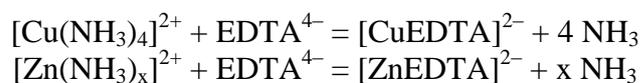
Acidify the titrated sample by adding 3 cm³ of 20 % (w/w) HCl and heat it to destroy the Murexide indicator, then cool the solution down and add 6 cm³ of 25 % (w/w) NH₃ solution and 0.1-0.3 g of solid Eriochrome Black T indicator. Titrate the sample with the Na₂EDTA titrant until its red-violet color becomes permanent blue. This is the second volume of titrant you should use for the calculation. Calculate the mass of Ca(II) and Mg(II) in your sample (mg's).

Molar weights: Ca: 40.08 g/mol; Mg: 24.32 g/mol

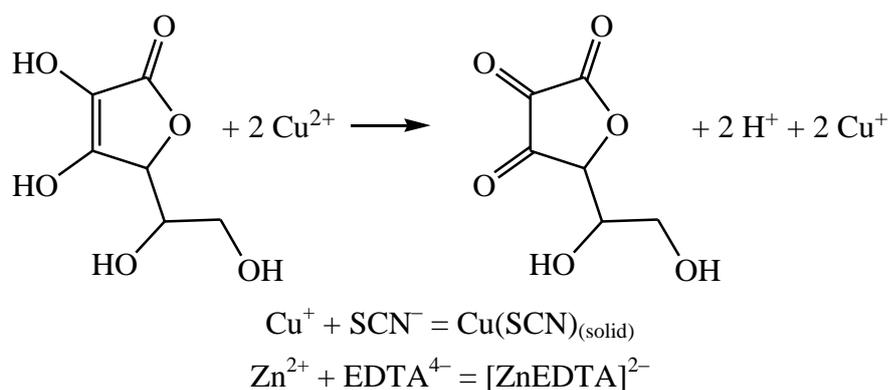
Simultaneous determination of Cu(II) and Zn(II) by complexometric titration

The ionic equations of the determination are:

For the first titration:



For the second titration:



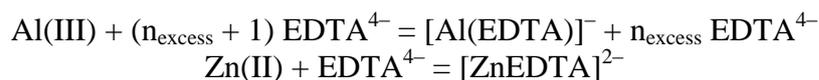
Description: An individual sample of Cu(II) and Zn(II) will be given in a vial. Transfer the sample without loss into a 100.00 cm³ volumetric flask and fill up the flask with distilled water up to the mark. Shake this stock solution well, then put 5.00 cm³ of the stock solution into a 100 cm³ titration flask using a pipette. Dilute the sample to approx. 40-50 cm³ with distilled water, add approx. 2 cm³ of 25 % (w/w) NH₃ and 0.1-0.2 g of solid Murexide indicator to the sample and titrate it with the Na₂EDTA titrant of known concentration until its color becomes permanent violet. This is the first volume of titrant you should use for the calculation.

Put 10.00 cm³ of the stock solution into another 100 cm³ titration flask using a pipette. Dissolve approx. 0.5 g of ascorbic acid in the sample and add 10 cm³ of 0.1 mol/dm³ KSCN to precipitate the Cu⁺ ions as Cu(SCN). Dilute the sample to approx. 50 cm³ with distilled water and add approx. 1 g of hexamethylenetetramine buffer (also called hexamine, urotropine or formin) and 0.1 g of solid Methylthymol Blue indicator. Titrate the sample with the Na₂EDTA titrant until its blue color becomes permanent yellow. This is the second volume of titrant you should use for the calculation. Calculate the mass of Cu(II) and Zn(II) in your sample (mg's).

Molar weights: Cu: 63.54 g/mol; Zn: 65.38 g/mol

Determination of Al(III) by complexometric titration

The ionic equations of the determination are:



Description: An individual sample of Al(III) will be given in a vial. Transfer the sample without loss into a 100.00 cm³ volumetric flask and fill up the flask with distilled water up to the mark. Shake this stock solution well, then put 10.00 cm³ of the stock solution into a 100 cm³ titration flask using a pipette. Adjust the pH of the solution to pH = 2-3 using HCl solution. Add 20.00 cm³ of 0.01 mol/dm³ Na₂EDTA solution to your sample using a 20.00 cm³ bulb pipette then boil the solution for some minutes. To ensure the complete complex formation, add 2-3 drops of phenolphthalein indicator, then add 5 % ammonia solution dropwise to the sample until its color becomes pale magenta. Boil the solution for another 1-2 minutes, then cool down, add some drops of 5 % HCl solution to acidify it, 1-2 g of hexamethylenetetramine buffer and 0.1-0.3 g of solid Methylthymol Blue indicator to the sample. Dilute the sample to approx. 50-60 cm³ with distilled water and titrate the excess of Na₂EDTA with approx. 0.1 mol/dm³ (but exactly known concentration) of Zn(II) titrant until its yellow color starts to become blue (not to permanent blue color). Calculate the mass of Al(III) in your sample (mg).

Molar weight of Al: 26.98 g/mol

Determination of aluminum content of aluminum acetate tartrate solution preparation (Aluminium aceticum tartaricum solutum, Alum. acet. tart. sol.)

This pharmaceutical preparation contains 0.58 – 0.65 % aluminum as aluminum acetate tartrate.

Preparation of the product:

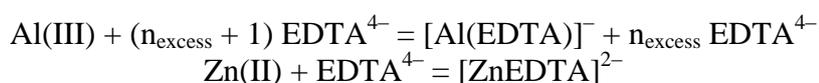
Aluminium sulfuricum solutum 25 %	300.00 g
Aqua destillata	605.00 g
Calcium carbonicum	36.00 g
Acidum aceticum dilutum 20 %	135.00 g
Acidum tartaricum	qu.s

Dilute the aluminum sulfate solution with the given amount of distilled water. Add the calcium carbonate to the solution in small portions and stir the solution continuously. When the intense gas formation stopped, add the 20 % acetic acid solution in small portions and stir the resulting solution continuously. Let the solution at room temperature and stir it frequently until the gas formation ceases and the precipitate settles down. Decant the pure solution, then collect the precipitate in a tamis (linen filter) and gently squeeze out the remaining solution. Mix the two portions of solution and add 1.75 g of tartaric acid to every 100 g of solution. Finally, filter the solution using a paper filter.

To prepare a 25 % aluminum sulfate solution, first prepare an aluminum sulfate of approx. 30 % and determine its $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ content by titration. If the $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ content of the solution is “X” %, dilute every 25 g of solution to “X” g with distilled water.

Determination of aluminum content:

The ionic equations of the determination are:



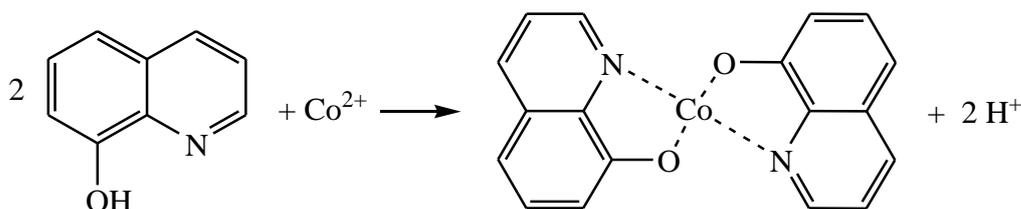
Description: Dilute approx. 0.5 g (accurately known mass) of preparation with 15.0 cm³ of distilled water in an Erlenmeyer flask. Add 10.00 cm³ of 0.05 mol/dm³ Na₂EDTA solution and approx. 30 cm³ of distilled water to the sample and boil it for 3 minutes. Cool down the solution and dissolve 2.0 g of hexamethylenetetramine buffer and 0.1-0.2 g of solid I-Methylthymol Blue indicator in the sample. Titrate the excess of Na₂EDTA with approx. 0.1 mol/dm³ (but exactly known concentration) of Zn(II) titrant until its yellow color becomes bluish. Calculate the mass of Al(III) in your preparation (mg).

Molar weight of Al: 26.98 g/mol

5. GRAVIMETRY

Determination of Co(II) using 8-hydroxy quinoline (oxine) by gravimetry (Berg method)

The chemical equation of the determination is:

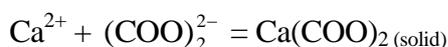


Description: An individual sample of cobalt(II) will be given in a vial. Transfer the sample without loss into a 100.00 cm³ volumetric flask and fill up the flask with distilled water up to the mark. Shake this stock solution well, then put 10.00 cm³ of the stock solution into a 250 cm³ beaker using a pipette. To adjust the pH to 5, add approx. 4 g of sodium acetate and 5 cm³ of 20 % (v/v) acetic acid to the solution and dilute it to approx. 100 cm³ with distilled water. Heat the mixture to approx. 60 °C and precipitate the solid cobalt oxinate by adding 10 cm³ of 2 % alcoholic oxine solution to the solution in the beaker while continuously stirring the solution. Boil up the solution then let it settle down and filter out the precipitate using a G3 glass filter. (Before filtering the precipitate, heat the glass filter at 180 °C in a drying oven and, after cooling down, weigh it on an analytical balance.) Wash the precipitate with approx. 50 cm³ of hot distilled water and dry it in a drying oven at 180-200 °C for 2 hours (until its weight becomes steady). After drying, let the filters with the precipitate cool for 10-15 minutes on air, then place it into a desiccator. After some hours, weigh its mass on an analytical balance. Calculate the mass of Co(II) in your sample (mg).
Molar weights: Co: 58.93 g/mol; CoC₁₈H₁₂N₂O₂: 347.23 g/mol

Determination of calcium as CaC₂O₄·H₂O (calcium oxalate monohydrate)

A well filterable and washable precipitate is formed when ammonium oxalate is added to a hot solution containing Ca(II) ions. The solubility of the calcium oxalate monohydrate precipitate in water is low ($K_{\text{sol}} = 2.6 \cdot 10^{-9}$). From a dilute solution of acetic acid (pH = 3), calcium precipitates quantitatively and the procedure is suitable for separating calcium(II) and magnesium(II) ions.

The chemical equation of the determination is:



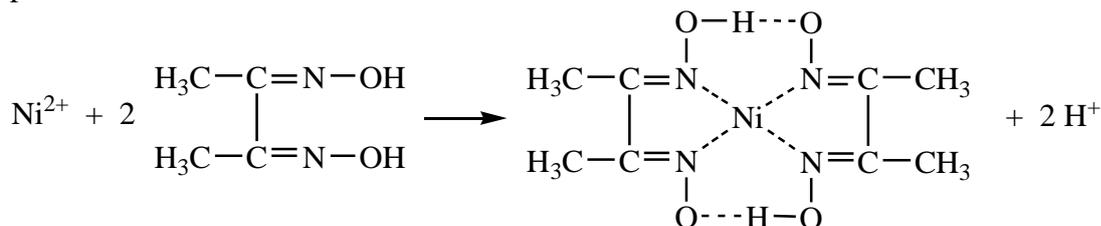
Description: An individual sample of calcium(II) will be given in a vial. Transfer the sample without loss into a 100.00 cm³ volumetric flask and fill up the flask with distilled water up to the mark. Shake this stock solution well, then put 10.00 cm³ of the stock solution into a 250 cm³ beaker using a pipette. Dilute the solution with distilled water to 100 cm³ and add approx. 3 g of ammonium chloride and 10 cm³ of 1 mol/dm³ acetic acid to the solution. Boil up the mixture and precipitate the solid calcium oxalate monohydrate by adding 20 cm³ of ammonium oxalate solution dropwise to the solution in the beaker (use a graduated pipette). Boil the solution for another 1-2 minutes then cover it with a clock glass and let the precipitate settle down for 2-3 hours. Filter the precipitate using a G4 glass filter, wash it with approx. 50 cm³ of cold distilled water and dry it in a drying oven at 100 °C for 3 hours. (Before filtering the precipitate, do not forget to weigh the glass filter without the precipitate on an analytical balance.) After drying, let the filters with the precipitate cool for 10-15 minutes on air, then weigh its mass on an analytical balance. Calculate the mass of Ca(II) in your sample (mg).

Molar weights: Ca: 40.08 g/mol; CaC₂O₄·H₂O: 146.11 g/mol

Determination of nickel(II) with dimethyl glyoxime

A weakly soluble precipitate, bis(glyoximate)nickel(II) chelate complex is formed in the reaction of dimethyl glyoxime (biacetyl glyoxime) and nickel(II) ions. During the procedure dimethyl glyoxime in ethyl alcohol is used. Too much alcoholic dimethyl glyoxime solution cannot be used because the scarlet colored precipitate is soluble in more concentrated alcoholic solutions. The precipitate is soluble in acids, too. Since the complex formation reaction produces acid as

well, the acid formed in the reaction should be neutralized, e.g. by using ammonia. The precipitate can be dried at 120 °C.



Description: An individual sample of nickel(II) will be given in a vial. The pH of the sample is neutral. Transfer the sample without loss into a 100.00 cm³ volumetric flask and fill up the flask with distilled water up to the mark. Shake this stock solution well, then put 10.00 cm³ of the stock solution (containing approximately 20 – 40 mg of nickel) into a 400 cm³ beaker using a pipette. Dilute the solution with distilled water to 150 cm³ and boil up the mixture. Precipitate the bis(glyoximato)nickel(II) complex by adding 60 cm³ of 1 % dimethyl glyoxime solution in 96 % ethanol slowly to the solution in the beaker. Add some 5 % ammonia solution to the sample until you can smell the ammonia in the solution in the beaker. Filter the hot precipitate using a G3 glass filter^{****}, wash it with approx. 50 cm³ of 30-40 °C distilled water and dry it in a drying oven at 120 °C for 2 hours. (Before filtering the precipitate, do not forget to weigh the glass filter without the precipitate on an analytical balance.) After drying, let the filters with the precipitate cool for 10-15 minutes on air, then weigh its mass on an analytical balance. Calculate the mass of Ni(II) in your sample (mg).
Molar weights: Ni: 58.69 g/mol; bis(glyoximato)nickel(II) (NiC₈H₁₄N₄O₄): 288.92 g/mol

Separation of iron(III) traces from chromium(III) by extraction. Determination of chromium(III) as oxide by gravimetric method

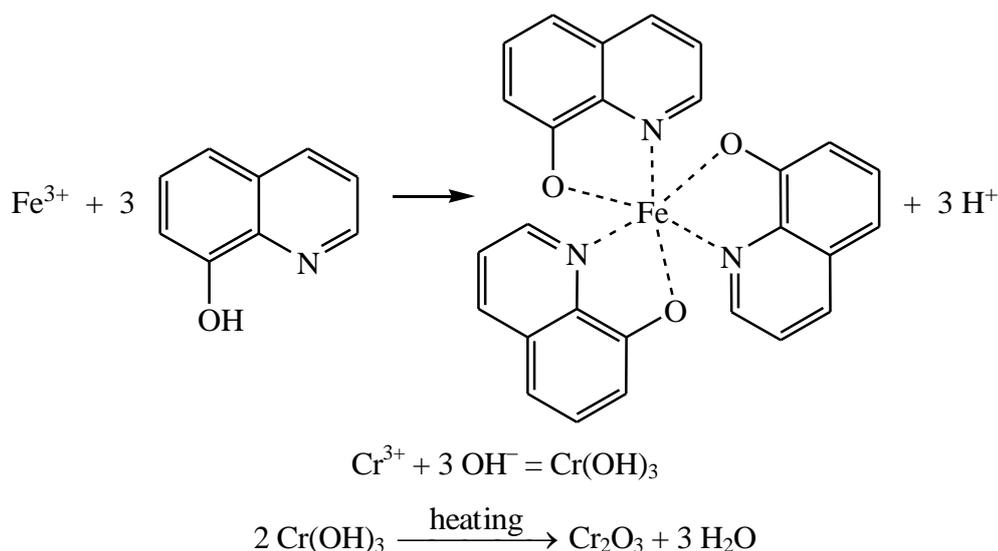
Extraction is often used for separating and concentrating trace elements. Extraction is based upon the fact that a substance has different solubilities in different solvents. Liquid-liquid extraction is a mass transfer operation in which a liquid solution (the feed, e.g. distilled water containing several solute components) is contacted with an immiscible or nearly immiscible liquid (solvent, e.g. an organic solvent) that exhibits preferential affinity or selectivity towards one or more of the components in the feed. Two streams result from this contact: the extract, which is the solvent rich solution containing the desired extracted solute, and the raffinate, the residual feed solution containing little solute. The solubility of the desired component can be increased in the organic solvent by adding a complexing agent much more soluble in the organic solvent than in water. In this case, the solubility of the neutral complex formed is also much higher in the organic solvent than in water. So, the selectivity of the extraction method can be increased by finding the ideal pH and complexing agent.

In this experiment, the studied sample contains a small amount (1-2 %) of iron(III) compared to its chromium(III) content. Under these conditions, iron(III) does not disturb the determination of chromium(III), but chromium(III) does disturb the determination of iron(III) by weight. So, extraction is necessary only when the amount of iron(III) needs to be measured. A 0.1 mol/dm³ solution of 8-hydroxyquinoline (oxine) in chloroform is well usable as an extracting solvent. Iron(III) ions quickly form stable complexes with oxine in a wide pH range (2.5 < pH < 11.0), while chromium(III) oxine complexes are inert and formed only at high temperature (when boiling the solution). When an aqueous sample containing chromium(III) and iron(III) traces is

^{****} After cooling down, dimethyl glyoxime excess may precipitate from the solution, so you should filter the bis(glyoximato)nickel(II) precipitate from the hot solution.

extracted with 0.1 mol/dm³ of oxine in chloroform, the iron(III) content of the aqueous solution is practically completely transferred to the organic solvent and chromium(III) stays in the water. The concentration of iron(III) in chloroform can be conveniently measured by a spectrophotometric method.^{††††} The concentration of chromium(III) in the water can be measured by any classical analytical method. During this laboratory practice, you should separate iron(III) and chromium(III) by extraction and determine the mass of chromium(III) in your sample by gravimetry.

The chemical equations of the determination are:



Description: An individual sample containing a relatively high amount of chromium(III) and iron(III) traces will be given in a vial. Transfer the sample without loss into a 100.00 cm³ volumetric flask and fill up the flask with distilled water up to the mark. Shake this stock solution well, then check whether it contains any iron(III) by adding ammonium thiocyanate (also called ammonium rhodanide, ammonium rhodanate or ammonium sulfocyanide) and ether to a small amount of the stock solution.^{††††} If the test is positive, put 50.00 cm³ of the stock solution into a 100 cm³ extraction funnel using a pipette. Add approx. 20 cm³ of 0.1 mol/dm³ oxine in chloroform and shake the mixture for 3 minutes. Let the two phases separate for some minutes, then let the bottom (organic) phase off. Check whether the upper, aqueous phase contains any iron(III) by testing some cm³ of it in the same way as before the extraction procedure. If the result is positive, repeat the extraction with additional 20 cm³ of 0.1 mol/dm³ oxine in chloroform. When the aqueous phase is iron(III)-free, remove the traces of oxine from the aqueous phase by extracting it four times with 20-20 cm³ of chloroform. Put 20.00 cm³ of the iron(III)-free aqueous phase into a high 250 cm³ beaker using a pipette. Dilute the solution with distilled water to 200 cm³. Dissolve 3.0 g of NH₄Cl in the solution and heat it up to 70-80 °C. Adjust the pH of the hot mixture to 6-8 by adding 1:4 ammonia solution (1 volume unit of concentrated ammonia mixed with 3 volume unit of distilled water) in small (0.5-1.0 cm³) portions with a graduated pipette.^{§§§§} Make sure that there is no ammonia solution on the wall of the beaker. Remove the ammonia gas over the solution by

^{††††} If the absorbance of the sample is too high, dilute the solution and measure the absorption spectrum again, or use a cell with shorter path length.

^{§§§§} If you add thiocyanate ions, SCN⁻, to a solution containing iron(III) ions, you get an intense blood red solution containing mainly the ion [Fe(SCN)(H₂O)₅]²⁺.

^{§§§§} This is the most “sensitive” part of the precipitation process: at pH < 6 the precipitate formation is not quantitative and at pH > 8 a significant portion of the precipitate can be dissolved as chromium(III) ammine or chromium(III) hydroxo complex.

blowing, then take a smell of the solution. If you can smell slight ammonia odor, the pH is suitable for the precipitation. Under these conditions, the precipitate quickly collects and settles. Heat the precipitated samples to 70-80 °C in a water bath, then filter it on Macherey-Nagel analytical filter paper. Remove the chloride content of the precipitate by washing it with $\text{NH}_4\text{NO}_3/\text{NH}_3$ buffer (pH = 7).***** Put the precipitate without loss into a porcelain cup which was earlier heated at 800-950 °C and then weighed on an analytical balance. Place the cup with the precipitate on a triangle and first cautiously dry, then burn the filter paper using a Bunsen burner. Place the cup with the precipitate into a heating furnace and heat it at 800-950 °C for approx. 2 hours (until its weight becomes steady). After heating, let the cup with the Cr_2O_3 formed cool for 10-15 minutes on air, then place it into a desiccator. After 30 minutes, weigh its mass on an analytical balance. Calculate the total mass of chromium(III) in your sample (mg).

Molar weights: Cr: 51.996 g/mol; Cr_2O_3 : 151.99 g/mol

***** Check whether the precipitate is chloride-free by adding AgNO_3 solution to the wash solution dropping off. Continue the washing with the $\text{NH}_4\text{NO}_3/\text{NH}_3$ buffer if a white AgCl precipitate was formed with AgNO_3 .