10A. Gravimetric determination of copper as CuSCN

Gravimetric analyses belong to the most precise, because contemporary analytical balances make possible determination of the mass of a sample with great accuracy. In these analyses one should obtain high purity compound of the analyzed element or a compound directly obtained from the analyzed substance). This reaction has to be exactly stoichiometric. It is also important that the weighed compound was non-hydroscopic and stable in air, it also better if it has relatively high molecular mass, because in this case the weighing is more precise.
Examples of gravimetric analyses of high precision and still often used in practice are, among others:

- Analysis of iron precipitated as $Fe(OH)_3$ and heated in electric oven at ca. 800^{o}C to oxide Fe_2O_3;
- Analysis of barium precipitated as $BaSO_4$ (or analysis of sulfates precipitated by Ba^{2+} salts), the precipitate is heated to ca. 500^{o}C;
- Analysis of nickel precipitated in form of its complex with dimethylglyoxime ($CH_3C(NOH)C(NOH)CH_3$, known also as "Chugaev salt", the precipitate has to be dried at 110^{o}C only.

In this exercise we will analyze an alloy containing copper to determine its percent content in it.
Copper will be precipitated as CuSCN (solubility product K_{so}=12.7). This means that Cu^{2+} ions will be reduced to Cu^+ before they are precipitated using SCN^-.

$2Cu^{2+} + HSO_3^- + H_2O \rightarrow 2Cu^+ + HSO_4^- + 2H^+$
$Cu^+ + SCN^- \rightarrow CuSCN$

This is an excellent method, since most thiocyanates of other metals are soluble, in particular thiocyanates of Bi, Cd, As, Sb, Sn, Fe, Ni, Co, Mn and Zn. In presence of moderate amounts of Bi, Sb or Sn it is desirable to add 2-3 g of tartaric acid to prevent of hydrolysis of their salts.
Solubility of CuSCN increases with pH, so excessive amounts of ammonium ions should be absent., as should also oxidizing agents. The solution should be only slightly acidic, since the solubility of CuSCN increases with decreasing pH because of complexing ability of thiocyanate anions. In this analysis, Pb, Hg, Se, Te and precious metals ions interefere and contaminate the precipitate.
Consequently, the conditions of experiment are as follows:

- Slight acidity with respect to HCl lub H_2SO_4.
- The presence of a reducing agent, for instance H_2SO_3 or NH_4HSO_3, to reduce Cu(II) to Cu(I).
- A slight excess of NH_4SCN. A large excess increases the solubility of the copper thiocyanate due to formation of a complex.
- The absence of oxidizing agents.

The precipitate is curdy and readily coagulates by boiling. It is washed with dilute ammonium thiocyanate with an addition of H_2SO_3 or NH_4HSO_3, to avoid oxidization of Cu(I).

Chemicals

1. 5-6% aqueous solution of NH_4HSO_3;
2. Freshly prepared 10% aqueous solution of NH_4SCN.

Procedure

Attention: if the sample is a mineral or alloy, discuss the procedure of its dissolution with your teacher.

This analysis should be done parallel for two independent samples, the final result will be the arithmetic mean of the partial ones.

1. Place the sample solution containing not more than 0.1 g of Cu^{2+} ions in a beaker á 250 mL. Add water to a total 50 mL, and next few drops of 2M HCl and 25 mL of NH_4HSO_3 solution.
2. Dilute the content of the beaker to 150-200 mL, heat nearly to boiling and add slowly, stirrling constantly with a glass rod, solution of NH_4SCN in slight excess. The precipitate should be white, the mother liquor should be colorless and smell of SO_2.

3. Leave the beaker covered to the next lesson[1].
4. (Next lesson) Filter through glass crucible G4, under vacuum[2]. Wash the precipitate at lest 10 times with cold solution made by adding 1 mL of solution of NH_4SCN and 1 mL of solution of NH_4HSO_3 to 100 mL of water.
5. Dry the crucibles at 110°C, during 90 min or more. Place them in dessicator for a 30 min and weigh using an analytical balance.

Attention:

- The glass rods In the beakers (each beaker should have its own rod) must be there all the time, to the end of analysis. Do not remove them even for a moment!
- Little amount of the precipitate on beaker's walls difficult to be washed down during filtering does not influence the result too much.
- After experiments, do not wash the crucibles – the laboratory staff will do it better. The beakers can be washed easily using a sponge and hot water with a detergent.

Calculations and report

The final report should contain masses of empty and full filters, calculated masses of the precipitated CuSCN, calculations made to achieve the final result, and – if necessary – the brief analysis of the results. The result is mass of elemental copper in each sample (in grams) and the averaged weight percent of Cu in the alloy or mineral under examination..
The ratio of molecular masses of Cu to CuSCN is 0.5225.

Sources:
Textbooks, In particular „Vogel's textbook of quantitative chemical analysis", G.H. Jeffery, J. Bassett, J. Mendham, R.C. Denney, Longman, Great Britain, 5th edition, 1989.

[1] This analysis is rather impossible to be completed during 3-4 hours of our laboratory session.

[2] Vacuum installation is in our main lab, but it can be operated only by the laboratory staff. The technique of vacuum filtering will be demonstrated by the teachers – do not begin in their absence.