1.1.2. Ion-exchange chromatography

Principle:
Ion exchange is reversible process that takes place between stationary phase- ionex exchange resin and liquid solution phase. Ion exchange resins are macromolecule compounds with ionizable functional groups in their main structure. They are insoluble in water and solutions of electrtolytes, but they expand and create macroporous support. The adsorption of the molecules to the solid support is driven by the ionic interaction between the oppositely charged ionic groups in the sample molecule and in the functional ligand on the support. Ions bounded to functional groups are mobile in expanded state and can diffuse to solution and are replaced by ions from solution. The strength of the interaction is determined by the number and location of the charges on the molecule and on the functional group. The absorption behavior of the ions is represented by equilibrium distribution coefficient. It is the ratio between concentration of ion in ion exchange resin and solution.Ion-exchange resins with acidic functional group, e.g. -SO3H, -COOH, -OH can exchange cations. It is qualified as catex. Anion-exchange resin (anex) has basic functional group (e.g., primary, secondary, terciary amines). According to ion that is bounded to functional group, ion-exchange resins can be various cycles (e.g., catex in H^+- cycle, anex in Cl^- -cycle).

1.1.1.1 Indirect alcalimetric determination of copper
The principle of neutralization determination is in the ion exchange of metal ion for the ion H+, during the transport of salt solution through the column filled with catex. Thus, equivalent amount of acid is created, that we determine by alkalimetric titration. Ion exchange is described by following chemical equation:
$2catex\text{-}H + M^{2+} = 2catex\text{-}M + 2\ H^+$

Chemicals and solutions. Chromatographic column filled with catex S X-8, solution of hydrochloric acid $c(HCl) = 2\ mol.dm^{-3}$, sodium hydroxide solution $c(NaOH) = 0.1\ mol.dm^{-3}$, nitric acid solution $c(HNO_3) = 2\ mol.dm^{-3}$, silver nitrate solution $c(AgNO_3) = 0.1\ mol.dm^{-3}$, potassium hexacyanoferrate solution $c(K_4Fe(CN)_6) = 0.1\ mol.dm^{-3}$.

Sieved fraction to 0.3-0.5mm particles Let the sorbent swell for 1-2 days in the beaker filled with water. After several decantations we fill the chromatographic column by the pure sorbent fraction. We fix the column into the stand and close the tap. We fill half of the column with water. With the aid of rod we place a piece of fiberglass to the bottom of column. We pour suspension of catex resin to the top of column. By opening the tap we let abundant water drain away with flow-rate 1-2 drops per second. Water can not fall under the top of resin, in order not to create air bubbles in the column. We continue to pour suspension till the height of resin achieve 15 cm. In order not to whirl the catex resin, we cover the top of it by piece of fiberglass. We switch catex to H^+ cycle by 200 ml of HCl solution $c(HCl) = 2\ mol.dm^{-3}$ with the flow-rate 1-2 drops per second.

1.1.1.2 Separation of copper and zinc

Principle.

For separation of metal ions ability of some cations to create anionic complexes is used. These are sorbed by ionexchange sorbent.

$M^{2+} + 4HCl = MCl_4^{2-} + 4\ H^+$

Creation of complex is dependent on its stability and concentration of HCl. Zinc cation is in solution of c (HCl)= 2 mol.dm^{-3} bounded in complex and it is quantitatively sorbed by anex, while copper ion doesn´t create complex and it flows through the column without interaction with sorbent. It is possible to determine Concentration of ions by suitable analytical method. Dependence of distribution coefficient D on pH is obvious from the graph in the fig. 1. After elution of Cu^{2+} from the column $ZnCl_4^{2-}$ complex is decomposed with diluted HCl c=0,005 mol.dm^{-3} and Zn^{2+} is quantitatively eluted.

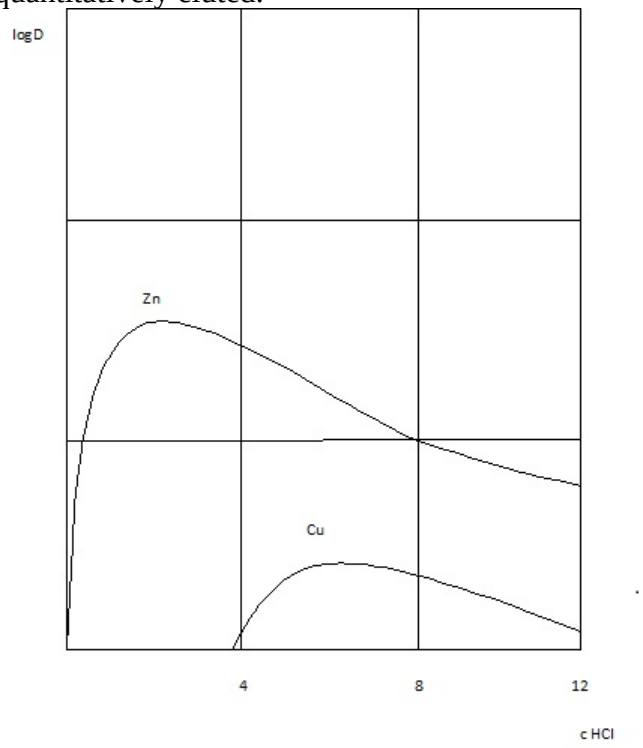


Fig 1. Dependence of distribution coefficient on HCl concentration.

Chemicals and solutions.

Chromatographic column with strong anex S X-8, solutions of hydrochloric acid of concentrations c(HCl)= 4 mol.dm^{-3}, 2 mol.dm^{-3}, 0,005 mol.dm^{-3}, solution of sodium thiosulfate c($Na_2S_2O_3$.5H2O) = 0.01 mol.dm^{-3}, chelatone 3 solution c(CH3) = 0.01 mol.dm^{-3}, indicator Eriochrome Black T (mixture with NaCl 1:100), solid KI, starch solution, buffer (to 54 g NH_4Cl add 350 ml concentrated NH_3 and fill with water to 1000ml).

Procedure.

Task1. Filling the column with ion-exchange resin

We use strong anex S X-8 (particle size 0.2 – 0.25 mm) for separation and determination of Zn^{2+} and Cu^{2+} . Let the sorbent swell for 1-2 days in the beaker filled with distilled water. After several decantations we fill the chromatographic column by the pure sorbent fraction. We fill the column by the procedure as written in task 1.1.1.1. We switch the column to OH- cycle by 100 ml of NaOH solution of c NaOH = 1 mol.dm^{-3}at first, then we rinse the column by 100 ml of HCl , c (HCl)= 1 mol.dm^{-3} to obtain the sorbent in Cl^- cycle. The flow-rate in all steps of the procedure should be 1-2 drops per second.

Task 2.Separation of copper and zinc

Let 25 ml of HCl of concentration c (HCl) = 2 $mol.dm^{-3}$ flow through the column at the flow-rate 1-2 drops per second. Liquid surface has **always** to remain above the sorbent, otherwise it is necessary to pack the column again, as the air bubbles insert the column. Let the HCl solution elute into the waste beaker.

We add 10ml of HCl c (HCl) = 4 $mol.dm^{-3}$ to the sample. Afterwards we insert the sample quantitatively into the column. To elute Cu^{2+} from the column we use HCl of concentration c (HCl)= 2 $mol.dm^{-3}$. We collect approximately 90 ml of eluate in 100ml volumetric flask. Then we fill the flask with distilled water up to mark.

Afterwards the Zinc complex is decomposed and free Zn^{2+} is eluted from the column by HCl c (HCl) = 0.005 $mol.dm^{-3}$. Collect the eluted Zn2+ into 200 ml volumetric flask. We complete the elution as in the case of Cu^{2+}.

We wash the column by 30 ml of HCl /c (HCl) = 2 $mol.dm^{-3}$/ to achieve the column in Cl^- - cycle. We close the column by the stopper to avoid of HCl evaporating.

Task3. Iodometric determination of Cu^{2+}

From 100 ml of solution containing Copper, we pipette 25 ml into titration flask. We add approximately 25ml of distilled water and 2 g of KI. We shake titration mixture and we titrate elementar iodine immediately with Na2S2O3 solution to light yellow color. Than we add 5 ml of starch solution and continue titration to colorless. We repeat titration 3 times.

Task4. Complexometric determination of Zn^{2+}

From 200 ml of solution containing Zinc, we pipette 50 ml into titration flask. We add indicator Eriochrome T, diluted ammonia solution drop by drop, till solution color turns to wine-red and 2 ml of buffer. We titrate with Chelatone 3 titrant solution till color turns to blue.