

EDTA Titration Techniques.

(1)

11-27 ~~Give~~ Give three circumstances in which an EDTA back titration might be necessary.

- * A back titration is necessary if the analyte precipitates in the absence of EDTA.
- * If it reacts too slowly with EDTA.
- * If it blocks the indicator.

11-28 ~~Describe~~ Describe what is done in a displacement titration and give an example:

Ans:

In a displacement titration, analyte displaces a metal ion from a complex. The displaced metal ion is then titrated.

Eg. The liberation of Ni^{2+} from $\text{Ni}(\text{CN})_4^{2-}$ by the analyte Ag^+ . The liberated Ni^{2+} is then titrated by EDTA to find out how much Ag^+ was present.

11-29. Give an example of the use of
a masking agent. (2)

Ans:

The Mg^{2+} in a solution of Mg^{2+} and Fe^{3+} can be titrated by EDTA if the Fe^{3+} is masked with CN^- to form $Fe(CN)_6^{3-}$, which does not react with EDTA.

11-30. What is meant by water hardness?

Explain the difference between temporary and permanent hardness.

Hardness refers to the total concentration of alkaline earth cations in water, which normally means $[Ca^{2+}] + [Mg^{2+}]$.

Hardness gets its name from the reaction of these cations with soap to form insoluble curds.

Temporary hardness, due to $Ca(HCO_3)_2$, is lost by precipitation of $CaCO_3(s)$ upon heating. Permanent hardness derived from other salts, such as $CaSO_4$, is not affected by heat.

(3)

11-31. How many milliliters of 0.050 M EDTA
 are required to react with 50.0 mL of 0.010 M Ca^{2+} ?
 with 50.0 mL of 0.010 M Al^{3+} ?

Ans:

$$50.0 \text{ mL} \times 0.010 \frac{\text{mmol } \text{Ca}^{2+}}{\text{mL}} = 0.500 \text{ mmol } \text{Ca}^{2+}$$

which requires 0.500 mmol EDTA = 10.0 mL EDTA

$\therefore 0.500 \text{ mmol } \text{Al}^{3+}$ requires the
 same amount of EDTA, 10.0 mL.

$$\therefore 1\text{mL} = 0.050 \text{ mmol EDTA}$$

$$\therefore 0.500 \text{ mmol} = \frac{0.500}{0.050} = 10 \text{ mL}$$

11-32. A 50.0-mL sample containing Ni^{2+} was
 treated with 25.0 mL of 0.050 M EDTA to complex
 all the Ni^{2+} and leave excess EDTA in solution.
 The excess EDTA was then back-titrated, requiring
 5.00 mL of 0.050 M Zn^{2+} . What was the concentration
 of Ni^{2+} in the original solution?

Ans:

$$\text{mmol EDTA} = \text{mmol } \text{Ni}^{2+} + \text{mmol } \text{Zn}^{2+}$$

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$$\text{mmol EDTA} = \text{mmol } \text{Ni}^{2+} + \text{mmol } \text{In}^{2+}$$

$$1.250 = x + 0.250$$

$$\therefore x = 1.000 \text{ mmol } \text{Ni}^{2+}$$

$$\therefore 1.000 \text{ mmol } \text{Ni}^{2+} \text{ in } 50.0 \text{ mL}$$

$$= 0.0200 \text{ M.}$$

$$\begin{aligned} \text{mmol EDTA} \\ = 25.0 \text{ mL} \times \frac{0.0500}{\text{mL}} \end{aligned}$$

$$= 1.250 \text{ mmol EDTA}$$

$$\text{mmol In}^{2+}$$

$$= 5.00 \text{ mL} \times \frac{0.0500}{\text{mL}}$$

$$= 0.250 \text{ mmol In}^{2+}$$

$$\begin{aligned} \text{concentration of} \\ \text{Ni}^{2+} &= \frac{1.000 \text{ mmol}}{50.0 \text{ mL}} \\ &= 0.0200 \text{ M.} \end{aligned}$$

(5)

11-33 A 50.0 mL aliquot of solution containing ~~0.450 g~~ of MgSO_4 (FM 120.37) in 0.500 L required 0.450 g of EDTA solution for titration. How many 37.6 mL of EDTA solution will react with milligrams of CaCO_3 (FM 100.09) will react with 1.00 mL of this EDTA solution.

Ans: The formula mass of MgSO_4 is 120.37.

The 50.0 mL aliquot contains

$$\left(\frac{50.0 \text{ mL}}{500 \text{ mL}} \right) \left(\frac{0.450 \text{ g}}{120.37 \text{ g/mol}} \right) = 0.3738 \text{ mmol/g Mg}^{2+}$$

Since 37.6 mL of EDTA reacts with this much

Mg^{2+} , the EDTA solution contains ~~0.27~~

$$\frac{0.3738 \text{ mmol}}{37.6 \text{ mL}} = 9.943 \times 10^{-3} \text{ mmol/mL of Mg}^{2+}$$

(b)

The formula mass of $\text{CaCO}_3 = 100.09$

$\therefore 1.00 \text{ mL of EDTA will react with } 9.943 \times 10^{-3} \text{ mmol}$
of CaCO_3

$\therefore \text{Amount of } \text{CaCO}_3 = \frac{(9.943 \times 10^{-3} \text{ mmol}) \times 100.09}{\text{m.mL}}$

$$\boxed{\text{CaCO}_3 = 0.995 \text{ mg.}}$$

11-85

A 1.000-mL sample of unknown ⑦

containing Co^{2+} and Ni^{2+} was treated with 25.00 mL of 0.03872 M EDTA. Back titration with 0.02127 M Zn^{2+} at $\text{pH } 5$ required 23.54 mL to reach the xylenol orange end point. A 2.000 mL sample of unknown was passed through an ion-exchange column that retards Co^{2+} more than Ni^{2+} . The Ni^{2+} that passed through the column was treated with 25.00 mL of 0.03872 M EDTA and required 25.63 mL of 0.02127 M Zn^{2+} for back titration. The Co^{2+} emerged from the column later. It, too, was treated with 25.00 mL of 0.03872 M EDTA. How many milliliters of 0.02127 M Zn^{2+} will be required for back titration?

Ans:

for 1.000 mL of unknown:

$$\begin{array}{rcl} \text{25.00 mL of EDTA} & = & 0.9680 \text{ mmol} \\ - 23.54 \text{ mL of } \text{Zn}^{2+} & = & 0.5007 \text{ mmol} \\ \hline \text{Co}^{2+} + \text{Ni}^{2+} & = & 0.4673 \text{ mmol} \end{array}$$

$$\begin{aligned} & \therefore \\ & 25.00 \text{ mL} \times 0.03872 \frac{\text{mmol}}{\text{mL}} \\ & = 0.9680 \text{ mmol} \\ & \cancel{-} \\ & 23.54 \text{ mL} \times 0.02127 \frac{\text{mmol}}{\text{mL}} \\ & = 0.5007 \text{ mmol} \end{aligned}$$

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for 2.000 mL of unknown:

$$25.00 \text{ mL of EDTA} = 0.968 \text{ mmol}$$

$$- 25.63 \text{ mL of } \text{Zn}^{2+} = 0.5452 \text{ mmol}$$

$$\text{Ni}^{2+} \text{ in 2.000 mL} = 0.4228 \text{ mmol}$$

Co^{2+} in 2.000 mL of unknown

$$= 2(0.4673) - 0.4228$$

$$= 0.5118 \text{ mmol.}$$

$\therefore \text{Co}^{2+}$ will react with 0.5118 mmol of EDTA,
leaving $0.9680 - 0.5118 = 0.4562 \text{ mmol EDTA.}$

$$\therefore \text{mL Zn needed} = \frac{0.4562 \text{ mmol}}{0.02127 \text{ mmol/mL}}$$

$$\boxed{\therefore \text{mL Zn needed} = 21.45 \text{ mL}}$$

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11-3b A 50.0 mL solution containing Ni^{2+} and Zn^{2+} was treated with 25.0 mL of 0.0452 M EDTA to bind all the metal. The excess reagent required 12.4 mL of 0.0123 M Mg^{2+} for complete reaction. An excess of the reagent 2,3-dimercapto-1-propanol was then added to displace the EDTA from zinc.

Another 25.2 mL of Mg^{2+} were required for reaction with the liberated EDTA. Calculate the molarity of Ni^{2+} and Zn^{2+} in the original solution.

Ans

$$\begin{aligned}
 \text{Total EDTA} &= (25.0 \text{ mL}) (0.0452 \text{ M}) = 1.130 \text{ mmol} \\
 -\text{Mg}^{2+} \text{ required} &= (12.4 \text{ mL}) (0.0123 \text{ M}) = 0.153 \text{ mmol} \\
 \hline
 \text{Ni}^{2+} + \text{Zn}^{2+} &= 0.977 \text{ mmol}
 \end{aligned}$$

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Zn^{2+} = EDTA displaced by 2,3-dimercapto-1-propanol

$$= (29.2 \text{ mL}) (0.0123 \text{ M})$$

$$= 0.359 \text{ mmol.}$$

$$\therefore \text{Ni}^{2+} = 0.977 - 0.359$$

$$= 0.618 \text{ mmol.}$$

$$\therefore [\text{Ni}^{2+}] = \frac{0.618 \text{ mmol}}{50.0 \text{ mL}}$$

$$[\text{Ni}^{2+}] = 0.0124 \text{ M.}$$

$$\therefore [\text{Zn}^{2+}] = \frac{0.359 \text{ mmol}}{50.0 \text{ mL}} = 0.00718 \text{ M}$$

$$\therefore [\text{Zn}^{2+}] = 0.00718 \text{ M}$$

(11)

11-87. Sulfide ion was determined by indirect titration with EDTA. To a solution containing 25.00 mL of 0.04332 M $\text{Cu}(\text{ClO}_4)_2$ plus 15 mL of 1M acetate buffer ($\text{pH } 4.5$) were added 25.00 mL of unknown sulfide solution with vigorous stirring. The CuS precipitate was filtered and washed with hot water. Then ammonia was added to the filtrate (which contains excess Cu^{2+}) until the blue color of $\text{Cu}(\text{NH}_3)_4^{2+}$ was observed. Titration with 0.03927 M EDTA required 12.11 mL to reach the equivalence end point. Calculate the molarity of sulfide in the unknown.

Ans:

The precipitation reaction is



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$$\begin{array}{l}
 \text{Total} \quad \text{Cr}^{2+} \text{ used} = (25.00 \text{ mL}) (0.04332 \text{ M}) = 1.083 \text{ mmol} \\
 -\text{Excess} \quad \text{Cr}^{2+} = (12.11 \text{ mL}) (0.03927 \text{ M}) = 0.475 \text{ mmol} \\
 \hline
 \text{mmol of } \text{S}^{2-} & = 0.6074 \text{ mmol}
 \end{array}$$

$$\therefore [\text{S}^{2-}] = \frac{0.607 \text{ mmol}}{25.00 \text{ mL}} = 0.02430 \text{ M}$$

$$\boxed{[\text{S}^{2-}] = 0.02430 \text{ M}}$$