potassium hydroxide solution with $0.5M$ hydrochloric acid using phenolphthalein indicator (record as titration a mL).

For the hydrolysis, accurately weigh approximately 2 g of the fat or oil into a 250 mL conical flask with a ground-glass joint and add 25 mL of the potassium hydroxide solution. Attach a reflux condenser and heat the flask contents on a steam bath for 1 h with occasional shaking. While the solution is still hot add phenolphthalein indicator and titrate the excess potassium hydroxide with the $0.5M$ hydrochloric acid (record as titration b mL).

$$\text{The saponification value} = \frac{(a-b)\times 0.5\times 56.1}{\text{Weight of sample (mg)}}$$

COMPLEXATION TITRATIONS

10.43 INTRODUCTION

The nature of complexes, their stabilities and the chemical characteristics of complexones have been dealt with in some detail in Sections 2.21 to 2.27. This particular section is concerned with the way in which complexation reactions can be employed in titrimetry, especially for determining the proportions of individual cations in mixtures.

The vast majority of complexation titrations are carried out using multidentate ligands such as EDTA or similar substances as the complexone. However, there are other more simple processes which also involve complexation using monodentate or bidentate ligands and which also serve to exemplify the nature of this type of titration. This is demonstrated in the determination outlined in Section 10.44.

10.44 A SIMPLE COMPLEXATION TITRATION

A simple example of the application of a complexation reaction to a titration procedure is the titration of cyanides with silver nitrate solution. When a solution of silver nitrate is added to a solution containing cyanide ions (e.g. an alkali cyanide) a white precipitate is formed when the two liquids first come into contact with one another, but on stirring it re-dissolves owing to the formation of a stable complex cyanide, the alkali salt of which is soluble:

$$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$$

When the above reaction is complete, further addition of silver nitrate solution yields the insoluble silver cyanoargentate (sometimes termed insoluble silver cyanide); the end point of the reaction is therefore indicated by the formation of a permanent precipitate or turbidity.

The only difficulty in obtaining a sharp end point lies in the fact that silver cyanide, precipitated by local excess concentration of silver ion somewhat prior to the equivalence point, is very slow to re-dissolve and the titration is time-consuming. In the Dénigès modification, iodide ion (usually as KI, *ca* $0.01M$) is used as the indicator and aqueous ammonia (*ca* $0.2M$) is introduced to dissolve the silver cyanide.

The iodide ion and ammonia solution are added before the titration is commenced; the formation of silver iodide (as a turbidity) will indicate the end point:

$$[Ag(NH_3)_2]^+ + I^- \rightleftharpoons AgI + 2NH_3$$

During the titration any silver iodide which would tend to form will be kept in solution by the excess of cyanide ion always present until the equivalence point is reached:

$$AgI + 2CN^- \rightleftharpoons [Ag(CN)_2]^- + I^-$$

The method may also be applied to the analysis of silver halides by dissolution in excess of cyanide solution and back-titration with standard silver nitrate. It can also be utilised indirectly for the determination of several metals, notably nickel, cobalt, and zinc, which form stable stoichiometric complexes with cyanide ion. Thus if a Ni(II) salt in ammoniacal solution is heated with excess of cyanide ion, the $[Ni(CN)_4]^{2-}$ ion is formed quantitatively; since it is more stable than the $[Ag(CN)_2]^-$ ion, the excess of cyanide may be determined by the Liebig–Denigès method. The metal ion determinations are, however, more conveniently made by titration with EDTA: see the following sections.

10.45 TITRATION CURVES

If, in the titration of a strong acid, pH is plotted against the volume of the solution of the strong base added, a point of inflexion occurs at the equivalence point (compare Section 10.12). Similarly, in the EDTA titration, if pM (negative logarithm of the 'free' metal ion concentration: $pM = -\log[M^{n+}]$) is plotted against the volume of EDTA solution added, a point of inflexion occurs at the equivalence point; in some instances this sudden increase may exceed 10 pM units. The general shape of titration curves obtained by titrating 10.0 mL of a 0.01*M* solution of a metal ion M with a 0.01*M* EDTA solution is shown in Fig. 10.11. The apparent stability constants (see Sections 2.21, 2.23 and 2.27) of various metal–EDTA complexes are indicated at the extreme right of the

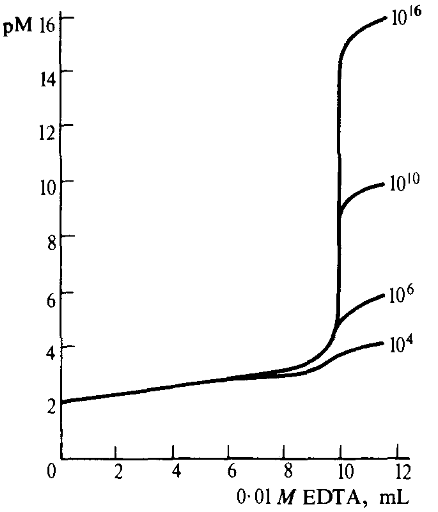

Fig. 10.11

curves. It is evident that the greater the stability constant, the sharper is the end point provided the pH is maintained constant.

In acid–base titrations the end point is generally detected by a pH-sensitive indicator. In the EDTA titration a metal ion-sensitive indicator (abbreviated, to **metal indicator** or **metal-ion indicator**) is often employed to detect changes of pM. Such indicators (which contain types of chelate groupings and generally possess resonance systems typical of dyestuffs) form complexes with specific metal ions, which differ in colour from the free indicator and produce a sudden colour change at the equivalence point. The end point of the titration can also be evaluated by other methods including potentiometric, amperometric, and spectrophotometric techniques.

10.46 TYPES OF EDTA TITRATIONS

The most important procedures for the titration of metal ions with EDTA are the following.

A. Direct titration. The solution containing the metal ion to be determined is buffered to the desired pH (e.g. to $\mathrm{pH} = 10$ with NH_4^+–aq. NH_3) and titrated directly with the standard EDTA solution. It may be necessary to prevent precipitation of the hydroxide of the metal (or a basic salt) by the addition of some auxiliary complexing agent, such as tartrate or citrate or triethanolamine. At the equivalence point the magnitude of the concentration of the metal ion being determined decreases abruptly. This is generally determined by the change in colour of a metal indicator or by amperometric, spectrophotometric, or potentiometric methods.

B. Back-titration. Many metals cannot, for various reasons, be titrated directly; thus they may precipitate from the solution in the pH range necessary for the titration, or they may form inert complexes, or a suitable metal indicator is not available. In such cases an excess of standard EDTA solution is added, the resulting solution is buffered to the desired pH, and the excess of the EDTA is back-titrated with a standard metal ion solution; a solution of zinc chloride or sulphate or of magnesium chloride or sulphate is often used for this purpose. The end point is detected with the aid of the metal indicator which responds to the zinc or magnesium ions introduced in the back-titration.

C. Replacement or substitution titration. Substitution titrations may be used for metal ions that do not react (or react unsatisfactorily) with a metal indicator, or for metal ions which form EDTA complexes that are more stable than those of other metals such as magnesium and calcium. The metal cation M^{n+} to be determined may be treated with the magnesium complex of EDTA, when the following reaction occurs:

$$M^{n+} + MgY^{2-} \rightleftharpoons (MY)^{(n-4)+} + Mg^{2+}$$

The amount of magnesium ion set free is equivalent to the cation present and can be titrated with a standard solution of EDTA and a suitable metal indicator.

An interesting application is the titration of calcium. In the direct titration of calcium ions, solochrome black gives a poor end point; if magnesium is present, it is displaced from its EDTA complex by calcium and an improved end point results (compare Section 10.51).

D. Alkalimetric titration. When a solution of disodium ethylenediaminetetraacetate, Na_2H_2Y, is added to a solution containing metallic ions, complexes are formed with the liberation of two equivalents of hydrogen ion:

$$M^{n+} + H_2Y^{2-} \rightleftharpoons (MY)^{(n-4)+} + 2H^+$$

The hydrogen ions thus set free can be titrated with a standard solution of sodium hydroxide using an acid–base indicator or a potentiometric end point; alternatively, an iodate–iodide mixture is added as well as the EDTA solution and the liberated iodine is titrated with a standard thiosulphate solution.

The solution of the metal to be determined must be accurately neutralised before titration; this is often a difficult matter on account of the hydrolysis of many salts, and constitutes a weak feature of alkalimetric titration.

E. Miscellaneous methods. Exchange reactions between the tetracyanonickelate(II) ion $[Ni(CN)_4]^{2-}$ (the potassium salt is readily prepared) and the element to be determined, whereby nickel ions are set free, have a limited application. Thus silver and gold, which themselves cannot be titrated complexometrically, can be determined in this way.

$$[Ni(CN)_4]^{2-} + 2Ag^+ \rightleftharpoons 2[Ag(CN)_2]^- + Ni^{2+}$$

These reactions take place with sparingly soluble silver salts, and hence provide a method for the determination of the halide ions Cl^-, Br^-, I^-, and the thiocyanate ion SCN^-. The anion is first precipitated as the silver salt, the latter dissolved in a solution of $[Ni(CN)_4]^{2-}$, and the equivalent amount of nickel thereby set free is determined by rapid titration with EDTA using an appropriate indicator (murexide, bromopyrogallol red).

Fluoride may be determined by precipitation as lead chlorofluoride, the precipitate being dissolved in dilute nitric acid and, after adjusting the pH to 5–6, the lead is titrated with EDTA using xylenol orange indicator.[10]

Sulphate may be determined by precipitation as barium sulphate or as lead sulphate. The precipitate is dissolved in an excess of standard EDTA solution, and the excess of EDTA is back-titrated with a standard magnesium or zinc solution using solochrome black as indicator.

Phosphate may be determined by precipitating as $Mg(NH_4)PO_4,6H_2O$, dissolving the precipitate in dilute hydrochloric acid, adding an excess of standard EDTA solution, buffering at pH = 10, and back-titrating with standard magnesium ion solution in the presence of solochrome black.

10.47 TITRATION OF MIXTURES, SELECTIVITY, MASKING AND DEMASKING AGENTS

EDTA is a very unselective reagent because it complexes with numerous doubly, triply and quadruply charged cations. When a solution containing two 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 is permissible, then the ratio of the stability constants of the EDTA complexes of the two metals M and N must be such that $K_M/K_N \geqq 10^6$ if N is not to interfere with the titration of M. Strictly, of course, the constants K_M and K_N 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 $K_M/K_N \geqq 10^8$.

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–EDTA complexes. Thus bismuth and thorium can be titrated in an acidic solution (pH = 2) with xylenol orange or methylthymol blue as indicator and most divalent cations do not interfere. A mixture of bismuth and lead ions can be successfully titrated by first titrating the bismuth at pH 2 with xylenol orange as indicator, and then adding hexamine to raise the pH to about 5, and titrating the lead (see Section 10.70).

(*b*) **Use of masking agents. Masking** may be defined as the process in which a substance, without physical separation of it or its reaction products, is so transformed that it does not enter into a particular reaction. **Demasking** is the process in which 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 the cyanide ion; this forms stable cyanide 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:

$$M^{2+} + 4CN^- \rightarrow [M(CN)_4]^{2-}$$

It is therefore possible to determine cations such as Ca^{2+}, Mg^{2+}, Pb^{2+}, and Mn^{2+} 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:

$$[Zn(CN)_4]^{2-} + 4H^+ + 4HCHO \rightarrow Zn^{2+} + 4HO{\cdot}CH_2{\cdot}CN$$

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 all the metals present.
2. Treat an aliquot portion with excess of KCN (**CARE!**)* and titrate as before. This gives Mg only.

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*Considerable care must be taken at all times when using potassium cyanide to avoid any form of physical contact and chemical antidotes must be kept permanently and easily available.

3. Add excess of chloral hydrate (or of formaldehyde–acetic acid solution, 3:1) 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.

(*d*) **Classical separation.** These may be applied if they are not tedious; thus the following precipitates may be used for separations in which, after being re-dissolved, the cations can be determined complexometrically: CaC_2O_4, nickel dimethylglyoximate, $Mg(NH_4)PO_4,6H_2O$, and CuSCN.

(*e*) **Solvent extraction.** This is occasionally of value. Thus zinc can be separated from copper and lead by adding excess of ammonium thiocyanate solution and extracting the resulting zinc thiocyanate with 4-methylpentan-2-one (isobutyl methyl ketone); the extract is diluted with water and the zinc content determined with EDTA solution.

(*f*) **Choice of indicators.** The indicator chosen should be one for which the formation of the metal–indicator complex is sufficiently rapid to permit establishment of the end point without undue waiting, and should preferably be reversible.

(*g*) **Removal of anions.** Anions, such as orthophosphate, which can interfere in complexometric titrations may be removed using ion exchange resins. For the use of ion exchange resins in the separation of cations and their subsequent EDTA titration, see Chapter 7.

(*h*) **'Kinetic masking'.** This is a special case in which a metal ion does not effectively enter into the complexation reaction because of its kinetic inertness (see Section 2.25). Thus the slow reaction of chromium(III) with EDTA makes it possible to titrate other metal ions which react rapidly, without interference from Cr(III); this is illustrated by the determination of iron(III) and chromium(III) in a mixture (Section 10.66).

10.48 METAL ION INDICATORS

General properties. 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 such that 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 at least selective.
(*c*) The metal–indicator complex must possess sufficient stability, otherwise, because of dissociation, a sharp colour change is not obtained. 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 such as to 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 the equivalence point as possible.

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

Dyestuffs which form complexes with specific metal cations can serve as indicators of pM values; 1:1-complexes (metal: dyestuff = 1:1) are common, but 1:2-complexes and 2:1-complexes also occur. The metal ion indicators, like EDTA itself, are chelating agents; this implies that the dyestuff molecule possesses several ligand atoms suitably disposed for coordination with a metal atom. They can, of course, equally take up protons, which also produces a colour change; metal ion indicators are therefore not only pM but also pH indicators.

Theory of the visual use of metal ion indicators. Discussion will be confined to the more common 1:1-complexes. The use of a metal ion indicator in an EDTA titration may be written as:

$$\text{M-In} + \text{EDTA} \rightarrow \text{M-EDTA} + \text{In}$$

This reaction will proceed if the metal–indicator complex M–In is less stable than the metal–EDTA complex M–EDTA. The former dissociates to a limited extent, and during the titration the free metal ions are progressively complexed by the EDTA until ultimately the metal is displaced from the complex M–In to leave the free indicator (In). The stability of the metal–indicator complex may be expressed in terms of the formation constant (or indicator constant) K_{In}:

$$K_{\text{In}} = [\text{M-In}]/[\text{M}][\text{In}]$$

The indicator colour change is affected by the hydrogen ion concentration of the solution, and no account of this has been taken in the above expression for the formation constant. Thus solochrome black, which may be written as H_2In^-, exhibits the following acid–base behaviour:

$$\underset{\text{Red}}{H_2In^-} \xrightleftharpoons[5.3-7.3]{\text{pH}} \underset{\text{Blue}}{HIn^{2-}} \xrightleftharpoons[10.5-12.5]{\text{pH}} \underset{\text{Yellow-orange}}{In^{3-}}$$

In the pH range 7–11, in which the dye itself exhibits a blue colour, many metal ions form red complexes; these colours are extremely sensitive, as is shown, for example, by the fact that $10^{-6} - 10^{-7}$ molar solutions of magnesium ion give a distinct red colour with the indicator. From the practical viewpoint, it is more convenient to define the apparent indicator constant K'_{In}, which varies with pH, as:

$$K'_{\text{In}} = [\text{MIn}^-]/[\text{M}^{n+}][\text{In}]$$

where

$[\text{MIn}^-]$ = concentration of metal–indicator complex,
$[\text{M}^{n+}]$ = concentration of metallic ion, and
$[\text{In}]$ = concentration of indicator not complexed with metallic ion.

(This, for the above indicator, is equal to $[H_2In^-] + [HIn^{2-}] + [In^{3-}]$.)
The equation may be expressed as:

$$\log K'_{\text{In}} = \text{pM} + \log[\text{MIn}^-]/[\text{In}];$$

log K'_{In} gives the value of pM when half the total indicator is present as the metal ion complex. Some values for log K'_{In} for CaIn^- and MgIn^- respectively (where H_2In^- is the anion of solochrome black) are: 0.8 and 2.4 at $\text{pH} = 7$; 1.9 and 3.4 at $\text{pH} = 8$; 2.8 and 4.4 at $\text{pH} = 9$; 3.8 and 5.4 at $\text{pH} = 10$; 4.7 and 6.3 at $\text{pH} = 11$; 5.3 and 6.8 at $\text{pH} = 12$. For a small titration error K'_{In} should be large ($> 10^4$), the ratio of the apparent stability constant of the metal–EDTA complex K'_{MY} to that of the metal-indicator complex K'_{In} should be large ($> 10^4$), and the ratio of the indicator concentration to the metal ion concentration should be small ($< 10^{-2}$).

The visual metallochromic indicators discussed above form by far the most important group of indicators for EDTA titrations and the operations subsequently described will be confined to the use of indicators of this type; nevertheless there are certain other substances which can be used as indicators.[11]

Some examples of metal ion indicators. Numerous compounds have been proposed for use as pM indicators; a selected few of these will be described. Where applicable, *Colour Index* (C.I.) references are given.[12] It has been pointed out by West,[11] that apart from a few miscellaneous compounds, the important visual metallochromic indicators fall into three main groups: (*a*) hydroxyazo compounds; (*b*) phenolic compounds and hydroxy-substituted triphenylmethane compounds; (*c*) compounds containing an aminomethyldicarboxymethyl group: many of these are also triphenylmethane compounds.

Note. In view of the varying stability of solutions of these indicators, and the possible variation in sharpness of the end point with the age of the solution, it is generally advisable (if the stability of the indicator solution is suspect), to dilute the solid indicator with 100–200 parts of potassium (or sodium) chloride, nitrate or sulphate (potassium nitrate is usually preferred) and grind the mixture well in a glass mortar. The resultant mixture is usually stable indefinitely if kept dry and in a tightly stoppered bottle.

Murexide (C.I. 56085). This is the ammonium salt of purpuric acid, and is of interest because it was probably the first metal-ion indicator to be employed in the EDTA titration. Murexide solutions are reddish violet up to $\text{pH} = 9$ (H_4D^-), violet from pH 9 to pH 11 (H_3D^{2-}), and blue–violet (or blue) above pH 11 (H_2D^{3-}). These colour changes are due to the progressive displacement of protons from imido groups; since there are four such groups, murexide may be represented as H_4D^-. Only two of these four acidic hydrogens can be removed by adding an alkali hydroxide, so that only two pK values need be considered; these are $\text{p}K_4 = 9.2$ ($\text{H}_2\text{D}^- \rightarrow \text{H}_3\text{D}^{2-}$) and $\text{p}K_3 = 10.5$ ($\text{H}_3\text{D}^{2-} \rightarrow \text{H}_2\text{D}^{3-}$). The anion H_4D^- can also take up a proton to yield the yellow and unstable purpuric acid, but this requires a pH of about 0.

Murexide forms complexes with many metal ions: only those with Cu, Ni, Co, Ca and the lanthanides are sufficiently stable to find application in analysis. Their colours in alkaline solution are orange (copper), yellow (nickel and cobalt), and red (calcium); the colours vary somewhat with the pH of the solution.

Murexide may be employed for the direct EDTA titration of calcium at $\text{pH} = 11$; the colour change at the end-point is from red to blue–violet, but is far from ideal. The colour change in the direct titration of nickel at pH 10–11 is from yellow to blue–violet.

Aqueous solutions of murexide are unstable and must be prepared each day. The indicator solution may be prepared by suspending 0.5 g of the powdered dyestuff in water, shaking thoroughly, and allowing the undissolved portion to settle. The saturated supernatant liquid is used for titrations. Every day the old supernatant liquid is decanted and the residue treated with water as before to provide a fresh solution of the indicator. Normally it is better to prepare a mixture of the indicator with pure sodium chloride in the ratio 1:500, and employ 0.2–0.4 g in each titration.

Solochrome black (eriochrome black T). This substance is sodium 1-(1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulphonate, and has the *Colour Index* reference C.I. 14645. In strongly acidic solutions the dye tends to polymerise to a red–brown product, and consequently the indicator is rarely applied in titrations of solutions more acidic than pH = 6.5.

The sulphonic acid group gives up its proton long before the pH range of 7–12, which is of immediate interest for metal-ion indicator use. Only the dissociation of the two hydrogen atoms of the phenolic groups need therefore be considered, and so the dyestuff may be represented by the formula H_2D^-. The two p*K* values for these hydrogen atoms are 6.3 and 11.5 respectively. Below pH = 5.5, the solution of solochrome black is red (due to H_2D^-), between pH 7 and 11 it is blue (due to HD^{2-}), and above pH = 11.5 it is yellowish–orange (due to D^{3-}). In the pH range 7–11 the addition of metallic salts produces a brilliant change in colour from blue to red:

$$M^{2+} + HD^{2-} \text{ (blue)} \rightarrow MD^- \text{ (red)} + H^+$$

This colour change can be observed with the ions of Mg, Mn, Zn, Cd, Hg, Pb, Cu, Al, Fe, Ti, Co, Ni, and the Pt metals. To maintain the pH constant (*ca* 10) a buffer mixture is added, and most of the above metals must be kept in solution with the aid of a weak complexing reagent such as ammonia or tartrate. The cations of Cu, Co, Ni, Al, Fe(III), Ti(IV), and certain of the Pt metals form such stable indicator complexes that the dyestuff can no longer be liberated by adding EDTA: direct titration of these ions using solochrome black as indicator is therefore impracticable, and the metallic ions are said to 'block' the indicator. However, with Cu, Co, Ni, and Al a back-titration can be carried out, for the rate of reaction of their EDTA complexes with the indicator is extremely slow and it is possible to titrate the excess of EDTA with standard zinc or magnesium ion solution.

Cu, Ni, Co, Cr, Fe, or Al, even in traces, must be absent when conducting a direct titration of the other metals listed above; if the metal ion to be titrated does not react with the cyanide ion or with triethanolamine, these substances can be used as masking reagents. It has been stated that the addition of 0.5–1 mL of 0.001*M* *o*-phenanthroline prior to the EDTA titration eliminates the 'blocking effect' of these metals with solochrome black and also with xylenol orange (see below).

The indicator solution is prepared by dissolving 0.2 g of the dyestuff in 15 mL of triethanolamine with the addition of 5 mL of absolute ethanol to reduce the viscosity; the reagent is stable for several months. A 0.4 per cent solution of the pure dyestuff in methanol remains serviceable for at least a month.

Patton and Reeder's indicator. The indicator is 2-hydroxy-1-(2-hydroxy-4-sulpho-1-naphthylazo)-3-naphthoic acid; the name may be abbreviated to HHSNNA. Its main use is in the direct titration of calcium, particularly in the presence of magnesium. A sharp colour change from wine red to pure blue is obtained when calcium ions are titrated with EDTA at pH values between 12 and 14. Interferences are similar to those observed with solochrome black, and can be obviated similarly. This indicator may be used as an alternative to murexide for the determination of calcium.

The dyestuff is thoroughly mixed with 100 times its weight of sodium sulphate, and 1 g of the mixture is used in each titration. The indicator is not very stable in alkaline solution.

Solochrome dark blue or calcon (C.I. 15705). This is sometimes referred to as eriochrome blue black RC; it is in fact sodium 1-(2-hydroxy-1-naphthylazo)-2-naphthol-4-sulphonate. The dyestuff has two ionisable phenolic hydrogen atoms; the protons ionise stepwise with pK values of 7.4 and 13.5 respectively. An important application of the indicator is in the complexometric titration of calcium in the presence of magnesium; this must be carried out at a pH of about 12.3 (obtained, for example, with a diethylamine buffer: 5 mL for every 100 mL of solution) in order to avoid the interference of magnesium. Under these conditions magnesium is precipitated quantitatively as the hydroxide. The colour change is from pink to pure blue.

The indicator solution is prepared by dissolving 0.2 g of the dyestuff in 50 mL of methanol.

Calmagite. This indicator, 1-(1-hydroxyl-4-methyl-2-phenylazo)-2-naphthol-4-sulphonic acid, has the same colour change as solochrome black, but the colour change is somewhat clearer and sharper. An important advantage is that aqueous solutions of the indicator are stable almost indefinitely. It may be substituted for solochrome black without change in the experimental procedures for the titration of calcium plus magnesium (see Sections 10.54 and 10.62).

Calmagite functions as an acid–base indicator:

$$\underset{\text{Bright red}}{H_3D} \xrightleftharpoons{\text{low pH}} \underset{\text{Bright red}}{H_2D^-} \xrightleftharpoons{\text{pH 7.1–9.1}} \underset{\text{Clear blue}}{HD^{2-}} \xrightleftharpoons{\text{pH 11.4–13.3}} \underset{\text{Reddish-orange}}{D^{3-}}$$

The hydrogen of the sulphonic acid group plays no part in the functioning of the dye as a metal ion indicator. The acid properties of the hydroxyl groups are expressed by $pK_1 = 8.14$ and $pK_2 = 12.35$. The blue colour of calmagite at pH = 10 is changed to red by the addition of magnesium ions, the change being reversible:

$$\underset{\text{Clear blue}}{HD^{2-}} \xrightleftharpoons{Mg^{2+}} \underset{\text{Red}}{MgD^{2-}}$$

This is the basis of the indicator action in the EDTA titration. The pH of 10 is attained by the use of an aqueous ammonia–ammonium chloride buffer mixture.

The combining ratio between calcium or magnesium and the indicator is 1:1; the magnesium compound is the more stable. Calmagite is similar to solochrome black in that small amounts of copper, iron, and aluminium interfere seriously in the titration of calcium and magnesium, and similar masking agents may be used. Potassium hydroxide should be employed for the neutralisation of large amounts of acid since sodium ions in high concentration cause difficulty.

The indicator solution is prepared by dissolving 0.05 g of calmagite in 100 mL of water. It is stable for at least 12 months when stored in a polythene bottle out of sunlight.

Calcichrome. This indicator, cyclotris-7-(1-azo-8-hydroxynaphthalene-3,6-disulphonic acid), is very selective for calcium. It is in fact not very suitable as an indicator for EDTA titrations because the colour change is not particularly sharp, but if EDTA is replaced by CDTA (see Section 2.26), then the indicator gives good results for calcium in the presence of large amounts of barium and small amounts of strontium.[13]

Fast sulphon black F (C.I. 26990). This dyestuff is the sodium salt of 1-hydroxy-8-(2-hydroxynaphthylazo)-2-(sulphonaphthylazo)-3,6-disulphonic acid. The colour reaction seems virtually specific for copper ions. In ammoniacal solution it forms complexes with only copper and nickel; the presence of ammonia or pyridine is required for colour formation. In the direct titration of copper in ammoniacal solution the colour change at the end point is from magenta or [depending upon the concentration of copper(II) ions] pale blue to bright green. The indicator action with nickel is poor. Metal ions, such as those of Cd, Pb, Ni, Zn, Ca, and Ba, may be titrated using this indicator by the prior addition of a reasonable excess of standard copper(II) solution.

The indicator solution consists of a 0.5 per cent aqueous solution.

Bromopyrogallol red. This metal ion indicator is dibromopyrogallol sulphonphthalein and is resistant to oxidation; it also possesses acid–base indicator properties. The indicator is coloured orange–yellow in strongly acidic solution, claret red in nearly neutral solution, and violet to blue in basic solution. The dyestuff forms coloured complexes with many cations. It is valuable for the determination, for example, of bismuth ($pH = 2-3$. nitric acid solution; end-point blue to claret red).

The indicator solution is prepared by dissolving 0.05 g of the solid reagent in 100 mL of 50 per cent ethanol.

Xylenol orange. This indicator is 3,3′-bis[*N*,*N*-di(carboxymethyl)aminomethyl]-*o*-cresolsulphonphthalein; it retains the acid–base properties of cresol red and displays metal indicator properties even in acid solution ($pH = 3-5$). Acidic solutions of the indicator are coloured lemon-yellow and those of the metal complexes intensely red.

Direct EDTA titrations of Bi, Th, Zn, Cd, Pb, Co, etc., are readily carried out and the colour change is sharp. Iron(III) and, to a lesser extent, aluminium interfere. By appropriate pH adjustment certain pairs of metals may be titrated successfully in a single sample solution. Thus bismuth may be titrated at $pH = 1-2$, and zinc or lead after adjustment to $pH = 5$ by addition of hexamine.

The indicator solution is prepared by dissolving 0.5 g of xylenol orange in 100 mL of water. For storage it is best kept as a solid mixture with potassium nitrate (page 316).

Thymolphthalein complexone (thymolphthalexone). This is thymolphthalein di(methyliminediacetic acid); it contains a stable lactone ring and reacts only in an alkaline medium. The indicator may be used for the titration of calcium; the colour change is from blue to colourless (or a slight pink). Manganese and also nickel may be determined by adding an excess of standard EDTA solution, and titrating the excess with standard calcium chloride solution; the colour change is from very pale blue to deep blue.

The indicator solution consists of a 0.5 per cent solution in ethanol. Alternatively, a finely ground mixture (1:100) with potassium nitrate may be used.

Methylthymol blue (methylthymol blue complexone). This compound is very similar in structure to the preceding one from which it is derived by replacement of the lactone grouping by a sulphonic acid group. By contrast, however, it will function in both acidic and alkaline media, ranging from pH = 0, under which condition bismuth may be titrated with a colour change from blue to yellow, to pH = 12; where the alkaline earths may be titrated with a colour change from blue to colourless. At intermediate pH values a wide variety of doubly charged metal ions may be titrated; of particular interest is its use as an indicator for the titration of Hg(II), an ion for which very few indicators are available. It is also suitable for determining calcium in the presence of magnesium provided that the proportion of the latter is not too high, and is therefore of value in determining the hardness of water. The indicator does not keep well in solution and is used as a solid mixture: 1 part to 100 of potassium nitrate.

Zincon. This is 1-(2-hydroxy-5-sulphophenyl)-3-phenyl-5-(2-carboxyphenyl) formazan, which is a specific indicator for zinc at pH 9–10. Its most important use, however, is as indicator for titration of calcium in the presence of magnesium, using the complexone EGTA (Section 2.26); the magnesium–EGTA complex is relatively weak and does not interfere with the calcium titration. Calcium and magnesium do not give coloured complexes with the indicator, and the procedure is to add a little of the zinc complex of EGTA. The titration is carried out in a buffer at pH 10, and under these conditions calcium ions decompose the Zn–EGTA complex, liberating zinc ions which give a blue colour with the indicator. As soon as all the calcium has been titrated, excess EGTA reconverts the zinc ions to the EGTA complex, and the solution acquires the orange colour of the metal-free indicator.

Variamine blue (C.I. 37255). The end point in an EDTA titration may sometimes be detected by changes in redox potential, and hence by the use of appropriate redox indicators. An excellent example is variamine blue (4-methoxy-4′-aminodiphenylamine), which may be employed in the complexometric titration of iron(III). When a mixture of iron(II) and (III) is titrated with EDTA the latter disappears first. As soon as an amount of the complexing agent equivalent to the concentration of iron(III) has been added, pFe(III) increases abruptly and consequently there is a sudden decrease in the redox potential (compare Section 2.33); the end point can therefore be detected either potentiometrically or with a redox indicator (10.91). The stability constant of the iron(III) complex FeY^- (EDTA = Na_2H_2Y) is about 10^{25} and that of the iron(II) complex FeY^{2-} is 10^{14}; approximate calculations show that the change of redox potential is about 600 millivolts at pH = 2 and that this will be almost independent of the concentration of iron(II) present. The jump in redox potential will also be obtained if no iron(II) salt is actually added, since the extremely minute amount of iron(II) necessary is always present in any 'pure' iron(III) salt.

The visual detection of the sharp change in redox potential in the titration of an iron(III) salt with EDTA is readily made with variamine blue as indicator.

The almost colourless leuco form of the base passes upon oxidation into the strongly coloured indamine. When titrating iron(III) at a pH of about 3 and the colourless hydrochloride of the leuco base is added, oxidation to the violet–blue indamine occurs with the formation of an equivalent amount of iron(II). At the end point of the EDTA titration, the small amount of iron(II) formed when the indicator was introduced is also transformed into the Fe(III)–EDTA complex FeY^-, whereupon the blue indamine is reduced back to the leuco base.

The indicator solution is a 1 per cent solution of the base in water.

10.49 STANDARD EDTA SOLUTIONS

Disodium dihydrogenethylenediaminetetra-acetate of analytical reagent quality is available commercially but this may contain a trace of moisture. After drying the reagent at 80 °C its composition agrees with the formula $Na_2H_2C_{10}H_{12}O_8N_2,2H_2O$ (relative molar mass 372.24), but it should not be used as a primary standard. If necessary, the commercial material may be purified by preparing a saturated solution at room temperature: this requires about 20 g of the salt per 200 mL of water. Add ethanol slowly until a permanent precipitate appears; filter. Dilute the filtrate with an equal volume of ethanol, filter the resulting precipitate through a sintered glass funnel, wash with acetone and then with diethyl ether. Air-dry at room temperature overnight and then dry in an oven at 80 °C for at least 24 hours.

Solutions of EDTA of the following concentrations are suitable for most experimental work: $0.1M$, $0.05M$, and $0.01M$. These contain respectively 37.224 g, 18.612 g, and 3.7224 g of the dihydrate per litre of solution. As already indicated, the dry analytical grade salt cannot be regarded as a primary standard and the solution must be standardised; this can be done by titration of nearly neutralised zinc chloride or zinc sulphate solution prepared from a known weight of zinc pellets, or by titration with a solution made from specially dried lead nitrate.

The water employed in making up solutions, particularly dilute solutions, of EDTA should contain no traces of multicharged ions. The distilled water normally used in the laboratory may require distillation in an all-Pyrex glass apparatus or, better, passage through a column of cation exchange resin in the sodium form — the latter procedure will remove all traces of heavy metals. De-ionised water is also satisfactory; it should be prepared from distilled water since tap water sometimes contains non-ionic impurities not removed by an ion exchange column. The solution may be kept in Pyrex (or similar borosilicate glass) vessels, which have been thoroughly steamed out before use. For prolonged storage in borosilicate vessels, the latter should be boiled with a strongly alkaline, 2 per cent EDTA solution for several hours and then repeatedly rinsed with de-ionised water. Polythene bottles are the most satisfactory, and should always be employed for the storage of very dilute (e.g. $0.001M$) solutions of EDTA. Vessels of ordinary (soda) glass should not be used; in the course of time such soft glass containers will yield appreciable amounts of cations (including calcium and magnesium) and anions to solutions of EDTA.

Water purified or prepared as described above should be used for the preparation of *all* solutions required for EDTA or similar titrations.

10.50 SOME PRACTICAL CONSIDERATIONS

The following points should be borne in mind when carrying out complexometric titrations.

A. Adjustment of pH. **For many EDTA titrations the pH of the solution is extremely critical**; often limits of ±1 unit of pH, and frequently limits of ±0.5 unit of pH must be achieved for a successful titration to be carried out. To achieve such narrow limits of control it is necessary to make use of a pH meter while adjusting the pH value of the solution, and even for those cases where the latitude is such that a pH test-paper can be used to control the adjustment of pH, only a paper of the narrow range variety should be used.

In some of the details which follow, reference is made to the addition of a buffer solution, and in all such cases, to ensure that the requisite buffering action is in fact achieved, it is necessary to make certain that the original solution has first been made almost neutral by the cautious addition of sodium hydroxide or ammonium hydroxide, or of dilute acid, before adding the buffer solution. When an acid solution containing a metallic ion is neutralised by the addition of alkali care must be taken to ensure that the metal hydroxide is not precipitated.

B. Concentration of the metal ion to be titrated. Most titrations are successful with 0.25 millimole of the metal ion concerned in a volume of 50–150 mL of solution. If the metal ion concentration is too high, then the end point may be very difficult to discern, and if difficulty is experienced with an end point then it is advisable to start with a smaller portion of the test solution, and to dilute this to 100–150 mL before adding the buffering medium and the indicator, and then repeating the titration.

C. Amount of indicator. The addition of too much indicator is a fault which must be guarded against: in many cases the colour due to the indicator intensifies considerably during the course of the titration, and further, many indicators exhibit dichroism, i.e. there is an intermediate colour change one to two drops before the real end-point. Thus, for example, in the titration of lead using xylenol orange as indicator at $\mathrm{pH} = 6$, the initial reddish-purple colour becomes orange-red, and then with the addition of one or two further drops of reagent, the solution acquires the final lemon yellow colour. This **end point anticipation**, which is of great practical value, may be virtually lost if too much of the indicator is added so that the colour is too intense. In general, a satisfactory colour is achieved by the use of 30–50 mg of a 1 per cent solid mixture of the indicator in potassium nitrate.

D. Attainment of the end point. In many EDTA titrations the colour change in the neighbourhood of the end point may be slow. In such cases, cautious addition of the titrant coupled with continuous stirring of the solution is advisable; the use of a magnetic stirrer is recommended. Frequently, a sharper end point may be achieved if the solution is warmed to about 40 °C. Titrations with CDTA (see Section 2.26) are always slower in the region of the end point than the corresponding EDTA titrations.

E. Detection of the colour change. With all of the metal ion indicators used in complexometric titrations, detection of the end point of the titration is dependent upon the recognition of a specified change in colour; for many observers this can be a difficult task, and for those affected by colour blindness it may be