

Fundamentals of Analytical Chemistry, CHC014011L

**Make up to the graduation mark** the obtained solution in the 200.0 cm<sup>3</sup> volumetric flask with distilled water (until the bottom of the meniscus is just in line with the graduation mark on the neck of the flask - use a dropping pipette for this), stopper the flask firmly and mix the solution by inverting the flask at least 10 times.

**Exercise 1:**

**Gravimetric analysis of Fe as Fe<sub>2</sub>O<sub>3</sub>**

Clean and mark two porcelain **crucibles**. Bring them to constant mass by drying them at 900°C in the muffle furnace for at least one hour.

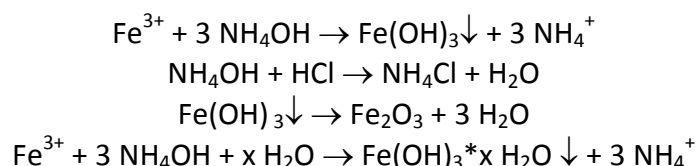
Keep the crucibles in desiccator.

If the mass of any of the crucibles will changed by more than 0.0010 g since the last weighing, you will need to bring that crucible through the heating and cooling process again.

All crucible masses are measured in grams (g):

crucible no	mass 1	mass 2	mass 3	average mass of crucible

**Equations:**



**CAUTION**

*Nitric acid (HNO<sub>3</sub>) is a powerful acid and oxidizing agent, particularly when hot.*

**Procedure:**

**Laboratory glassware has to be perfectly clean before it can be used for any type of analytical work.**

Pipette 25.00 cm<sup>3</sup> of your unknown into clean, 250 cm<sup>3</sup> beaker (do not forget to rinse pipette with the sample being tested, first!). Add to each of the beaker 1 cm<sup>3</sup> (use a dropping pipette for this) of concentrated HNO<sub>3</sub> and heat near to boiling.

Dilute each sample to about 150 cm<sup>3</sup> with distilled water and heat sample near to boiling (about 70 °C). Then add ammonium hydroxide (NH<sub>4</sub>OH) solution (1:1) very slowly (dropwise) and with constant stirring (use a glass rod) until the first permanent precipitate is formed and a slight excess of exists (characteristic odour of NH<sub>3</sub>), plus an additional 1 cm<sup>3</sup> of NH<sub>4</sub>OH solution. Add to the sample 20 cm<sup>3</sup> of 1M buffer solution. Heat the suspensions (without boiling) with constant stirring to coagulation of precipitate.

Let the beaker with its content stand on the desk for some time. Decant the solution from the sample through the filter paper. Add to the precipitate in the beaker about 50 cm<sup>3</sup> of the wash solution (hot water + buffer; 100:1) stir well, let the precipitate to settle and decant the solution through the filter. Repeat the washing by decantation 3 times and finally bring precipitate onto the filter, use small portions of the wash solution for transfer. Continue washing the filter with hot water until the least portion of washing give a negative test for iron ion. Dissolve the precipitate in 25 cm<sup>3</sup> of the hot HCl (1:5) collecting the filtrate in a beaker.

Dilute the filtrate with distilled water to about 150 cm<sup>3</sup>, heat to 70 °C with good stirring add concentrated NH<sub>4</sub>OH to adjust the pH (about 5 cm<sup>3</sup>), then add diluted NH<sub>4</sub>OH solution (1:1) until permanent precipitate is formed. Next, add the mixture 10 cm<sup>3</sup> of buffer solution. Heat the suspension to coagulate the Fe(OH)<sub>3</sub>·x H<sub>2</sub>O. Wash the precipitate by decantation with the 50 cm<sup>3</sup> of wash solution (3 x). Decant supernatant through ashless filter paper.

Bring the precipitate onto the filter paper with small portions of the wash solution. Continue washing the precipitate on the filter with hot distilled water until the last portions of washing give a negative test for chloride ions.

Remove the filter paper with the precipitate from the funnel and place into the crucible. (*Flatten and fold the filter paper with the precipitate and place it inside a crucible for ignition. Continue folding paper so that the entire sample fits at the bottom of the crucible. Be careful not to puncture the paper.*). Allow filter paper to dry for at least 24 hours protected from dust.

Ash the filter paper by heating in the small flame.

Place the crucible containing the precipitate in the muffle furnace and heat them at 900-1000°C for 1 hour. Cool the crucible in desiccator and weight accurately. (The crucible needs to cool completely before its mass can be accurately measured.)

Reheat the crucible and its content for 1 hour periods to obtain constant weights.

Calculate and report the mass of iron contained in your unknown.

Report each individual result and the mean.

### Expression of results:

all masses are measured in grams (g):

Crucible No.			
Mass of:			
empty crucible			
crucible and precipitate - 1			
crucible and precipitate - 2			
crucible and precipitate - 3			
crucible and precipitate - 4			
Fe <sub>2</sub> O <sub>3</sub>			

Calculations:

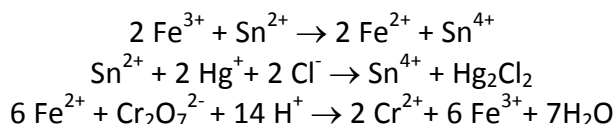
mass of iron (in mg) per 200 cm<sup>3</sup> of solution:

## Exercise 2:

### Redox titration of Fe with $K_2Cr_2O_7$

Iron may be determined by a redox titration with an oxidant such as  $K_2Cr_2O_7$  that converts Fe(II) to Fe(III).

#### Equations:



#### Procedure:

Three samples can be taken up to the point to just before addition of  $SnCl_3$  and then must be treated one at a time up through the titration.

Transfer (using pipette)  $25.00\text{ cm}^3$  of the unknown (containing Fe and Ni) into  $250\text{ cm}^3$  conical flask. Add  $5\text{ cm}^3$  of 6M HCl and heat the flask nearly to boiling. Add, by drops,  $SnCl_2$  to the hot solution to eliminate the yellow colour and 1-2 drops excess. Cool the solution to the room temperature by immersing the bottom of the flask in cold water. Add  $10\text{ cm}^3$  6%  $HgCl_2$  and mix solution thoroughly. A slight white precipitate should form (if a heavy grey or black precipitate or no precipitate form the sample must be discarded).

Add about  $100\text{ cm}^3$  of distilled water,  $30\text{ cm}^3$  of the  $H_3PO_4 - H_2SO_4$  mixture and 3 drops of 1% diphenylamine sulfonate indicator. Titrate immediately with  $K_2Cr_2O_7$  solution, stirring constantly until the green colour changes into purple or violet-blue that remains for at least 1 minute.

Calculate and report the milligrams of iron in each portion of the unknown analysed along with the mean and the precision.

#### Expression of results:

**molarity of  $K_2Cr_2O_7$  [ $\text{mol}/\text{dm}^3$ ]:**

titration no.	initial burette reading [ $\text{cm}^3$ ]	final burette reading [ $\text{cm}^3$ ]	titration [ $\text{cm}^3$ ]

Calculations:

mean titration [ $\text{cm}^3$ ]:

mass of iron (in mg) per  $200\text{ cm}^3$  of solution:

### Exercise 3:

#### Indirect complexometric titration of Fe and Ni with EDTA

Metal ions in an aliquot are complexed with EDTA and the excess EDTA is back titrated with lead nitrate at pH 5.0-6.0 (hexamine) using xylenol orange as the indicator.

#### Procedure:

Pipette 25.00 cm<sup>3</sup> of your unknown sample into a conical flask.

Add 20.00 cm<sup>3</sup> of standard 0.05M EDTA solution and 1g (half a spoon) of hexamine (hexamethylenetetramine, (CH<sub>2</sub>)<sub>6</sub>N<sub>4</sub>) and 5 drops of xylene orange solution (indicator). The hexamine buffers the solution at pH 5-6.

Back-titrate with standardised Pb(NO<sub>3</sub>)<sub>2</sub> until the colour of the indicator changes from greenish yellow into brownish yellow. Repeat to obtain consistent trite values.

From the moles EDTA taken and number of moles excess EDTA found in the back-titration, calculate and report the content on nickel in your unknown sample.

#### Expression of results:

molarity of EDTA (in mol/dm<sup>3</sup>):

volume of EDTA (in cm<sup>3</sup>):

molarity of Pb(NO<sub>3</sub>)<sub>2</sub> (in mol/dm<sup>3</sup>):

titration no.	initial burette reading [cm <sup>3</sup> ]	final burette reading [cm <sup>3</sup> ]	titration [cm <sup>3</sup> ]

Calculations:

mean titration [cm<sup>3</sup>]:

number of moles (nickel and iron):

number of iron moles taken from redox titration (Fe with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>):

number of nickel moles:

mass of nickel (in mg) per 200 cm<sup>3</sup> of solution:

Write up a report for the exercises. Your report should include:

- the underlying chemical principle of your method,
- procedures,
- tables summarizing titration results,
- treatment of data involving calculations,
- a conclusion of the investigation and
- comment on the results obtained.

**Tasks for pre-lab quizzes:**

**gravimetry**

precipitation methods; steps in a gravimetric analysis; properties of precipitates and precipitating agents; coprecipitation; application of gravimetric methods; gravimetric calculations

**redox titrations**

redox reactions; redox titration principles; redox titration curves; redox indicators; permanganometry (titrant: potassium permanganate); chromotometry (titrant: potassium dichromate); preparation and standardization of permanganate solutions; determination of iron by redox titration (by potassium dichromate and by potassium permanganate); calculations

**complexometric titrations**

complexation titration principles; classification of complexation titration including types of complexometric titrations; chelate compound or chelate; factors influencing EDTA reactions; stability of complexes; stability constant  $K$ ; EDTA titration; EDTA titration curves; methods of end point detection; indicators; quantitative applications of complexometric titrations including determination of hardness of water; calculations.

**[http://www.zcha.pwr.wroc.pl/dydaktyka/Fundamentals of analytical chemistry](http://www.zcha.pwr.wroc.pl/dydaktyka/Fundamentals%20of%20analytical%20chemistry)**