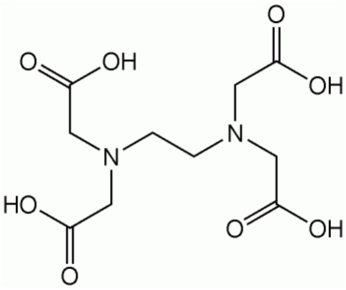
14. The complexometric determination of calcium and magnesium in the same sample

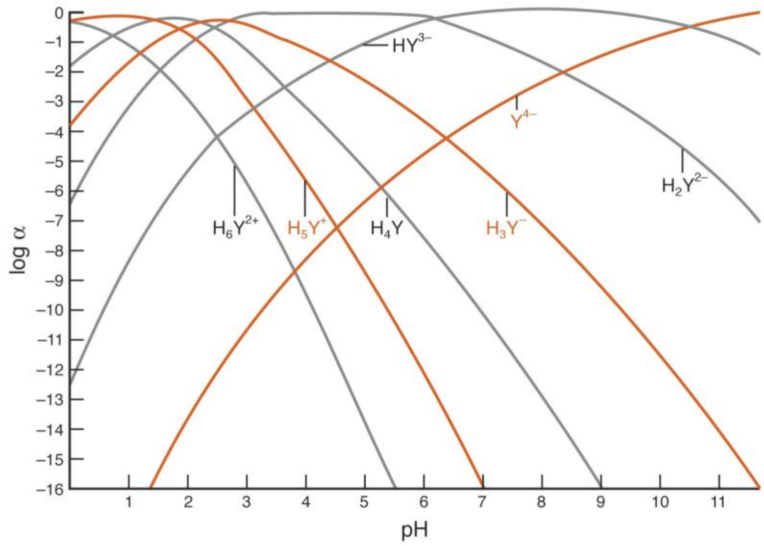
Complexometry is a chemical technique using the formation of a colored complex to indicate the end of a titration. Complexes (also called "coordination compounds" or "metal complexes") are structures consisting of a central atom or molecule connected to surrounding atoms or molecules (ligands) by coordination bonds. Most often used reagent in complexometric analyses is EDTA - EthyleneDiamineTetraAcetic acid.

EDTA is a chelating ligand. ("Chelate" is from Latin *chele*=claw, like the pincer of a lobster. "Ligand" is from Latin *ligare*=to bind). There are also other similar chelating agents (EGTA, CDTA and so on) widely used.



EDTA itself is almost insoluble in water. Because of that, in analytical chemistry one uses its disodium salt, Na_2EDTA. The titrants are usually very diluted, the typical concentration is 0.01 M. EDTA contains four carboxyl groups and two basic (alkaline) nitrogens in molecule. So, it is dissociating in complicated manner.

However, it is the completely dissociated form (Y^{-4}) which forms stable complexes with metals. It is dominating only in very high pH:



Distribution of dissociated species of EDTA vs. pH

The bonding energy of H^+ by EDTA is much lower than that of metals, and during complexation deprotonation occurs (exchange reaction). Thus, ions H_2Y^{-2} formed when the sodium salt of EDTA is dissolved in water react with cations in the following way: $H_2Y^{-2}+Mg^{+2} \leftrightarrow 2H^+ + MgY^{-2}$ or $H_2Y^{-2}+Fe^{+3} \leftrightarrow 2H^+ + FeY^-$ etc.

It is clear that higher pH will shift this equilibrium right, towards formation of complex.

In analyses of metal ions detection of the endpoint is mainly based on substances that change color when creating complexes with determined metals. An example of such indicators is Eriochrome Black T, substance used at pH between 7 and 11. It is blue when free, and red-orange when forming complex with a metal ion. Other examples of complexometric indicators are Pyrocatechin Violet and Murexide.

The formation constant of complexes metal:indicator should be low, so that titrant displaces it easily.

Both magnesium and calcium can be easily determined by EDTA titration in the pH 10 against Eriochrome Black T. If the sample solution initially contains also other metal ions, one should first remove or mask them, as EDTA react easily with most of the cations (with the exception of alkali metals). Reactions taking place during titration are: $[MeIn]^+ + H_2EDTA^{2-} \rightarrow [MeEDTA]^{2-} + 2H^+ + In^-$ (where Me – Mg or Ca, In - indicator).

The end point of magnesium titration can be easily detected with Eriochrome Black T, which forms red-orange complex with both Ca^{2+} and Mg^{2+} ions. Addition of EDTA causes gradual expulsion of indicator from complexes (because those with EDTA are stronger). Finally, only blue color of free (non-bonded) indicator is present. The change of color is, however, gradual, and titration should be carried with overtitrated sample as color reference.

Another indicator, Murexide, forms red complexes with calcium at pH=12 (and higher). At this pH, magnesium precipitates as $Mg(OH)_2$. So, for simultaneous determination of Mg and Ca one needs two titrations: one at pH=10 and using Eriochrome Black T (the sum of moles of both metals is obtained) and second, at pH=12 and using Murexide (only calcium is titrated).

Important: the change of indicator's color is gradual. So, the titration has to be carried to total change of color, using overtitrated sample as the color reference.

Determination of magnesium and calcium is important in many fields. The examples are:

1. Analysis of drinking (technological, etc.) water. Surface waters always contain dissolved minerals, in particular well soluble bicarbonates of Mg and Ca. Because there is always CO_2 present in air, when rains fall of the limestone, the following reaction occurs: $CaCO_3 + H_2O + CO_2 \rightarrow Ca^{+2} + 2HCO_3^{-2}$
   This reaction can be reversed by boiling and the carbonate precipitates forming so called "fur" or "boiler scale". Moreover, metal ions in water react with soap causing its increased consumption when washing. So, the content of Ca and Mg is one of the most important factors, known as "water hardness". Look in textbooks for information how this factor is calculated.
2. Analysis of minerals – the content of magnesium in limestone/dolomite determines sometimes its technological usefulness. Cations of other metals can disturb these analyses – sometimes it is necessary to mask them using a ligand forming colorless complexes with these ions, but not with magnesium or calcium ones (CN^-, F^- etc.). Find in textbooks additional information about masking.

Procedure

The first titration should always be reference. Overtitrate the sample, i.e. add 2-3 mL of the titrant in excess to have pure blue (Eriochrome Black T, pH=10) or violet (Murexide, pH=12) color of the non-bonded indicator. Further titrations should always end when the sample has color identical to that of the reference.

1. Weigh ca. 0,2 g of the mineral, dissolve it in ca. 3 mL of 2 M acetic acid, transfer (quantitatively!) the solution to your volumetric flask and dilute with water to the mark. Mix the content carefully. If your are analyzing water (river, mineral), simply measure 100 mL to Erlenmeyer flask using the measuring cylinder and skip point 2.
2. Transfer a portion of sample solution from volumetric flask to Erlenmeyer flask using the pipette. Dilute to about 100 mL with distilled water.
3. Add 15-20 mL of pH 10 ammonia buffer solution and a pinch of Eriochrome Black T.
4. Titrate with EDTA solution till the color changes from red to blue.
5. Calculate the sum of moles of Ca and Mg (n_{Ca+Mg}).
6. Perform points 2-5 at least twice.
7. Transfer a portion of sample solution from volumetric flask to Erlenmeyer flask using the pipette. Dilute to about 100 mL with distilled water.
8. Add 2-3 granules of solid NaOH and a pinch of Murexide (not too much!).
9. Titrate with EDTA solution till the color changes from red to violet.
10. Calculate the number of moles of Ca (n_{Ca}).
11. Perform points 7-10 at least twice.

Report

List the data obtained.

Calculate the average number of sums of moles of Ca and Mg n_{Ca+Mg} (points 2-6).

Calculate the average number of moles of Ca n_{Ca} (points 7-11).

Calculate the average number of moles of Mg $n_{Mg}= n_{Ca+Mg} - n_{Ca}$.

Calculate the masses of Ca and Mg in the total sample received and their molar ratio (Mg:Ca). If the sample is water – calculate the masses of Ca and Mg in 1 dm^3 of it.

Sources:

Internet: Wikipedia and http://www.titrations.info/complexometric-titration textbooks