

Problem 28. Titrimetric determination of lead and silver in their mixture

Lead and silver are often both present in alloys (such as tin-lead-silver or lead-silver), which are successfully applied in bearing assembly, ballast, casting, step soldering, and radiation shielding. The alloys usually contain 30–90 % of lead and 1–5 % of silver. Redox titration was found to be a precise standardless method allowing determination of these metals.

In this work, you will determine lead and silver in a solution by redox titration.

Chemicals and reagents:

- A sample of lead and silver containing alloy, or test solution simulating a dissolved alloy (a standard solution containing about 500–1000 mg Pb and 70–190 mg Ag in 0.1 L)
- Ammonia aqueous solution (25% ammonium solution and water, 1:1 v/v)
- Oxalic acid, saturated solution at room temperature
- Potassium permanganate, 0.0100 M standard solution
- Nitric acid, 4 M solution
- Ammonium iron(III) sulfate, saturated solution
- Ammonium thiocyanate, 0.0100M standard solution.

Substance	Name	State	GHS Hazard Statement
NH ₃	Ammonia	aqueous solution	H314, H400
C ₂ H ₂ O ₄	Oxalic acid	aqueous solution	H314, H318
KMnO ₄	Potassium permanganate	aqueous solution	H272, H302, H400, H410
HNO ₃	Nitric acid	aqueous solution	H290, H314, H318
NH ₄ Fe(SO ₄) ₂	Ammonium iron(III) sulfate	aqueous solution	H315, H319
NH ₄ SCN	Ammonium thiocyanate	aqueous solution	H332, H412

Equipment and glassware:

- Analytical balance (± 0.0001 g)
- Hot plate
- Filter paper or glass filter
- Burette, 25 mL (2 ea.)
- Funnels (to fill the burettes)
- Volumetric pipette, 10.00 mL
- Pipette filler
- Erlenmeyer flask, 100 mL
- Volumetric flask, 100 mL
- Glass beaker, 100 and 250 mL
- Graduated cylinders
- Waste bottle for oxalate solution

Procedure**A. Decomposition of the alloy sample**

(Optional and may be omitted; if so, a model solution of metal salts is to be prepared; see *Chemicals and reagents* for the solution composition)

Take a precise weight of the metal (~250 mg) and place it in a beaker. Carefully add 5 mL of concentrated nitric acid (to be done under a fume hood because of gaseous NO_2 evolution). Heat the beaker slightly on the hot plate to provide for an effective dissolution. When the digestion is complete evaporate the solution to near dryness to remove the major part of the acid (avoid evaporating to dry salts, since hydrolysis may occur. If still so, add a minimal amount of HNO_3 to dissolve the residue). Allow the beaker cooling down to room temperature.

***ATTENTION!** Nitric acid is very corrosive! You will have to deal with hot solutions in the above and subsequent steps. Be careful and beware of steam!*

B1. Separation of lead

Using the hot plate, remove the excess of the acid by evaporating the solution obtained at stage A to dryness and dissolve the residue in water (skip this step if a model test solution is used rather than a real alloy solution). Bring the solution to boiling, then add about 10 mL of the saturated solution of oxalic acid and observe a precipitate formation. Avoid large excess of oxalic acid. To partially dissolve the precipitate, add aqueous ammonia solution (1:1 v/v) dropwise.

***ATTENTION!** The ammonia solution is corrosive and has a very strong smell! Keep the bottle stoppered when not in use.*

C. Determination of lead

Heat the solution above the precipitate on the hot plate to remove the excess of ammonia, and cool the mixture quickly under the running tap water. Filter the slurry through the glass filter. Keep the filtrate for next step. Wash the filter cake with cold water and then dissolve it in hot 0.5M HNO_3 adding the acid in small portions. Collect the obtained solution in the 100-mL volumetric flask and make it up to the mark with water. Titrate oxalate in the prepared solution (take 10.00 mL aliquots) with 0.0100 M solution of potassium permanganate.

ATTENTION! Oxalate solutions are toxic. Do not pour the solutions down a sink. Instead, dispose these in a special waste bottle.

D. Determination of silver

Add 10 mL of 4M nitric acid solution and 1–2 mL of saturated iron(III) ammonium sulfate solution to the filtrate (from step C). Use burette to add the standard solution of ammonium thiocyanate until vanishing reddish-brown color is observed. Shake the flask and continue titrating until the color is stable.

Questions and Data Analysis

1. Write down balanced chemical equations for the reactions that take place upon:
 - a) formation of the precipitate (step B),
 - b) partial dissolution of the precipitate in ammonia (step B),
 - c) dissolution of lead oxalate (step C),
 - d) oxalate titration with permanganate (step C).
2. Explain the role of iron(III) at step D.
3. Calculate the lead and silver content in the sample (starting alloy or test solution).

Problem 29. Complexometric determination of iron, chromium, and zinc in an alloy

Chemicals and reagents:

- Test solution simulating a digested sample of galvanized steel (a standard solution containing Fe^{3+} , Zn^{2+} and Cr^{3+} ions within the concentration range of 0.1–0.3 M)
- Hydrochloric acid, 1 M
- $\text{Na}_2\text{H}_2\text{EDTA}$ standard solution, 0.025 M
- Acetate buffer solution, pH 5.5–6.0, 1.7 M in acetate
- Copper(II) sulfate standard solution, 0.025 M
- Ethanol, 96%
- Distilled water
- Indicators:
 - aqueous solution of 5-sulfosalicylic acid, 5% (w/w)
 - solution of 1-(2-pyridylazo)-2-naphthol (PAN) in ethanol, 0.1% (w/w)
 - universal pH indicator paper

Equipment and glassware:

- Hot plate
- Funnels (to fill the burettes)
- Paper filters
- Volumetric flask, 100 mL
- Volumetric pipettes, 1 and 10 mL
- Burette, 25 or 50 mL (2 ea.)
- Erlenmeyer flask, 200 mL (3 ea.)
- Graduated cylinder, 10 mL (2 ea.)
- Glass dropper

Procedure**A. Sample preparation**

Prepare 100 mL of your working solution by a 10-fold dilution of the test solution provided. Use the 100 mL volumetric flask and distilled water. The Fe^{3+} , Zn^{2+} and Cr^{3+} ions content in the working solution would be within the concentration range of 0.01 – 0.03 M.

B. Determination of Fe^{3+}

Place 10.00 mL of the working solution into a 200 mL Erlenmeyer flask, add about 20 mL of distilled water and adjust the pH to 1 by adding about 5 mL of 1M HCl (check the pH value against the indicator paper). Finally, supplement 1 mL of 5% aqueous solution of sulfosalicylic acid (the indicator) and mix thoroughly.

Titrate the flask contents with 0.025 M EDTA standard solution until the color changes from violet to yellow-green. Record the volume of the standard solution (V_1 , mL). Repeat the titration as necessary.

C. Determination of Zn^{2+}

Adjust the pH of the solution obtained in step **B** to 5–6 by adding 5–6 mL of the acetate buffer solution, then add 3–5 drops of PAN solution (the indicator), 2 mL of ethanol (by cylinder) and mix thoroughly.

Titrate the flask contents with 0.025 M EDTA standard solution until the color changes from pink to yellow-green. Record the volume of the standard solution (V_2 , mL). Repeat the titration as necessary.

D. Determination of Cr³⁺

Direct titration of Cr³⁺ with EDTA solution is impossible because of the low rate of complex formation. Thus, the method of back titration is used: an excess of EDTA standard solution is introduced, and the unreacted EDTA is titrated with Cu²⁺.

Supplement an excess of 0.025 M standard solution of EDTA (20 mL) to the solution obtained in step C, mix thoroughly and boil the mixture for 5 min. Add 3-5 drops of PAN solution (the indicator) to the cooled mixture and mix thoroughly.

Titrate the flask contents with 0.025 M CuSO₄ standard solution until the color changes from wine-red to blue-violet. Record the volume of the standard solution (V₃, mL). Repeat the titration as necessary.

Questions and Data Analysis

- Write down balanced chemical equations for the reactions that take upon:
 - the sample of alloy is dissolved in concentrated nitric acid
 - the working solution is titrated with Na₂H₂EDTA
- Derive the formulae for calculation of the Fe³⁺, Zn²⁺ and Cr³⁺ concentration in the test solution. Calculate the concentrations of the ions.
- Calculate the molar fraction of H₂EDTA²⁻ at pH 1. EDTA is a weak acid with the following acidity constants: $K_1 = 1.0 \cdot 10^{-2}$, $K_2 = 2.1 \cdot 10^{-3}$, $K_3 = 6.9 \cdot 10^{-7}$, $K_4 = 5.5 \cdot 10^{-11}$.