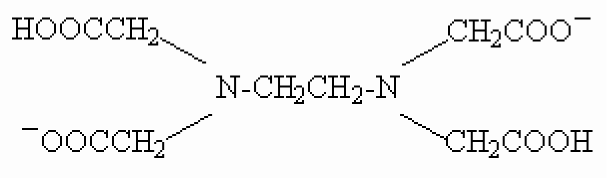
WATER HARDNESS
DETERMINATION OF Ca^{2+} AND Mg^{2+} IN PARALLEL

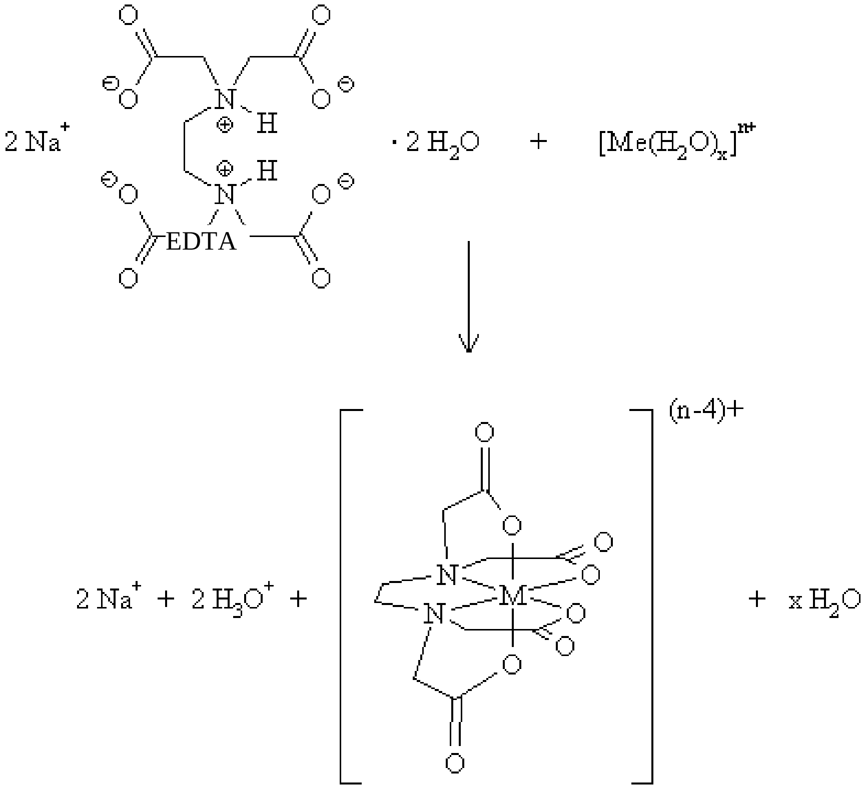
Complexometric titrations

In complexometric titrations, the most frequent titration agent is ethylenediamine-tetraacetic acid (abbr. EDTA). Dihydrate of disodium salt is often referred to as Chelaton 3 (abbr. Na_2H_2Y).



In aqueous solution Na_2H_2Y dissociates:
$Na_2H_2Y \rightarrow 2Na^+ + H_2Y^{2-}$

EDTA reacts with metal ions in the molar ratio always 1:1, according to the following reaction:
$M^{z+} + H_2Y^{2-} \leftrightarrow MY^{z-4} + 2H^+$



Complex of EDTA with metal

e.g.
$Ca^{2+} + H_2Y^{2-} \leftrightarrow [CaY]^{2-} + 2H^+$
$Fe^{3+} + H_2Y^{2-} \leftrightarrow [FeY]^- + 2H^+$
In the course of the reaction, protons are released; i.e. **the reaction is pH-dependent!**

Common metalochromic indicators

Indicator	Type	Form	**Determined metals**
murexid	Ammonium salt Purpure acids	H_4,Ind^-	Cu, Ni, Co; pH 8-9 Ca; pH 12
Eriochrome black T	azodye	H_2Ind^-	Cd, Zn, Mg, Mn'', Pb; pH 10
PAN	azodye	H_2Ind^+	Cu, Ni, Zn; pH 4-5 Bi, Th; pH 2-3
methylthymol blue	sulphophtalein	H_2Ind^+	Bi, Th, Zr; pH 2-4 Cu, Pb'', Sn''; pH 6 Ca, Cu, Mg; pH 9-12
xylenol orange	sulphophtalein	H_7Ind^+	Zr (1M-$HN0_3$) Bi, Fe''', Th; pH 2.5-3 Cu, Cd, Co, Pb, Zn; pH 5
calcein	derivative of fluoresceine	H_6Ind	Ca; pH 12.5 (KOH)

Indication of the end point of the titration

To indicate the end poind in complexometric titrations, the metalochromic indicators are often used. These compounds are organic dyes, usually polyvalent acids H_xInd, the anions of which bear different charges and are intensively colored. The color of the indicator is strictly pH-dependent. The anion forms a complex with metal ions and the color of these complexes is different from the color of uncomplexed anions.

In a complexometric titration, a small amount of metalochromic indicator is added to the reaction mixture of defined pH containing the metal ion to be determined. The anionic form of the indicator is generated by protolysis:

$$H_xInd \rightarrow H_{x-i}Ind^{i-} + iH^+$$

Then, the anionic form of the indicator forms a complex with metal cation and the solution displays a color change (it gets the color of the complex):

$$M^{z+} + H_{x-i}Ind^{i-} \rightarrow MH_{x-i}Ind^{z-i}$$

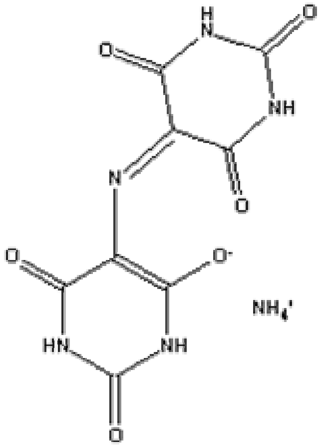
In the solution, there are free metal ions and metal ions bound in the complex with the indicator. In the beginning of the titration, the free metal ion reacts with the titration agent (Chelaton) and forms a complex (usually colorless or weakly colored); in the course of titration, the concentration of free metal ion decreases but the color of the solution remains unchanged. Protons released by occurring reactions are neutralized by alkaline components of the buffer. When approaching the end point, concentration of metal ions drastically decreases and the equilibrium of the reaction of complex $MH_{x-i}Ind^{z-i}$ formation is shifted to the left and consequently the released M^{z+} ions immediately react with Chelaton; i.e., close to the end point, the following displacement reaction occurs:

$$MH_{x-i}Ind^{z-i} + H_2Y^{2-} \rightarrow MY^{z-4} + H_{x-i}Ind^{i-} + (1 + i)\ H^+$$

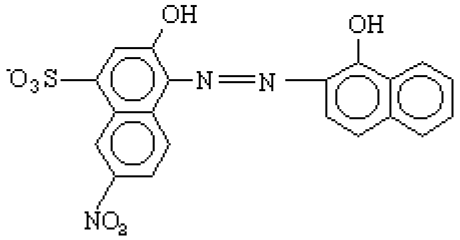
This reaction occurs provided the stability of complex of metal with Chelaton (MY^{z-4}) is higher that that of complex of metal with indicator ($MH_{x-i}Ind^{z-i}$).

The indication of end point in complexometric titrations may be performed by potenciometry using appropriate indication electrode, the potential of which depends on the concentration of free metal M^{z+}.

Parallel complexometric determination of Ca^{2+} and Mg^{2+} is based on the simultaneous titration of both ions by Chelaton in ammonia-buffered solution (pH 10), using Eriochrome black T as metalochromic indicator (i.e. the sum Ca^{2+} + Mg^{2+} is determined). Calcium is determined subsequently by titration in a strongly alkaline buffer (pH 11-12), where magnesium is precipitated in the form of $Mg(OH)_2$ (a transparent gel precipitates) that does not react with the titration agent nor interferes with the reaction (unless in large quantity). Murexid is now used as metalochromic indicator. The concentration of Mg^{2+} is calculated from the difference between both titrations.



Murexid



Eriochrome black T

Reagents

1. Buffer, pH 10 (NH_3+NH_4^+)
2. 2M-NaOH
3. Metalochromic indicator Eriochrome black T (0.1 g + 10 g NaCl)
4. Metalochromic indicator Murexid (0.1 g + 10 g NaCl)
5. Chelaton - $NaH_2Y.2H_2O$ p.a. (0.02 mol l^{-1})

Procedure

1. Determination of total content of Ca^{2+} and Mg^{2+} in water (total water hardness)

Pipette 25 ml of the sample; add 2 ml of buffer (pH 10) and a small amount of mixture Eriochrome black T and NaCl (the color of solution will get intensively wine-red). Immediately titrate with Chelaton solution until the first marked change of color (wine-red → blue-violet). When approaching end point, it is recommended to titrate slowly because the color change occurs with a time-lag. Observe the change of color carefully to detect the end point properly. Perform the titration 2x in parallel (consumption A, ml). For the blank, pipette 25 ml of distilled water instead of the sample and titrate as the sample (consumption A_o, ml).
The hardness of water is calculated according to the following equation and is expressed in German degrees (i.e. 1 mg of CaO in 100 ml) and as mmols of Ca in 1 litre of sample.

Total hardness [mg CaO in 100 ml] $= M_{rCaO} \cdot c_{ch} \cdot (A\text{-}A_o) \cdot f$

M_r CaO = 56.08; Mr Ca = 40.08
c_{ch} – concentration of Chelaton [0.02 mol l^{-1}]
A – consumption of Chelaton for determination of the sum Ca^{2+} + Mg^{2+} [ml]
A_o, - consumption of Chelaton for the blank [ml]
f = 4 (titrated 25 ml; Hardness degrees are expressed as mg per 100 ml)

Total hardness	German scale for drinking water
0 - 4	Very soft
4 - 6	Soft
6 - 9	Medium hard
9 - 12	Fairly hard
12 - 18	Hard
> 18	Very hard

Calculate molar concentration of Ca in the sample using the value of total water hardness.

3. Determination of Ca in a sample

Pipette 25 ml of sample; add 2 ml of 2M-NaOH and a small amount of metalochromic indicator Murexid + NaCl; mix well and immediately titrate with Chelaton (0.02 mol l^{-1}) until the development of violet color. Perform the titration 2x in parallel (consumption B, ml). For the blank, pipette 25 ml of distilled water instead of sample and titrate as the sample (consumption B_o, ml).

4. Calculation of Ca^{2+} and Mg^{2+} concentrations

$$m_{Ca} = \frac{Mr_{Ca}}{1000} \cdot c_{ch} \cdot (B\text{-}B_o)$$

$$m_{Mg} = \frac{Mr_{Mg}}{1000} \cdot c_{ch} \cdot [(A\text{-}A_o) - (B\text{-}B_o)]$$

m_{Ca} – content of Ca^{2+} in the sample [g]
m_{Mg} - content of Mg^{2+} in the sample [g]
Mr_{Ca} = 40.08; Mr_{Mg} = 24.31
C_{ch} – concentration of Chelaton [0.02 mol l^{-1}]
B – consumption of titration agent for Ca only [ml]
A - consumption of titration agent for sum Ca^{2+} + Mg^{2+} [ml]
A_o,B_o – consumptions of titration agent in corresponding blank assays [ml]

Express the results as **mg** of Ca and Mg in 1 litre of the sample.