# Laboratory exercise no. 12A. The manganometric determination of iron (only full-semester course)

Oxidimetric determinations are based on complete redox reactions in which electrons are transferred from a donor ion (or molecule) to an acceptor ion (or molecule):

- Iodometry (e.g. for Cl_2, Br_2, Cu(I)...) $2 S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$ (thiosulphate + I_2) $\rightarrow$ (tetrathionate + I^-)
- Bromatometry (e.g. for Sb(III), As(III), Cu(I)...) $BrO_3^- + 6 H^+ + 6 e \rightarrow Br^- + 3 H_2O$
- Manganometry (e. g. for Ca^{2+}, Fe^{2+}, H_2O_2, oxalate...) $MnO_4^- + 8 H^+ + 5 e \rightarrow Mn^{2+} + 4 H_2O$

In manganometric determination of iron the first step is conversion of all the iron ions into Fe^{+2} (reduced form), because only this can be oxidized further by permanganate MnO_4^-. This is done using $SnCl_2$ solution in hot environment containing HCl, the process of reduction can be easily seen because Fe^{+3} ions form dark-brown complex with chloride anions, which disappear gradually during reaction. Some excess of $SnCl_2$ solution should be added to ensure the completeness of reduction.

$Sn^{+2} + 2Fe^{+3} \rightarrow Sn^{+4} + 2Fe^{+2}$
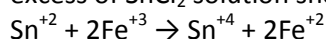
This excess of reductor, i.e. of Sn^{+2} cations, is after removed by their oxidation by $HgCl_2$. The latter reduces to Hg_2^{+2} ions which form calomel (Hg_2Cl_2), insoluble in water and thus not oxidized by permanganate during the titration.

$Sn^{+2} + 2 HgCl_2 \rightarrow Hg_2Cl_2\downarrow + Sn^{+4} + 2Cl^-$
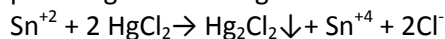
Titration is done in large beakers (800-1000 mL) in presence of so-called Reinhard-Zimmermann mixture, using permanganate as the titrant.

$5Fe^{+2} + MnO_4^- + 8H^+ \rightarrow 5Fe^{+3} + Mn^{+2} + 4H_2O$
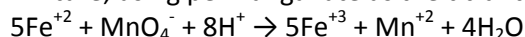
The R-Z mixture contains H_2SO_4 (to ensure low pH of the reaction medium), phosphoric acid H_3PO_4 (ions Fe^{+3} formed during titration are colored, brown-yellow, but they form with phosphoric anions colorless complex; this is important because of the end-point detection, see below), and $MnCl_2$ (ions Mn^{+2} present in solution lower the oxidizing potential of permanganates at the initial stage of titration) [1].

Titration is carried out until the titrant $KMnO_4$ colors the reaction solution to light red color.

Procedure

Students receive two identical samples of $FeCl_3$ in two beakers (at least 800 mL capacity each). Put glass bars to the beakers. Attention: these bars should never been removed from the beakers or exchanged between them until the analysis was finished!

1. Add 10 mL of concentrated HCl to each sample. Samples become darker.
2. Heat the sample almost to boiling and take off the fire. Add slowly $SnCl_2$ solution to it, drop by drop, stirring the content continuously with the glass bar. When the solution becomes colorless, add 2-3 drops of $SnCl_2$ more and leave to cool.
3. Add ca. 100 mL water and 10 mL of 5% $HgCl_2$ and stir shortly with the glass bar. Delicate, silk-like precipitate appears. If it becomes dark, the excess of $SnCl_2$ was too big, metallic Hg was formed, the analysis is lost and should be repeated.
4. Add 50-80 mL of R-Z mixture.
5. Titrate using 0.02 M $KMnO_4$, stirring continuously the content of beaker with your glass rod. When the solution is colored light red or pink and the color does not disappear during 10-15 seconds, the titration is finished.
6. The result is the arithmetic average of two independent titrations. If they differ by more than 3%, analysis should be repeated.

Source: textbooks

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[1] The oxidizing potential of MnO_4^- is (Nernst equation): $E_{ox} = E^0_{MnO_4^-/Mn^{+2}} + \dfrac{0.059}{5} \log_{10} \dfrac{[MnO_4^-]\cdot[H^+]^8}{[Mn^{+2}]}$. For $[Mn^{+2}]$

close to zero, E_{ox} becomes very high and permanganate oxidizes chlorides: $2Cl^- \rightarrow Cl_2 + 2e^-$. This leads to error.