15D-7  Titration Methods Employing EDTA

Several different types of titration methods can be used with EDTA as described below.

Direct Titration

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

Methods Based on Indicators for the Analyte.  Reilley and Barnard\textsuperscript{6} list 40 elements that can be determined by direct titration with EDTA using metal-ion indicators.


indicators. Indicators that respond to the metal directly cannot be used in all cases either because no indicator with an appropriate transition range is available or because the reaction between the metal ion and EDTA is so slow as to make titration impractical.

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

Potentiometric Methods. Potential measurements can be used for end-point detection in the EDTA titration of those metal ions for which specific ion electrodes are available. Electrodes of this type are described in Section 19D. In addition, a mercury electrode can be made sensitive to EDTA ions and used in titrations with this reagent.

Spectrophotometric Methods. Measurement of UV/visible absorption can also be used to determine the end points of titrations (see Section 23A-2). In these cases, an instrument responds to the color change in the titration rather than relying on a visual determination of the end point.

Back-Titration Methods

Back-titration are useful for the determination of cations that form stable EDTA complexes and for which a satisfactory indicator is not available; the determination of thallium is an extreme example. The method is also useful for cations such as Cr(III) and Co(III) that react only slowly with EDTA. A measured excess of standard EDTA solution is added to the analyte solution. After the reaction is judged complete, the excess EDTA is back-titrated with a standard magnesium or zinc ion solution to an Eriochrome Black T or Calmagite end point. For this procedure to be successful, it is necessary that the magnesium or zinc ions form an EDTA complex that is less stable than the corresponding analyte complex.

Back-titration is also useful for analyzing samples that contain anions that would otherwise form sparingly soluble precipitates with the analyte under the analytical conditions. Here, the excess EDTA prevents precipitate formation.

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Displacement Methods

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

\[ \text{MgY}^{2-} + M^{2+} \rightarrow \text{MY}^{2-} + \text{Mg}^{2+} \]

where \( M^{2+} \) represents the analyte cation. The liberated \( \text{Mg}^{2+} \) or, in some cases \( \text{Zn}^{2+} \), is then titrated with a standard EDTA solution. Displacement titrations are used when no indicator for an analyte is available.

15D-8 The Scope of EDTA Titrations

Complexometric titrations with EDTA have been applied to the determination of virtually every metal cation with the exception of the alkali metal ions. Because EDTA complexes most cations, the reagent might appear at first glance to be totally lacking in selectivity. In fact, however, considerable control over interferences can be realized by pH regulation. For example, trivalent cations can usually be titrated without interference from divalent species by maintaining the solution at a pH of about 1 (Figure 15-12). At this pH, the less stable divalent chelates do not form to any significant extent, but the trivalent ions are quantitatively complexed.

Similarly, ions such as cadmium and zinc, which form more stable EDTA chelates than does magnesium, can be determined in the presence of the latter ion by buffering the mixture to pH 7 before titration. Eriochrome Black T serves as an indicator for the cadmium or zinc end points without interference from magnesium because the indicator chelate with magnesium is not formed at this pH.

Finally, interference from a particular cation can sometimes be eliminated by adding a suitable masking agent, an auxiliary ligand that preferentially forms highly stable complexes with the potential interfering ion. Thus, cyanide ion is often employed as a masking agent to permit the titration of magnesium and calcium ions in the presence of ions such as cadmium, cobalt, copper, nickel, zinc, and palladium. The latter all form sufficiently stable cyanide complexes to prevent reaction with EDTA. Feature 15-4 illustrates how masking and demasking reagents are used to improve the selectivity of EDTA reactions.

A masking agent is a complexing agent that reacts selectively with a component in a solution to prevent that component from interfering in a determination.