Complexometric titration

Complexometric titration (sometimes **chelatometry**) is a form of volumetric analysis in which the formation of a colored complex is used to indicate the end point of a titration. Complexometric titrations are particularly useful for the determination of a mixture of different metal ions in solution. An indicator capable of producing an unambiguous color change is usually used to detect the end-point of the titration.

Reactions for Complexometric Titration

In theory, any complexation reaction can be used as a volumetric technique provided that:

1. the reaction reaches equilibrium rapidly after each portion of titrant is added.
2. interfering situations do not arise. For instance, the stepwise formation of several different complexes of the metal ion with the titrant, resulting in the presence of more than one complex in solution during the titration process.
3. a complexometric indicator capable of locating equivalence point with fair accuracy is available.

In practice, the use of EDTA as a titrant is well established

Complex titration with EDTA

EDTA, ethylenediaminetetraacetic acid, has four carboxyl groups and two amine groups that can act as electron pair donors, or Lewis bases. The ability of EDTA to potentially donate its six lone pairs of electrons for the formation of coordinate covalent bonds to metal cations makes EDTA a **hexadentate** ligand. However, in practice EDTA is usually only partially ionized, and thus forms fewer than six coordinate covalent bonds with metal cations.

Disodium EDTA is commonly used to standardize aqueous solutions of transition metal cations. Disodium EDTA (often written as **Na_2H_2Y**) only forms four coordinate covalent bonds to metal cations at pH values $\leq$ 12. In this pH range, the amine groups remain protonated and thus unable to donate electrons to the formation of coordinate covalent bonds. Note that the shorthand form **$Na_{4-x}H_xY$** can be used to represent any species of EDTA, with **x** designating the number of acidic protons bonded to the EDTA molecule.

EDTA forms an octahedral complex with most 2+ metal cations, M^{2+}, in aqueous solution. The main reason that EDTA is used so extensively in the standardization of metal cation solutions is that the formation constant for most metal cation-EDTA complexes is very high, meaning that the equilibrium for the reaction:

$$M^{2+} + H_4Y \rightarrow MH_2Y + 2H^+$$
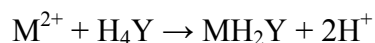
lies far to the right. Carrying out the reaction in a basic buffer solution removes H^+ as it is formed, which also favors the formation of the EDTA-metal cation complex reaction product. For most purposes it can be considered that the formation of the metal cation-EDTA complex goes to completion, and this is chiefly why EDTA is used in titrations / standardizations of this type.

Indicators

To carry out metal cation titrations using EDTA, it is almost always necessary to use a complexometric indicator to determine when the end point has been reached. Common indicators are organic dyes such as Fast Sulphon Black, Eriochrome Black T. Color change shows that the indicator has been displaced (usually by EDTA) from the metal cations in solution when the endpoint has been reached. Thus, the free indicator (rather than the metal complex) serves as the endpoint indicator.

TITRATION OF MIXTURES, SELECTIVITY, MASKING AND DEMASKING AGENTS
EDTA is a very unselective reagent because it complexes with numerousdoubly, triply and quadruply charged cations. When a solution containingtwo cations which complex with EDTA is titrated without the addition of a complex-forming indicator, and if a titration error of 0.1 per cent ispermissible, then the ratio of the stability constants of the EDTA complexesof the two metals M and N must be such that KM/KN > 106 if N is not to interfere with the titration of M. Strictly, of course, the constants KM and KN considered in the above expression should be the apparent stability constants of the complexes. If complex-forming indicators are used, then for a similar titration error KM/KN > 108.The following procedures will help to increase the selectivity :

(a) Suitable control of the pH of the solution.
This, of course, makes use of the different stabilities of metal-EDTAcomplexes. Thus bismuth and thorium can be titrated in an acidicsolution (pH = 2) with xylenol orange or methylthymol blue as indicatorand most divalent cations do not interfere.A mixture of bismuth and lead ions can be successfully titrated by firsttitrating the bismuth at pH 2 with xylenol orange as indicator, and thenadding hexamine to raise the pH to about 5, and titrating the lead.
(b) Use of masking agents.
Masking may be defined as the process in which a substance, withoutphysical separation of it or its reaction products, is so transformed that it does not enter into a particular reaction. Demasking is the process inwhich the masked substance regains its ability to enter into a particular reaction. By the use of masking agents, some of the cations in a mixture can often be 'masked' so that they can no longer react with EDTA or with the indicator. An effective masking agent is thecyanide ion; this forms stablecyanide complexes with the cations of Cd, Zn, Hg(II), Cu, Co, Ni, Ag, and the platinum metals, but not with the alkaline earths, manganese, and lead

It is therefore possible to determine cations such as Ca2+, Mg2+, Pb2+, and Mn2+ in the presence of the above-mentioned metals by masking with an excess of potassium or sodium cyanide. A small amount of iron may be masked by cyanide if it is first reduced to the iron(II) state by the addition of ascorbic acid. Titanium(IV), iron(III), and aluminium can be masked with triethanolamine; mercury with iodide ions; and aluminium, iron(III), titanium(IV), and tin(II) with ammonium fluoride (the cations of the alkaline-earth metals yield slightly soluble fluorides). Sometimes the metal may be transformed into a different oxidation state: thus copper(II) may be reduced in acid solution by hydroxylamine or ascorbic acid. After rendering ammoniacal, nickel or cobalt can be titrated using, for example, murexide as indicator without interference from the copper, which is now present as Cu(I). Iron(III) can often be similarly masked by reduction with ascorbic acid.

(c) Selective demasking.
The cyanide complexes of zinc and cadmium may be demasked with formaldehyde-acetic acid solution or, better, with chloral hydrate : The use of masking and selective demasking agents permits the successive titration of many metals. Thus a solution containing Mg, Zn, and Cu can be titrated as follows:
1. Add excess of standard EDTA and back-titrate with standard Mg
solution using solochrome black as indicator. This gives the sum of al1
the metals present.
2. Treat an aliquot portion with excess of KCN (Poison !) and titrate as
before. This gives Mg only.
3. Add excess of chloral hydrate (or of formaldehyde-acetic acid solution,
to the titrated solution in order to liberate the Zn from the cyanide
complex, and titrate until the indicator turns blue. This gives the Zn only.
The Cu content may then be found by difference.

METAL ION INDICATORS
The success of an EDTA titration depends upon the precise determination of the end point. The most common procedure utilises metal ion indicators. The requisites of a metal ion indicator for
use in the visual detection of end points include :
(a) The colour reaction must be before the end point, when nearly all the metal ion is complexed with EDTA, the solution is strongly coloured.
(b) The colour reaction should be specific or selective.
(c) The metal-indicator complex must possess sufficient stability, otherwise, due to dissociation, a sharp colour change is not attained. The metal-indicator complex must, however, be less stable than the metal-EDTA complex to ensure that, at the end point, EDTA removes metal ions from the metal indicator-complex. The change in equilibrium from the metal indicator complex to the metal-EDTA complex should be sharp and rapid.
(d) The colour contrast between the free indicator and the metal-indicator complex should be readily observed.
(e) The indicator must be very sensitive to metal ions (i.e. to pM) so that the colour change occurs as near to equivalence point as possible.

(f) The above requirements must be fulfilled within the pH range at which the titration is performed.

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