XVIII Baltic Chemistry Olympiad

Practical Problems-

- Analytical Chemistry

Code: .....

16-18 April 2010

Tartu, Estonia

Instructions

- **Safety rules** – follow them as in the Preparatory problems described, no eating or drinking is allowed in the lab. You should wear safety glasses and lab coats.
- **Violating safety rules** – you get one warning, offend again: you are out.
- **Total time** – 2.5 hours for first task and one break (30 min) for rest after it.
- Write your **student code** on first sheet.
- **Answers** – only in the appropriate places of the sheets, nothing else will be marked. Relevant calculations have to be shown.
- **Results.** The number of significant figures in numerical answers must conform to the rules of evaluation of experimental error. Mistakes will result in penalty points even if your experimental technique is flawless.
- **Questions** concerning safety, apparatus, chemicals, organization, toilet break: **ask your lab assistant.**
- **You must stop your work immediately after the stop signal has been given. A delay of 5 minutes will result in zero points for the current task.**
- Do not leave the room until permitted by the supervisors.
- This examination has **5** pages.
- The official English version of this examination is available on request only for clarification.

Analysis of zinc-aluminum alloy by EDTA titration

Alloys containing aluminum and zinc as primary alloying elements have been developed in Japan for use in industry. The most famous example—extra super duralumin "7075"—is the strongest aluminum alloy used in aircraft manufacturing. Recently, a novel zinc-aluminum alloy that exhibits an interesting mechanical property has also been developed. The alloy exists as a solid at room temperature but is easily spread like a starch syrup under appropriate mechanical tension. This property is known as "super-plasticity," which facilitates industrial uses of the alloy, including use as a high-performance and semi-permanent seismic damper for protecting buildings from earthquakes. This unique property arises from the alloy's fine-grained microstructure containing 7%–50% aluminum by weight.

Composition is a fundamental parameter for developing such advanced alloys. In this experiment, assuming the composition assay of this type of alloy, you will be given a test solution which simulates a digested sample of the alloy; 50 mL of the solution contains 30–35 mg of zinc and 10–15 mg of aluminum, and is acidified to pH 1 using hydrochloric acid. You will be required to determine the concentrations of Zn^{2+} and Al^{3+} in the sample solution by titration utilizing ethylenediaminetetraacetic acid (EDTA) as a chelating agent. Masking and back-titration techniques should also be employed.

Chemicals

- test solution (prepare as described above)
- 0.1 mol L^{-1} acetic acid solution
- ammonium fluoride
- 0.012 mol L^{-1} ethylenediamine-N,N,N',N'-tetraacetic acid, disodium salt, dihydrate ($Na_2EDTA{\cdot}2H_2O$) standard solution (accurately prepared)
- 10% (w/v) hexamethylenetetramine (hexamine) solution
- 0.1% methyl orange (MO) solution
- 0.1% xylenol orange (XO) ethanol/water (20/80) solution
- 0.01 mol L^{-1} Zn^{2+} standard solution (accurately prepared using $ZnSO_4{\cdot}7H_2O$)

Apparatuses and glassware

- burette (50 mL, 1 rack) with stative
- Erlenmeyer flask (250 ml × 2)
- hot-plate
- magnetic stirrer, stirring bar (coated with Teflon)
- pipette (10 mL, 25 mL)
- safety bulb

Procedures

1. Pipette 10 mL of the sample solution into a 200 mL Erlenmeyer flask and place a stirring bar in the flask. Start stirring the solution on a magnetic stirrer and add a few drops of MO indicator.
2. Add 25 mL of a 0.012 mol L^{-1} EDTA standard solution. To adjust the pH of the mixture to ca. 3.5, introduce (dropwise) a 10% hexamine solution into the flask until the MO indicator shows a slight color change, from red to orange.
3. Place the flask on a hot-plate and boil the mixture for a few minutes; then place the flask in an ice bath to cool the mixture. After cooling, place the flask on the magnetic stirrer and add a few drops of the XO indicator solution to the mixture.
4. Adjust the pH to ca. 5.5 as follows: stir the mixture gently, deliver the 10% hexamine solution dropwise into the flask until the XO indicator changes color from yellow to slightly purplish, and then, add a 0.1 mol L^{-1} acetic acid solution in drops until a clear yellow color reappears.
5. Next, titrate the mixture using 0.01 mol L^{-1} Zn^{2+} standard solution until the color turns to purple. The volume of titrant used in step this is defined as “A” mL. (Caution: Do not discard the titrated mixture; you will need to titrate it in the following steps.)
   Note: Determining the end point is somewhat difficult, since the color changes gradually from yellow to purple as the end point is approached. When the color is close to purple, read the burette and then add another drop of titrant; if there is a perceptible color change, read the burette again and add another drop. Repeat this process until a drop of titrant causes no color change, and then record the preceding burette reading. If EDTA is still present, the yellow color will return; add more titrant until the color remains purple for at least one minute.
6. Add ca. 1.0 g of NH_4F to the mixture titrated in step 5, and heat it on the hot-plate until the mixture boils; note that heating results in the mixture’s color returning to yellow.
7. Remove the flask to an ice bath, and after the mixture cools, place the flask on the magnetic stirrer. If the clear yellow color has disappeared after cooling, add a 0.1 mol L^{-1} acetic acid solution dropwise until the color reappears.
8. Next, titrate the mixture again using a 0.01 mol L^{-1} Zn^{2+} standard solution. The volume of the titrant used in step 8 is defined as “B” mL.

Questions

1. Report the titrant volume A (ml):

2. Report the titrant volume B (ml):

3. In steps 2 to 4, why is the pH adjusted to ca. 3.5 and ca. 5.5 in a stepwise manner? Explain the reason considering the difference in the stability of each metal-EDTA and -hydroxyl complex.

4. What is the role of the ammonium fluoride added to the mixture in step 6?

5. Show the formula for calculating the concentration of the Al^{3+} and Zn^{2+} ions in the sample solution based on the results of each titration (A and B).

6. Calculate the concentrations of Al^{3+} and Zn^{2+} ions in the sample solution in mol L^{-1}.

Concentration of Al^{3+}:

Concentration of Zn^{2+}:

7. Assuming that the alloy contains only Al and Zn, calculate the composition of the alloy in percent by weight.

Percent weight of Al^{3+}:

Percent weight of Zn^{2+}: