**Estimation of Ca2+ and Fe3+ from a mixture of Fe(III) and Ca(II)**

**(Students are requested to estimate Ca(II) on 23rd February and Fe(III) on 1st March from same mixture)**

1. **Separation of Fe(III) from the mixture:**

Pipette out 20 mL of the mixture in a 250 mL beaker and add 1 g of NH4Cl to it. Heat the solution to 80 OC - 90 OC and then add liquor ammonia to completely precipitate Fe(OH)3 (red). The solution should smell ammonia. Filter the hot solution using a funnel and Whatman No. 1 filter paper and collect the filtrate in a 250 mL beaker. Wash the filtrate with hot distilled water thoroughly.

1. **Estimation of Ca2+ present in the filtrate by complexometric titration with EDTA:**
2. Add pH 10 Ammonium buffer to the filtrate to maintain a pH of 10 so that EDTA as well as EBT remain in their corresponding ionized form of pH 10. This keeps the titration concordant and does not propagate errors. We will maintain this pH for all our complexometric titrations today. Another reason of maintaining pH 10 is to keep Ca-EDTA complex stable whereas Mg-EDTA complex relatively unstable.
3. Add 10 drops of EBT to turn the mixture wine red
4. Titrate with standard 0.050 M stock EDTA solution from a burette until the red colour solution turns into a permanent blue.

**Supplied Solution**

1. 0.050 M stock EDTA solution at pH 8 with a trace amount of MgCl2•6H2O. The reason to add MgCl2 here is to get a sharp end point. The Ca-HIn complex is unstable in presence of Mg2+ ions.
2. pH 10 ammonia-ammonium chloride buffer
3. 0.1% (w/v) EBT in ethanol
4. **Estimation of Fe3+ present in the ppt by Redox titration with Dichromate using BDS indicator:**

**Determination of iron using potassium dichromate: Redox indicators**

**Theory**
As an oxidant, dichromate has some advantages over permanganate, but, as it is less powerful, its use is much more limited. It is obtainable in a state of high purity and can be used as a primary standard. Solutions of dichromate in water are stable indefinitely. The half reaction for the dichromate system is:

Cr2O72- + 14H+ + 6e- → 2Cr3+ + 7H2O      E° = 1.33 V

The most important application of dichromate is in its reaction with iron(II) in which it is often preferred to permanganate.

The relevant half reaction is :

Fe2+ → Fe3+ + e-      E° = -0.77 V

and the total reaction is:

Cr2O72- + 6 Fe2+ + 14H+ → 2Cr3+ + 6 Fe3+ + 7H2O      E° = 0.56 V

Unlike permanganate, dichromate titrations require an indicator. There are three indicators that may be used for the titration of Fe2+ with K2Cr2O7. These are diphenylamine, diphenylbenzidine and diphenylamine sulfonate. The colour change for all three indicators is green to violet and the standard electrode potentials are all ca 0.78 V. According to Kolthoff and Sandell, this should lie between the electrode potentials of the two reduction reactions. This not being the case, phosphoric acid is added to reduce the electrode potential for the Fe3+ → Fe2+ reaction by stabilising the ferric ion.

Method
Prepare a standard dichromate solution by dissolving an accurately weighed sample of about 0.4 g in water and make up to 100 cm3 in a volumetric flask. Into flasks or beakers weigh out accurately duplicate portions of about 0.7 g of the iron(II) solid `M' provided. Add 30 cm3 of dil. sulfuric acid, 100 cm3 of water, 7 cm3 of 85% phosphoric acid and 5 drops of diphenylamine sulfonate indicator. Titrate with dichromate to a purple colour. Calculate the percentage of iron in the solid `M'.