Separation by extraction

1. Execution of the exercise

Attention – all residues of dithizone and amyl alcohol should be placed into their respective, specially dedicated tanks !!!

Attention ! It is recommended to wear protection gloves !!!

1.1. Extraction of dithizone depending on the pH value.

1.1.1. Approx. 2.5 cm^3 of distilled water should be introduced into a test tube and then approx. 1 cm^3 of dithizone solution should be added (the solution is green). Then, add 3 – 4 drops of **2 M NH_3 aq.**; gently shake the tube – write down any eventual changes observed, next add 5 – 6 drops of concentrated **H_2SO_4** and gently shake the tube again. Observe and write down the occurring changes of colour.

1.2. Separation by extraction at regulated pH.

1.2.1. Extraction of zinc dithizonate.

Introduce approx. 2 cm^3 of distilled water into the test tube and add 3 drops of a specially prepared and separated solution of zinc salt [on the windowsill] and a couple of drops of **2 M H_2SO_4**, next add approx. 2 cm^3 of **dithizone** solution. Shake the tube, then add a couple of drops of aqueous ammonia in order to change the pH value of the solution. After the equilibrium between the organic and water phases is established, acidify the sample again using **2 M H_2SO_4** and shake it. The extraction of **Zn^{2+}** ions back into the water phase occurs and the green colour of dithizone solution should appear again.

1.2.2. Separation of **Zn^{2+}** and **Hg^{2+}**.

If the studied solution includes **Zn^{2+}** and **Hg^{2+}***cations, then it is possible to extract the* ***Hg^{2+}****ions first by changing the pH value to 0.5 – 2.5 and to extract* ***Zn^{2+}*** *ions next at pH =6.5 – 10 in the form of dithizonates to carbon tetrachloride. The orange mercury dithizonate is extracted even from very acidic solutions (pH equal to approx. 0).*

Approx. 2 cm^3 of water are introduced into the separator, followed by 3 drops of a specially prepared and separated solution of **$Hg(NO_3)_2$** salt and 6 drops of a **$Zn(NO_3)_2$** solution; next 2 drops of concentrated **H_2SO_4** should be added and mercury dithizonate is extracted using 2 – 3 cm^3 of **dithizone** solution. The organic phase is separated into a test tube. The activity described above should be repeated until complete extraction of **Hg^{2+}** from the aqueous solution is achieved, i.e. until a green colour of the added portion of dithizone is achieved [it is not discoloured after shaking]. After complete extraction of mercury, ammonia is added to the sample and zinc dithizonate is extracted three times using dithizone. The changes in the aqueous and organic phase after the addition of a new portion of the reagent should be observed and written down.

1.2.3. Influence of the precipitation reaction on extraction – separation of **Ag^+**.

The formation of poorly soluble compounds in one of the phases is a hindrance for the extraction to the second phase, e.g. silver dithizonate may be extracted over a wide range of pH value, however if ***Cl^-*** *or* ***SCN^-*** *ions are added to the aqueous phase, the precipitation of* ***AgCl*** *or* ***AgSCN*** *interferes with the extraction of silver dithizonate at the same pH value.*

Approx. 5 cm^3 of water should be introduced to a test tube, followed by 1 drop of a **$AgNO_3$** solution, 1 – 2 drops of concentrated **H_2SO_4** and approx. 1 cm^3 of **dithizone**. Shake the test tube. Under such conditions silver dithizonate (yellow) is extracted. Next, add an excess of chlorides in the form of solid **KCl** and stir the solution. Silver dithizonate decomposes.

1.2.4. Shifting the equilibrium of complexes in an aqueous solution.

*Cobalt (II) thiocyanate complexes are poorly stable in an aqueous solution. In the presence of an organic solvent **$(NH_4)_2Co(SCN)_4$** are extracted and a blue complex appears in the organic phase (all equilibrium states are shifted right).*

Approx. 1 cm^3 of a **$CoCl_2$** solution should be introduced into the test tube, followed by solid **NH_4SCN**. Initially, the pale-pink solution of cobalt ions becomes red. Next, approx. 1 cm^3 of amyl alcohol should be added (available in the fume cupboard) and the tube should be stirred – this causes the appearance of a blue colour in the organic solvent phase. Next, 1 – 2 cm^3 of a 10% **EDTA** solution should be added to the water solution in contact with the organic phase, which includes the **Co^{2+}** complex. After stirring the blue colour should disappear. **The solution should be placed into a special tank located in the fume cupboard !!!**

Explanation: The addition of **EDTA**, strongly complexes cobalt ions in the water phase. Addition of **EDTA** decomposes the thiocyanate complex and causes the introduction of cobalt ions back into the **aqueous phase**.

2. Preparation of results

- Describe the behaviour of dithizone depending on the pH value based on the test carried out in section 1.1.
- Describe the conditions for extraction and re-extraction of zinc dithizonate.
- How can we determine that mercury was completely extracted from the water phase?
- Describe the colours of solutions at specific stages of conducting the exercise.
- Which changes may be observed in a solution which includes silver dithizonate (organic phase) after the addition of solid **KCl** in the exercise section 1.2.3?
- Fill the table after finishing the exercise:

Cation	Characteristic reactions	pH	Dithizonate colour in CCl_4
Zn^{2+}			
Hg^{2+}			
Ag^{+}			

- Write down the formation and equilibrium reactions for **Co^{2+}** complexes with **SCN^-** ions in the aqueous and organic phase and describe their colour.
- Write down the characteristic reactions for detection of cations.
- What are the other methods for separation and detection of **Ag^+** and **Hg^{2+}** cations? Describe them using chemical reactions.

3. Conclusions

4. Scope of the material

- Which parameters characterize the extraction process?
- Characteristics of extraction systems?
- What is the basis for extraction in ionic-associative and internal chelate systems?
- What is the role of masking reactions in extraction?
- Which conditions must be met by organic solvents used for extraction processes?
- What is re-extraction? Specify the methods and describe extraction techniques.

5. Literature

- M. D. Joesten, J. L. Wood, *World of Chemistry*, second edition, Thomson, USA 1996
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- D. W. Oxtoby, N. H. Nachtrieb, *Principles of modern Chemistry*, Saunders College Publishing, USA 1996