Titrimetric Analysis: *Methods*

Titrimetric methods of analysis are capable of rapid and convenient analyte determinations with high accuracy and precision. Titrimetric analysis is based on the complete reaction between the analyte and a reagent, the *titrant*:

$$aA + tT \rightarrow \text{products}$$

where A and T represent the analyte and titrant, respectively, and a and t are the stoichiometric coefficients. Titrations are often classified by the nature of this titration reaction: acid-base, redox, precipitation and complexation reactions are the most common reaction types.

For volumetric titrations, the amount, n_A, of analyte in the sample can be calculated using

$$n_A = \frac{a}{t} C_T V_T$$

where C_T is the concentration of the titrant, and V_T is the volume of titrant needed to reach the endpoint. Thus, quantitative determination of the analyte concentration requires the following:

1. There is a stoichiometric reaction between analyte and titrant. This reaction should be fast and complete, and the values of a and t must be known.
2. The concentration of the titrant solution, C_T, must be known accurately. The titrant solution must be *standardized* either by preparing it using a primary standard or, more commonly, titrating it against a solution prepared with a primary standard.
3. The endpoint volume must be measured accurately using an appropriate chemical indicator or instrumental method. If an instrumental method is used to follow the progress of the titration reaction, a titration curve may be generated, which allows for the analysis of mixtures and/or the detection of interferences.

In this document, we will examine some of the specifics of titrimetric analysis: the most common titrants and the types of analytes they react with, methods of titrant standardization, the stability of titrant solutions, methods of endpoint detection, and any other details that might be important. Finally, a few important examples of the application of titrimetric analysis will be given. These applications will be taken from the field of water and wastewater analysis.

Much of the material in this handout was taken from the following references:

- GH Jeffery, J Bassett, J Mendham, RC Denney, *Vogel's Textbook of Quantitative Chemical Analysis*, 5th edition
- HA Laitinen, WE Harris, *Chemical Analysis*, 2nd edition
- *Standard Methods for the Examination of Water and Wastewater*, edited by AD Eaton, LS Clesceri, AE Greenber, 19th edition

The relevant chapters in your textbook are:

- Harris chapters 7, 12, 13, 16

Titrimetry Methods
Acid-Base Titrations

Aqueous Acid-Base Titrations

General

Proton transfer reactions in aqueous solutions are quite fast. Aqueous acid-base titrations are thus suitable for the analysis of any Bronsted acid or base. Practically, the pK_a or pK_b of the analyte should be less than about 10 (i.e., pK_a or pK_b < 10) for a complete reaction between analyte and titrant.

Common Titrants

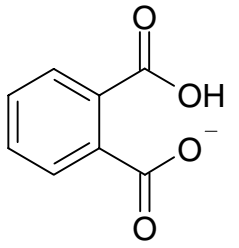
In order for the titration reaction to go to completion, a strong acid or a strong base is the usual choice for a titrant in acid-base titrations. The levelling effect in aqueous solutions should be kept in mind, however: the strongest acid that can exist at a substantial concentration is the hydronium ion, H_3O^+, since any strong acid HA will react completely with water:

$$HA + H_2O \rightarrow A^- + H_3O^+$$

Thus, titrating with any strong acid is equivalent to titrating the analyte with hydronium ion. Similarly, the strongest base that can exist in water is the hydroxide ion, OH^-.

For the analysis of bases, the most common aqueous titrant is HCl; sometimes H_2SO_4 or $HClO_4$ are also used. Any of these may be standardized by tris(hyddroxymethyl)aminomethane, $(HOCH_2)_3CNH_2$, which is sometimes referred to simply as **tris**. Sodium carbonate, Na_2CO_3, can also serve as a primary standard, but it is less desirable than tris due to its lower equivalent weight. Titrations of bases are sometimes called ***alkalimetric titrations***.

For the analysis of acids, NaOH is usually used; KOH or $Ba(OH)_2$ may also be used. Any of these may be standardized against potassium hydrogen phthalate (KHP). The hydrogen phthalate anion is shown below.



Titrations of acids are sometimes called ***acidimetric titrations***.

Any alkaline solution will absorb substantial amounts of carbon dioxide from the atmosphere, resulting in the following net reaction:

$$CO_2 + 2OH^- \rightleftharpoons CO_3^{2-} + 2H_2O$$

Exposure of aqueous NaOH or KOH titrant to the atmosphere results in *carbonate error*. Solid hydroxide salts may also contain significant amounts of carbonate impurities due to absorption of atmospheric CO_2. A NaOH titrant solution is best prepared by dilution from a concentrated (approximately 50 $^{w}/_{w}\%$) solution. Sodium carbonate is insoluble in this solution. The diluted titrant solutions are sometimes boiled to drive dissolved CO_2 out of the solution and then protected from exposure to air. The absorption process is fairly slow, occurring over a period of hours and days. Ideally, acidimetric titrations should be performed with a freshly prepared and standardized solution of NaOH.

Nonaqueous Acid-Base Titrations

General

Sometimes acid-base titrations are performed using a solvent other than water. There are several reasons why nonaqueous acid-base titrations may be used instead of aqueous titrations:

1. The sample is insoluble in water.
2. Sample and/or titrant reacts with water in undesirable ways.
3. For the analysis of very weak acids or bases. As mentioned previously, an aqueous acidimetric titration is limited to bases with pK_b less than about 10. Otherwise, the reaction between titrant (i.e., H_3O^+) and analyte will be incomplete. One solution to this problem for weak bases would be to use a stronger titrant – an impossibility in aqueous solutions. However, using glacial acetic acid as the solvent would solve that problem, since the strongest possible acid is H_2OAc^+ (a strong acid indeed). Most strong acids do not completely dissociate in acetic acid. Thus, perchloric acid in acetic acid is a much stronger titrant than the same acid in water. Similar considerations apply to alkalimetric titrations.
4. Selectivity is sometimes enhanced in nonaqueous solutions (analysis of analytes with similar dissociation constants). In aqueous solutions, a difference of 2 pK units is necessary to observe distinct endpoints. However, careful choice of solvent can sometimes allow the observation of distinct endpoints that cannot be measured in aqueous solution.

Common Titrants for Nonaqueous Acid-Base Titrations

Alkalimetry in Nonaqueous Solutions

- HCl in isopropanol
- $HClO_4$ in glacial acetic acid
- these titrants may be standardized by tris, just as in aqueous titrations

Acidimetry in Nonaqueous Solutions

- KOH in ethanol, methanol, or isopropanol
- sodium methylate, $NaOCH_3$, in methanol or chlorobenzene

• nonaqueous alkalimetric titrants may usually be standardized by benzoic acid, which is soluble in most of the solvents commonly used

Instrumental Endpoint Detection in Acid-Base Titrations

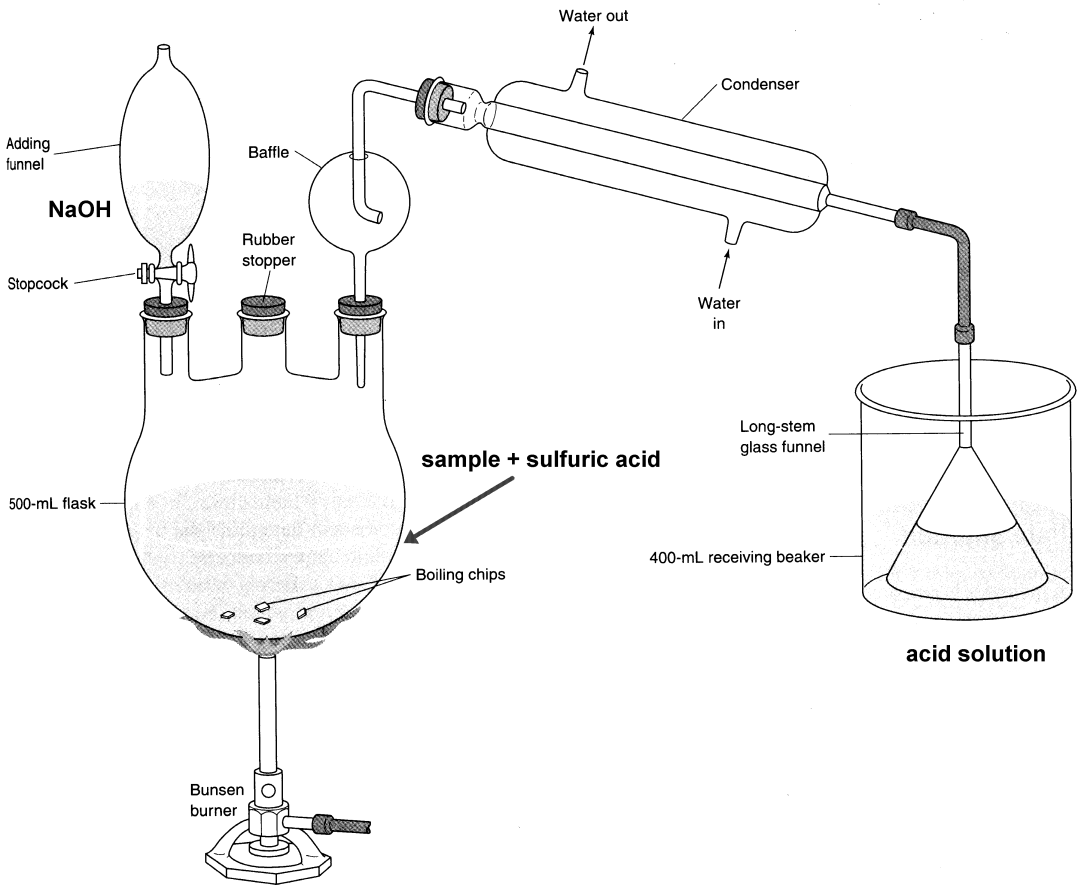
Potentiometric endpoint detection using a pH meter is the universal instrumental method used for acid-base titrations, both in aqueous and nonaqueous solvents. Special care of the pH electrode is necessary for nonaqueous titrations – in particular, the electrode must not be allowed to become dehydrated.

Example Applications of Acid-Base Titrations

KJeldahl Analysis of Organic Nitrogen

The Kjeldahl procedure is a method for the analysis of organic nitrogen in the –3 oxidation state. The sample is digested with sulfuric acid to convert the organic nitrogen to ammonium, NH_4^+. The digested sample is then basified and ammonia is then distilled into acid. The ammonia may be distilled into excess standard HCl; the amount of HCl remaining after the distillation is determined by alkalimetric titration. Alternately, ammonia may be distilled into excess boric acid, H_3BO_3; the dihydrogen borate, $H_2BO_3^-$, formed by reaction with ammonia is determined by acidimetric titration.

The following figure shows apparatus that can be used for Kjeldahl analysis.



Kjeldahl analysis is often used in the analysis of surface water and wastewater. The ***total Kjeldahl nitrogen*** (TKN) content of a water sample is a measure of the total concentration of nitrogen in the –3 oxidation state in the sample: ammonia/ammonium plus organic nitrogen. Kjeldahl analysis is also widely used to determine the protein content of food samples.

Buffering of Natural Waters

The ability of an aqueous solution to resist changes in pH upon the addition of acid or base is termed the *buffering capability* of the solution. The ability of a natural water body to resist a decrease in pH is very important due to the ubiquitous presence of acid rain. The ***alkalinity*** of a water body is defined as the number of moles of H^+ needed to bring a 1L sample to pH = 4.5. The higher the *acid neutralizing capacity* (ANC) of the water, the more acid must be added to the 1L sample to bring the pH to 4.5.

Acidimetric titration to pH=4.5 (rather than to an endpoint) is thus widely used to characterize the ability of a water body to resist acidification. If potentiometric detection is not used, bromcresol green (perhaps mixed with methyl red) is used as a chemical indicator; the color change signifies the end of the titration.

Titrimetry Methods
Precipitation Titrations

Precipitation reactions in aqueous solution range from rapid to slow, depending on the identity of the precipitant. Many precipitations are sufficiently rapid and complete to form the basis of quantitation by titration. Precipitation titrimetry has several advantages over precipitation gravimetry, including speed, sensitivity, and convenience.

Common Titrants

Argentometric Titrations

Most precipitation reactions involve the silver cation, Ag^+. Silver precipitations are rapid and quantitative, and silver nitrate, $AgNO_3$, is used for the direct titration of a number of anions that precipitate silver: all the halides except $F^–$; $SCN^–$, $CNO^–$, $AsO_4^{3–}$, $PO_4^{3–}$, $CN^–$, $C_2O_4^{2–}$, $CO_3^{2–}$, $S^{2–}$, $CrO_4^{2–}$. See table 7-1 on page 167 in Harris for more detail. Titrations using $AgNO_3$ as titrant are termed ***argentometric titrations***.

Sodium chloride is suitable as a primary standard, and is most often used for standardization of the titrant in argentometric titrations. Solid silver nitrate is also available in high enough purity to serve as a primary standard, but it is more expensive.

Silver nitrate solutions are stable in the dark, and amber bottles are used for storage. Exposure to light can cause photoreduction of the silver cations, particular in the presence of trace impurities that may catalyze the reaction.

Sulfate Analysis

The sulfate content of an aqueous solution may be determined by titration with aqueous barium chloride, $BaCl_2$. The titrant is usually standardized using sodium sulfate.

Fluoride Analysis

Fluoride cannot be analyzed by argentometric titration (AgF is soluble); instead, the sample may be titrated with lanthanum nitrate, $La(NO_3)_3$, or lead nitrate, $Pb(NO_3)_2$, since both LaF_3 (pK_{sp} = 16.2) and PbF_2 (pK_{sp} = 7.57) are insoluble. Sodium fluoride is a suitable primary standard.

Endpoint Detection

A variety of chemical indicators are used to indicate the endpoint of argentometric titrations: the Fajans, Volhard, and Mohr methods are discussed in some detail in the lab handout *Titrimetric Analysis of Chloride*, and in your textbook (Harris chapter 7).

A silver wire or ring is a sufficient indicator electrode for potentiometric titrations using $AgNO_3$, while a fluoride ISE is suitable for potentiometric endpoint detection for fluoride analysis using La^{3+} or Pb^{2+} titrant solutions.

Example Application: Analysis of Chloride in Surface Waters

Chloride is frequently a major anion in surface and groundwater; certainly is a major constituent of seawater. Although chloride in freshwater is usually of geological origin, runoff from roads salted during the winter may significantly increase the chloride content of surrounding streams, rivers and lakes. A high chloride concentration may impart a noticeably salty taste to potable water, and can also damage metallic pipes and growing plants.

Argentometric titration of water samples is a standard method for chloride determination; concentrations in the low ppm range may be detected using potentiometric titration.

Titrimetry Methods
Redox Titrations

Redox reactions are the most diverse of the four main classes of inorganic aqueous reactions (acid-base, pptn, complexation and redox). In principle, then, redox titrations can be used to analyze for any oxidizing or reducing agent. However, many redox reactions are either too slow or have inconsistent stiochiometry. The stability of titrant and analyte solutions can also be a problem. Nevertheless, a wide variety of analytes can be conveniently determined by redox titrations.

General Considerations

Consider a generic redox half-reaction (charges omitted for clarity):

$$ox + ne^- \rightleftharpoons red$$

A chemical (i.e., **ox** in this equation) that pulls electrons from another substance is an ***oxidizing agent***, while a chemical (**red**) that forces another substance to accept electrons is a ***reducing agent***. Together, *ox*/*red* form a ***redox couple***; redox couples are analogous to acid/base conjugate pairs. And just like acid-base reactions, the "conjugate" of a strong oxidizing agent is a weak reducing agent. The strength of oxidizing/reducing agents can be deduced by the standard reduction potential: a very positive standard potential indicates a strong oxidizing agent, while a low positive or a negative potential is characteristic of a strong reducing agent.

The strength of an oxidizing or reducing agent is very often dependent on pH. There is a general rule of thumb: *acidic conditions tend to make oxidizing agents more powerful and render reducing agents less reactive*. Some few redox reagents are relatively insensitive to pH, which can be an advantage. Most redox reagents are stable (if they are stable at all!) only within a certain pH range.

Sample treatment is often necessary to adjust the oxidation state of the analyte. The analyte is either *pre-reduced* or *pre-oxidized*. For pre-reduction of the analyte, many metals (many of which are strong reducing agents) can be used. It is common to use a *reductor*, which is a column of granulated metal through which the sample solution is poured. Two common reductors are: the *Jones Reductor*, which uses amalgamated zinc (ZnHg) granules, and the *Walden Reductor*, which uses silver granules (chloride is added to the sample, usually as HCl). The Walden Reductor is more selective (i.e., a less powerful reducing agent) than the Jones Reductor.

Pre-oxidation is not as common as pre-reduction, since the analyte is usually desired in a reduced form for titration with an oxidizing agent. However, when pre-oxidation is necessary, sodium bismuthate, $NaBiO_3$, ammonium peroxydisulfate, $(NH_4)_2S_2O_8$, or hydrogen peroxide may be used.

Common Titrants

Reducing Agents

- reducing agents are not stable in air (undergo air oxidation) and so are not often used. Here are a few titrants

• the two most common reducing titrants are ferrous ammonium sulfate (FAS) and sodium thiosulfate. Procedures using these titrants are capable of determining the concentrations analytes that are (at least) moderately strong oxidizing agents.

Ferrous Ammonium Sulfate (FAS or Mohr's salt), $(NH_4)_2Fe(SO_4)_2$

• the ferrous ion is a fairly weak reducing agent:

$$Fe^{2+} \rightarrow Fe^{3+} + e^- \qquad E^\circ = 0.771V$$

The use of ferrous ion as a titrant is limited to the analysis of moderately strong oxidizing agents; it is used for the direct titration of a few metals such as U(VI), Mo(VI) and V(IV). Probably the most important use of FAS is in back-titrations of dichromate and other reasonably strong oxidants.

• solutions of FAS are most stable under acidic conditions (in 0.5M H_2SO_4); still, the solution is stable only for about a day. Standardization is with potassium dichromate, $K_2Cr_2O_7$.

Sodium Thiosulfate, $Na_2S_2O_3$

• thiosulfate is a moderately strong reducing agent:

$$2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^- \qquad E^\circ = 0.09\ V$$

• thiosulfate is actually not suitable for the direct analysis of most oxidizing agents, since reactions with thiosulfate tend to produce also produce sulfite and sulfate. However, it is widely used in back-titrations of iodine that is produced by the reactions of oxidizing agents with iodide, another reducing agent (this procedure is called *iodometry*).

• thiosulfate solutions are standardized with iodine which has been prepared by acidifying primary standard potassium iodate in the presence of a slight excess of potassium iodide:

acidic solution $$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2(aq) + 3H_2O$$

The titration reaction between iodine and thiosulfate is fairly straightforward:

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

• alkaline solutions of sodium thiosulfate are fairly stable

Oxidizing Agents

• used for the analysis of reducing agents. Pre-reduction of analyte is common; analyte is often unstable in reduced form, and care must be taken in sample handling

Potassium Permanganate, $KMnO_4$

• used since the mid-1800's - one of the earliest titrimetric agents

• a strong oxidant

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2(s) + 2H_2O \qquad E^\circ = 1.692\ V$$

• standardized with sodium oxalate, $Na_2C_2O_4$. Not a very stable titrant unless precautions are taken; should be standardized fairly often.

• can be used for the analysis of many reducing agents, weak or strong. Examples are given in table 16-3 in Harris: e.g., Br^-, H_2O_2, NO_2^-, Fe^{2+}, As^{3+}, Sb^{3+}, Mo^{3+}, W^{3+}, U^{4+}, Ti^{3+}

Ceric Sulfate, $Ce(SO_4)_2$

• another strong oxidant, just about as strong as permanganate

$$Ce^{4+} + e^- \rightarrow Ce^{3+} \qquad E^\circ = 1.44 \text{ V (in } H_2SO_4)$$

• standardized with $Na_2C_2O_4$. Alternately, primary standard $(NH_4)_2Ce(NO_3)_6$ can be used (expensive!). Titrant is very stable in acid solutions; it ppts in alkaline solutions.

• almost anything that can be done with potassium permanganate can be done more conveniently with ceric sulfate.

Potassium Dichromate, $K_2Cr_2O_7$

• historically important; like permanganate, used since mid-1800's

• a moderately strong oxidizing agent; oxidizing ability depends strongly on pH, decreasing rapidly as solution becomes more neutral

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \qquad E^\circ = 1.36 \text{ V}$$

• available in sufficient purity to be its own primary standard; in fact, it is the most common reagent used to standardize reducing titrants. If necessary, dichromate solutions can be standardized with $Na_2C_2O_4$.

• most common applications: analysis of iron content of ores and COD of wastewaters. Advantage for iron ore analysis: no problem with HCl solutions, unlike permanganate (which oxidizes chloride to chlorine). Back-titrations involving FAS are also common: FAS may be added in excess for the analysis of oxidizing agents (back-titration with dichromate) or FAS may be used for to analyze excess dichromate (as in COD measurements).

Titrations involving Iodine, I_2

General Applicability

• an important class of techniques: can be used to analyze moderately strong oxidants or reductants. Advantage of moderate strength as a redox reagent: better selectivitity. Permanganate and ceric oxidize almost everything present.

• the standard reduction of iodine is

$$I_2(aq) + 2e^- \rightarrow 2I^- \qquad E^\circ = 0.621 \text{ V}$$

• iodine is a moderate oxidizing agent; iodide is a moderate reducing agent. There are two classes of titrations involving iodine:

1. ***Iodimetry***, which is based on the direct reaction between the analyte and iodine. Since iodine is an oxidizing agent, *iodimetry is used for the analysis of reductants*.

2. ***Iodometry***, which is based on the reaction between the analyte and an unmeasured excess of iodide to *produce* iodine, which is measured by titration with thiosulfate. The amount of iodine produced by this reaction is stoichiometrically related to the amount of analyte originally present in the solution. Since iodide is an reductant, *iodometry is used for the analysis of oxidants*.

- applications of iodimetry and iodometry are extensive; see Harris table 16-4 for more details. Remember: iodimetry (analyte reacts with iodine) is for the analysis of reducing agents, while iodometry (production of iodine by reaction of analyte with iodide, followed by back-titration with thiosulfate) is for the analysis of oxidizing agents. Titrations involving iodine are more selective than those involving more powerful redox reagents.

Iodine Aquatic Chemistry

Iodine crystals are only sparingly soluble in water, so the standard potential listed earlier for iodine gives a misleading impression of the strength of iodine as an oxidizing agent. Usually iodine is prepared by dissolution in a solution of concentrated potassium iodide, due to the formation of the *triiodide* ion:

$$I_2(aq) + I^- \rightleftharpoons I_3^- \qquad K = 710$$

This reaction allows iodine to dissolve. However, the actual concentration of $I_2(aq)$ remains low; thus, the oxidizing power still does not approach that of 1M $I_2(aq)$. Due to the presence of triiodide, the following reaction is often used to represent iodine oxidation during a titration:

$$I_3^-(aq) + 2e^- \rightarrow 3I^-(aq) \qquad E^\circ = 0.545\ V$$

The oxidizing ability of iodine solutions is not very dependent on pH; however, in alkaline solutions (pH > 8), iodine disproportionates to iodate and iodide:

alkaline solution $$3I_2 + 3H_2O \rightleftharpoons IO_3^- + 5I^- + 6H^+$$

Note that this reaction is quite reversible: upon acidification, the reaction shifts to the left as iodate reacts with iodide to form iodine.

Preparation of Titrant Solutions

- iodine titrant solutions are usually prepared by dissolving solid iodine in potassium iodide solutions. The solution may be standardized with primary standard sodium oxalate or with sodium thiosulfate that has been previously standardized.
- sodium thiosulfate is the reducing agent that is universally used for the back-titration of iodine produced in iodometry. This titration reaction is stoichiometric and fairly rapid:

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

- sodium thiosulfate titrant is prepared simply by dissolving the salt in water and storing under slightly basic conditions. It is standardized with potassium iodate that has been acidified in excess iodide.

Iodine/triiodide solutions are unstable for a variety of reasons. First of all, aqueous iodine exerts a significant vapor pressure. Also, under acidic conditions iodide is slowly air-oxidized to produce iodine. Finally, under alkaline conditions, iodine will disproportionate to produce iodide and iodate,

as mentioned previously. Thus, iodine solutions are generally most stable at neutral pH values. Iodine titrant solutions must be standardized fairly frequently.

Endpoint Detection for Redox Titrations

- it is probably worthwhile to mention that starch is an excellent chemical indicator for titrations involving iodine
- potentiometric detection with an inert indicator electrode (e.g., Pt) is a general method for following redox titrations
- amperometric detection can also be used in many cases
- many redox titrants are colored (e.g., permanganate or iodine) and so photometric detection can also be used to follow the course of the titration

Applications of Redox Titrations

Example Applications

- DO by Winkler (iodometric) titration
- COD by dichromate back-titration (using FAS)
- analysis of iron in ores by dichromate titration
- analysis of residual chlorine by iodometric titration
- analysis of ascorbic acid (vitamin C), hydrogen peroxide, bleach, ...

Summary of Applications of Redox Reactions

- analytes that are oxidizing agents are most conveniently analyzed by addition of excess reducing agent and then back-titrating. There are two common ways of doing this: (i) addition of a measured excess of ferrous ammonium sulfate and back-titrating the unreacted excess with dichromate titrant; (ii) addition of an unmeasured excess of potassium iodide and using thiosulfate to back-titrate the iodine produced by reaction of iodide with analyte.
- analytes that are reducing agents may be analyzed by a variety of oxidizing agents: potassium permanganate and ceric sulfate are strong oxidants, potassium dichromate is a moderately strong oxidizing titrant (especially suitable for the analysis of ferrous iron, or back-titrations with FAS) and iodine is a milder, more selective oxidizing agent that may be used for the direct analysis of a number of reducing agents (iodimetry), as well as the indirect analysis of reducing agents (back-titration with thiosulfate in iodometry; see above)
- pre-treatment of the analyte with an oxidizing agent or a reducing agent is often needed in redox titrations

Titrimetry Methods
EDTA Titrations

General Scope and Applicability of EDTA Titrations

Complexometric titrations are based on the reaction between Lewis acids (usually metal cations) and Lewis bases.

$$M + :L \rightarrow M:L$$

Lewis acids and bases react to form a *complex*. The base donates two electrons to form a bond with the acid. Since the proton, H^+, is a good Lewis acid, by definition any Bronsted base will be a Lewis base. Lewis bases will possess at least a single lone pair of electrons that it will donate to the Lewis acid. Lewis bases are also sometimes called *ligands*, and the atoms containing the lone pair is the ligand binding site.

A special subset of ligands are those that contain more than one binding site on the molecule; these are called ***chelating agents***. Chelating agents form particularly strong complexes – called ***chelates*** – with Lewis acids. By far the most common complexometric titrant is *ethylenediaminetetraacetic acid*, EDTA. This is a hexadentate chelating ligand, meaning that there are six ligand binding sites on EDTA molecule. EDTA titrations are very versatile: they can be used for the analysis of all the metal cations except the alkali metals, and can even be used (through back-titration and similar methods) for the analysis of many anions. EDTA titrations are also fairly sensitive, capable of detecting concentrations of some metals at levels of approximately 10 ppm (i.e., 10 mg/L).

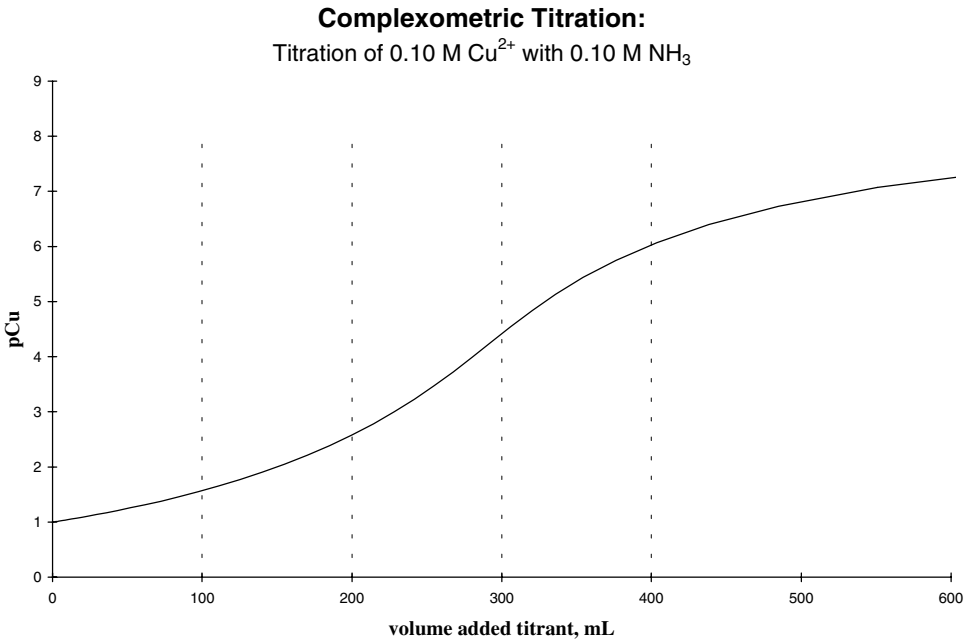
EDTA Chemistry

Advantages of EDTA as a Complexing Titrant

Complexation of metal cations with unidentate ligands is not useful as the basis for a quantitative titration. Let's imagine that we have a solution of Cu^{2+} to be analyzed by complexometric titration. We can use a titrant such as aqueous ammonia, a unidentate ligand. The following equations show the stepwise formation of complexes between the metal and the ligand:

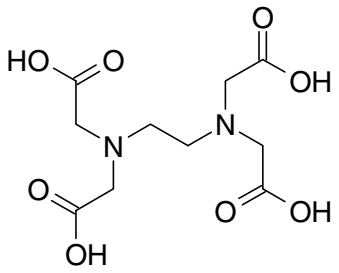
$$Cu^{2+} + NH_3 \rightleftharpoons CuNH_3^{2+} \qquad \log K = 3.99$$
$$CuNH_3^{2+} + NH_3 \rightleftharpoons Cu(NH_3)_2^{2+} \qquad \log K = 3.34$$
$$Cu(NH_3)_2^{2+} + NH_3 \rightleftharpoons Cu(NH_3)_3^{2+} \qquad \log K = 2.73$$
$$Cu(NH_3)_3^{2+} + NH_3 \rightleftharpoons Cu(NH_3)_4^{2+} \qquad \log K = 1.97$$

Since the coordination number of Cu^{2+}, ideally we would observe four distinct endpoints during the titration with NH_3. The following figure shows the titration curve that would actually be observed.



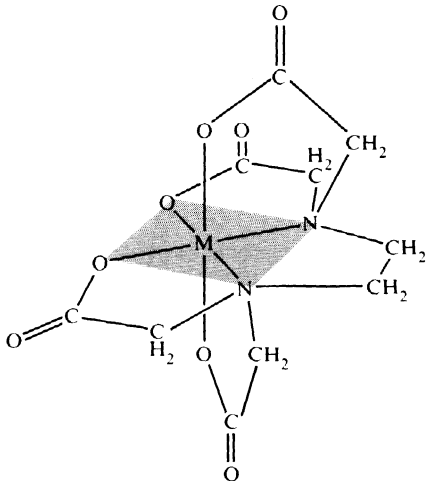
The dashed lines indicate the equivalence points for the four complexation reactions. However, the equilibrium constants of those reactions are not different enough to observe four distinct endpoints. In addition, the equilibrium constants themselves are not large enough for the titration; we would like the complexation to go more to completion.

As mentioned previously, EDTA is a hexadentate chelating agent. The structure of the neutral EDTA molecule is given below.



ethylenediaminetetraacetic acid
(EDTA)

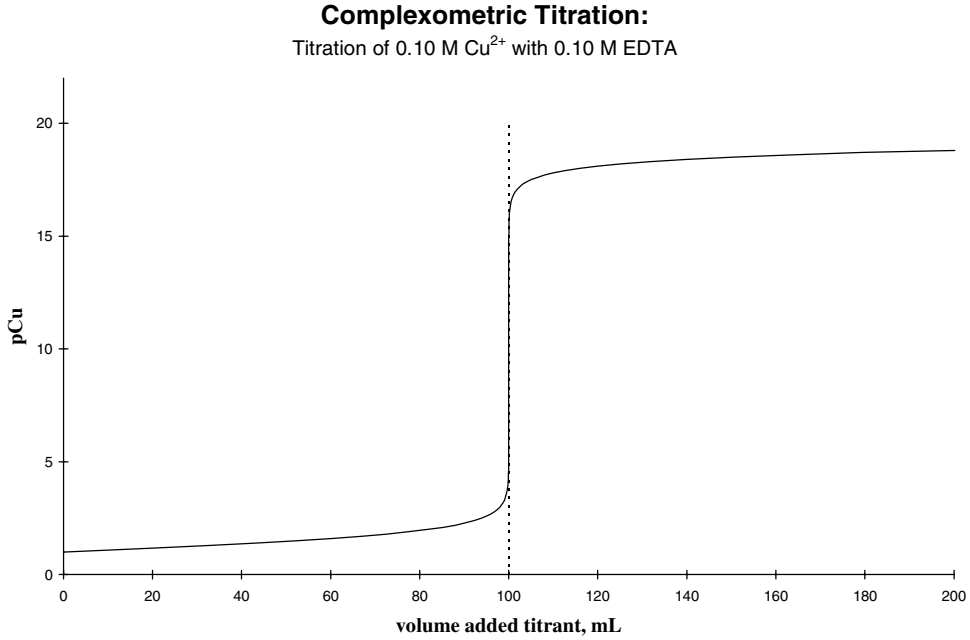
The two nitrogen atoms contain lone pairs that can be donated to the metal cation. In addition, a metal cation can displace the proton on the four carboxyl acid groups. The structure of an EDTA-metal chelate is illustrated in the next figure for a metal (M) that has a coordination number of six. The EDTA forms a "cage" around the metal cation, binding the metal with the two amine nitrogens and the four carboxylate groups.



Compared to unidentate ligands, EDTA has two very important advantages as a titrant:

1. It reacts with most metal cations (as long as the coordination number is six or less, which is true of most metals) in a 1:1 stoichiometry, meaning that only a single endpoint will be observed.
2. It complexes very strongly to almost every metal (see table 13-2 in Harris, p313). This means that the endpoint of the EDTA titration will be sharp.

The following is the titration curve that would be observed in titrating the same Cu^{2+} solution with EDTA instead of aqueous ammonia. Obviously this titration is much better suited for the quantitative analysis of the copper in the solution.



EDTA is a hexaprotic acid (as it must be, since it is a hexadentate ligand and H^+ is a Lewis acid). The dissociation constants of EDTA are: pK_a = 0.0, 1.5, 2.0, 2.66, 6.16, 10.24. The neutral form of EDTA is usually abbreviated as H_4Y. The dominant uncomplexed form of EDTA will depend on the pH, as shown in the following table.

pH	0 – 1.5	1.5 – 2.0	2.0 – 2.66	2.66 – 6.16	6.16 – 10.24	> 10.24
dominant	H_5Y^+	H_4Y	H_3Y^-	H_2Y^-	HY^{3-}	Y^{4-}

The chemical equation for the reaction of EDTA with a metal cation is often written as that between the fully deprotonated form of EDTA and the cation. For example, the titration equation for the reaction between Cu^{2+} and EDTA is generally written as

$$Cu^{2+} + Y^{4-} \rightarrow CuY^{2-}$$

regardless of which form of EDTA is dominant at the pH of the sample solution. The equilibrium expression for this reaction is:

$$K_T = \frac{[CuY^{2-}]}{[Cu^{2+}][Y^{4-}]}$$

This is not to say that a metal cation can only react with the deprotonated form of EDTA. For example, at a pH of 7, the following reaction would certainly occur:

$$Cu^{2+} + HY^{3-} \rightarrow CuY^{2-} + H^+$$

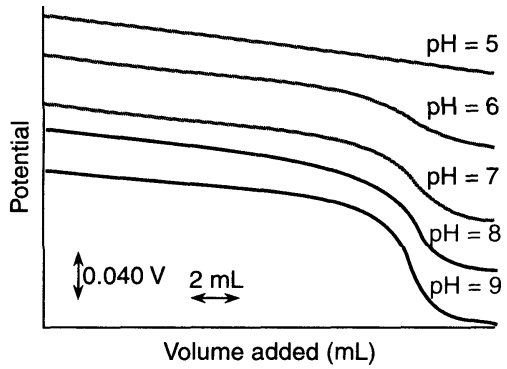
We will soon discuss the effect of pH on the titration in more detail.

Preparation and Standardization of EDTA Solutions

The neutral EDTA molecule (H_4Y) is not very soluble in water, so that aqueous EDTA titrant solutions are usually prepared by dissolving the disodium (Na_2H_2Y) or magnesium (MgH_2Y) salt of EDTA. The concentration of free EDTA in the solution is decreased by contamination of the solution by metals that may be present in normal glassware. EDTA titrant solutions are generally stored in polyethylene or borosilicate glass containers. A fresh solution should be prepared at least monthly, and the solution should be standardized fairly often (every one or two weeks) against using calcium carbonate, which is available in purity high enough to be used as a primary standard.

Effect of pH on EDTA Titrations

Since H^+ is a Lewis acid, it competes with metal cations for binding sites on the EDTA molecule. Thus, the pH of the sample solution will have significant effect on the sharpness of the titration. The following series of titration curves show the effect of pH on the EDTA titration of Ca^{2+}. As can be seen, the endpoint becomes more distinct at higher pH values due to less competition from H^+ for EDTA.



Consider the generic equation representing the reaction of a metal cation with EDTA (the charge on the chelate MY is omitted for clarity):

$$M^{n+} + Y^{4-} \rightleftharpoons MY(aq) \qquad K_T$$

The equilibrium constant for the titration reaction is:

$$K_T = \frac{[MY]}{[M^{n+}][Y^{4-}]}$$

This is the formation constant for the complexation of the metal cation by unprotonated EDTA. We can account for the effect of pH on the titration by considering how the pH affects the dissociation of uncomplexed EDTA. The fraction of the fully deprotonated EDTA is given by α_Y, where

$$\alpha_Y = \frac{[Y^{4-}]}{C_{EDTA}} = \frac{K_1K_2K_3K_4}{[H^+]^4+[H^+]^3K_1+[H^+]^2K_1K_2+[H^+]K_1K_2K_3+K_1K_2K_3K_4}$$

where C_{EDTA} is the total concentration of all EDTA species (i.e., the "formal" or "analytical" concentration) and K_i is the i^{th} acid dissociation constant. This expression shows that the fraction of EDTA that is fully deprotonated depends only on the pH.

Since $[Y^{4-}] = \alpha_Y C_{EDTA}$, then we may write the titration equilibrium constant

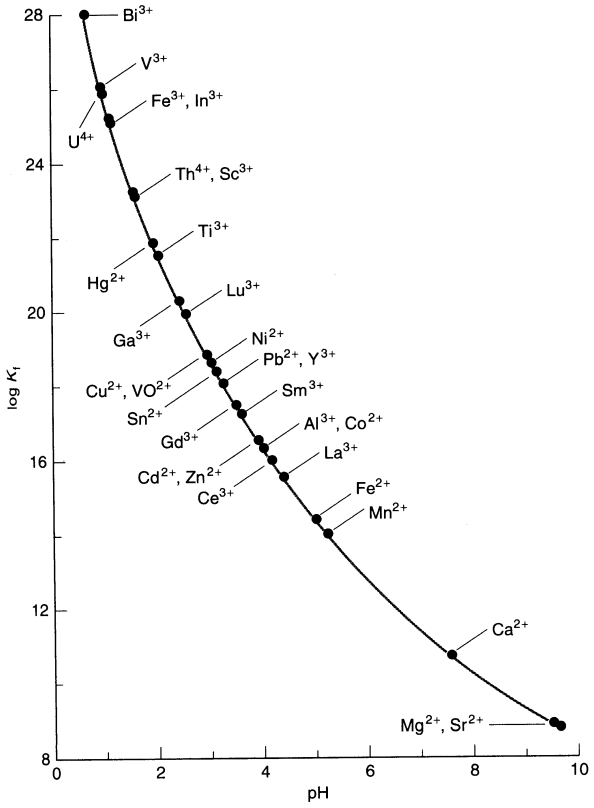
$$K_T = \frac{[MY]}{[M^{n+}]\alpha_Y C_{EDTA}}$$

Rearranging, we have

$$K'_T = \alpha_Y K_T = \frac{[MY]}{[M^{n+}]C_{EDTA}}$$

where K'_T is the *conditional formation constant* for the titration reaction. This constant, which depends on solution pH (unlike a normal equilibrium constant), can be thought of as an "effective" titration equilibrium constant that accounts for the effects of the competition of H^+ and metal cation for the same ligand binding sites.

The following figure (from Harris, p 315) gives the minimum pH needed to give a conditional formation constant of 10^8, which can be considered a minimum value necessary to give a satisfactory endpoint for typical analyte concentrations.



The figure illustrates how pH might affect the titration of a mixture of metal cations. For example, imagine we are to titrate a mixture of Cu^{2+} and Ca^{2+}. If we buffer the solutions at pH=4, only the cupric ions would react with the EDTA, since calcium cations would be effectively out-competed by the hydronium ions. However, a pH greater than about 7.5 would allow both analytes to react with the titrant.

The effect of pH is actually more complicated than the previous figure indicates. Most metal cations will undergo hydrolysis and/or may precipitate at higher pH values. For example, the aqueous ferric cation is not really a "free" cation but is actually complexed by water molecules (which are weak Lewis bases, after all). Thus, "Fe^{3+}" is actually more truthfully written as $Fe(H_2O)_6^{3+}$.

In the reaction between hydrated Fe^{3+} and EDTA, the chelating agent actually *displaces* the water molecules from the coordinate sites of the metal:

$$Fe(H_2O)_6^{3+} + Y^{4-} \rightleftharpoons FeY^{-} + 6H_2O \qquad \log K = 24.23$$

Thus, we may look at this reaction as a competition for the metal cation between two Lewis bases: EDTA (Y^{4-}) and water. The aquo (H_2O) ligand is a much weaker Lewis base than the EDTA, and so the formation constant for the above reaction is large.

Most metal cations that are hydrated in this manner are Bronsted acids, and the ferric ion is no exception. In aqueous solutions, hydrated ferric cation may lose protons in the following sequence of reactions.

$$Fe(H_2O)_6^{3+} \rightleftharpoons Fe(H_2O)_5(OH)^{2+} + H^+ \qquad pK_1 = 3.05$$
$$Fe(H_2O)_5(OH)^{+} \rightleftharpoons Fe(H_2O)_4(OH)_2^{+} + H^+ \qquad pK_2 = 3.26$$
$$Fe(H_2O)_4(OH)_2^{+} \rightleftharpoons Fe(H_2O)_3(OH)_3 + H^+ \qquad pK_3 = 7.49$$
$$Fe(H_2O)_3(OH)_3 \rightleftharpoons Fe(H_2O)_2(OH)_4^{-} + H^+ \qquad pK_4 = 8.9$$

These reactions are called *metal hydrolysis* reactions. What is happening is that, at higher pH values, the H_2O ligands in the complex are being replaced by OH^- ligands, which bond more strongly to the metal. Since the hydroxo (OH) ligand binds the metal more strongly, they are harder for EDTA to displace during a titration.

Thus, the effect of metal hydrolysis is to decrease the effective equilibrium constant of the EDTA titration reaction. Since metal hydrolysis is more complete at higher pH values, we would predict that lower pH values will favor sharper endpoints.

So there are actually two opposing effects of pH on EDTA titrations:

- there is a competition between protons and the analyte for the EDTA ligand, with higher pH values favoring more complete reaction of analyte and EDTA;
- hydrolysis of the analyte at higher pH values, with lower pH values favoring more complete reaction of analyte with EDTA.

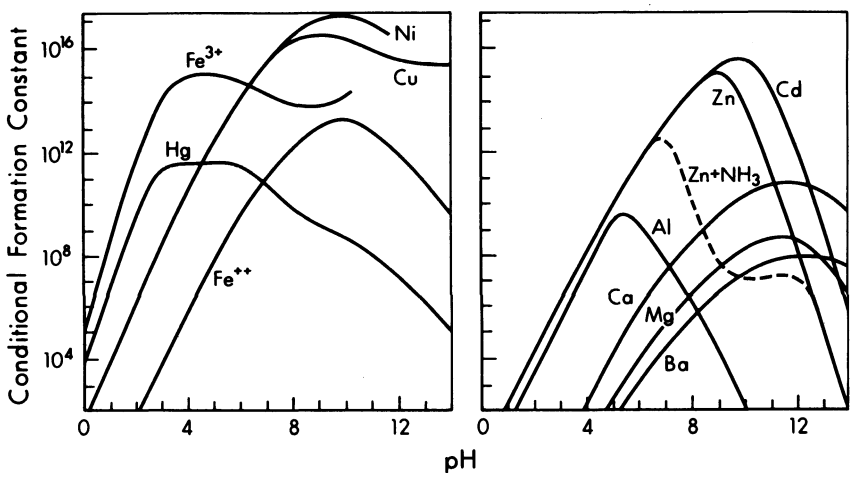
We can represent the effect of pH on the titration equilibrium constant mathematically. Let α_M represent the fraction of hydrated metal complex that has not lost a proton (i.e., not undergone hydrolysis):

$$\alpha_M = \frac{[M^{n+}]}{C_M}$$

where C_M is the formal concentration of the dissolved metal cation (all hydrated species). The value of α_M will depend only on the pH. We may rewrite a conditional formation constant for the EDTA titration as

$$K_f'' = \alpha_M \alpha_Y K_f = \frac{[MY]}{C_M C_{EDTA}}$$

This is the "effective" equilibrium constant of the EDTA titration. Lower pH values will cause α_M to increase but α_Y to decrease, while more alkaline conditions will have the opposite effect. Thus, for many metal cations, there will be an optimum pH range for EDTA titration, as shown in the next figure when K_f'' is plotted as a function of pH.



Selectivity of EDTA Titrations

EDTA reacts with so many different metals that interferences are common. Indeed, contamination of the sample can be a real problem in EDTA titrations, particularly for low concentrations of analyte.

Effect of pH on Selectivity

Due to the effect of pH on the endpoint sharpness, the pH is almost always buffered in EDTA titrations. In fact, the proper selection of the pH can often be used to improve selectivity in the titration of metal cation mixtures. The pH is chosen to maximize the conditional formation constant for the reaction of EDTA and the analyte and minimize the conditional formation constant for all other components of the solution.

Auxiliary Complexing Agents; Masking and Demasking

There are times when another Lewis base is added to the sample solution to enhance the selectivity of EDTA titrations. The added Lewis base will compete with EDTA for metal cations, hence further altering the effective equilibrium constant.

As mentioned above, the pH of the solution may be altered to enhance selectivity of the EDTA titration for the analyte. Sometimes, however, the desired pH will cause the analyte to precipitate from the solution as the hydroxide or oxide salt. Addition of an ***auxiliary complexing agent*** is necessary in such cases to keep the analyte from precipitating. For titrations at higher pH's, an ammonia/ammonium chloride buffer is sometimes used. This solution has the dual purpose of buffering the pH to the desired value *and* keeping the analyte in solution (since ammonia will complex with the metal cation).

Simple adjustment of the pH is sometimes not always enough for selective EDTA titrations. A **masking agent** may be added to bind to specific metal cations so strongly they won't react with EDTA. Examples of masking agents:

- cyanide, CN^-, can be used for the analysis of Mg, Ca, Mn or Pb in the presence of many other cations (masks Cd, Zn, Hg, Co, Cu (I), Ag, Ni, Pd, Pt, Fe)
- fluoride, F^-, masks Al, Fe (III), Ti (IV), Be
- triethanolamine, $N(EtOH)_3$, masks Al, Fe and Mn (II)

After the titration, demasking agents may be added to release the metal cation from the "masked" complex. For example, formaldehyde can de-mask cyanide complexes, allowing for their subsequent analysis.

Types of EDTA Titrations

A wide variety of different types of EDTA titrations have been developed, most commonly based on one of the following: (i) *direct titration* of the analyte with EDTA, (ii) *back-titration* of a measured excess of EDTA added to the sample solution, and (iii) *substitution titration* of the metal liberated with an excess of EDTA-metal chelate is added to the sample solution.

Direct Titrations

Direct EDTA titrations are straightforward: the EDTA titrant is added to the sample solution until the endpoint is reached.

Back-Titrations

EDTA back-titrations are generally used for one of three reasons: (i) reaction kinetics are too slow for the direct titration of the analyte; (ii) the metal precipitates at the desired pH; or (iii) there is no suitable chemical indicator for the direct titration.

In the back-titration, a measured excess of EDTA is added to the sample solution. The amount of unreacted excess EDTA is measured by back-titration, usually with a standard solution of a metal cation, usually Mg^{2+}. The metal cation used in the back-titration must not displace the analyte from its EDTA complex. Magnesium is usually used because it does not bind too strongly to EDTA (compared to most other metal cations) and several excellent chemical indicators are available for the Mg^{2+} - EDTA titration.

Displacement Titrations

Displacement titrations are also called *substitution* or *replacement* titrations. An unmeasured excess of an EDTA-metal complex is added to the sample solution; the analyte displaces the metal from the complex, and the displaced metal is measured by titration with EDTA. For example, if excess MgY^{2-} titrant is added to the sample solution, Mg^{2+} is displaced by the analyte metal

$$M + MgY^{2-} \rightarrow MY + Mg^{2+}$$

where M is the analyte and MY is the analyte-EDTA complex (charges are omitted for clarity). In order for this method to work, the analyte must have a larger affinity for EDTA than the magnesium cation. The amount of Mg^{2+} displaced is equal to the amount of analyte originally present in the solution, assuming 1:1 stoichiometry. Thus, titration by EDTA to determine the concentration of liberated Mg^{2+} will determine the amount of analyte originally present.

Endpoint Detection

A number of chemical indicators are available for EDTA titrations. These are generally chelating agents (like EDTA) that bind to the analyte and are displaced near the endpoint. Obviously the bound and free forms of the indicator must be different colors. Your textbook (Harris) lists a number of these indicators.

Potentiometry is the most common instrumental method of endpoint detection. The most general form of detection is to use (as the indicator electrode) a wire that has been amalgamated so that a thin film of mercury coats the wire. A small amount of mercuric ion, Hg^{2+}, is added to the sample solution, forming the following galvanic cell

$$\text{reference} \,\|\, HgY^{2-}, Hg^{2+} \,|\, Hg$$

The measured potential difference is controlled by the indicator electrode potential, which reponds to the thermodynamic driving force for the reduction of the mercuric cation:

$$Hg^{2+} + 2e^- \rightleftharpoons Hg(l)$$

According to the Nernst equation, the indicator electrode potential will depend on the concentration of mercuric cation, as follows.

$$E_{ind} = E^0 - \frac{0.0592}{n} \log \frac{1}{[Hg^{2+}]}$$

The concentration of Hg^{2+} is affected by the concentration of titrant EDTA due to the following complexation reaction:

$$Hg^{2+} + Y^{4-} \rightleftharpoons HgY^{2-}$$

As the concentration of EDTA rises near (and past) the endpoint, the concentration of free Hg^{2+} decreases, causing a corresponding decrease in the indicator electrode potential. A typical titration curve will be recorded by plotting the measured potential against the volume of added titrant.

Example Application: Determination of Water Hardness

EDTA titrations has been used for the analysis of almost every metal in the periodic table; a number of anions can also be analyzed using a variety of back-titrations or displacement titrations. One of the most common applications of EDTA titrations is the measurement of *water hardness* in a water sample.

Historically, water hardness has been a measure of the ability of the water to precipitate detergents, usually as calcium and magnesium salts. The hardness of a water sample is defined as the sum of the concentrations of Ca^{2+} and Mg^{2+} cations. Even though many modern detergents are no longer precipitated by these cations, hardness continues to be an important and commonly measured environmental and industrial water quality parameter. Calcium and/or magnesium are often two of the most concentrated cations in surface freshwater samples, and their environmental significance extends beyond their ability to precipitate soap.

The total hardness of a water sample is usually determined by EDTA titration at pH=10; at this pH, the endpoint occurs after the titrant has reacted with all the Ca^{2+} and Mg^{2+} present in the sample. It is possible to determine calcium only by basifying the sample solution to pH 12 or 13 before titration, which precipitates any magnesium present as the hydroxide.