

Complexometric Titrations

Titrations based on complex formation, sometimes called **complexometric titrations**.

Most metal ions react with electron-pair donors to form coordination compounds or complexes. The donor species, or ligand, must have at least one pair of unshared electrons available for bond formation.

A **ligand** is an ion or a molecule that forms a covalent bond with a cation or a neutral metal atom by donating a pair of electrons, which are then shared by the two.

The number of covalent bonds that a cation tends to form with electron donors is its **coordination number**.

A **chelate** is produced when a metal ion coordinates with two or more donor groups of a single ligand to form a five- or six-membered heterocyclic ring.

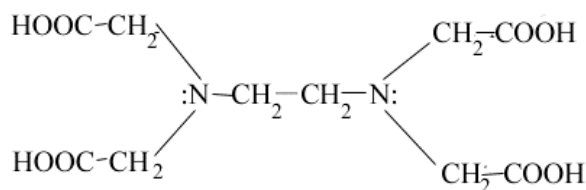
A ligand that has a single donor group, such as ammonia, is called unidentate (single-toothed), whereas one such as glycine, which has two groups available for covalent bonding, is called bidentate. Tridentate, tetradentate, pentadentate, and hexadentate chelating agents are also known.

As titrants, multidentate ligands, particularly those having four or six donor groups, have two advantages over their unidentate counterparts.

1. They generally react more completely with cations and thus provide sharper end points.
2. They ordinarily react with metal ions in a single-step process, whereas complex formation with unidentate ligands usually involves two or more intermediate species.

Ethylenediaminetetraacetic Acid (EDTA)

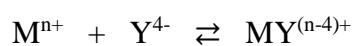
EDTA, a hexadentate ligand, is among the most important and widely used reagents in titrimetry.



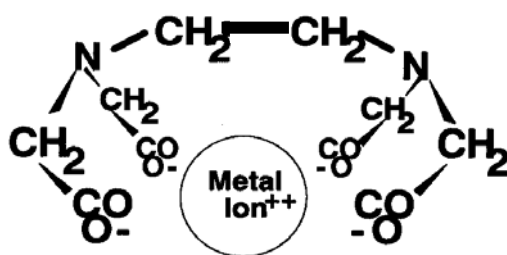
- The EDTA molecule has six potential sites for bonding a metal ion: the four carboxyl groups and the two amino groups, each of the latter with an unshared pair of electrons. Thus, EDTA is a hexadentate ligand.

The dissociation constants for the acidic groups in EDTA are $K_1=1.02 \times 10^{-2}$, $K_2=2.14 \times 10^{-3}$, $K_3=6.92 \times 10^{-7}$, and $K_4=5.50 \times 10^{-11}$. Note that the first two constants are of the same order of magnitude. This similarity suggests that the two protons involved dissociate from opposite ends of the rather long molecule. Because the protons are several atoms apart, the negative charge resulting from the first dissociation does not greatly influence the removal of the second proton. Note, however, that the dissociation constants of the other two protons are much smaller and different from one another. These protons are closer to the negatively charged carboxylate ions resulting from the dissociations of the first two protons, and they are more difficult to remove from the ion because of electrostatic attraction.

- The various EDTA species are often abbreviated H_4Y , H_3Y^- , H_2Y^{2-} , HY^{3-} , and Y^{4-} .
- EDTA combines with metal ions in a 1:1 ratio regardless of the charge on the cation.
- In general, we can write the reaction of the EDTA anion with a metal ion:



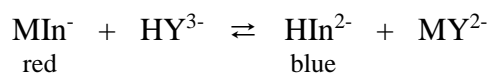
- EDTA is a remarkable reagent not only because it forms chelates with all cations but also because most of these chelates are sufficiently stable for titrations. This great stability undoubtedly results from the several complexing sites within the molecule that give rise to a cage-like structure in which the cation is effectively surrounded and isolated from solvent molecules.



Indicators for EDTA titrations;

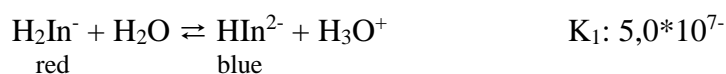
- Eriochrome Black T
- Calmagite

The metal complexes of Eriochrome Black T are generally red. Until the equivalence point in a titration, the indicator complexes the excess metal ion so that the solution is red. With the first slight excess of EDTA, the solution turns blue as a result of the reaction



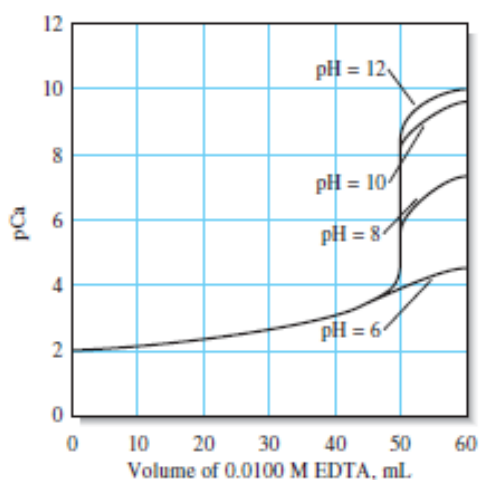
It is necessary to adjust the pH to 10. Because,

1. Eriochrome Black T behaves as an acid/base indicator as well as a metal-ion indicator.



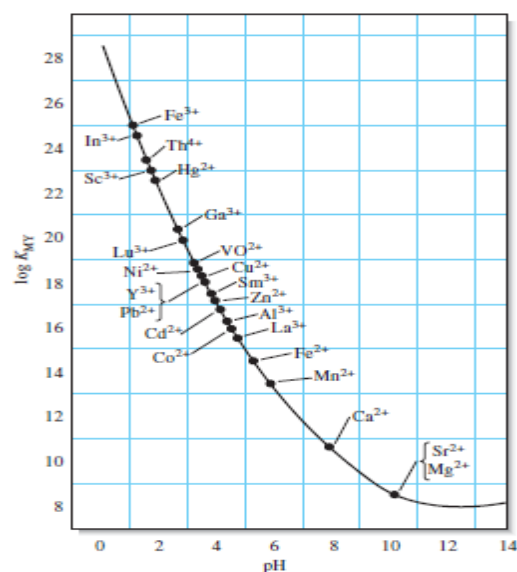
If the pH is 7 or above, the blue form of the species, HIn^{2-} , predominates in the absence of a metal ion.

2. Titrations with EDTA are highly dependent on pH.



Influence of pH on the titration of 0.0100 M Ca^{2+} with 0.0100 M EDTA

It shows that an adequate end point in the titration of calcium requires that the pH be greater than about 8.0.



Minimum pH needed for satisfactory titration of various cations with EDTA.

Titration Methods Involving EDTA

1. Direct Titration

Many of the metals in the periodic table can be determined by titration with standard EDTA solutions. Some methods are based on indicators that respond to the analyte itself, while others are based on an added metal ion.

- a) Methods Based on Indicators for the Analyte.
- b) Methods Based on Indicators for an Added Metal Ion.

In cases where a good, direct indicator for the analyte is unavailable, a small amount of a metal ion for which a good indicator is available can be added. The metal ion must form a complex that is less stable than the analyte complex. For example, indicators for calcium ion are generally less satisfactory than those we have described for magnesium ion. Consequently, a small amount of magnesium chloride is often added to an EDTA solution that is to be used for the determination of calcium. In this case, Eriochrome Black T can be used as indicator. In the initial stages of the titration, magnesium ions are displaced from the EDTA complex by calcium ions and are free to combine with the Eriochrome Black T, therefore imparting a red color to the solution. When all of the calcium ions have been complexed, however, the liberated magnesium ions again combine with the EDTA until the end point is observed.

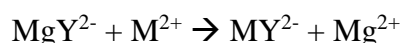
2. Back-Titration Methods

Back-titration procedures are used when no suitable indicator is available, when the reaction between analyte and EDTA is slow, or when the analyte forms precipitates at the pH required for its titration.

A measured excess of standard EDTA solution is added to the analyte solution. After the reaction is judged complete, the excess EDTA is back-titrated with a standard magnesium or zinc ion solution to an Eriochrome Black T or Calmagite end point. For this procedure to be successful, it is necessary that the magnesium or zinc ions form an EDTA complex that is less stable than the corresponding analyte complex.

3. Displacement Methods

In displacement titrations, an unmeasured excess of a solution containing the magnesium or zinc complex of EDTA is introduced into the analyte solution. If the analyte forms a more stable complex than that of magnesium or zinc, the following displacement reaction occurs:



where M^{2+} represents the analyte cation. The liberated Mg^{2+} or, in some cases Zn^{2+} , is then titrated with a standard EDTA solution.

Determination of Water Hardness

Hardness is the concentration of calcium carbonate that is equivalent to the total concentration of all the multivalent cations in the sample.

Calcium and magnesium bicarbonates → Temporary hardness

Chlorides, nitrates, sulphates, phosphates and silicates of these elements → Permanent Hardness

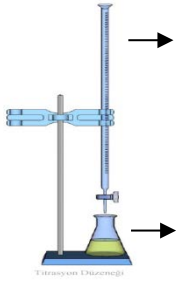
Classification of Water Hardness

Soft Water	→	0-75 mg/L	→	0-7.5 Fr
Medium Hard Water	→	75-150 mg/L	→	7.5-15 Fr
Hard Water	→	150-300 mg/L	→	15-30 Fr
Very Hard Water	→	> 300 mg/L	→	> 30 Fr

Water Hardness Degrees:

- French Degree of Hardness : 10 mg CaCO_3 / L
- German Degree of Hardness : 10 mg CaO / L
- English Degree of Hardness : 10 mg CaCO_3 / 700 mL
- American Degree of Hardness : 1 mg CaCO_3 / L (ppm CaCO_3)

Experimental Procedure:



→ 0.0100 M EDTA

- Mg^{2+} sample + 30 mL of purified water + 2 mL of $\text{NH}_3/\text{NH}_4\text{Cl}$ buffer + 2 drops of Eriochrome Black T → Pink solution
- The solution is titrated until the blue color is observed in the solution