ESTIMATION OF HARDNESS

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Estimation of hardness by EDTA method

Principle

Preparation of solutions

Experimental procedure

Calculations

1.4 PROBLEMS BASED ON EDTA METHOD

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1.3 ESTIMATION OF HARDNESS

The estimation of hardness of water is of great importance for the chemical industry in general. There are various methods available for estimating the hardness of water.

Some of them are

- Soap titration method
- Alkali titration method
- EDTA method

Here, let us discuss the determination of hardness of water by using EDTA method.

ESTIMATION OF HARDNESS BY EDTA METHOD

EDTA is Ethylene Di-amine Tetra Acetic acid. The structure of EDTA is

Figure 1.3.1 Structure of EDTA

Source: https://www.toppr.com/ask/question/the-correct-structure-of-ethylenediamineteraaceticacid-edta-is/

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Since, EDTA is insoluble in water; its disodium salt is used as a complexing agent.

Principle

The amount of hardness causing ions (Ca^{2+} and Mg^{2+}) can be estimated by titrating the water sample against EDTA using Eriochrome-Black-T indicator (EBT) at a pH of 8-10. In order tomaintain the pH, buffer solution (NH4Cl − NH4OH mixture) is added. Only at this pH such a complexation is possible.

When the EBT indicator is added to the water sample, it forms wine red coloured weak complex with Ca^{2+} and Mg^{2+} ions.

$$[Ca^{2+}\ Mg^{2+}] + EBT \xrightarrow{pH = 8 - 10} [Ca\ Mg\ EBT]\ complex$$

Wine red colored weak complex

When this solution is titrated against EDTA, it replaces the indicator from the weak complex form stable EDTA complex. When all the hardness causing ions are complexed by EDTA,the indicator is set free. The color of the free indicator is steel blue. Thus the end point is the changeof color from wine red to steel blue.

$$\text{[Ca Mg EBT] complex + EDTA} \xrightarrow{pH = 8-10} \text{[Ca Mg EDTA]+ EBT}$$

Wine red colored weak complex — Stable complex Steel blue

Preparation of solutions

EDTA Solution

It is prepared by dissolving 4 gms of EDTA in 1000 ml of distilled water.

Standard hard water

1 gm of pure $CaCO_3$ is dissolved in minimum quantity of HCl and then made up to 1000 ml using distilled water.

$\therefore$ 1 ml of standard hard water $\equiv$ 1 mg of $CaCO_3$ equivalent hardness.

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EBT indicator

0.5 gms of EBT is dissolved in 100 ml of alcohol.

Buffer solution

67.5 gms of NH_4Cl and 570 ml of NH_3 are dissolved and the solution is made up to 1000 mlusing distilled water.

Experimental procedure

Standardization of EDTA

Pipette out 50 ml of standard hard water into a clean conical flask. Add 10 ml of buffer solution and 4-5 drops of EBT indicator and titrate it against EDTA solution taken in the burette. The end point is the change of colour from wine red to steel blue.

➢ Let the volume of EDTA consumed be V_1 ml

Estimation of total hardness of water sample

Pipette out 50 ml of the given hard water sample into a clean conical flask and titrate it against EDTA as before.

➢ Let the volume of EDTA consumed be V_2 ml

Estimation of permanent hardness of water sample

Take 100 ml of the same hard water sample in a 250 ml beaker. Boil it for 15 minutes. During boiling temporary hardness gets removed. Cool and filter the solution and make up to 100 ml in a standard flask by adding distilled water.

Pipette out 50 ml of the made up solution into a clean conical flask and titrate it against EDTA as before.

➢ Let the volume of EDTA consumed be V_3 ml.

Calculations

Standardization of EDTA

1 ml of Std. hard water = 1 mg of $CaCO_3$

50 ml of Std. hard water = 50 mgs of $CaCO_3$

50 ml of Std. hard water consumes = V_1 ml of EDTA

∴ V_1 ml of EDTA ≡ 50 mgs of $CaCO_3$ equivalent hardness

(or)

1 ml of EDTA ≡ 50 V_1 mgs of $CaCO_3$ equivalent hardness

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Estimation of total hardness of water sample

50 ml of the given hard water sample consumes = V_2 ml of EDTA

= $V_2 \times 50/V_1$ mgs of $CaCO_3$ equivalent hardness

[∴ 1 ml of EDTA = 50 V_1 mgs of $CaCO_3$]

∴ 1000 ml of the given hard water sample = $V_2 \times 50 / V_1 \times 1000 / 50$

= $1000 \times V_2 / V_1$ mgs of $CaCO_3$ equivalent hardness

∴ Total hardness = $1000 \times V_2 / V_1$ ppm

Estimation of permanent hardness of water sample

50 ml of the same hard water sample after boiling, filtering, etc., consumes = V_3 ml of EDTA

= $V_3 \times 50/V_1$ mgs of $CaCO_3$ equivalent hardness

∴ 1000 ml of the given hard water sample = $V_3 \times 50/V_1 \times 1000/50$

= $1000 \times V_3/V_1$ mgs of $CaCO_3$ equivalent hardness

∴ Permanent hardness = $1000 \times V_3/V_1$ ppm

Temporary hardness

Temporary hardness = Total hardness − Permanent hardness

$$= [1000 \times V_2 / V_1] - [1000 \times V_3 / V_1]$$

$\therefore$ Temporary hardness = $1000/V_1(V_2 - V_3)$ ppm

1.4 Problems based on EDTA method

Problem 1

100 ml of a water sample requires 20 ml of EDTA solution for titration. 1 ml of EDTA solution is equivalent to 1.1 mgs of $CaCO_3$. Calculate hardness in ppm.

Solution

Given 1 ml of EDTA solution = 1.1 mgs of $CaCO_3$

$\therefore$ 20 ml of EDTA solution = 20×1.1 mgs of $CaCO_3$

$= 22$ mgs of $CaCO_3$

100 ml of water sample requires = 20 ml of EDTA

$= 22$ mgs of $CaCO_3$

$\therefore$ 1000 ml of water sample = 22×1000 100 mgs of $CaCO_3$

Hardness = 220 mgs/lit or ppm.

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Problem 2

100 ml of a sample of water requires 18 ml of an EDTA solution for titration. 22 ml of thesame EDTA solution was required for the titration of 100 ml of standard hard water containing 1 gm $CaCO_3$ per litre. Calculate hardness of water sample in ppm.

Solution

Given 1 litre of std. hard water contains 1 gm of $CaCO_3$

i.e. 1000 ml of std. hard water contains 1000 mgs of $CaCO_3$

$\therefore$ 1 ml of std. hard water = 1 mg of $CaCO_3$

22 ml of EDTA = 100 ml of std. hard water

$= 100 \times 1$ mg of $CaCO_3$

$\therefore$ 1 ml of EDTA = 100/22mgs of $CaCO_3$

100 ml of sample of water = 18 ml of EDTA

= 18 × 100 /22 mgs of $CaCO_3$

∴ for 1000 ml of sample of water = 18 × 100 / 22 × 1000

x100 Hardness = 818.18 mgs/lit or ppm.

Problem 3

0.28 gm of CaCO3 was dissolved in HCl and the solution was made up to one litre with distilled water. 100 ml of the above solution required 28 ml of EDTA solution on titration. 100 ml of hard water sample required 33 ml of same EDTA solution on titration. 100 ml of this water, after boilingcooling and filtering required 10 ml of EDTA solution on titration. Calculate the temporary and permanent harness of water.

Solution

Given 1000 ml of std. hard water contains = 0.28 gm of $CaCO_3$

ie., 1000 ml of std. hard water contains = 0.28 × 1000 mgs of $CaCO_3$

= 280 mgs of $CaCO_3$

∴ 1 ml of std. hard water = 0.28 mg of $CaCO_3$

28 ml of EDTA = 100 ml of the std. hard water

= 100 × 0.28 mgs of $CaCO_3$

= 100 × 0.28 x28

1 ml of EDTA = 1 mgs of $CaCO_3$.

Total hardness

100 ml of hard water = 33 ml of EDTA

= 33 × 1 mgs of $CaCO_3$

= 33 mgs of $CaCO_3$

∴ 1000 ml of hard water = 33 ×

1000/100 Total hardness = 330 mgs/lit

(or) ppm.

Permanent hardness (NCH)

100 ml of the same water, after boiling, cooling and filtering required = 10 ml of EDTA

= 10 × 1 mgs of $CaCO_3$

= 10 mgs of $CaCO_3$

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∴ 1000 ml of the water = 10 × 1000 100 mgs of $CaCO_3$

Permanent hardness = 100 mgs/lit (or) ppm.

Temporary hardness (CH)

Temporary hardness = Total hardness − permanent hardness

= 330 − 100

Temporary hardness = 230 mgs/lit (or) ppm.

Problem 4

100 ml of a sample of water required 25.0 ml of 0.01 M EDTA for the titration using Eriochrome-Black-T indicator. Calculate the total hardness.

Solution

We know that,

1 ml of 0.01 M EDTA = 1 mg of $CaCO_3$

25 ml of 0.01 M EDTA = 25 mgs of $CaCO_3$

100 ml of sample of water required = 25.0 ml of 0.01 M EDTA

= 25.0 mgs of $CaCO_3$ equivalent

∴ 1000 ml of water is equal to = 25.0 × 1000 100 mgs of $CaCO_3$ equivalent

Total hardness = 250 mgs/lit or ppm.

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Problem 5

Calculate permanent hardness from the following. 500 ml of a water sample is boiled for 1 hr. It isthen cooled and filtered. The filtrate is made up to 500 ml again with distilled water. 50 ml of this solution requires 10 ml of N/50 EDTA with EBT-indicator and NH_4Cl − NH_4OH buffer.

Solution

Given50 ml of water sample after boiling, filtering requires 10 ml of N /50 EDTA

We know that,

1 ml of N /50 EDTA ≡ 1 mg of $CaCO_3$ equivalent hardness

∴ 10 ml of N /50 EDTA ≡ 10 mgs of $CaCO_3$

50 ml of the boiled water sample requires = 10 ml of N/ 50 EDTA

= 10 mgs of $CaCO_3$

∴ 1000 ml of the water sample = 10 × 1000 /50

Permanent hardness = 200 mgs/lit or ppm.

Problem 6

100 ml of a sample of water required 15.0 ml of 0.01 M EDTA for titration using Erio-chrome Black-T indicator. In another experiment, 100 ml of the same sample was boiled to remove the CH, the precipitate was removed and the cold solution required 8.0 ml of 0.01 M EDTA using Erio- chrome Black-T indicator. Calculate (i) the total hardness, (ii) permanent hardness or NCH, (iii) carbonate hardness (CH), in terms of mg/lit of $CaCO_3$.

Solution

We know that,

1 ml of 1 M EDTA ≡ 100 mgs of $CaCO_3$

1 ml of 0.01 M EDTA ≡ 1 mg of $CaCO_3$

Total Hardness

100 ml of a sample of water required = 15 ml of 0.01 M EDTA

= 15 × 1 mgs

= 15 mgs of $CaCO_3$

∴ 1000 ml of sample of water is equivalent to = 15 × 1000/100 mgs of $CaCO_3$

= 150 mgs of $CaCO_3$ equivalents

Total hardness = 150 mgs/lit or ppm.

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Permanent Hardness (NCH)

100 ml of the same water sample after boiling, filtering consumes = 8.0 ml of 0.01 M EDTA

= 8.0 × 1 mgs

= 8.0 mgs of $CaCO_3$

∴ 1000 ml of sample of water is equal to = 8.0 × 1000/100 mgs

= 80 mgs of $CaCO_3$ equivalents

Permanent hardness of the water sample = 80 ppm.

Temporary Hardness (CH)

Temporary hardness = Total hardness − Permanent hardness

= 150 − 80 = 70 ppm

Temporary hardness = 70 ppm.

Problem 7

100 ml of a water sample required 20 ml of 0.01 M EDTA for the titration with Eriochrome Black- T indicator 100 ml of the same water sample after boiling and filtering required 10 ml of 0.01 M EDTA. Calculate the total, carbonate and non-carbonate hardness of the sample.

Solution

We know that ,

1 ml of 1 M EDTA ≡ 100 mgs of $CaCO_3$

1 ml of 0.01 M EDTA ≡ 1 mg of $CaCO_3$

Total Hardness 100 ml of a sample of water required = 20 ml of 0.01 M EDTA

$= 20 \times 1$ mgs

= 20 mgs of $CaCO_3$

∴ 1000 ml of sample of water is equivalent to = $20 \times 1000/100$ mgs of $CaCO_3$

= 200 mgs of $CaCO_3$ equivalent

Total hardness = 200 mgs/lit or ppm.

Non-carbonate Hardness (NCH)

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100 ml of the same water sample after boiling, filtering consumes = 10 ml of 0.01 M EDTA

$= 10 \times 1$ mgs

= 10 mgs of $CaCO_3$

∴ 1000 ml of sample of water is equal to = $10 \times 1000 /100$ mgs

= 100 mgs of $CaCO_3$ equivalent

Permanent hardness of the water sample = 100 ppm.

Carbonate Hardness (CH)

Carbonate hardness = Total hardness – Non-carbonate hardness

$= 200 - 100$

=100 ppm

Carbonate hardness = 100 ppm.

Problem 8

In an estimation of hardness of water by EDTA titration, 250 ml of a sample of water required 15ml of 0.025 M EDTA solution to get the end point. Calculate the hardness of water.

Solution

We know that 1 ml of 1 M EDTA ≡ 100 mgs of $CaCO_3$

1 ml of 0.01 M EDTA ≡ 1 mg of $CaCO_3$

∴ 1 ml of 0.0β5 M EDTA ≡ 2.5 mgs of $CaCO_3$ equivalent

Total Hardness

250 ml of a sample of water required = 15 ml of 0.025 M EDTA

= 15 × 2.5 mgs

= 37.5 mgs of $CaCO_3$ equivalent

∴ 1000 ml of a sample of water required = 37.5 × 1000 250 mgs

= 150 mgs of $CaCO_3$ equivalent

Total hardness = 150 ppm.

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