

10. The gravimetric determination of nickel in alloys

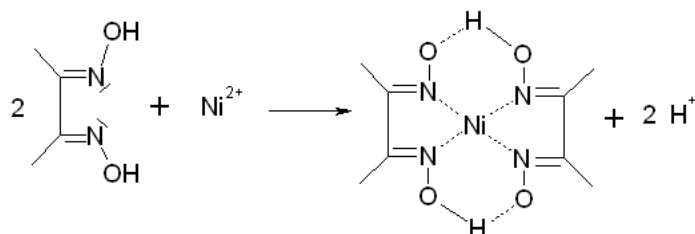
Gravimetric analyses belong to the most precise, because contemporary analytical balances make possible determination of the mass of a sample with great accuracy. In these analyses one should obtain high purity compound of the analyzed element or a compound directly obtained from the analyzed substance). This reaction has to be exactly stoichiometric. It is also important that the weighed compound was non-hygroscopic 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 $\text{Fe}(\text{OH})_3$ and heated in electric oven at ca. 800°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°C ;
- Analysis of nickel precipitated in form of its complex with dimethylglyoxime ($\text{CH}_3\text{C}(\text{NOH})\text{C}(\text{NOH})\text{CH}_3$, known also as "Chugaev salt"¹, the precipitate has to be dried at 110°C only.

In this exercise we will analyze an alloy containing Ni to determine its percent content in it.

Nickel(II) forms a precipitate with the organic compound dimethylglyoxime, $\text{C}_4\text{H}_6(\text{NOH})_2$. The formation of the red chelate occurs quantitatively in a solution in which the pH is buffered in the range of 5 to 9. The chelation reaction that occurs is illustrated below.



Although the loss of one proton occurs from one oxime group (NOH) on each of the two molecules of dimethylglyoxime, the chelation reaction occurs due to donation of the electron pairs on the four nitrogen atoms, not by electrons on the oxygen atoms. The reaction is performed in a solution buffered by either an ammonia or citrate buffer to prevent the pH of the solution from falling below 5. If the pH does become too low the equilibrium of the above reaction favors the formation of the nickel(II) ion, causing the dissolution of $\text{Ni}(\text{dmgl})_2$ back into the mother liquor.

Adding tartarate or citrate ions before the precipitation of the red nickel complex prevents interference from Cr, Fe and other metals². These anions selectively form tightly bound soluble complexes with the metals and prevent the formation of insoluble metal hydroxides in the buffered solution.

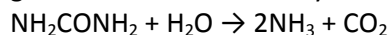
An alcoholic solution of dimethylglyoxime (*dmgl*) is used as the precipitating reagent during the experiment because *dmgl* is only slightly soluble in water (0.063 g in 100 mL at 25°C). It is therefore crucial to avoid the addition of too large an excess of the reagent because it may crystallize out with the chelate. It is also important to know that the complex itself is slightly soluble to some extent in alcoholic solutions. By keeping the volume added of the chelating reagent small, the errors from these sources are minimized. The amount of the reagent added is also governed by the presence of other metals such as cobalt, which form soluble complexes with the reagent. If a high quantity of these ions is present, a greater amount of *dmgl* must be added.

The nickel dimethylglyoximate is a precipitate that is very bulky in character. Therefore, the sample weight used in the analysis must be carefully controlled to allow more convenient handling of the precipitate during transferal to the filtering crucible. To improve the compactness of the precipitate, homogeneous precipitation is often performed in the analytical scheme. This is accomplished by the

¹ L.A. Chugaev discovered this reagent as useful in detection of nickel in 1905.

² In our analysis the interfering ions are probably present, alas!

adjustment of the pH to 3 or 4, followed by the addition of urea. The solution is heated to cause the generation of ammonia by the hydrolysis of the added urea, as indicated by the following reaction:



A slow increase in the concentration of ammonia in the solution causes the pH to rise slowly and results in the gradual precipitation of the complex. The result is the formation of a more dense, easily handled precipitate. We will, however, simply add ammonia to increase pH gradually. Once the filtrate has been collected and dried, the nickel content of the solution is calculated stoichiometrically from the weight of the precipitate.

Chemicals

1. Alcoholic solution of dimethylglyoxime (1% mass);
2. 2 M HCl (bottles in main lab);
3. 2 M ammonia in water (bottles in main lab);
4. Solid citrate or tartarate (bottles in main lab);

Procedure

1. Two (marked!) glass filters (crucibles) of density (i.e. pore sizes) G4 keep in dryer at 110° during 15-20 min., after this store them in essicator until the room temperature was achieved (ca. 30 min.) and weigh them on analytical balance.
2. At the same time weigh two samples of alloy (0.1-0.15 g), place them in 600-800 mL beakers, add few mL of 2 HCl. Place glass rods in beakers. Wait until the samples are dissolved (mixing gently).
3. Add water to beakers to the volume of ca. 50 mL, next add 1 g of solid tartarate or citrate and finally ca. 100 mL 1% alcoholic dimethylglyoxime. The mixture heat to ca. 60°C in water bath and add slowly and gradually, mixing continuously, 2M ammonia. Huge amount of red precipitate appears. At the end, the smell of ammonia should be well scented. Add 2-3 mL of 2M ammonia in excess. Leave the beakers in water bath for 15-30 min.
4. Filter the precipitate under vacuum³. Wash it with little amount of water.
5. Store the glass filter with precipitate in essicator for the week⁴.
6. (Next week) Place the filters with precipitate in dryer for not less than 90 min., at 110°C. After this move them to essicator for not less than 30 min. and weigh.

Attention:

- The glass rods in beakers (each has its own) must be there until the end of precipitation and filtering; do not remove them!
- Small amount of precipitate on walls of filter will not influence the result.
- After the analysis, do not wash glass filters – this will be done by our laboratory staff. The beakers can be washed easily with sponge and hot water and a detergent.

Calculations and report

The final report should contain masses of empty and full filters, calculated masses of the precipitated chelates, calculations made to achieve the final result, and – if necessary – the brief analysis of the results. The result is mass of elemental nickel in each sample (in grams) and the averaged weight percent of Ni in the ally under examination..

The ratio of molecular masses of Ni to Ni(dmgI)₂ is 0.2032.

Source: <http://chemlab.truman.edu/CHEM222manual/pdf/nickelgrav.pdf> (2012-02-11) and textbooks

³ 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.

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