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SUPPLEMENTARY MATERIAL

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A Novel pH-Sensitive Method for the Quantification of Ca^{+2} Ions by Complexometric Titration with Na_3HEDTA

Rahul Bhochiya,[a] Pradip Kumar Mondal,[b] Shah Jaimin Balkrishna*[a]

[a] Department of Chemistry, Government Commerce and Science College Dahej, Bharuch, Gujarat 392 130, India (Affiliated with Veer Narmad South Gujarat University, Surat, Gujarat, India)

[b] Elettra Sincrotrone Trieste, S.S. 14 Km 163.5 in Area Science Park, 34149 Basovizza Trieste, Italy

jaiminshah02@gail.com

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Experimental Section

Calcium Carbonate ($CaCO_3$), disodium salt of EDTA (Na_2H_2EDTA) and bromothymol blue indicator solution were purchased from Loba Chemie. Hydrochloric acid (HCl) and Sodium Hydroxide (NaOH) were purchased from Finar. Eriochrome Black –T (EBT) indicator was purchased from Finar and freshly prepared just before the experiment by dissolving 0.4 g EBT in 10.0 mL ethanol and 30.0 mL triethanolamine. Buffer solution having pH 10 was prepared by mixing 68.0 g NH_4Cl, 568.0 mL liquor ammonia and 364.0 mL water. Aqueous solutions in all the experiments were prepared by using Bisleri packaged drinking water. Marble stone, egg shells and sea shells were thoroughly washed, dried and grinded to have homogeneous powder. Calcium tablets (Caldison-500, Unison Pharmaceuticals Pvt. Ltd) were purchased from local market (Batch No. 220910770, Manufacturing Date: Sept 2022, Expiry Date: August 2024). All the pH-Metric experiments were conducted on digital pH meter (Brand: Digitronics, Model: 213) having pH range of 0-14 and resolution 0.01 unit of pH. Combined glass electrode Digitronics CE24 was used. The inner reference electrode is Ag/AgCl electrode in 3 mol/L KCl solution with porous liquid junction. pH electrode was calibrated with the use of buffer solutions having pH 4.00, pH 7.00 and pH 9.00 before each new experiment. All the pH-Metric titrations and volumetric analysis with bromothymol blue were performed with three sets of solutions and three experiments were performed with each set of solution in order to check the reproducibility of results.

1) pH-Metric Estimation of Calcium as Calcium Carbonate ($CaCO_3$) by using Aq. Solution of Ca^{+2} (pH 7) as titrand and Aq. Solution of Na_2H_2EDTA (pH 4.4) as titrant

0.0375 g $CaCO_3$ was dissolved in 0.1 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 100.0 mL beaker. Then, pH electrode was inserted to this solution and pH value was found to be 2.5. pH of this solution was adjusted to 7 by adding 2.0 mL 0.33 M NaOH solution (**Solution B**). 0.01M

Na_2H_2EDTA solution was filled in 25.0 mL burette. Now, 0.5 mL 0.01M Na_2H_2EDTA was added to Solution B having pH 7. Solution was shaken well with the help of glass rod and then pH reading was measured. Same process was repeated by adding 0.5 mL 0.01M Na_2H_2EDTA from burette up to 12.0 mL and pH reading was measured after each 0.5 mL addition of burette solution. Obtained readings and graph are described below.

Table 1: pH-Metric Titration Readings between Aq. Solutions of Ca^{+2} and Na_2H_2EDTA

Sr. No.	Volume of 0.01M Na_2H_2EDTA (in mL)	pH
1	0.0	7.05
2	0.5	6.49
3	1.0	5.95
4	1.5	5.20
5	2.0	4.52
6	2.5	4.32
7	3.0	4.19
8	3.5	4.11
9	4.0	4.03
10	4.5	4.00
11	5.0	3.98
12	5.5	3.95
13	6.0	3.92
14	6.5	3.90
15	7.0	3.89
16	7.5	3.87

17	8.0	3.84
18	8.5	3.82
19	9.0	3.80
20	9.5	3.79
21	10.0	3.77
22	10.5	3.75
23	11.0	3.74
24	11.5	3.73
25	12.0	3.72

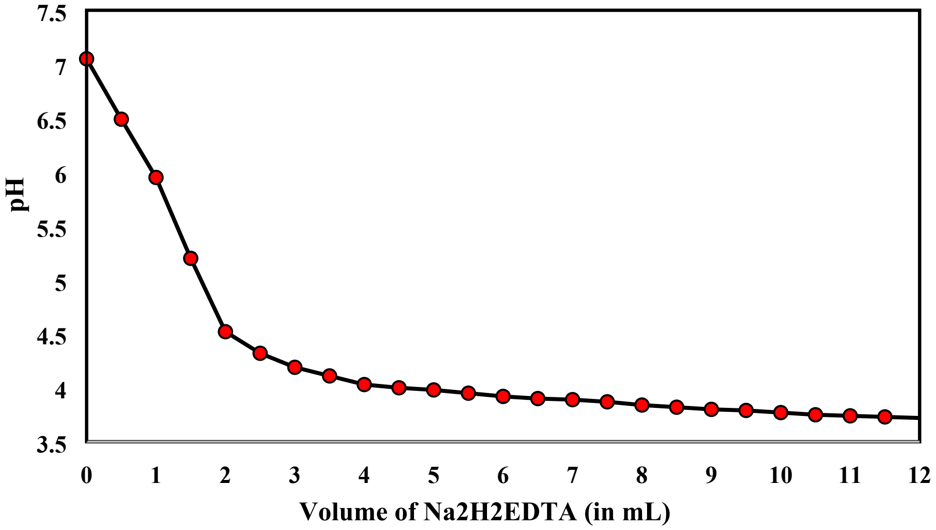


Figure 1: Effect of Aq.Na$_2$H$_2$EDTA Addition on pH of Ca^{+2} Solution

Observations: Initially, decrease in pH was observed with the progress of titration, but even after passing the stage of equivalence point, a constant small decrease in pH was observed and hence we could not find out the exact & sharp equivalence point. It may be because of weak acidic nature of Aq. Na$_2$H$_2$EDTA solution.

2) pH-Metric Estimation of Calcium as Calcium Carbonate ($CaCO_3$) by using Aq. Solution of Ca^{+2} (pH 7) as titrand and Aq. Solution of Na_3HEDTA (pH 11) as titrant (Stock solution of $CaCO_3$ was prepared by dissolving 37.5 mg of $CaCO_3$)

0.0375 g $CaCO_3$ was dissolved in 0.1 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 100.0 mL beaker. Then, pH electrode was inserted to this solution and pH value was found to be 2.5. pH of this solution was adjusted to 7 by adding 2.0 mL 0.33 M NaOH solution (**Solution B**). Aqueous solution of 0.01M Na_3HEDTA (pH 11) was prepared by mixing 250.0 mL 0.01M Na_2H_2EDTA and 15.0 mL 0.33M NaOH solutions. This solution was filled in 25.0 mL burette as titrant. Then, 0.5 mL 0.01M Na_3HEDTA was added to Solution B having pH 7. Solution was shaken well with the help of glass rod and then pH reading was measured. Same process was repeated by adding 0.5 mL 0.01M Na_3HEDTA from burette up to 12.0 mL and pH reading was measured after each 0.5 mL addition of burette solution. Obtained readings and graph are described below.

Table 2: pH-Metric Titration Readings between Aq. Solutions of Ca^{+2} and Na_3HEDTA

Sr. No.	Volume of 0.01M Na_3HEDTA (in mL)	pH
1	0.0	7.06
2	0.5	6.99
3	1.0	6.94
4	1.5	6.86
5	2.0	6.79
6	2.5	6.73
7	3.0	6.68

8	3.5	6.62
9	4.0	6.56
10	4.5	6.50
11	5.0	6.44
12	5.5	6.39
13	6.0	6.34
14	6.5	6.31
15	7.0	6.28
16	**7.5**	**6.24**
17	8.0	7.15
18	8.5	7.79
19	9.0	8.39
20	9.5	9.39
21	10.0	9.70
22	10.5	10.02
23	11.0	10.12
24	11.5	10.28
25	12.0	10.34

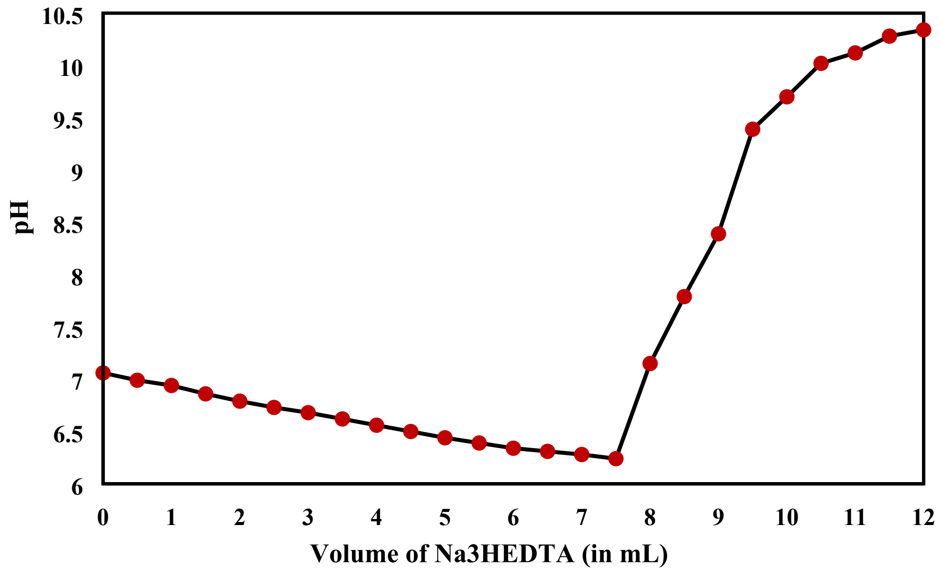


Figure 2: Effect of Aq.Na_3HEDTA Addition on pH of Ca^{+2} Solution

Observations: During this titration, formation of Ca-EDTA complex and release of one H^+ ion was taking place and hence decrease in pH from 7.06 to 6.24 was observed. At equivalence point, release of H^+ ion was stopped and sharp increase in pH was observed from 6.24 to 7.15 with further 0.5 mL addition of Na_3HEDTA (pH 11). Upon subsequent addition of Na_3HEDTA solution, pH value of solution significantly jumped to 7.79, 8.39 and 9.39. **So sharp equivalence point for the titration was observed at 7.5 mL.**

Theoretical Calculations:

Solution B contains 7.5 mg of $CaCO_3$ (Theoretical Amount)

Solution A contains (7.5 x 5) = 37.5 mg of $CaCO_3$ (Theoretical Amount)

Experimental Calculations:

1000.0 mL 1M Na_3HEDTA ≡ 100.0 g $CaCO_3$ ≡ 40.0 g Ca^{+2}

1000.0 mL 0.01M Na_3HEDTA ≡ 1.0 g $CaCO_3$ ≡ 0.4 g Ca^{+2}

1.0 mL 0.01M Na_3HEDTA ≡ 1.0 mg $CaCO_3$ ≡ 0.4 mg Ca^{+2}

7.5 mL 0.01M Na_3HEDTA ≡ 7.5 mg $CaCO_3$

Solution B contains 7.5 mg of $CaCO_3$ (Experimental Amount)

Solution A contains (7.5 x 5) = 37.5 mg of $CaCO_3$ (Experimental Amount)

Theoretical and experimental amount for the estimation of $CaCO_3$ matches well.

3) Estimation of Calcium as Calcium Carbonate ($CaCO_3$) by using conventional complexometric titration method (Stock solution of $CaCO_3$ was prepared by dissolving 37.5 mg of $CaCO_3$)

0.0375 g $CaCO_3$ was dissolved in 0.1 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 250.0 mL conical flask (**Solution B**). To this, 1.5 test tube (Approx. 10-12 mL) NH_4OH-NH_4Cl buffer (pH 10) was added. Then, 4-5 drops of Eriochrome Black-T indicator was added. Solution in the conical flask was turned wine red and it was shaken well. Aq. Solution of Na_2H_2EDTA was filled in 25.0 mL burette. Then, titration was performed by drop wise addition of burette solution to the conical flask. A sharp colour change from wine red to blue was observed at the end point. This experiment was repeated three times. Obtained observations are listed below.

Table 3: Readings of complexometric titration between Aq. Solutions of Ca^{+2} and Na_2H_2EDTA by using Eriochrome Black-T as indicator

Experiment No.	Initial Reading (in mL)	Final Reading (in mL)	Difference (in mL)	Concordant Reading (in mL)
1	0.0	7.8	7.8	7.8
2	0.0	7.8	7.8	
3	0.0	7.8	7.8	

<u>Theoretical Calculations:</u>

Solution B contains 7.5 mg of $CaCO_3$ (Theoretical Amount)

Solution A contains (7.5 x 5) = 37.5 mg of $CaCO_3$ (Theoretical Amount)

Experimental Calculations:

1000.0 mL $1M\ Na_2H_2EDTA$ ≡ 100.0 g $CaCO_3$ ≡ 40.0 g Ca^{+2}

1000.0 mL $0.01M\ Na_2H_2EDTA$ ≡ 1.0 g $CaCO_3$ ≡ 0.4 g Ca^{+2}

1.0 mL $0.01M\ Na_2H_2EDTA$ ≡ 1.0 mg $CaCO_3$ ≡ 0.4 mg Ca^{+2}

7.8 mL $0.01M\ Na_2H_2EDTA$ ≡ 7.8 mg $CaCO_3$

Solution B contains 7.8 mg of $CaCO_3$ (Experimental Amount)

Solution A contains (7.8 x 5) = 39.0 mg of $CaCO_3$ (Experimental Amount)

4) Gravimetric estimation of Calcium Carbonate (Stock solution of Calcium Carbonate was prepared by digesting 37.5 mg of Calcium Carbonate Powder with 1.0 mL Con. HCl)[1]

37.5 mg of calcium carbonate powder was taken in 100.0 mL beaker. To this, 1.0 mL Con. HCl was added with stirring followed by addition of 10.0 mL water. Beaker was covered with watch glass and then heated till the solution became clear and carbon dioxide expelled completely. Sides of beaker and watch glass were rinsed with distilled water and diluted up to 50.0 mL. Then, solution was heated to boiling and 2 drops of methyl red indicator was added. To this, 5.0 mL 5% ammonium oxalate solution was added. To the resulted hot solution, (1:1) ammonia solution was added drop wise and with constant stirring until the mixture became neutral (color of solution changes to yellow from red). Formed precipitates were allowed to settle without further heating for one hour. Precipitates were filtered through previously weighed Whatman filter paper 40 and washed with 0.1% ammonium oxalate solution till it became free from chloride. Precipitates were dried on metallic cone on sand bath. Weight the amount of (Precipitate + Whatmann filter paper) and subtract it from the weight of empty Whatmann filter paper. This experiment was repeated three times and the results are reported below.

Experiment No.	Weight of Filter Paper (in g)	Weight of (Filter Paper + Precipitates) (in g)	Weight of Precipitates (in g)	Concordant Reading (in mg)
01	1.1130 g	1.1676	0.0546	54.6
02	1.1271 g	1.1817	0.0546	
03	1.0864 g	1.1415	0.0551	

Calculations:

1.0 mole of $CaCO_3$ ≡ 1.0 mole of $CaC_2O_4.H_2O$

100.0 g $CaCO_3$ ≡ 146.08 g $CaC_2O_4.H_2O$

0.0375 g $CaCO_3$ ≡ 0.0547 g $CaC_2O_4.H_2O$

Therefore, for obtained 54.6 mg $CaC_2O_4.H_2O$, the equivalent amount of $CaCO_3$ is 37.4 mg

5) **pH-Metric Estimation of Calcium as Calcium Carbonate ($CaCO_3$) by using Aq. Solution of Ca^{+2} (pH 7) as titrand and Aq. Solution of Na_3HEDTA (pH 11) as titrant (Stock solution of $CaCO_3$ was prepared by dissolving 75.0 mg of $CaCO_3$)**

0.075 g $CaCO_3$ was dissolved in 0.2 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 100.0 mL beaker. Then, pH electrode was inserted to this solution and pH value was found to be 2.4. pH of this solution was adjusted to 7 by adding 4.0 mL 0.33 M NaOH solution (**Solution B**). Aqueous solution of 0.01M Na_3HEDTA (pH 11) was prepared by mixing 250.0 mL 0.01M Na_2H_2EDTA and 15.0 mL 0.33M NaOH solutions. This solution was filled in 25.0 mL burette as titrant. Then, 0.5 mL 0.01M Na_3HEDTA was added to Solution B having pH 7. Solution was shaken well with the help of glass rod and then pH reading was measured. Same process was repeated by adding 0.5 mL 0.01M Na_3HEDTA from burette up to 20.0 mL and pH reading was measured after each 0.5 mL addition of burette solution. Obtained readings and graph are described below.

Table 4: pH-Metric Titration Readings between Aq. Solutions of Ca^{+2} and Na_3HEDTA

Sr. No.	Volume of 0.01M Na_3HEDTA (in mL)	pH
1	0.0	7.07
2	0.5	6.90
3	1.0	6.73
4	1.5	6.66
5	2.0	6.59
6	2.5	6.51
7	3.0	6.44
8	3.5	6.39
9	4.0	6.34
10	4.5	6.30
11	5.0	6.26
12	5.5	6.22
13	6.0	6.18
14	6.5	6.13
15	7.0	6.08
16	7.5	6.05
17	8.0	6.01

18	8.5	5.96
19	9.0	5.92
20	9.5	5.89
21	10.0	5.86
22	10.5	5.83
23	11.0	5.80
24	11.5	5.76
25	12.0	5.71
26	12.5	5.68
27	13.0	5.65
28	13.5	5.62
29	14.0	5.60
30	14.5	5.58
31	**15.0**	**5.56**
32	15.5	5.86
33	16.0	6.12
34	16.5	6.31
35	17.0	6.57
36	17.5	6.84
37	18.0	7.09
38	18.5	7.34
39	19.0	7.72
40	19.5	8.10
41	20.0	8.38

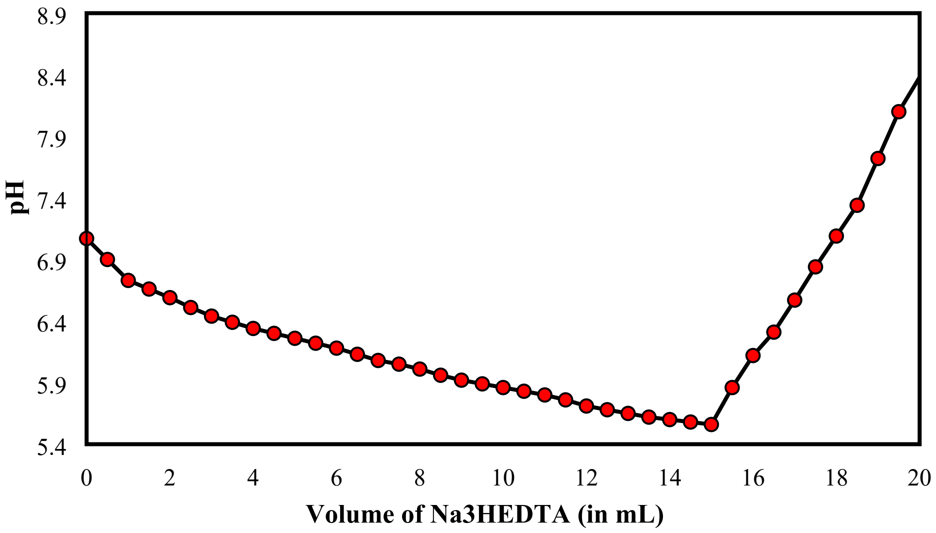


Figure 3: Effect of Aq.Na_3HEDTA Addition on pH of Ca^{+2} Solution

Observations: During this titration, formation of Ca-EDTA complex and release of one H^+ ion was taking place and hence decrease in pH from 7.07 to 5.56 was observed. At equivalence point, release of H^+ ion was stopped and sharp increase in pH was observed from 5.56 to 5.86 with further 0.5 mL addition of Na_3HEDTA (pH 11). Upon subsequent addition of Na_3HEDTA solution, pH value of solution significantly jumped to 6.12, 6.31 and 6.57. **So sharp equivalence point for the titration was observed at 15.0 mL.**

Theoretical Calculations:

Solution B contains 15.0 mg of $CaCO_3$ (Theoretical Amount)

Solution A contains (15.0 x 5) = 75.0 mg of $CaCO_3$ (Theoretical Amount)

Experimental Calculations:

1000.0 mL 1M Na_3HEDTA ≡ 100.0 g $CaCO_3$ ≡ 40.0 g Ca^{+2}

1000.0 mL 0.01M Na_3HEDTA ≡ 1.0 g $CaCO_3$ ≡ 0.4 g Ca^{+2}

1.0 mL 0.01M Na_3HEDTA ≡ 1.0 mg $CaCO_3$ ≡ 0.4 mg Ca^{+2}

15.0 mL 0.01M Na_3HEDTA ≡ 15.0 mg $CaCO_3$

Solution B contains 15.0 mg of $CaCO_3$ (Experimental Amount)

Solution A contains (15.0 x 5) = 75.0 mg of $CaCO_3$ (Experimental Amount)

6) Estimation of Calcium as Calcium Carbonate ($CaCO_3$) by using conventional complexometric titration method (Stock solution of $CaCO_3$ was prepared by dissolving 75.0 mg of $CaCO_3$)

0.075 g $CaCO_3$ was dissolved in 0.2 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 250.0 mL conical flask (**Solution B**). To this, 1.5 test tube (Approx. 10-12 mL) NH_4OH-NH_4Cl buffer (pH 10) was added. Then, 4-5 drops of Eriochrome Black-T indicator was added. Solution in the conical flask was turned wine red and it was shaken well. Aq. Solution of Na_2H_2EDTA was filled in 25.0 mL burette. Then, titration was performed by drop wise addition of burette solution to the conical flask. A sharp colour change from wine red to blue was observed at the end point. This experiment was repeated three times. Obtained observations are listed below.

Table 5: Readings of complexometric titration between Aq. Solutions of Ca^{+2} and Na_2H_2EDTA by using Eriochrome Black-T as indicator

Experiment No.	Initial Reading (in mL)	Final Reading (in mL)	Difference (in mL)	Concordant Reading (in mL)
1	0.0	15.4	15.4	15.4
2	0.0	15.4	15.4	
3	0.0	15.4	15.4	

<u>Theoretical Calculations:</u>

Solution B contains 15.0 mg of $CaCO_3$ (Theoretical Amount)

Solution A contains (15.0 x 5) = 75.0 mg of $CaCO_3$ (Theoretical Amount)

Experimental Calculations:

1000.0 mL 1M Na_2H_2EDTA ≡ 100.0 g $CaCO_3$ ≡ 40.0 g Ca^{+2}

1000.0 mL 0.01M Na_2H_2EDTA ≡ 1.0 g $CaCO_3$ ≡ 0.4 g Ca^{+2}

1.0 mL 0.01M Na_2H_2EDTA ≡ 1.0 mg $CaCO_3$ ≡ 0.4 mg Ca^{+2}

15.4 mL 0.01M Na_2H_2EDTA ≡ 15.4 mg $CaCO_3$

Solution B contains 15.4 mg of $CaCO_3$ (Experimental Amount)

Solution A contains (15.4 x 5) = 77.0 mg of $CaCO_3$ (Experimental Amount)

7) Gravimetric Estimation of Calcium Carbonate (Stock solution of Calcium Carbonate was prepared by digesting 75.0 mg of Calcium Carbonate Powder with 2.0 mL Con. HCl)

75.0 mg of calcium carbonate powder was taken in 100.0 mL beaker. To this, 2.0 mL Con. HCl was added with stirring followed by addition of 10.0 mL water. Beaker was covered with watch glass and then heated till the solution became clear and carbon dioxide expelled completely. Sides of beaker and watch glass were rinsed with distilled water and diluted up to 50.0 mL. Then, solution was heated to boiling and 2 drops of methyl red indicator was added. To this, 7.0 mL 5% ammonium oxalate solution was added. To the resulted hot solution, (1:1) ammonia solution was added drop wise and with constant stirring until the mixture became neutral (color of solution changes to yellow from red). Formed precipitates were allowed to settle without further heating for one hour. Precipitates were filtered through previously weighed Whatman filter paper 40 and washed with 0.1% ammonium oxalate solution till it became free from chloride. Precipitates were dried on metallic cone on sand bath. Weight the amount of (Precipitate + Whatmann filter paper) and subtract it from the weight of empty Whatmann filter paper. This experiment was repeated three times and the results are reported below.

Experiment No.	Weight of Filter Paper (in g)	Weight of (Filter Paper + Precipitates) (in g)	Weight of Precipitates (in g)	Concordant Reading (in mg)
01	1.0683 g	1.1772	0.1089	108.9
02	1.0878 g	1.1972	0.1094	
03	1.1292 g	1.2381	0.1089	

Calculations:

1.0 mole of $CaCO_3$ ≡ 1.0 mole of $CaC_2O_4.H_2O$

100.0 g $CaCO_3$ ≡ 146.08 g $CaC_2O_4.H_2O$

0.075 g $CaCO_3$ ≡ 0.1095 g $CaC_2O_4.H_2O$

Therefore, for obtained 108.9 mg $CaC_2O_4.H_2O$, the equivalent amount of $CaCO_3$ is 74.6 mg

8) pH-Metric Estimation of Calcium as Calcium Carbonate ($CaCO_3$) by using Aq. Solution of Ca^{+2} (pH 7) as titrand and Aq. Solution of Na_3HEDTA (pH 11) as titrant (Stock solution of $CaCO_3$ was prepared by dissolving 112.5 mg of $CaCO_3$)

0.112 g $CaCO_3$ was dissolved in 0.3 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 100.0 mL beaker. Then, pH electrode was inserted to this solution and pH value was found to be 2.2. pH of this solution was adjusted to 7 by adding 6.0 mL 0.33 M NaOH solution (**Solution B**). Aqueous solution of 0.01M Na_3HEDTA (pH 11) was prepared by mixing 250.0 mL 0.01M Na_2H_2EDTA and 15.0 mL 0.33M NaOH solutions. This solution was filled in 25.0 mL burette as titrant. Then, 0.5 mL 0.01M Na_3HEDTA was added to Solution B having pH 7. Solution was shaken well with the help of glass rod and then pH reading was measured. Same process was repeated by adding 0.5 mL 0.01M Na_3HEDTA from burette up to 25.0 mL and pH reading

was measured after each 0.5 mL addition of burette solution. Obtained readings and graph are described below.

Table 6: pH-Metric Titration Readings between Aq. Solutions of Ca^{+2} and Na_3HEDTA

Sr. No.	Volume of 0.01M Na_3HEDTA (in mL)	pH
1	0.0	7.01
2	0.5	6.97
3	1.0	6.93
4	1.5	6.92
5	2.0	6.91
6	2.5	6.90
7	3.0	6.89
8	3.5	6.88
9	4.0	6.87
10	4.5	6.86
11	5.0	6.85
12	5.5	6.84
13	6.0	6.83
14	6.5	6.82
15	7.0	6.81
16	7.5	6.80
17	8.0	6.79
18	8.5	6.78
19	9.0	6.77

20	9.5	6.75
21	10.0	6.74
22	10.5	6.73
23	11.0	6.72
24	11.5	6.70
25	12.0	6.68
26	12.5	6.67
27	13.0	6.66
28	13.5	6.65
29	14.0	6.64
30	14.5	6.61
31	15.0	6.58
32	15.5	6.56
33	16.0	6.54
34	16.5	6.52
35	17.0	6.49
36	17.5	6.46
37	18.0	6.44
38	18.5	6.42
39	19.0	6.41
40	19.5	6.39
41	20.0	6.37
42	20.5	6.35
43	21.0	6.33

44	21.5	6.31
45	22.0	6.29
46	**22.5**	**6.27**
47	23.0	6.40
48	23.5	6.65
49	24.0	6.82
50	24.5	6.95
51	25.0	7.17

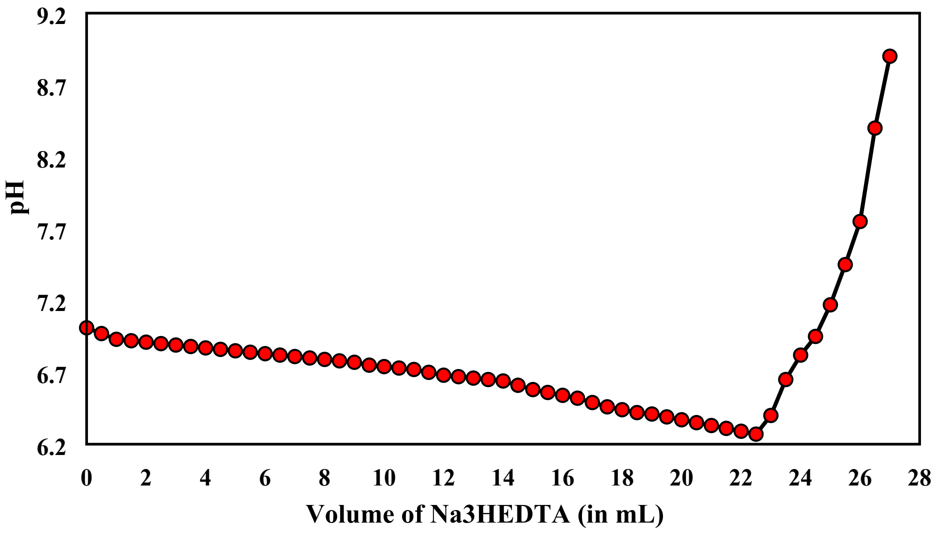


Figure 4: Effect of Aq.Na_3HEDTA Addition on pH of Ca^{+2} Solution

Observations: During this titration, formation of Ca-EDTA complex and release of one H^+ ion was taking place and hence decrease in pH from 7.01 to 6.27 was observed. At equivalence point, release of H^+ ion was stopped and sharp increase in pH was observed from 6.27 to 6.40 with further 0.5 mL addition of Na_3HEDTA (pH 11). Upon subsequent addition of Na_3HEDTA solution, pH value of solution significantly jumped to 6.65, 6.82 and 6.95. **So sharp equivalence point for the titration was observed at 22.5 mL**

Theoretical Calculations:

Solution B contains 22.5 mg of $CaCO_3$ (Theoretical Amount)

Solution A contains (22.5 x 5) = 112.5 mg of $CaCO_3$ (Theoretical Amount)

Experimental Calculations:

1000.0 mL 1M Na_3HEDTA ≡ 100.0 g $CaCO_3$ ≡ 40.0 g Ca^{+2}

1000.0 mL 0.01M Na_3HEDTA ≡ 1.0 g $CaCO_3$ ≡ 0.4 g Ca^{+2}

1.0 mL 0.01M Na_3HEDTA ≡ 1.0 mg $CaCO_3$ ≡ 0.4 mg Ca^{+2}

22.5 mL 0.01M Na_3HEDTA ≡ 22.5 mg $CaCO_3$

Solution B contains 22.5 mg of $CaCO_3$ (Experimental Amount)

Solution A contains (22.5 x 5) = 112.5 mg of $CaCO_3$ (Experimental Amount)

Theoretical and experimental amount for the estimation of $CaCO_3$ matches well.

9) Estimation of Calcium as Calcium Carbonate ($CaCO_3$) by using conventional complexometric titration method (Stock solution of $CaCO_3$ was prepared by dissolving 112.5 mg of $CaCO_3$)

0.1125 g $CaCO_3$ was dissolved in 0.3 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 250.0 mL conical flask (**Solution B**). To this, 1.5 test tube (Approx. 10-12 mL) NH_4OH-NH_4Cl buffer (pH 10) was added. Then, 4-5 drops of Eriochrome Black-T indicator was added. Solution in the conical flask was turned wine red and it was shaken well. Aq. Solution of Na_2H_2EDTA was filled in 25.0 mL burette. Then, titration was performed by drop wise addition of burette solution to the conical flask. A sharp colour change from wine red to blue was observed at the end point. This experiment was repeated three times. Obtained observations are listed below.

Table 7: Readings of complexometric titration between Aq. Solutions of Ca^{+2} and Na_2H_2EDTA by using Eriochrome Black-T as indicator

Experiment No.	Initial Reading (in mL)	Final Reading (in mL)	Difference (in mL)	Concordant Reading (in mL)
1	0.0	23.0	23.0	23.0
2	0.0	23.0	23.0	
3	0.0	22.9	22.9	

Theoretical Calculations:

Solution B contains 22.5 mg of $CaCO_3$ (Theoretical Amount)

Solution A contains (22.5 x 5) = 112.5 mg of $CaCO_3$ (Theoretical Amount)

Experimental Calculations:

1000.0 mL 1M Na_2H_2EDTA ≡ 100.0 g $CaCO_3$ ≡ 40.0 g Ca^{+2}

1000.0 mL 0.01M Na_2H_2EDTA ≡ 1.0 g $CaCO_3$ ≡ 0.4 g Ca^{+2}

1.0 mL 0.01M Na_2H_2EDTA ≡ 1.0 mg $CaCO_3$ ≡ 0.4 mg Ca^{+2}

23.0 mL 0.01M Na_2H_2EDTA ≡ 23.0 mg $CaCO_3$

Solution B contains 23.0 mg of $CaCO_3$ (Experimental Amount)

Solution A contains (23.0 x 5) = 115.0 mg of $CaCO_3$ (Experimental Amount)

10) Gravimetric Estimation of Calcium Carbonate (Stock solution of Calcium Carbonate was prepared by digesting 112.5 mg of Calcium Carbonate Powder with 3.0 mL Con. HCl)

112.5 mg of calcium carbonate powder was taken in 100.0 mL beaker. To this, 3.0 mL Con. HCl was added with stirring followed by addition of 10.0 mL water. Beaker was covered with watch glass and then heated till the solution became clear and carbon dioxide expelled completely. Sides of beaker and watch glass were rinsed with distilled water and diluted up to 50.0 mL. Then, solution was heated to boiling and 2 drops of methyl red indicator was added. To this, 10.0 mL 5% ammonium oxalate solution was added. To the resulted hot solution, (1:1) ammonia solution was added drop wise and with constant stirring until the mixture became neutral (color of solution changes to yellow from red). Formed precipitates were allowed to settle without further heating for one hour. Precipitates were filtered through previously weighed Whatman filter paper 40 and washed with 0.1% ammonium oxalate solution till it became free from chloride. Precipitates were dried on metallic cone on sand bath. Weight the amount of (Precipitate + Whatmann filter paper) and subtract it from the weight of empty Whatmann filter paper. This experiment was repeated three times and the results are reported below.

Experiment No.	Weight of Filter Paper (in g)	Weight of (Filter Paper + Precipitates) (in g)	Weight of Precipitates (in g)	Concordant Reading (in mg)
01	1.1282 g	1.2933	0.1651	164.5
02	1.0891 g	1.2536	0.1645	
03	1.0664 g	1.2309	0.1645	

Calculations:

1.0 mole of $CaCO_3$ ≡ 1.0 mole of $CaC_2O_4.H_2O$

100.0 g $CaCO_3$ ≡ 146.08 g $CaC_2O_4.H_2O$

0.1125 g $CaCO_3$ ≡ 0.1643 g $CaC_2O_4.H_2O$

Therefore, for obtained 164.5 mg $CaC_2O_4.H_2O$, the equivalent amount of $CaCO_3$ is 112.6 mg

11) pH-Metric Estimation of Calcium in White Marble Stone as Calcium Carbonate ($CaCO_3$) by using Aq. Solution of Ca^{+2} (pH 7) as titrand and Aq. Solution of Na_3HEDTA (pH 11) as titrant (Stock solution of White Marble Stone was prepared by dissolving 46.2 mg of Dry White Marble Stone Powder)

0.0462 g white marble stone powder was dissolved in 0.1 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 100.0 mL beaker. Then, pH electrode was inserted to this solution and pH value was found to be 2.4. pH of this solution was adjusted to 7 by adding 2.0 mL 0.33 M NaOH solution (**Solution B**). Aqueous solution of 0.01M Na_3HEDTA (pH 11) was prepared by mixing 250.0 mL 0.01M Na_2H_2EDTA and 15.0 mL 0.33M NaOH solutions. This solution was filled in 25.0 mL burette as titrant. Then, 0.5 mL 0.01M Na_3HEDTA was added to Solution B having pH 7. Solution was shaken well with the help of glass rod and then pH reading was measured. Same process was repeated by adding 0.5 mL 0.01M Na_3HEDTA from burette up to 12.0 mL and pH reading was measured after each 0.5 mL addition of burette solution.

Table 8: Readings of pH-Metric Titration between Aq. Solutions of Ca^{+2} (present in White Marble Stone) and Na_3HEDTA

Sr. No.	Volume of 0.01M Na_3HEDTA (in mL)	pH
1	0.0	7.02
2	0.5	6.98
3	1.0	6.96
4	1.5	6.90
5	2.0	6.84
6	2.5	6.79

7	3.0	6.75
8	3.5	6.69
9	4.0	6.62
10	4.5	6.59
11	5.0	6.56
12	5.5	6.51
13	6.0	6.46
14	6.5	6.42
15	7.0	6.38
16	7.5	6.33
17	8.0	6.28
18	8.5	6.24
19	**9.0**	**6.18**
20	9.5	7.13
21	10.0	7.74
22	10.5	8.45
23	11.0	9.27
24	11.5	9.68
25	12.0	10.24

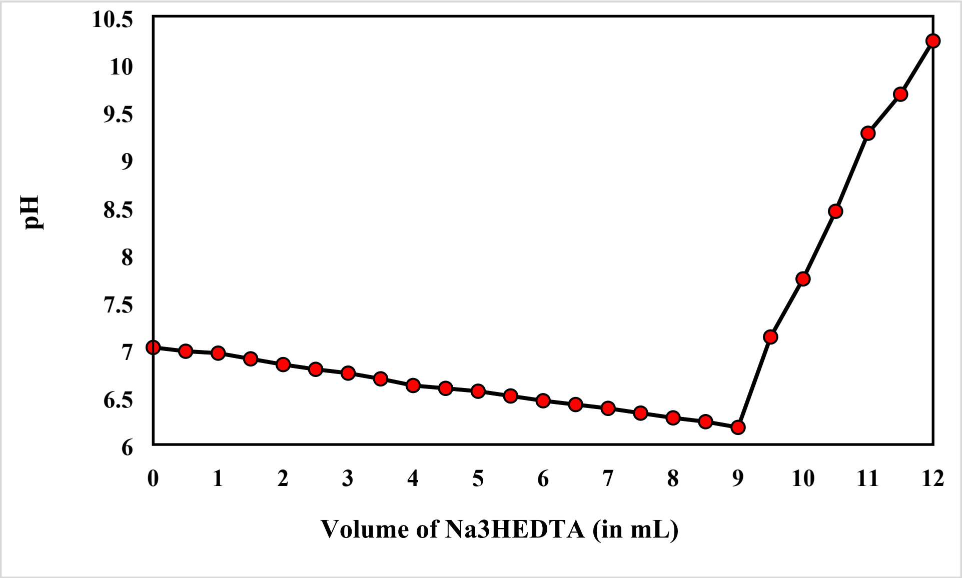


Figure 5: Effect of Aq.Na_3HEDTA Addition on pH of Ca^{+2} Solution

Observations: During this titration, formation of Ca-EDTA complex and release of one H^+ ion was taking place and hence decrease in pH from 7.02 to 6.18 was observed. At equivalence point, release of H^+ ion was stopped and sharp increase in pH was observed from 6.18 to 7.13 with further 0.5 mL addition of Na_3HEDTA (pH 11). Upon subsequent addition of Na_3HEDTA solution, pH value of solution significantly jumped to 7.74, 8.45 and 9.27. **So sharp equivalence point for the titration was observed at 9.0 mL**

Experimental Calculations:

1000.0 mL 1M Na_3HEDTA ≡ 100.0 g $CaCO_3$ ≡ 40.0 g Ca^{+2}

1000.0 mL 0.01M Na_3HEDTA ≡ 1.0 g $CaCO_3$ ≡ 0.4 g Ca^{+2}

1.0 mL 0.01M Na_3HEDTA ≡ 1.0 mg $CaCO_3$ ≡ 0.4 mg Ca^{+2}

9.0 mL 0.01M Na_3HEDTA ≡ 9.0 mg $CaCO_3$

Solution B contains 9.0 mg of $CaCO_3$ (Experimental Amount)

Solution A contains (9.0 x 5) = 45.0 mg of $CaCO_3$ (Experimental Amount)

12) Estimation of Calcium as Calcium Carbonate ($CaCO_3$) by using conventional complexometric titration method (Stock solution of Marble Stone was prepared by dissolving 46.2 mg of Dry White Marble Stone Powder)

0.0462 g white marble stone powder was dissolved in 0.1 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 250.0 mL conical flask (**Solution B**). To this, 1.5 test tube (Approx. 10-12 mL) NH_4OH-NH_4Cl buffer (pH 10) was added. Then, 4-5 drops of Eriochrome Black-T indicator was added. Solution in the conical flask was turned wine red and it was shaken well. Aq. Solution of Na_2H_2EDTA was filled in 25.0 mL burette. Then, titration was performed by drop wise addition of burette solution to the conical flask. A sharp colour change from wine red to blue was observed at the end point. This experiment was repeated three times. Obtained observations are listed below.

Table 9: Readings of complexometric titration between Aq. Solutions of Ca^{+2} and Na_2H_2EDTA by using Eriochrome Black-T as indicator

Experiment No.	Initial Reading (in mL)	Final Reading (in mL)	Difference (in mL)	Concordant Reading (in mL)
1	0.0	9.4	9.4	9.4
2	0.0	9.4	9.4	
3	0.0	9.4	9.4	

Experimental Calculations:

1000.0 mL 1M Na_2H_2EDTA ≡ 100.0 g $CaCO_3$ ≡ 40.0 g Ca^{+2}

1000.0 mL 0.01M Na_2H_2EDTA ≡ 1.0 g $CaCO_3$ ≡ 0.4 g Ca^{+2}

1.0 mL 0.01M Na_2H_2EDTA ≡ 1.0 mg $CaCO_3$ ≡ 0.4 mg Ca^{+2}

9.4 mL 0.01M Na_2H_2EDTA ≡ 9.4 mg $CaCO_3$

Solution B contains 9.4 mg of $CaCO_3$ (Experimental Amount)

Solution A contains (9.4 x 5) = 47.0 mg of $CaCO_3$ (Experimental Amount)

13) Gravimetric Estimation of Calcium in White Marble Stone as Calcium Carbonate ($CaCO_3$) (Stock solution of White Marble Stone was prepared by digesting 46.2 mg of Dry White Marble Stone Powder with 1.0 mL Con. HCl)

46.2 mg of dry white marble stone powder was taken in 100.0 mL beaker. To this, 1.0 mL Con. HCl was added with stirring followed by addition of 10.0 mL water. Beaker was covered with watch glass and then heated till the solution became clear and carbon dioxide expelled completely. Sides of beaker and watch glass were rinsed with distilled water and diluted up to 50.0 mL. Then, solution was heated to boiling and 2 drops of methyl red indicator was added. To this, 5.0 mL 5% ammonium oxalate solution was added. To the resulted hot solution, (1:1) ammonia solution was added drop wise and with constant stirring until the mixture became neutral (color of solution changes to yellow from red). Formed precipitates were allowed to settle without further heating for one hour. Precipitates were filtered through previously weighed Whatman filter paper 40 and washed with 0.1% ammonium oxalate solution till it became free from chloride. Precipitates were dried on metallic cone on sand bath. Weight the amount of (Precipitate + Whatmann filter paper) and subtract it from the weight of empty Whatmann filter paper. This experiment was repeated three times and the results are reported below.

Experiment No.	Weight of Filter Paper (in g)	Weight of (Filter Paper + Precipitates) (in g)	Weight of Precipitates (in g)	Concordant Reading (in mg)
01	1.0723 g	1.1394	0.0671	67.1
02	1.1091 g	1.1763	0.0672	
03	1.0774 g	1.1445	0.0671	

Calculations:

1.0 mole of $CaCO_3$ ≡ 1.0 mole of $CaC_2O_4.H_2O$

100.0 g $CaCO_3$ ≡ 146.08 g $CaC_2O_4.H_2O$

0.0462 g $CaCO_3$ ≡ 0.0675 g $CaC_2O_4.H_2O$

Therefore, for obtained 67.1 mg $CaC_2O_4.H_2O$, the equivalent amount of $CaCO_3$ is 45.9 mg

14) pH-Metric Estimation of Calcium in Egg Shell as Calcium Carbonate ($CaCO_3$) by using Aq. Solution of Ca^{+2} (pH 7) as titrand and Aq. Solution of Na_3HEDTA (pH 11) as titrant (Stock solution of Egg Shell was prepared by dissolving 49.7 mg of Dry Egg Shell Powder)

0.0497 g dry egg shell powder was dissolved in 0.1 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 100.0 mL beaker. Then, pH electrode was inserted to this solution and pH value was found to be 2.3. pH of this solution was adjusted to 7 by adding 2.2 mL 0.33 M NaOH solution (**Solution B**). Aqueous solution of 0.01M Na_3HEDTA (pH 11) was prepared by mixing 250.0 mL 0.01M Na_2H_2EDTA and 15.0 mL 0.33M NaOH solutions. This solution was filled in 25.0 mL burette as titrant. Then, 0.5 mL 0.01M Na_3HEDTA was added to Solution B having pH 7. Solution was shaken well with the help of glass rod and then pH reading was measured. Same process was repeated by adding 0.5 mL 0.01M Na_3HEDTA from burette up to 13.0 mL and pH reading was measured after each 0.5 mL addition of burette solution. Obtained readings and graph are described below.

Table 10: Readings of pH-Metric Titration between Aq. Solutions of Ca^{+2} (present in Egg Shell) and Na_3HEDTA

Sr. No.	Volume of 0.01M Na_3HEDTA (in mL)	pH
1	0.0	7.05
2	0.5	7.0
3	1.0	6.96
4	1.5	6.88
5	2.0	6.82
6	2.5	6.76
7	3.0	6.70
8	3.5	6.63
9	4.0	6.57
10	4.5	6.54
11	5.0	6.50
12	5.5	6.45
13	6.0	6.41
14	6.5	6.39
15	7.0	6.36
16	7.5	6.32
17	8.0	6.28
18	8.5	6.25
19	9.0	6.22
20	9.5	6.16

21	**10.0**	**6.10**
22	10.5	6.47
23	11.0	6.95
24	11.5	7.53
25	12.0	8.40
26	12.5	9.20
27	13.0	9.73

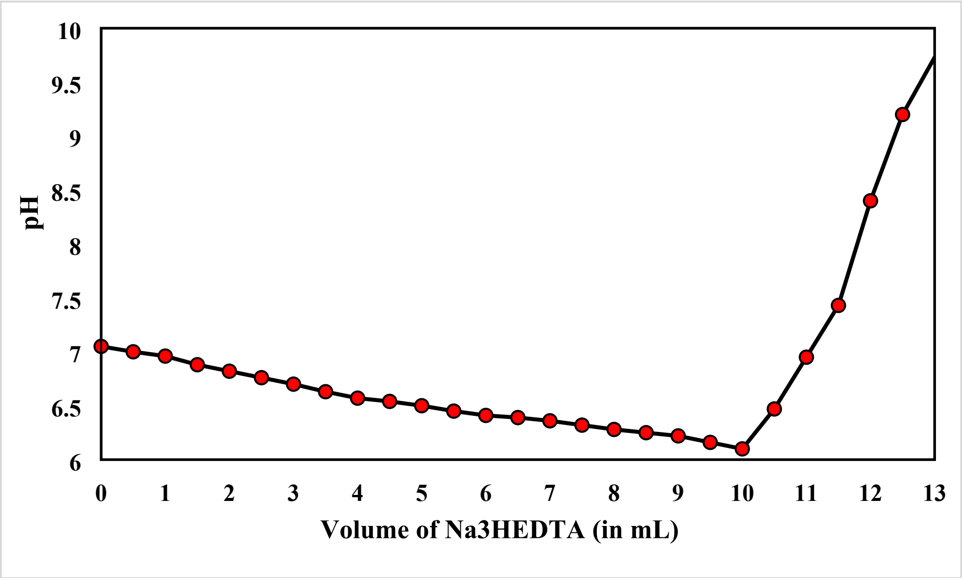


Figure 6: Effect of Aq.Na_3HEDTA Addition on pH of Ca^{+2} Solution

Observations: During this titration, formation of Ca-EDTA complex and release of one H^+ ion was taking place and hence decrease in pH from 7.05 to 6.10 was observed. At equivalence point, release of H^+ ion was stopped and sharp increase in pH was observed from 6.10 to 6.47 with further 0.5 mL addition of Na_3HEDTA (pH 11). Upon subsequent addition of Na_3HEDTA solution, pH value of solution significantly jumped to 6.95, 7.53 and 8.40. **So sharp equivalence point for the titration was observed at 10.0 mL**

Experimental Calculations:

1000.0 mL 1M Na_3HEDTA ≡ 100.0 g $CaCO_3$ ≡ 40.0 g Ca^{+2}

1000.0 mL 0.01M Na_3HEDTA ≡ 1.0 g $CaCO_3$ ≡ 0.4 g Ca^{+2}

1.0 mL 0.01M Na_3HEDTA ≡ 1.0 mg $CaCO_3$ ≡ 0.4 mg Ca^{+2}

10.0 mL 0.01M Na_3HEDTA ≡ 10.0 mg $CaCO_3$

Solution B contains 10.0 mg of $CaCO_3$ (Experimental Amount)

Solution A contains (10.0 x 5) = 50.0 mg of $CaCO_3$ (Experimental Amount)

15) Estimation of Calcium as Calcium Carbonate ($CaCO_3$) by using conventional complexometric titration method (Stock solution of Egg Shell was prepared by dissolving 49.7 mg of Dry Egg Shell Powder)

0.0497 g dry egg shell powder was dissolved in 0.1 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 250.0 mL conical flask (**Solution B**). To this, 1.5 test tube (Approx. 10-12 mL) NH_4OH-NH_4Cl buffer (pH 10) was added. Then, 4-5 drops of Eriochrome Black-T indicator was added. Solution in the conical flask was turned wine red and it was shaken well. Aq. Solution of Na_2H_2EDTA was filled in 25.0 mL burette. Then, titration was performed by drop wise addition of burette solution to the conical flask. A sharp colour change from wine red to blue was observed at the end point. This experiment was repeated three times. Obtained observations are listed below.

Table 11: Readings of complexometric titration between Aq. Solutions of Ca^{+2} and Na_2H_2EDTA by using Eriochrome Black-T as indicator

Experiment No.	Initial Reading (in mL)	Final Reading (in mL)	Difference (in mL)	Concordant Reading (in mL)
1	0.0	10.2	10.2	10.2
2	0.0	10.2	10.2	

3	**0.0**	**10.2**	**10.2**	

Experimental Calculations:

1000.0 mL	**1M Na_2H_2EDTA**	≡	**100.0 g $CaCO_3$**	≡	**40.0 g Ca^{+2}**
1000.0 mL	**0.01M Na_2H_2EDTA**	≡	**1.0 g $CaCO_3$**	≡	**0.4 g Ca^{+2}**
1.0 mL	**0.01M Na_2H_2EDTA**	≡	**1.0 mg $CaCO_3$**	≡	**0.4 mg Ca^{+2}**
10.2 mL	**0.01M Na_2H_2EDTA**	≡	**10.2 mg $CaCO_3$**		

Solution B contains 10.2 mg of $CaCO_3$ (Experimental Amount)

Solution A contains (10.2 x 5) = 51.0 mg of $CaCO_3$ (Experimental Amount)

16) Gravimetric Estimation of Calcium in Egg-Shell as Calcium Carbonate ($CaCO_3$) (Stock solution of Egg-Shell was prepared by digesting 49.7 mg of Dry Egg-Shell Powder with 1.0 mL Con. HCl)

49.7 mg of dry Egg-Shell powder was taken in 100.0 mL beaker. To this, 1.0 mL Con. HCl was added with stirring followed by addition of 10.0 mL water. Beaker was covered with watch glass and then heated till the solution became clear and carbon dioxide expelled completely. Sides of beaker and watch glass were rinsed with distilled water and diluted up to 50.0 mL. Then, solution was heated to boiling and 2 drops of methyl red indicator was added. To this, 5.0 mL 5% ammonium oxalate solution was added. To the resulted hot solution, (1:1) ammonia solution was added drop wise and with constant stirring until the mixture became neutral (color of solution changes to yellow from red). Formed precipitates were allowed to settle without further heating for one hour. Precipitates were filtered through previously weighed Whatman filter paper 40 and washed with 0.1% ammonium oxalate solution till it became free from chloride. Precipitates were dried on metallic cone on sand bath. Weight the amount of (Precipitate + Whatmann filter paper) and subtract it from the weight of empty Whatmann filter paper. This experiment was repeated three times and the results are reported below.

Experiment No.	Weight of Filter Paper (in g)	Weight of (Filter Paper + Precipitates) (in g)	Weight of Precipitates (in g)	Concordant Reading (in mg)
01	1.1385 g	1.2106	0.0721	72.1
02	1.1428 g	1.2149	0.0721	
03	1.0882 g	1.1606	0.0724	

Calculations:

1.0 mole of $CaCO_3$ ≡ 1.0 mole of $CaC_2O_4.H_2O$

100.0 g $CaCO_3$ ≡ 146.08 g $CaC_2O_4.H_2O$

0.0497 g $CaCO_3$ ≡ 0.0726 g $CaC_2O_4.H_2O$

Therefore, for obtained 72.1 mg $CaC_2O_4.H_2O$, the equivalent amount of $CaCO_3$ is 49.3 mg

17) pH-Metric Estimation of Calcium in Sea Shell as Calcium Carbonate ($CaCO_3$) by using Aq. Solution of Ca^{+2} (pH 7) as titrand and Aq. Solution of Na_3HEDTA (pH 11) as titrant (Stock solution of Sea Shell was prepared by dissolving 41.7 mg of Dry Sea Shell Powder)

0.0417 g dry sea shell powder was dissolved in 0.1 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 100.0 mL beaker. Then, pH electrode was inserted to this solution and pH value was found to be 2.2. pH of this solution was adjusted to 7 by adding 2.0 mL 0.33 M NaOH solution (**Solution B**). Aqueous solution of 0.01M Na_3HEDTA (pH 11) was prepared by mixing 250.0 mL 0.01M Na_2H_2EDTA and 15.0 mL 0.33M NaOH solutions. This solution was filled in 25.0 mL burette as titrant. Then, 0.5 mL 0.01M Na_3HEDTA was added to Solution B having pH 7. Solution was shaken well with the help of glass rod and then pH reading was measured. Same process was repeated by adding 0.5 mL 0.01M Na_3HEDTA from burette up to 12.0 mL and pH reading

was measured after each 0.5 mL addition of burette solution. Obtained readings and graph are described below.

Table 12: Readings of pH-Metric Titration between Aq. Solutions of Ca^{+2} (present in Sea Shell Powder) and Na_3HEDTA

Sr. No.	Volume of 0.01M Na_3HEDTA (in mL)	pH
1	0.0	7.05
2	0.5	6.99
3	1.0	6.94
4	1.5	6.88
5	2.0	6.82
6	2.5	6.77
7	3.0	6.73
8	3.5	6.69
9	4.0	6.65
10	4.5	6.61
11	5.0	6.58
12	5.5	6.52
13	6.0	6.45
14	6.5	6.39
15	7.0	6.34
16	7.5	6.29
17	8.0	6.24
18	**8.5**	**6.16**

19	9.0	6.55
20	9.5	7.13
21	10.0	7.66
22	10.5	8.49
23	11.0	9.13
24	11.5	9.47
25	12.0	9.85

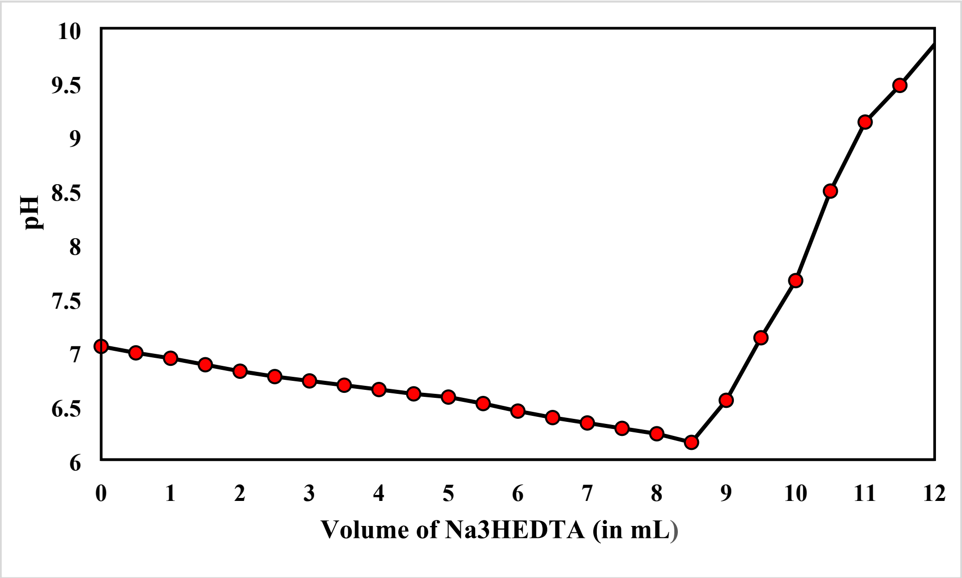


Figure 7: Effect of Aq.Na_3HEDTA Addition on pH of Ca^{+2} Solution

Observations: During this titration, formation of Ca-EDTA complex and release of one H^+ ion was taking place and hence decrease in pH from 7.05 to 6.16 was observed. At equivalence point, release of H^+ ion was stopped and sharp increase in pH was observed from 6.16 to 6.55 with further 0.5 mL addition of Na_3HEDTA (pH 11). Upon subsequent addition of Na_3HEDTA solution, pH value of solution significantly jumped to 7.13, 7.66 and 8.49. **So sharp equivalence point for the titration was observed at 8.5 mL**

Experimental Calculations:

1000.0 mL 1M Na_3HEDTA ≡ 100.0 g $CaCO_3$ ≡ 40.0 g Ca^{+2}

1000.0 mL 0.01M Na_3HEDTA ≡ 1.0 g $CaCO_3$ ≡ 0.4 g Ca^{+2}

1.0 mL 0.01M Na_3HEDTA ≡ 1.0 mg $CaCO_3$ ≡ 0.4 mg Ca^{+2}

8.5 mL 0.01M Na_3HEDTA ≡ 8.5 mg $CaCO_3$

Solution B contains 8.5 mg of $CaCO_3$ (Experimental Amount)

Solution A contains (8.5 x 5) = 42.5 mg of $CaCO_3$ (Experimental Amount)

18) Estimation of Calcium as Calcium Carbonate ($CaCO_3$) by using conventional complexometric titration method (Stock solution of Sea Shell was prepared by dissolving 41.7 mg of Dry Sea Shell Powder)

0.0417 g dry sea shell powder was dissolved in 0.1 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 250.0 mL conical flask (**Solution B**). To this, 1.5 test tube (Approx. 10-12 mL) NH_4OH-NH_4Cl buffer (pH 10) was added. Then, 4-5 drops of Eriochrome Black-T indicator was added. Solution in the conical flask was turned wine red and it was shaken well. Aq. Solution of Na_2H_2EDTA was filled in 25.0 mL burette. Then, titration was performed by drop wise addition of burette solution to the conical flask. A sharp colour change from wine red to blue was observed at the end point. This experiment was repeated three times. Obtained observations are listed below.

Table 13: Readings of complexometric titration between Aq. Solutions of Ca^{+2} and Na_2H_2EDTA by using Eriochrome Black-T as indicator

Experiment No.	Initial Reading (in mL)	Final Reading (in mL)	Difference (in mL)	Concordant Reading (in mL)
1	0.0	8.7	8.7	8.7
2	0.0	8.7	8.7	
3	0.0	8.7	8.7	

Experimental Calculations:

1000.0 mL 1M Na_2H_2EDTA ≡ 100.0 g $CaCO_3$ ≡ 40.0 g Ca^{+2}

1000.0 mL 0.01M Na_2H_2EDTA ≡ 1.0 g $CaCO_3$ ≡ 0.4 g Ca^{+2}

1.0 mL 0.01M Na_2H_2EDTA ≡ 1.0 mg $CaCO_3$ ≡ 0.4 mg Ca^{+2}

8.7 mL 0.01M Na_2H_2EDTA ≡ 8.7 mg $CaCO_3$

Solution B contains 8.7 mg of $CaCO_3$ (Experimental Amount)

Solution A contains (8.7 x 5) = 43.5 mg of $CaCO_3$ (Experimental Amount)

19) Gravimetric Estimation of Calcium in Sea-Shell as Calcium Carbonate ($CaCO_3$)

(Stock solution of Sea-Shell was prepared by digesting 41.7 mg of Dry Sea-Shell Powder with 1.0 mL Con. HCl)

41.7 mg of dry Sea-Shell powder was taken in 100.0 mL beaker. To this, 1.0 mL Con. HCl was added with stirring followed by addition of 10.0 mL water. Beaker was covered with watch glass and then heated till the solution became clear and carbon dioxide expelled completely. Sides of beaker and watch glass were rinsed with distilled water and diluted up to 50.0 mL. Then, solution was heated to boiling and 2 drops of methyl red indicator was added. To this, 5.0 mL 5% ammonium oxalate solution was added. To the resulted hot solution, (1:1) ammonia solution was added drop wise and with constant stirring until the mixture became neutral (color of solution changes to yellow from red). Formed precipitates were allowed to settle without further heating for one hour. Precipitates were filtered through previously weighed Whatman filter paper 40 and washed with 0.1% ammonium oxalate solution till it became free from chloride. Precipitates were dried on metallic cone on sand bath. Weight the amount of (Precipitate + Whatmann filter paper) and subtract it from the weight of empty Whatmann filter paper. This experiment was repeated three times and the results are reported below.

Experiment No.	Weight of Filter Paper (in g)	Weight of (Filter Paper + Precipitates)	Weight of Precipitates	Concordant Reading

		(in g)	(in g)	(in mg)
01	1.0662	1.1279	0.0617	61.7
02	1.0743	1.1363	0.0620	
03	1.0545	1.1162	0.0617	

Calculations:

1.0 mole of $CaCO_3$ ≡ 1.0 mole of $CaC_2O_4.H_2O$

100.0 g $CaCO_3$ ≡ 146.08 g $CaC_2O_4.H_2O$

0.0417 g $CaCO_3$ ≡ 0.0609 g $CaC_2O_4.H_2O$

Therefore, for obtained 61.7 mg $CaC_2O_4.H_2O$, the equivalent amount of $CaCO_3$ is 42.2 mg

20) pH-Metric Estimation of Calcium in Tablet as Calcium Carbonate ($CaCO_3$) by using Aq. Solution of Ca^{+2} (pH 7) as titrand and Aq. Solution of Na_3HEDTA (pH 11) as titrant (Stock solution of Calcium Tablet was prepared by dissolving 50.0 mg of Dry Calcium Tablet Powder)

0.050 g dry calcium tablet powder was dissolved in 0.2 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 100.0 mL beaker. Then, pH electrode was inserted to this solution and pH value was found to be 2.2. pH of this solution was adjusted to 7 by adding 2.5 mL 0.33 M NaOH solution (**Solution B**). Aqueous solution of 0.01M Na_3HEDTA (pH 11) was prepared by mixing 250.0 mL 0.01M Na_2H_2EDTA and 15.0 mL 0.33M NaOH solutions. This solution was filled in 25.0 mL burette as titrant. Then, 0.5 mL 0.01M Na_3HEDTA was added to Solution B having pH 7. Solution was shaken well with the help of glass rod and then pH reading was measured. Same process was repeated by adding 0.5 mL 0.01M Na_3HEDTA from burette up to 12.0 mL and pH reading

was measured after each 0.5 mL addition of burette solution. Obtained readings and graph are described below.

Table 14: Readings of pH-Metric Titration between Aq. Solutions of Ca^{+2} (present in Calcium Tablet) and Na_3HEDTA

Sr. No.	Volume of 0.01M Na_3HEDTA (in mL)	pH
1	0.0	7.06
2	0.5	7.0
3	1.0	6.96
4	1.5	6.92
5	2.0	6.89
6	2.5	6.83
7	3.0	6.78
8	3.5	6.72
9	4.0	6.66
10	4.5	6.60
11	5.0	6.55
12	5.5	6.48
13	6.0	6.42
14	6.5	6.35
15	7.0	6.29
16	7.5	6.24
17	8.0	6.19
18	8.5	6.13

19	9.0	6.08
20	9.5	6.03
21	**10.0**	**5.98**
22	10.5	6.31
23	11.0	6.72
24	11.5	7.45
25	12.0	7.84
26	12.5	8.24
27	13.0	9.31

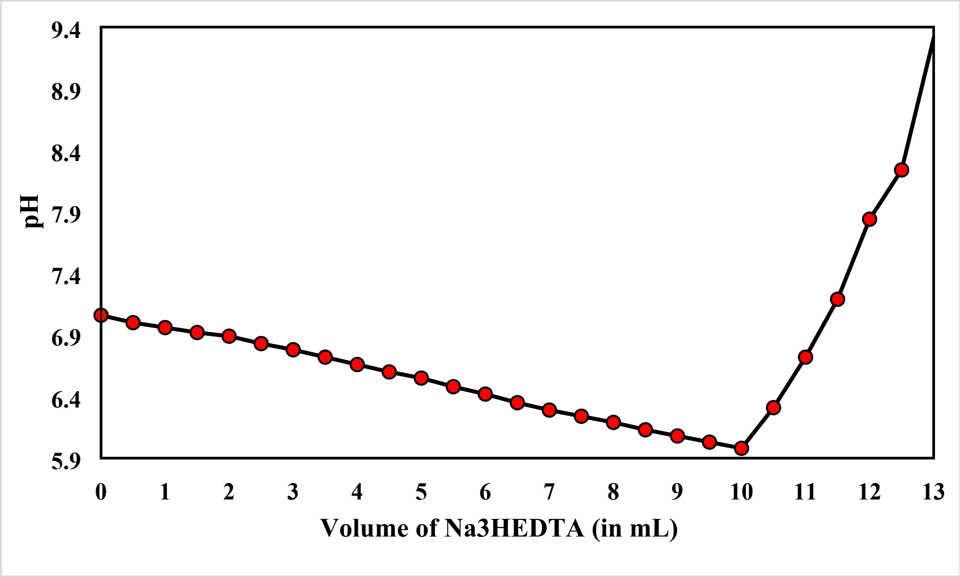


Figure 8: Effect of Aq.Na_3HEDTA Addition on pH of Ca^{+2} Solution

Observations: During this titration, formation of Ca-EDTA complex and release of one H^+ ion was taking place and hence decrease in pH from 7.06 to 5.98 was observed. At equivalence point, release of H^+ ion was stopped and sharp increase in pH was observed from 5.98 to 6.31 with further 0.5 mL addition of Na_3HEDTA (pH 11). Upon subsequent addition of Na_3HEDTA solution, pH value of solution significantly jumped to 6.72, 7.45 and 7.84. **So sharp equivalence point for the titration was observed at 10.0 mL**

Experimental Calculations:

1000.0 mL 1M Na_3HEDTA ≡ 100.0 g $CaCO_3$ ≡ 40.0 g Ca^{+2}

1000.0 mL 0.01M Na_3HEDTA ≡ 1.0 g $CaCO_3$ ≡ 0.4 g Ca^{+2}

1.0 mL 0.01M Na_3HEDTA ≡ 1.0 mg $CaCO_3$ ≡ 0.4 mg Ca^{+2}

10.0 mL 0.01M Na_3HEDTA ≡ 10.0 mg $CaCO_3$

Solution B contains 10.0 mg of $CaCO_3$ (Experimental Amount)

Solution A contains (10.0 x 5) = 50.0 mg of $CaCO_3$ (Experimental Amount)

21) Estimation of Calcium as Calcium Carbonate ($CaCO_3$) by using conventional complexometric titration method (Stock solution of Calcium Tablet was prepared by dissolving 50.0 mg of Dry Calcium Tablet Powder)

0.050 g dry calcium tablet powder was dissolved in 0.2 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 250.0 mL conical flask (**Solution B**). To this, 1.5 test tube (Approx. 10-12 mL) NH_4OH-NH_4Cl buffer (pH 10) was added. Then, 4-5 drops of Eriochrome Black-T indicator was added. Solution in the conical flask was turned wine red and it was shaken well. Aq. Solution of Na_2H_2EDTA was filled in 25.0 mL burette. Then, titration was performed by drop wise addition of burette solution to the conical flask. A sharp colour change from wine red to blue was observed at the end point. This experiment was repeated three times. Obtained observations are listed below.

Table 15: Readings of complexometric titration between Aq. Solutions of Ca^{+2} and Na_2H_2EDTA by using Eriochrome Black-T as indicator

Experiment No.	Initial Reading (in mL)	Final Reading (in mL)	Difference (in mL)	Concordant Reading (in mL)
1	0.0	10.4	10.4	10.4
2	0.0	10.4	10.4	
3	0.0	10.4	10.4	

<u>Experimental Calculations:</u>

1000.0 mL 1M Na_2H_2EDTA ≡ 100.0 g $CaCO_3$ ≡ 40.0 g Ca^{+2}

1000.0 mL 0.01M Na_2H_2EDTA ≡ 1.0 g $CaCO_3$ ≡ 0.4 g Ca^{+2}

1.0 mL 0.01M Na_2H_2EDTA ≡ 1.0 mg $CaCO_3$ ≡ 0.4 mg Ca^{+2}

10.4 mL 0.01M Na_2H_2EDTA ≡ 10.4 mg $CaCO_3$

Solution B contains 10.4 mg of $CaCO_3$ (Experimental Amount)

Solution A contains (10.4 x 5) = 52.0 mg of $CaCO_3$ (Experimental Amount)

22) Gravimetric Estimation of Calcium in Calcium Tablet as Calcium Carbonate ($CaCO_3$) (Stock solution of Calcium Tablet was prepared by digesting 50.0 mg of Dry Calcium Tablet Powder with 1.0 mL Con. HCl)

50.0 mg of dry Calcium Tablet powder was taken in 100.0 mL beaker. To this, 1.0 mL Con. HCl was added with stirring followed by addition of 10.0 mL water. Beaker was covered with watch glass and then heated till the solution became clear and carbon dioxide expelled completely. Sides of beaker and watch glass were rinsed with distilled water and diluted up to 50.0 mL. Then, solution was heated to boiling and 2 drops of methyl red indicator was added. To this, 5.0 mL 5% ammonium oxalate solution was added. To the resulted hot solution, (1:1) ammonia solution was added drop wise and with constant stirring until the mixture became neutral (color of solution changes to yellow from red). Formed precipitates

were allowed to settle without further heating for one hour. Precipitates were filtered through previously weighed Whatman filter paper 40 and washed with 0.1% ammonium oxalate solution till it became free from chloride. Precipitates were dried on metallic cone on sand bath. Weight the amount of (Precipitate + Whatmann filter paper) and subtract it from the weight of empty Whatmann filter paper. This experiment was repeated three times and the results are reported below.

Experiment No.	Weight of Filter Paper (in g)	Weight of (Filter Paper + Precipitates) (in g)	Weight of Precipitates (in g)	Concordant Reading (in mg)
01	1.1201	1.1932	0.0731	0.0724
02	1.0983	1.1707	0.0724	
03	1.0654	1.1378	0.0724	

Calculations:

1.0 mole of $CaCO_3$ ≡ 1.0 mole of $CaC_2O_4.H_2O$

100.0 g $CaCO_3$ ≡ 146.08 g $CaC_2O_4.H_2O$

0.0500 g $CaCO_3$ ≡ 0.0730 g $CaC_2O_4.H_2O$

Therefore, for obtained 72.4 mg $CaC_2O_4.H_2O$, the equivalent amount of $CaCO_3$ is 49.5 mg

23) pH-Metric Estimation of Calcium as Calcium Carbonate ($CaCO_3$) by using Aq. Solution of Ca^{+2} (pH 7) as titrand and Aq. Solution of Na_3HEDTA (pH 11) as titrant (Stock solution of Ca^{+2} was prepared by dissolving 5.0 mg of $CaCO_3$ in 250.0 mL water)

0.005g $CaCO_3$ was dissolved in minimum amount of conc. HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 100.0

mL beaker. Then, pH electrode was inserted to this solution and pH value was measured and adjusted to 7.0 by adding 0.33 M NaOH solution (**Solution B**). Aqueous solution of 0.01M Na_3HEDTA (pH 11) was prepared by mixing 250.0 mL 0.01M Na_2H_2EDTA and 15.0 mL 0.33M NaOH solutions. This solution was filled in 25.0 mL burette as titrant. Then, 0.5 mL 0.01M Na_3HEDTA was added to Solution B having pH 7. Solution was shaken well with the help of glass rod and then pH reading was measured. Same process was repeated by adding 0.5 mL 0.01M Na_3HEDTA from burette up to 2.0 mL and pH reading was measured after each 0.5 mL addition of burette solution. Obtained readings and graph are described below.

Table 16: Readings of pH-Metric Titration between Aq. Solutions of Ca^{+2} (present in Calcium Tablet) and Na_3HEDTA

Sr. No.	**Volume of 0.01M Na_3HEDTA (in mL)**	**pH**
1	0.0	7.03
2	0.5	6.82
3	**1.0**	**6.71**
4	1.5	7.33
5	2.0	9.11
6	2.5	9.64

Observations: During this titration, formation of Ca-EDTA complex and release of one H^+ ion was taking place and hence decrease in pH from 7.03 to 6.71 was observed. At equivalence point, release of H^+ ion was stopped and sharp increase in pH was observed from 6.71 to 7.33 with further 0.5 mL addition of Na_3HEDTA (pH 11). Upon subsequent addition of Na_3HEDTA solution, pH value of solution significantly jumped to 9.11 and 9.64. **<u>So sharp equivalence point for the titration was observed at 1.0 mL</u>**

<u>Experimental Calculations:</u>

1000.0 mL 1M Na_3HEDTA ≡ 100.0 g $CaCO_3$ ≡ 40.0 g Ca^{+2}

1000.0 mL 0.01M Na_3HEDTA ≡ 1.0 g $CaCO_3$ ≡ 0.4 g Ca^{+2}

1.0 mL 0.01M Na_3HEDTA ≡ 1.0 mg $CaCO_3$ ≡ 0.4 mg Ca^{+2}

Solution B contains 1.0 mg of $CaCO_3$ (Experimental Amount)

Solution A contains (1.0 x 5) = 5.0 mg of $CaCO_3$ (Experimental Amount)

24) pH-Metric Titration of Calcium as Calcium Carbonate ($CaCO_3$) by using Aq. Solution of Ca^{+2} (pH 7) as titrand and Aq. Solution of Na_4EDTA (pH 12) as titrant (Stock solution of Ca^{+2} was prepared by dissolving 37.7 mg of $CaCO_3$ in 250.0 mL water)

0.0377 g $CaCO_3$ was dissolved in 0.1 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 100.0 mL beaker. Then, pH electrode was inserted to this solution and pH value was found to be 2.4. pH of this solution was adjusted to 7 by adding 2.0 mL 0.33 M NaOH solution (**Solution B**). Aqueous solution of 0.01M Na_4EDTA (pH 12) was prepared by mixing 0.01M Na_2H_2EDTA and 0.33M NaOH solutions. This solution was filled in 25.0 mL burette as titrant. Then, 0.5 mL 0.01M Na_4EDTA was added to Solution B having pH 7. Solution was shaken well with the help of glass rod and then pH reading was measured. Same process was repeated by adding 0.5 mL 0.01M Na_4EDTA from burette up to 12.0 mL and pH reading was measured after each 0.5 mL addition of burette solution. Obtained readings and graph are described below.

Table 17: pH-Metric Titration Readings between Aq. Solutions of Ca^{+2} and Na_4EDTA

Sr. No.	Volume of 0.01M Na_3HEDTA (in mL)	pH
1	0.0	7.04
2	0.5	7.69
3	1.0	8.25
4	1.5	8.63
5	2.0	9.03
6	2.5	9.18
7	3.0	9.40
8	3.5	9.52
9	4.0	9.66
10	4.5	9.78
11	5.0	9.89
12	5.5	9.98
13	6.0	10.08
14	6.5	10.19
15	7.0	10.24
16	7.5	10.30
17	8.0	10.37
18	8.5	10.43
19	9.0	10.49
20	9.5	10.53
21	10.0	10.59

22	10.5	10.63
23	11.0	10.67
24	11.5	10.72
25	12.0	10.76

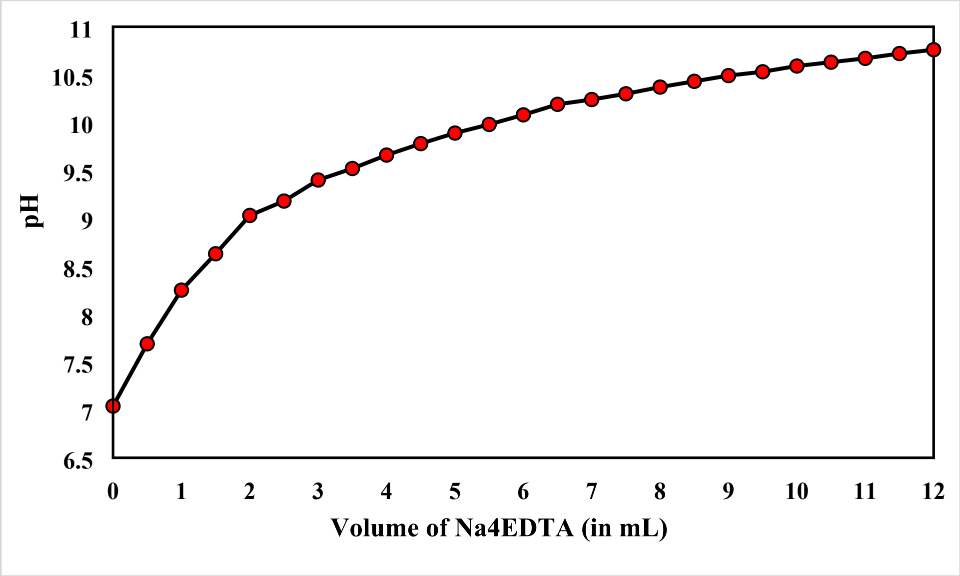


Figure 9: Effect of Aq.Na_4EDTA Addition on pH of Ca^{+2} Solution

During this titration, release of one H^+ ion was not taking place and hence decrease in pH was not observed. However, continuous increase in pH was observed. No sharp equivalence point was observed.

25) Estimation of Calcium as Calcium Carbonate ($CaCO_3$) by using Aq. Solution of Ca^{+2} (pH 7) as titrand, Aq. Solution of Na_3HEDTA (pH 11) as titrant and bromothymol blue as indicator (Stock solution of $CaCO_3$ was prepared by dissolving 37.5 mg of $CaCO_3$)

0.0375 g $CaCO_3$ was dissolved in 0.1 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 250.0 mL beaker. Then, pH electrode was inserted to this solution and pH value was found to be 2.5. pH of this solution was adjusted to 7 by adding 2.0 mL 0.33 M NaOH solution (**Solution B**). 50.0 mL of solution B was transferred to 250.0 mL conical flask. To this, 3-4 drops of bromothymol blue indicator was added. Colour of solution was colourless to pale green. Aqueous solution of 0.01M Na_3HEDTA (pH 11) was prepared by mixing 250.0 mL 0.01M Na_2H_2EDTA and 15.0 mL 0.33M NaOH solutions. This solution was filled in 25.0 mL burette as titrant. Then, titration was performed by drop wise addition of burette solution to the conical flask. With progress of titration, pH of solution decreases and colour of solution changed from light green to yellow. After surpassing the equivalence point, further addition of Na_3HEDTA solution caused sharp increase in the pH of solution i.e $pH \geq 7.5$ and its colour changed from yellow to intense blue which was detected as end point of the titration. This experiment was repeated three times. Obtained observations are listed below.

Table 18A (Solution Set-I): Readings of complexometric titration between Aq. Solutions of Ca^{+2} and Na_3HEDTA by using bromothymol blue as indicator

Experiment No.	Initial Reading (in mL)	Final Reading (in mL)	Difference (in mL)	Concordant Reading (in mL)
1	0.0	8.3	8.3	8.3
2	0.0	8.3	8.3	
3	0.0	8.3	8.3	

Table 18B (Solution Set-II): Readings of complexometric titration between Aq. Solutions of Ca^{+2} and Na_3HEDTA by using bromothymol blue as indicator

Experiment No.	Initial Reading (in mL)	Final Reading (in mL)	Difference (in mL)	Concordant Reading (in mL)
1	0.0	8.3	8.3	8.3
2	0.0	8.4	8.4	
3	0.0	8.3	8.3	

Table 18C (Solution Set-III): Readings of complexometric titration between Aq. Solutions of Ca^{+2} and Na_3HEDTA by using bromothymol blue as indicator

Experiment No.	Initial Reading (in mL)	Final Reading (in mL)	Difference (in mL)	Concordant Reading (in mL)
1	0.0	8.5	8.5	8.3
2	0.0	8.3	8.3	
3	0.0	8.3	8.3	

Relative Standard Deviation of Above Nine Readings: 0.85%

Theoretical Calculations:

Solution B contains 7.5 mg of $CaCO_3$ (Theoretical Amount)

Solution A contains (7.5 x 5) = 37.5 mg of $CaCO_3$ (Theoretical Amount)

Experimental Calculations:

1000.0 mL 1M Na_2H_2EDTA ≡ 100.0 g $CaCO_3$ ≡ 40.0 g Ca^{+2}

1000.0 mL 0.01M Na_2H_2EDTA ≡ 1.0 g $CaCO_3$ ≡ 0.4 g Ca^{+2}

1.0 mL 0.01M Na_2H_2EDTA ≡ 1.0 mg $CaCO_3$ ≡ 0.4 mg Ca^{+2}

8.3 mL 0.01M Na_2H_2EDTA ≡ 8.3 mg $CaCO_3$

Solution B contains 8.3 mg of $CaCO_3$ (Experimental Amount)

Solution A contains (8.3 x 5) = 41.5 mg of $CaCO_3$ (Experimental Amount)

26) Estimation of Calcium as Calcium Carbonate ($CaCO_3$) by using Aq. Solution of Ca^{+2} (pH 7) as titrand, Aq. Solution of Na_3HEDTA (pH 11) as titrant and bromothymol blue as indicator (Stock solution of $CaCO_3$ was prepared by dissolving 50.0 mg of Marble Stone Powder)

0.050 g marble stone powder was dissolved in 0.2 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 250.0 mL beaker. Then, pH electrode was inserted to this solution and pH value was found to be 2.4. pH of this solution was adjusted to 7 by adding 2.2 mL 0.33 M NaOH solution (**Solution B**). 50.0 mL of solution B was transferred to 250.0 mL conical flask. To this, 3-4 drops of bromothymol blue indicator was added. Colour of solution was colourless to pale green. Aqueous solution of 0.01M Na_3HEDTA (pH 11) was prepared by mixing 250.0 mL 0.01M Na_2H_2EDTA and 15.0 mL 0.33M NaOH solutions. This solution was filled in 25.0 mL burette as titrant. Then, titration was performed by drop wise addition of burette solution to the conical flask. With progress of titration, pH of solution decreases and colour of solution changed from light green to yellow. After surpassing the equivalence point, further addition of Na_3HEDTA solution caused sharp increase in the pH of solution i.e pH≥7.5 and its colour changed from yellow to intense blue which was detected as end point of the titration. This experiment was repeated three times. Obtained observations are listed below.

Table 19A (Solution Set-I): Readings of complexometric titration between Aq. Solutions of Ca^{+2} and Na_3HEDTA by using bromothymol blue as indicator

Experiment No.	Initial Reading (in mL)	Final Reading (in mL)	Difference (in mL)	Concordant Reading (in mL)
1	0.0	10.7	10.7	10.7
2	0.0	10.7	10.7	
3	0.0	10.7	10.7	

Table 19B (Solution Set-II): Readings of complexometric titration between Aq. Solutions of Ca^{+2} and Na_3HEDTA by using bromothymol blue as indicator

Experiment No.	Initial Reading (in mL)	Final Reading (in mL)	Difference (in mL)	Concordant Reading (in mL)
1	0.0	10.8	10.8	10.7
2	0.0	10.7	10.7	
3	0.0	10.7	10.7	

Table 19C (Solution Set-III): Readings of complexometric titration between Aq. Solutions of Ca^{+2} and Na_3HEDTA by using bromothymol blue as indicator

Experiment No.	Initial Reading (in mL)	Final Reading (in mL)	Difference (in mL)	Concordant Reading (in mL)
1	0.0	10.7	10.7	10.7
2	0.0	10.8	10.8	
3	0.0	10.7	10.7	

Relative Standard Deviation of Above Nine Readings: 0.41%

Theoretical Calculations:

Solution B contains 10.0 mg of $CaCO_3$ (Theoretical Amount)

Solution A contains (10.0 x 5) = 50.0 mg of $CaCO_3$ (Theoretical Amount)

Experimental Calculations:

1000.0 mL 1M Na_2H_2EDTA ≡ 100.0 g $CaCO_3$ ≡ 40.0 g Ca^{+2}

1000.0 mL 0.01M Na_2H_2EDTA ≡ 1.0 g $CaCO_3$ ≡ 0.4 g Ca^{+2}

1.0 mL 0.01M Na_2H_2EDTA ≡ 1.0 mg $CaCO_3$ ≡ 0.4 mg Ca^{+2}

10.7 mL 0.01M Na_2H_2EDTA ≡ 10.7 mg $CaCO_3$

Solution B contains 10.7 mg of $CaCO_3$ (Experimental Amount)

Solution A contains (10.7 x 5) = 53.5 mg of $CaCO_3$ (Experimental Amount)

27) Estimation of Calcium as Calcium Carbonate ($CaCO_3$) by using conventional complexometric Titration Method (Stock solution of White Marble Stone was prepared by dissolving 50.0 mg of Dry White Marble Stone Powder)

0.050 g marble stone powder was dissolved in 0.2 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 250.0 mL conical flask (**Solution B**). To this, 1.5 test tube (Approx. 10-12 mL) NH_4OH-NH_4Cl buffer (pH 10) was added. Then, 4-5 drops of Eriochrome Black-T indicator was added. Solution in the conical flask was turned wine red and it was shaken well. Aq. Solution of Na_2H_2EDTA was filled in 25.0 mL burette. Then, titration was performed by drop wise addition of burette solution to the conical flask. A sharp colour change from wine red to blue was observed at the end point. This experiment was repeated three times. Obtained observations are listed below.

Table 20: Readings of complexometric titration between Aq. Solutions of Ca^{+2} and Na_2H_2EDTA by using Eriochrome Black-T as indicator

Experiment No.	Initial Reading (in mL)	Final Reading (in mL)	Difference (in mL)	Concordant Reading (in mL)
1	0.0	10.2	10.2	10.2
2	0.0	10.2	10.2	
3	0.0	10.2	10.2	

Experimental Calculations:

1000.0 mL 1M Na_2H_2EDTA ≡ 100.0 g $CaCO_3$ ≡ 40.0 g Ca^{+2}

1000.0 mL 0.01M Na_2H_2EDTA ≡ 1.0 g $CaCO_3$ ≡ 0.4 g Ca^{+2}

1.0 mL 0.01M Na_2H_2EDTA ≡ 1.0 mg $CaCO_3$ ≡ 0.4 mg Ca^{+2}

10.2 mL 0.01M Na_2H_2EDTA ≡ 10.2 mg $CaCO_3$

Solution B contains 10.2 mg of $CaCO_3$ (Experimental Amount)

Solution A contains (10.2 x 5) = 51.0 mg of $CaCO_3$ (Experimental Amount)

28) Gravimetric Estimation of Calcium in White Marble Stone as Calcium Carbonate ($CaCO_3$) (Stock solution of White Marble Stone was prepared by digesting 50.0 mg of Dry White Marble Stone Powder with 1.0 mL Con. HCl)

50.0 mg of dry white marble stone powder was taken in 100.0 mL beaker. To this, 1.0 mL Con. HCl was added with stirring followed by addition of 10.0 mL water. Beaker was covered with watch glass and then heated till the solution became clear and carbon dioxide expelled completely. Sides of beaker and watch glass were rinsed with distilled water and diluted up to 50.0 mL. Then, solution was heated to boiling and 2 drops of methyl red indicator was added. To this, 5.0 mL 5% ammonium oxalate solution was added. To the resulted hot solution, (1:1) ammonia solution was added drop wise and with constant stirring until the mixture became neutral (color of solution changes to yellow from red). Formed precipitates were allowed to settle without further heating for one hour. Precipitates were filtered through previously weighed Whatman filter paper 40 and washed with 0.1% ammonium oxalate solution till it became free from chloride. Precipitates were dried on metallic cone on sand bath. Weight the amount of (Precipitate + Whatmann filter paper) and subtract it from the weight of empty Whatmann filter paper. This experiment was repeated three times and the results are reported below.

Experiment No.	Weight of Filter Paper (in g)	Weight of (Filter Paper + Precipitates) (in g)	Weight of Precipitates (in g)	Concordant Reading (in mg)
01	1.1192 g	1.1916	0.0724	0.0724
02	1.0884 g	1.1613	0.0729	
03	1.0906 g	1.1630	0.0724	

Calculations:

1.0 mole of $CaCO_3$ ≡ 1.0 mole of $CaC_2O_4.H_2O$

100.0 g $CaCO_3$ ≡ 146.08 g $CaC_2O_4.H_2O$

0.050 g $CaCO_3$ ≡ 0.0730 g $CaC_2O_4.H_2O$

Therefore, for obtained 72.4 mg $CaC_2O_4.H_2O$, the equivalent amount of $CaCO_3$ is 49.6 mg

29) Estimation of Calcium as Calcium Carbonate ($CaCO_3$) by using Aq. Solution of Ca^{+2} (pH 7) as titrand, Aq. Solution of Na_3HEDTA (pH 11) as titrant and bromothymol blue as indicator (Stock solution of $CaCO_3$ was prepared by dissolving 42.0 mg of Egg Shell Powder)

0.0420 g egg shell powder was dissolved in 0.1 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 250.0 mL beaker. Then, pH electrode was inserted to this solution and pH value was found to be 2.2. pH of this solution was adjusted to 7 by adding 2.0 mL 0.33 M NaOH solution (**Solution B**). 50.0 mL of solution B was transferred to 250.0 mL conical flask. To this, 3-4 drops of bromothymol blue indicator was added. Colour of solution was colourless to pale green. Aqueous solution of 0.01M Na_3HEDTA (pH 11) was prepared by mixing 250.0 mL 0.01M Na_2H_2EDTA and 15.0 mL 0.33M NaOH solutions. This solution was filled in 25.0 mL burette as titrant. Then, titration was performed by drop wise addition of burette solution to the conical flask. With progress of titration, pH of solution decreases and colour of solution changed from light green to yellow. After surpassing the equivalence point, further addition of Na_3HEDTA solution caused sharp increase in the pH of solution i.e $pH \geq 7.5$ and its colour changed from yellow to intense blue which was detected as end point of the titration. This experiment was repeated three times. Obtained observations are listed below.

Table 21A (Solution Set-I): Readings of complexometric titration between Aq. Solutions of Ca^{+2} and Na_3HEDTA by using bromothymol blue as indicator

Experiment No.	Initial Reading (in mL)	Final Reading (in mL)	Difference (in mL)	Concordant Reading (in mL)
1	0.0	9.2	9.2	9.2
2	0.0	9.2	9.2	
3	0.0	9.2	9.2	

Table 21B (Solution Set-II): Readings of complexometric titration between Aq. Solutions of Ca^{+2} and Na_3HEDTA by using bromothymol blue as indicator

Experiment No.	Initial Reading (in mL)	Final Reading (in mL)	Difference (in mL)	Concordant Reading (in mL)
1	0.0	9.2	9.2	9.2
2	0.0	9.2	9.2	
3	0.0	9.4	9.4	

Table 21C (Solution Set-III): Readings of complexometric titration between Aq. Solutions of Ca^{+2} and Na_3HEDTA by using bromothymol blue as indicator

Experiment No.	Initial Reading (in mL)	Final Reading (in mL)	Difference (in mL)	Concordant Reading (in mL)
1	0.0	9.2	9.2	9.2
2	0.0	9.4	9.4	
3	0.0	9.2	9.2	

Relative Standard Deviation of Above Nine Readings: 0.95%

Theoretical Calculations:

Solution B contains 8.4 mg of $CaCO_3$ (Theoretical Amount)

Solution A contains (8.4 x 5) = 42 mg of $CaCO_3$ (Theoretical Amount)

Experimental Calculations:

1000.0 mL 1M Na_2H_2EDTA ≡ 100.0 g $CaCO_3$ ≡ 40.0 g Ca^{+2}

1000.0 mL 0.01M Na_2H_2EDTA ≡ 1.0 g $CaCO_3$ ≡ 0.4 g Ca^{+2}

1.0 mL 0.01M Na_2H_2EDTA ≡ 1.0 mg $CaCO_3$ ≡ 0.4 mg Ca^{+2}

9.2 mL 0.01M Na_2H_2EDTA ≡ 9.2 mg $CaCO_3$

Solution B contains 9.2 mg of $CaCO_3$ (Experimental Amount)

Solution A contains (9.2 x 5) = 46.0 mg of $CaCO_3$ (Experimental Amount)

30) Estimation of Calcium as Calcium Carbonate ($CaCO_3$) by using conventional complexometric titration method (Stock solution of Egg Shell was prepared by dissolving 42.0 mg of Dry Egg Shell Powder)

0.042 g dry egg shell powder was dissolved in 0.1 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 250.0 mL conical flask (**Solution B**). To this, 1.5 test tube (Approx. 10-12 mL) NH_4OH-NH_4Cl buffer (pH 10) was added. Then, 4-5 drops of Eriochrome Black-T indicator was added. Solution in the conical flask was turned wine red and it was shaken well. Aq. Solution of Na_2H_2EDTA was filled in 25.0 mL burette. Then, titration was performed by drop wise addition of burette solution to the conical flask. A sharp colour change from wine red to blue was observed at the end point. This experiment was repeated three times. Obtained observations are listed below.

Table 22: Readings of complexometric titration between Aq. Solutions of Ca^{+2} and Na_2H_2EDTA by using Eriochrome Black-T as indicator

Experiment No.	Initial Reading (in mL)	Final Reading (in mL)	Difference (in mL)	Concordant Reading (in mL)
1	**0.0**	**8.6**	**8.6**	**8.6**
2	**0.0**	**8.6**	**8.6**	
3	**0.0**	**8.6**	**8.6**	

<u>Experimental Calculations:</u>

1000.0 mL 1M Na_2H_2EDTA ≡ 100.0 g $CaCO_3$ ≡ 40.0 g Ca^{+2}

1000.0 mL 0.01M Na_2H_2EDTA ≡ 1.0 g $CaCO_3$ ≡ 0.4 g Ca^{+2}

1.0 mL 0.01M Na_2H_2EDTA ≡ 1.0 mg $CaCO_3$ ≡ 0.4 mg Ca^{+2}

8.6 mL 0.01M Na_2H_2EDTA ≡ 8.6 mg $CaCO_3$

Solution B contains 8.6 mg of $CaCO_3$ (Experimental Amount)

Solution A contains (8.6 x 5) = 43.0 mg of $CaCO_3$ (Experimental Amount)

31) Gravimetric Estimation of Calcium in Egg-Shell as Calcium Carbonate ($CaCO_3$) (Stock solution of Egg-Shell was prepared by digesting 42.0 mg of Dry Egg-Shell Powder with 1.0 mL Con. HCl)

42.0 mg of dry Egg-Shell powder was taken in 100.0 mL beaker. To this, 1.0 mL Con. HCl was added with stirring followed by addition of 10.0 mL water. Beaker was covered with watch glass and then heated till the solution became clear and carbon dioxide expelled completely. Sides of beaker and watch glass were rinsed with distilled water and diluted up to 50.0 mL. Then, solution was heated to boiling and 2 drops of methyl red indicator was added. To this, 5.0 mL 5% ammonium oxalate solution was added. To the resulted hot solution, (1:1) ammonia solution was added drop wise and with constant stirring until the mixture became neutral (color of solution changes to yellow from red). Formed precipitates

were allowed to settle without further heating for one hour. Precipitates were filtered through previously weighed Whatman filter paper 40 and washed with 0.1% ammonium oxalate solution till it became free from chloride. Precipitates were dried on metallic cone on sand bath. Weight the amount of (Precipitate + Whatmann filter paper) and subtract it from the weight of empty Whatmann filter paper. This experiment was repeated three times and the results are reported below.

Experiment No.	Weight of Filter Paper (in g)	Weight of (Filter Paper + Precipitates) (in g)	Weight of Precipitates (in g)	Concordant Reading (in mg)
01	1.0672 g	1.1281	0.0609	60.9
02	1.0728 g	1.1337	0.0609	
03	1.0989 g	1.1604	0.0615	

Calculations:

1.0 mole of $CaCO_3$ ≡ 1.0 mole of $CaC_2O_4.H_2O$

100.0 g $CaCO_3$ ≡ 146.08 g $CaC_2O_4.H_2O$

0.042 g $CaCO_3$ ≡ 0.0613 g $CaC_2O_4.H_2O$

Therefore, for obtained 60.9 mg $CaC_2O_4.H_2O$, the equivalent amount of $CaCO_3$ is 41.7 mg

32) Estimation of Calcium as Calcium Carbonate ($CaCO_3$) by using Aq. Solution of Ca^{+2} (pH 7) as titrand, Aq. Solution of Na_3HEDTA (pH 11) as titrant and bromothymol blue as Indicator (Stock solution of $CaCO_3$ was prepared by dissolving 48.0 mg of Sea Shell Powder)

0.048 g sea shell powder was dissolved in 0.2 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 250.0

mL beaker. Then, pH electrode was inserted to this solution and pH value was found to be 2.2. pH of this solution was adjusted to 7 by adding 2.0 mL 0.33 M NaOH solution (**Solution B**). 50.0 mL of solution B was transferred to 250.0 mL conical flask. To this, 3-4 drops of bromothymol blue indicator was added. Colour of solution was colourless to pale green. Aqueous solution of 0.01M Na_3HEDTA (pH 11) was prepared by mixing 250.0 mL 0.01M Na_2H_2EDTA and 15.0 mL 0.33M NaOH solutions. This solution was filled in 25.0 mL burette as titrant. Then, titration was performed by drop wise addition of burette solution to the conical flask. With progress of titration, pH of solution decreases and colour of solution changed from light green to yellow. After surpassing the equivalence point, further addition of Na_3HEDTA solution caused sharp increase in the pH of solution i.e pH≥7.5 and its colour changed from yellow to intense blue which was detected as end point of the titration. This experiment was repeated three times. Obtained observations are listed below.

Table 23A (Solution Set-I): Readings of complexometric titration between Aq. Solutions of Ca^{+2} and Na_3HEDTA by using bromothymol blue as indicator

Experiment No.	Initial Reading (in mL)	Final Reading (in mL)	Difference (in mL)	Concordant Reading (in mL)
1	0.0	10.5	10.5	10.5
2	0.0	10.5	10.5	
3	0.0	10.5	10.5	

Table 23B (Solution Set-II): Readings of complexometric titration between Aq. Solutions of Ca^{+2} and Na_3HEDTA by using bromothymol blue as indicator

Experiment No.	Initial Reading (in mL)	Final Reading (in mL)	Difference (in mL)	Concordant Reading (in mL)
1	0.0	10.7	10.7	10.5
2	0.0	10.5	10.5	

3	**0.0**	**10.5**	**10.5**	

Table 23C (Solution Set-III): Readings of complexometric titration between Aq. Solutions of Ca^{+2} and Na_3HEDTA by using bromothymol blue as indicator

Experiment No.	Initial Reading (in mL)	Final Reading (in mL)	Difference (in mL)	Concordant Reading (in mL)
1	0.0	10.5	10.5	10.5
2	0.0	10.5	10.5	
3	0.0	10.7	10.7	

Relative Standard Deviation of Above Nine Readings: 0.84%

<u>Theoretical Calculations:</u>

Solution B contains 9.6 mg of $CaCO_3$ (Theoretical Amount)

Solution A contains (9.6 x 5) = 48 mg of $CaCO_3$ (Theoretical Amount)

<u>Experimental Calculations:</u>

1000.0 mL 1M Na_2H_2EDTA ≡ 100.0 g $CaCO_3$ ≡ 40.0 g Ca^{+2}

1000.0 mL 0.01M Na_2H_2EDTA ≡ 1.0 g $CaCO_3$ ≡ 0.4 g Ca^{+2}

1.0 mL 0.01M Na_2H_2EDTA ≡ 1.0 mg $CaCO_3$ ≡ 0.4 mg Ca^{+2}

10.5 mL 0.01M Na_2H_2EDTA ≡ 10.5 mg $CaCO_3$

Solution B contains 10.5 mg of $CaCO_3$ (Experimental Amount)

Solution A contains (10.5 x 5) = 52.5 mg of $CaCO_3$ (Experimental Amount)

33) Estimation of Calcium as Calcium Carbonate ($CaCO_3$) by using conventional complexometric titration method (Stock solution of $CaCO_3$ was prepared by dissolving 48.0 mg of Dry Sea Shell Powder)

0.048 g sea shell powder was dissolved in 0.2 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 250.0 mL conical flask (**Solution B**). To this, 1.5 test tube (Approx. 10-12 mL) NH_4OH-NH_4Cl buffer (pH 10) was added. Then, 4-5 drops of Eriochrome Black-T indicator was added. Solution in the conical flask was turned wine red and it was shaken well. Aq. Solution of Na_2H_2EDTA was filled in 25.0 mL burette. Then, titration was performed by drop wise addition of burette solution to the conical flask. A sharp colour change from wine red to blue was observed at the end point. This experiment was repeated three times. Obtained observations are listed below.

Table 24: Readings of complexometric titration between Aq. Solutions of Ca^{+2} and Na_2H_2EDTA by using Eriochrome Black-T as indicator

Experiment No.	Initial Reading (in mL)	Final Reading (in mL)	Difference (in mL)	Concordant Reading (in mL)
1	0.0	9.8	9.8	9.8
2	0.0	9.8	9.8	
3	0.0	9.8	9.8	

<u>Experimental Calculations:</u>

1000.0 mL 1M Na_2H_2EDTA ≡ 100.0 g $CaCO_3$ ≡ 40.0 g Ca^{+2}

1000.0 mL 0.01M Na_2H_2EDTA ≡ 1.0 g $CaCO_3$ ≡ 0.4 g Ca^{+2}

1.0 mL 0.01M Na_2H_2EDTA ≡ 1.0 mg $CaCO_3$ ≡ 0.4 mg Ca^{+2}

9.8 mL 0.01M Na_2H_2EDTA ≡ 9.8 mg $CaCO_3$

Solution B contains 9.8 mg of $CaCO_3$ (Experimental Amount)

Solution A contains (9.8 x 5) = 49.0 mg of $CaCO_3$ (Experimental Amount)

34) Gravimetric Estimation of Calcium in Sea-Shell as Calcium Carbonate ($CaCO_3$) (Stock solution of Sea-Shell was prepared by digesting 48.0 mg of Dry Sea-Shell Powder with 1.0 mL Con. HCl)

48.0 mg of dry Sea-Shell powder was taken in 100.0 mL beaker. To this, 1.0 mL Con. HCl was added with stirring followed by addition of 10.0 mL water. Beaker was covered with watch glass and then heated till the solution became clear and carbon dioxide expelled completely. Sides of beaker and watch glass were rinsed with distilled water and diluted up to 50.0 mL. Then, solution was heated to boiling and 2 drops of methyl red indicator was added. To this, 5.0 mL 5% ammonium oxalate solution was added. To the resulted hot solution, (1:1) ammonia solution was added drop wise and with constant stirring until the mixture became neutral (color of solution changes to yellow from red). Formed precipitates were allowed to settle without further heating for one hour. Precipitates were filtered through previously weighed Whatman filter paper 40 and washed with 0.1% ammonium oxalate solution till it became free from chloride. Precipitates were dried on metallic cone on sand bath. Weight the amount of (Precipitate + Whatmann filter paper) and subtract it from the weight of empty Whatmann filter paper. This experiment was repeated three times and the results are reported below.

Experiment No.	Weight of Filter Paper (in g)	Weight of (Filter Paper + Precipitates) (in g)	Weight of Precipitates (in g)	Concordant Reading (in mg)
01	1.1071	1.1778	0.0707	70.7
02	1.0803	1.1515	0.0712	
03	1.0821	1.1528	0.0707	

Calculations:

1.0 mole of $CaCO_3$ ≡ 1.0 mole of $CaC_2O_4.H_2O$

100.0 g $CaCO_3$ ≡ 146.08 g $CaC_2O_4.H_2O$

0.0480 g $CaCO_3$ ≡ 0.0701 g $CaC_2O_4.H_2O$

Therefore, for obtained 70.7 mg $CaC_2O_4.H_2O$, the equivalent amount of $CaCO_3$ is 48.4 mg

35) Estimation of Calcium as Calcium Carbonate ($CaCO_3$) by using Aq. Solution of Ca^{+2} (pH 7) as titrand, Aq. Solution of Na_3HEDTA (pH 11) as titrant and bromothymol blue as indicator (Stock solution of $CaCO_3$ was prepared by dissolving 40.0 mg of Calcium Tablet Powder)

0.040 g calcium tablet powder was dissolved in 0.1 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 250.0 mL beaker. Then, pH electrode was inserted to this solution and pH value was found to be 2.2. pH of this solution was adjusted to 7 by adding 2.0 mL 0.33 M NaOH solution (**Solution B**). 50.0 mL of solution B was transferred to 250.0 mL conical flask. To this, 3-4 drops of bromothymol blue indicator was added. Colour of solution was colourless to pale green. Aqueous solution of 0.01M Na_3HEDTA (pH 11) was prepared by mixing 250.0 mL 0.01M Na_2H_2EDTA and 15.0 mL 0.33M NaOH solutions. This solution was filled in 25.0 mL burette as titrant. Then, titration was performed by drop wise addition of burette solution to the conical flask. With progress of titration, pH of solution decreases and colour of solution changed from light green to yellow. After surpassing the equivalence point, further addition of Na_3HEDTA solution caused sharp increase in the pH of solution i.e $pH \geq 7.5$ and its colour changed from yellow to intense blue which was detected as end point of the titration. This experiment was repeated three times. Obtained observations are listed below.

Table 25A (Solution Set-I): Readings of complexometric titration between Aq. Solutions of Ca^{+2} and Na_3HEDTA by using bromothymol blue as indicator

Experiment No.	Initial Reading (in mL)	Final Reading (in mL)	Difference (in mL)	Concordant Reading (in mL)
1	0.0	8.9	8.9	8.9
2	0.0	8.9	8.9	
3	0.0	8.9	8.9	

Table 25B (Solution Set-II): Readings of complexometric titration between Aq. Solutions of Ca^{+2} and Na_3HEDTA by using bromothymol blue as indicator

Experiment No.	Initial Reading (in mL)	Final Reading (in mL)	Difference (in mL)	Concordant Reading (in mL)
1	0.0	9.0	9.0	8.9
2	0.0	8.9	8.9	
3	0.0	8.9	8.9	

Table 25C (Solution Set-III): Readings of complexometric titration between Aq. Solutions of Ca^{+2} and Na_3HEDTA by using bromothymol blue as indicator

Experiment No.	Initial Reading (in mL)	Final Reading (in mL)	Difference (in mL)	Concordant Reading (in mL)
1	0.0	8.9	8.9	8.9
2	0.0	9.1	9.1	
3	0.0	8.9	8.9	

Relative Standard Deviation of Above Nine Readings: 0.99%

Theoretical Calculations:

Solution B contains 8.0 mg of $CaCO_3$ (Theoretical Amount)

Solution A contains (8.0 x 5) = 40 mg of $CaCO_3$ (Theoretical Amount)

Experimental Calculations:

1000.0 mL 1M Na_2H_2EDTA ≡ 100.0 g $CaCO_3$ ≡ 40.0 g Ca^{+2}

1000.0 mL 0.01M Na_2H_2EDTA ≡ 1.0 g $CaCO_3$ ≡ 0.4 g Ca^{+2}

1.0 mL 0.01M Na_2H_2EDTA ≡ 1.0 mg $CaCO_3$ ≡ 0.4 mg Ca^{+2}

8.9 mL 0.01M Na_2H_2EDTA ≡ 8.9 mg $CaCO_3$

Solution B contains 8.9 mg of $CaCO_3$ (Experimental Amount)

Solution A contains (8.9 x 5) = 44.5 mg of $CaCO_3$ (Experimental Amount)

36) Estimation of Calcium as Calcium Carbonate ($CaCO_3$) by using conventional complexometric titration method (Stock solution of $CaCO_3$ was prepared by dissolving 40.0 mg of Dry Calcium Tablet Powder)

0.040 g sea shell powder was dissolved in 0.1 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 250.0 mL conical flask (**Solution B**). To this, 1.5 test tube (Approx. 10-12 mL) NH_4OH-NH_4Cl buffer (pH 10) was added. Then, 4-5 drops of Eriochrome Black-T indicator was added. Solution in the conical flask was turned wine red and it was shaken well. Aq. Solution of Na_2H_2EDTA was filled in 25.0 mL burette. Then, titration was performed by drop wise addition of burette solution to the conical flask. A sharp colour change from wine red to blue was observed at the end point. This experiment was repeated three times. Obtained observations are listed below.

Table 26: Readings of complexometric titration between Aq. Solutions of Ca^{+2} and Na_2H_2EDTA by using Eriochrome Black-T as indicator

Experiment No.	Initial Reading (in mL)	Final Reading (in mL)	Difference (in mL)	Concordant Reading (in mL)
1	0.0	8.2	8.2	8.2
2	0.0	8.2	8.2	
3	0.0	8.2	8.2	

Experimental Calculations:

1000.0 mL	**1M Na_2H_2EDTA**	≡	**100.0 g $CaCO_3$**	≡	**40.0 g Ca^{+2}**
1000.0 mL	**0.01M Na_2H_2EDTA**	≡	**1.0 g $CaCO_3$**	≡	**0.4 g Ca^{+2}**
1.0 mL	**0.01M Na_2H_2EDTA**	≡	**1.0 mg $CaCO_3$**	≡	**0.4 mg Ca^{+2}**
8.2 mL	**0.01M Na_2H_2EDTA**	≡	**8.2 mg $CaCO_3$**		

Solution B contains 8.2 mg of $CaCO_3$ (Experimental Amount)

Solution A contains (8.2 x 5) = 41.0 mg of $CaCO_3$ (Experimental Amount)

37) Gravimetric Estimation of Calcium in Calcium Tablet as Calcium Carbonate ($CaCO_3$) (Stock solution of Calcium Tablet was prepared by digesting 40.0 mg of Dry Calcium Tablet Powder with 1.0 mL Con. HCl)

40.0 mg of dry Calcium Tablet powder was taken in 100.0 mL beaker. To this, 1.0 mL Con. HCl was added with stirring followed by addition of 10.0 mL water. Beaker was covered with watch glass and then heated till the solution became clear and carbon dioxide expelled completely. Sides of beaker and watch glass were rinsed with distilled water and diluted up to 50.0 mL. Then, solution was heated to boiling and 2 drops of methyl red indicator was added. To this, 5.0 mL 5% ammonium oxalate solution was added. To the resulted hot solution, (1:1) ammonia solution was added drop wise and with constant stirring until the mixture became neutral (color of solution changes to yellow from red). Formed precipitates

were allowed to settle without further heating for one hour. Precipitates were filtered through previously weighed Whatman filter paper 40 and washed with 0.1% ammonium oxalate solution till it became free from chloride. Precipitates were dried on metallic cone on sand bath. Weight the amount of (Precipitate + Whatmann filter paper) and subtract it from the weight of empty Whatmann filter paper. This experiment was repeated three times and the results are reported below.

Experiment No.	Weight of Filter Paper (in g)	Weight of (Filter Paper + Precipitates) (in g)	Weight of Precipitates (in g)	Concordant Reading (in mg)
01	1.0772	1.1352	0.0580	58.0
02	1.1129	1.1717	0.0588	
03	1.0697	1.1277	0.0580	

Calculations:

1.0 mole of $CaCO_3$ ≡ 1.0 mole of $CaC_2O_4.H_2O$

100.0 g $CaCO_3$ ≡ 146.08 g $CaC_2O_4.H_2O$

0.0400 g $CaCO_3$ ≡ 0.0584 g $CaC_2O_4.H_2O$

Therefore, for obtained 58.0 mg $CaC_2O_4.H_2O$, the equivalent amount of $CaCO_3$ is 39.7 mg

38) pH-Metric Estimation of Lithium as Lithium Carbonate (Li_2CO_3) by using Aq. Solution of Li^+ (pH 7) as titrand and Aq. Solution of Na_3HEDTA (pH 11) as titrant (Stock solution of Lithium Carbonate was prepared by dissolving 55.0 mg of Dry Lithium Carbonate Powder)

0.055 g dry lithium carbonate powder was dissolved in 0.2 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 100.0 mL beaker. Then, pH electrode was inserted to this solution and pH value was found to be 3.2. pH of this solution was adjusted to 7 by adding 2.0 mL 0.33 M NaOH solution (**Solution B**). Aqueous solution of 0.01M Na_3HEDTA (pH 11) was prepared by mixing 250.0 mL 0.01M Na_2H_2EDTA and 15.0 mL 0.33M NaOH solutions. This solution was filled in 25.0 mL burette as titrant. Then, 0.5 mL 0.01M Na_3HEDTA was added to Solution B having pH 7. Solution was shaken well with the help of glass rod and then pH reading was measured. Same process was repeated by adding 0.5 mL 0.01M Na_3HEDTA from burette up to 9.0 mL and pH reading was measured after each 0.5 mL addition of burette solution. Obtained readings and graph are described below.

Table 27: Readings of pH-Metric Titration between Aq. Solutions of Li^+ (present in Lithium Carbonate) and Na_3HEDTA

Sr. No.	**Volume of 0.01M Na_3HEDTA (in mL)**	**pH**
1	0	7.06
2	0.5	7.49
3	1	8.2
4	1.5	8.59
5	2	9.02
6	2.5	9.42
7	3	9.74
8	3.5	9.82
9	4	9.93
10	4.5	9.97
11	5	10.04
12	5.5	10.08
13	6	10.12
14	6.5	10.15
15	7	10.19
16	7.5	10.24
17	8	10.34
18	8.5	10.42
19	9	10.52

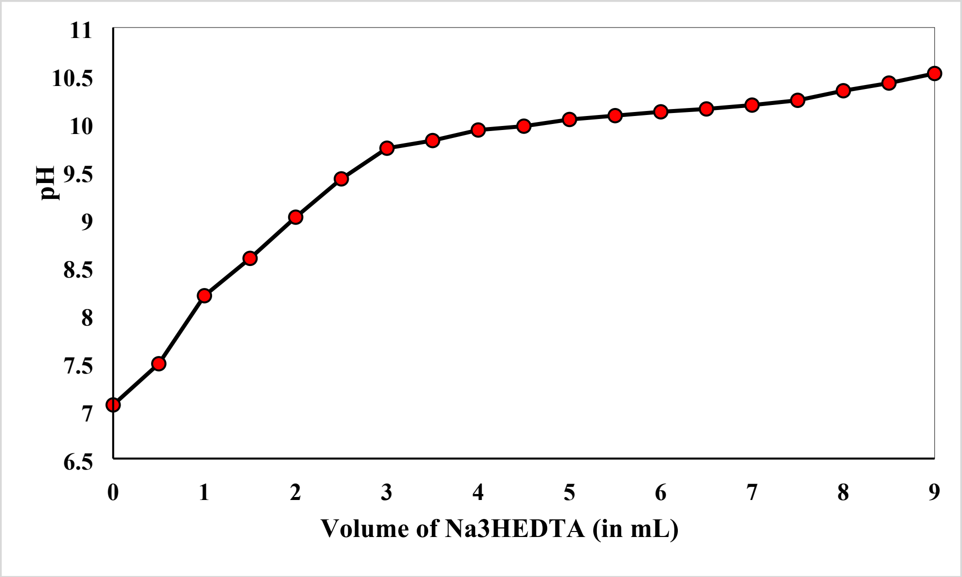


Figure 10: Effect of Aq.Na_3HEDTA Addition on pH of Li^+ Solution

During this titration, release of one H^+ ion was not taking place and hence decrease in pH was not observed. However, continuous increase in pH was observed. No sharp equivalence point was observed.

39) pH-Metric Estimation of Sodium as Sodium Chloride (NaCl) by using Aq. Solution of Na^+ (pH 7) as titrand and Aq. Solution of Na_3HEDTA (pH 11) as titrant (Stock solution of Sodium Chloride was prepared by dissolving 29.2 mg of Sodium Chloride Powder)

0.0292 g dry sodium chloride powder was dissolved in pure water. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 100.0 mL beaker. Then, pH electrode was inserted to this solution and pH value was found to be 6.7. pH of this solution was adjusted to 7 by adding 0.2 mL 0.33 M NaOH solution (**Solution B**). Aqueous solution of 0.01M Na_3HEDTA (pH 11) was prepared by mixing 250.0 mL 0.01M Na_2H_2EDTA and 15.0 mL 0.33M NaOH solutions. This solution was filled in 25.0 mL burette as titrant. Then, 0.5 mL 0.01M Na_3HEDTA was added to Solution B having pH 7. Solution was shaken well with the help of glass rod and then pH reading was measured. Same process was repeated by adding 0.5 mL 0.01M Na_3HEDTA from burette up to 12.0 mL and pH reading was measured after each 0.5 mL addition of burette solution. Obtained readings and graph are described below.

Table 28: Readings of pH-Metric Titration between Aq. Solutions of Na^+ (present in Sodium Chloride) and Na_3HEDTA

Sr. No.	Volume of 0.01M Na_3HEDTA (in mL)	pH
1	0	7.09
2	0.5	7.2
3	1	7.3
4	1.5	7.6
5	2	8.3
6	2.5	8.75
7	3	9.3
8	3.5	9.47
9	4	9.72
10	4.5	9.77
11	5	9.85
12	5.5	9.91
13	6	9.98
14	6.5	10.03
15	7	10.08
16	7.5	10.12
17	8	10.16
18	8.5	10.2
19	9	10.26

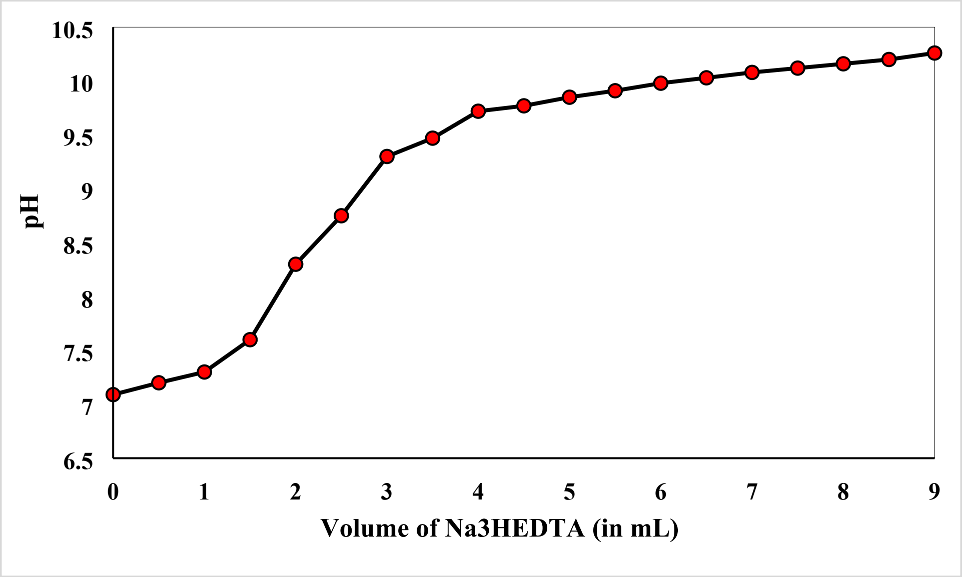


Figure 11: Effect of Aq.Na_3HEDTA Addition on pH of Na^+ Solution

During this titration, release of one H^+ ion was not taking place and hence decrease in pH was not observed. However, continuous increase in pH was observed. No sharp equivalence point was observed.

40) pH-Metric Estimation of Potassium as Potassium Chloride (KCl) by using Aq. Solution of K^+ (pH 7) as titrand and Aq. Solution of Na_3HEDTA (pH 11) as titrant (Stock solution of Potassium Chloride was prepared by dissolving 37.2 mg of Potassium Chloride Powder)

0.0372 g dry potassium chloride powder was dissolved in pure water. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 100.0 mL beaker. Then, pH electrode was inserted to this solution and pH value was found to be 6.5. pH of this solution was adjusted to 7 by adding 0.2 mL 0.33 M NaOH solution (**Solution B**). Aqueous solution of 0.01M Na_3HEDTA (pH 11) was prepared by mixing 250.0 mL 0.01M Na_2H_2EDTA and 15.0 mL 0.33M NaOH solutions. This solution was filled in 25.0 mL burette as titrant. Then, 0.5 mL 0.01M Na_3HEDTA was added to Solution B having pH 7. Solution was shaken well with the help of glass rod and then pH reading was measured. Same process was repeated by adding 0.5 mL 0.01M Na_3HEDTA from burette up to 12.0 mL and pH reading was measured after each 0.5 mL addition of burette solution. Obtained readings and graph are described below.

Table 29: Readings of pH-Metric Titration between Aq. Solutions of K^+ (present in Potassium Chloride) and Na_3HEDTA

Sr. No.	Volume of 0.01M Na_3HEDTA (in mL)	pH
1	0	7.08
2	0.5	7.2
3	1	7.3
4	1.5	7.41
5	2	7.67
6	2.5	8.1
7	3	9.11
8	3.5	9.41
9	4	9.61
10	4.5	9.74
11	5	9.83
12	5.5	9.89
13	6	9.99
14	6.5	10.05
15	7	10.09
16	7.5	10.13
17	8	10.17
18	8.5	10.2
19	9	10.24

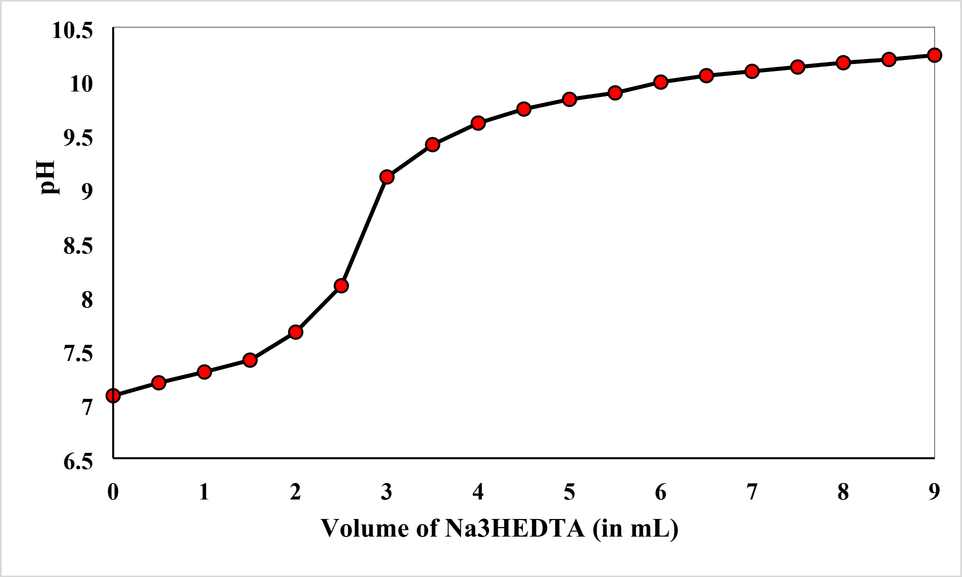


Figure 12: Effect of Aq.Na_3HEDTA Addition on pH of K^+ Solution

During this titration, release of one H^+ ion was not taking place and hence decrease in pH was not observed. However, continuous increase in pH was observed. No sharp equivalence point was observed.

41) pH-Metric Estimation of Metal Ions from the mixture of (Ca^{+2} and Mg^{+2}). Aq. Solution of Ca^{+2} and Mg^{+2} was prepared by mixing 0.0375 g $CaCO_3$ and 0.0298 g $MgCO_3$ respectively. pH of this solution was adjusted to 7 and then it was taken as titrand and Aq. Solution of Na_3HEDTA (pH 11) was taken as titrant

0.0375 g $CaCO_3$ and 0.0298 g $MgCO_3$ powder was mixed well and then dissolved in 0.2 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 100.0 mL beaker. Then, pH electrode was inserted to this solution and pH value was found to be 2.2. pH of this solution was adjusted to 7 by adding 3.0 mL 0.33 M NaOH solution (**Solution B**). Aqueous solution of 0.01M Na_3HEDTA (pH 11) was prepared by mixing 250.0 mL 0.01M Na_2H_2EDTA and 15.0 mL 0.33M NaOH solutions. This solution was filled in 25.0 mL burette as titrant. Then, 0.5 mL 0.01M Na_3HEDTA was added to Solution B having pH 7. Solution was shaken well with the help of glass rod and then pH reading was measured. Same process was repeated by adding 0.5 mL 0.01M Na_3HEDTA from burette up to 19.0 mL and pH reading was measured after each 0.5 mL addition of burette solution. Obtained readings and graph are described below.

Table 30: pH-Metric Titration Readings between Aq. Solutions of (Ca^{+2} + Mg^{+2}) and Na_3HEDTA

Sr. No.	Volume of 0.01M Na_3HEDTA (in mL)	pH
1	0	7.05
2	0.5	7
3	1	6.96
4	1.5	6.89
5	2	6.84
6	2.5	6.79
7	3	6.73
8	3.5	6.68
9	4	6.64
10	4.5	6.6
11	5	6.55
12	5.5	6.53
13	6	6.49
14	6.5	6.45
15	7	6.43
16	7.5	6.4
17	8	6.37
18	8.5	6.34
19	9	6.31
20	9.5	6.29
21	10	6.27
22	10.5	6.25
23	11	6.22
24	11.5	6.2
25	12	6.18
26	12.5	6.16
27	13	6.15
28	13.5	6.13
29	14	6.12
30	14.5	6.1
31	15	6.68
32	15.5	6.98

33	16	7.3
34	16.5	8.22
35	17	8.74
36	17.5	9.28
37	18	9.59
38	18.5	9.75
39	19	9.89

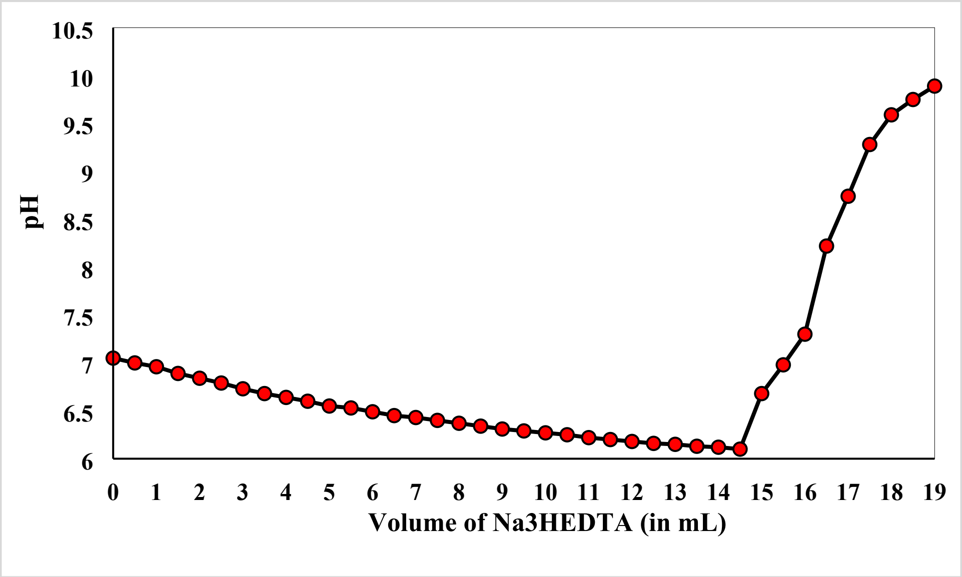


Figure 13: Effect of Aq.Na_3HEDTA Addition on pH of (Ca^{+2} + Mg^{+2}) Solution

Observations: During this titration, formation of Ca- and Mg-EDTA complexes and release of one H^+ ion was taking place and hence decrease in pH from 7.04 to 6.10 was observed. At equivalence point, release of H^+ ion was stopped and sharp increase in pH was observed from 6.10 to 6.68 with further 0.5 mL addition of Na_3HEDTA (pH 11). Upon subsequent addition of Na_3HEDTA solution, pH value of solution significantly jumped to 6.98, 7.30 and 8.22. **So sharp equivalence point for the titration was observed at 14.5 mL.**

Theoretical Calculations:

Solution B contains 7.5 mg of $CaCO_3$ (Theoretical Amount)

Solution B contains 5.9 mg of $MgCO_3$ (Theoretical Amount)

1.0 mL 0.01M Na_3HEDTA ≡ 1.0 mg $CaCO_3$ ≡ 0.84 mg $MgCO_3$

Expected equivalence point is (7.5 + 7.0) mL = 14.5 mL Na_3HEDTA (Theoretical)

Solution A contains (13.4 x 5) = 67.0 mg of Total (Ca^{+2} + Mg^{+2}) content (Theoretical Amount)

Experimental Calculations:

1000.0 mL 1M Na_3HEDTA ≡ 100.0 g $CaCO_3$ ≡ 40.0 g Ca^{+2}

1000.0 mL 1M Na_3HEDTA ≡ 84.31 g $MgCO_3$ ≡ 24.3 g Mg^{+2}

1000.0 mL 0.01M Na_3HEDTA ≡ 1.0 g $CaCO_3$ ≡ 0.84 g $MgCO_3$

1.0 mL 0.01M Na_3HEDTA ≡ 1.0 mg $CaCO_3$ ≡ 0.84 mg $MgCO_3$

Experimental equivalence point: 14.5 mL, which was utilized to form complexes with 7.4 mg $CaCO_3$ and 5.9 mg of $MgCO_3$

Theoretical and experimental equivalence point shows very good agreement

42) pH-Metric Estimation of Metal Ions from the mixture of (Ca^{+2} and Ba^{+2}). Aq. Solution of Ca^{+2} and Ba^{+2} was prepared by mixing 0.0375 g $CaCO_3$ and 0.0490 g $BaCO_3$ respectively. pH of this solution was adjusted to 7 and then it was taken as titrand and Aq. Solution of Na_3HEDTA (pH 11) was taken as titrant

0.0375 g $CaCO_3$ and 0.0490 g $BaCO_3$ powder was mixed well and then dissolved in 0.2 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 100.0 mL beaker. Then, pH electrode was inserted to this solution and pH value was found to be 2.5. pH of this solution was adjusted to 7 by adding 3.0 mL 0.33 M NaOH solution (**Solution B**). Aqueous solution of 0.01M Na_3HEDTA (pH 11) was prepared by mixing 250.0 mL 0.01M Na_2H_2EDTA and 15.0 mL 0.33M NaOH solutions. This solution was filled in 25.0 mL burette as titrant. Then, 0.5 mL 0.01M Na_3HEDTA was added to Solution B having pH 7. Solution was shaken well with the help of glass rod and then pH reading was measured. Same process was repeated by adding 0.5 mL 0.01M Na_3HEDTA from burette up to 17.0 mL and pH reading was measured after each 0.5 mL addition of burette solution. Obtained readings and graph are described below.

Table 31: pH-Metric Titration Readings between Aq. Solutions of (Ca^{+2} + Ba^{+2}) and Na_3HEDTA

Sr. No.	Volume of 0.01M Na_3HEDTA (in mL)	pH
1	0	7.09
2	0.5	7.02
3	1	6.98
4	1.5	6.94
5	2	6.9
6	2.5	6.85
7	3	6.81
8	3.5	6.78
9	4	6.73
10	4.5	6.69
11	5	6.65
12	5.5	6.61
13	6	6.57
14	6.5	6.52
15	7	6.48
16	7.5	6.44
17	8	6.39
18	8.5	6.34
19	9	6.31
20	9.5	6.29
21	10	6.28
22	10.5	6.26
23	11	6.24
24	11.5	6.22
25	12	6.2
26	12.5	6.18
27	13	6.77
28	13.5	7.08
29	14	7.39
30	14.5	7.64
31	15	7.92
32	15.5	8.38
33	16	8.85
34	16.5	9.05
35	17	9.39

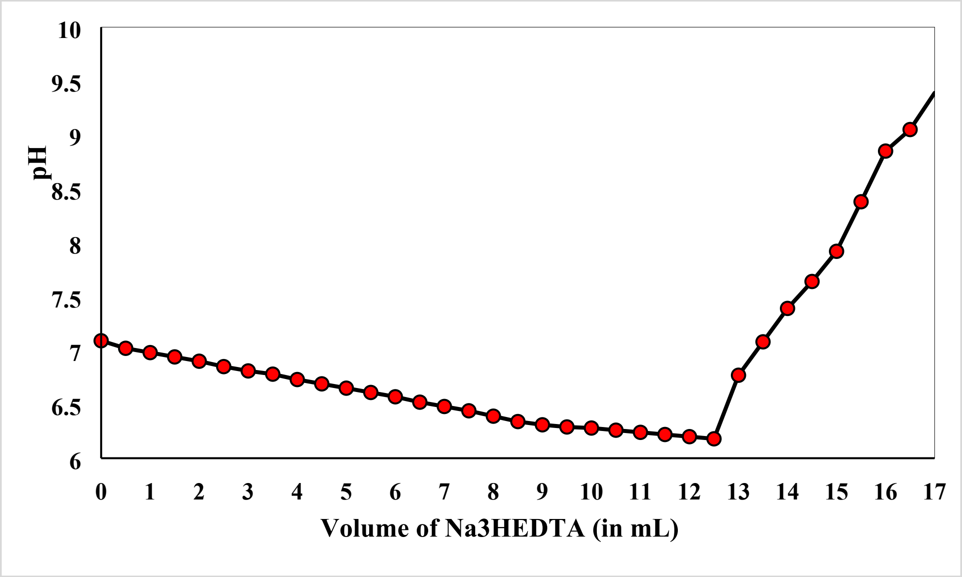


Figure 14: Effect of Aq.Na_3HEDTA Addition on pH of (Ca^{+2} + Ba^{+2}) Solution

Observations: During this titration, formation of Ca- and Ba-EDTA complexes and release of one H^+ ion was taking place and hence decrease in pH from 7.09 to 6.18 was observed. At equivalence point, release of H^+ ion was stopped and sharp increase in pH was observed from 6.18 to 6.77 with further 0.5 mL addition of Na_3HEDTA (pH 11). Upon subsequent addition of Na_3HEDTA solution, pH value of solution significantly jumped to 7.08, 7.39 and 7.64. **So sharp equivalence point for the titration was observed at 12.5 mL.**

Theoretical Calculations:

Solution B contains 7.5 mg of $CaCO_3$ (Theoretical Amount)

Solution B contains 9.8 mg of $BaCO_3$ (Theoretical Amount)

1.0 mL 0.01M Na_3HEDTA ≡ 1.0 mg $CaCO_3$ ≡ 1.97 mg $BaCO_3$

Expected equivalence point is (7.5 + 5.0) mL = 12.5 mL Na_3HEDTA (Theoretical)

Solution A contains (17.3 x 5) = 86.5 mg of Total (Ca^{+2} + Ba^{+2}) content (Theoretical Amount)

Experimental Calculations:

1000.0 mL 1M Na_3HEDTA ≡ 100.0 g $CaCO_3$ ≡ 40.0 g Ca^{+2}

1000.0 mL 1M Na_3HEDTA ≡ 197.35 g $BaCO_3$ ≡ 137.32 g Ba^{+2}

1000.0 mL 0.01M Na_3HEDTA ≡ 1.0 g $CaCO_3$ ≡ 1.97 g $BaCO_3$

1.0 mL 0.01M Na_3HEDTA ≡ 1.0 mg $CaCO_3$ ≡ 1.97 mg $BaCO_3$

Experimental equivalence point: 12.5 mL, which was utilized to form complexes with 7.5 mg $CaCO_3$ and 9.8 mg of $BaCO_3$

Theoretical and experimental equivalence point shows very good agreement

43) pH-Metric Estimation of Metal Ions from the mixture of (Ca^{+2} and Sr^{+2}). Aq. Solution of Ca^{+2} and Sr^{+2} was prepared by mixing 0.0375 g $CaCO_3$ and 0.050 g $SrCl_2$.6H2O respectively. pH of this solution was adjusted to 7 and then it was taken as titrand and Aq. Solution of Na_3HEDTA (pH 11) was taken as titrant

0.0375 g $CaCO_3$ and 0.050 g $SrCl_2$.6H2O powder was mixed well and then dissolved in 0.3 mL 11.3N HCl. It was transferred to a 250.0 mL standard volumetric flask and diluted up to the mark with water. Solution was shaken well to make it homogeneous (**Solution A**). Then, 50.0 mL of Solution A was transferred to a 100.0 mL beaker. Then, pH electrode was inserted to this solution and pH value was found to be 2.5. pH of this solution was adjusted to 7 by adding 3.0 mL 0.33 M NaOH solution (**Solution B**). Aqueous solution of 0.01M Na_3HEDTA (pH 11) was prepared by mixing 250.0 mL 0.01M Na_2H_2EDTA and 15.0 mL 0.33M NaOH solutions. This solution was filled in 25.0 mL burette as titrant. Then, 0.5 mL 0.01M Na_3HEDTA was added to Solution B having pH 7. Solution was shaken well with the help of glass rod and then pH reading was measured. Same process was repeated by adding 0.5 mL 0.01M Na_3HEDTA from burette up to 15.0 mL and pH reading was measured after each 0.5 mL addition of burette solution. Obtained readings and graph are described below.

Table 32: pH-Metric Titration Readings between Aq. Solutions of (Ca^{+2} + Sr^{+2}) and Na_3HEDTA

Sr. No.	Volume of 0.01M Na_3HEDTA (in mL)	pH
1	0	7.06

2	0.5	6.99
3	1	6.95
4	1.5	6.92
5	2	6.89
6	2.5	6.86
7	3	6.83
8	3.5	6.8
9	4	6.77
10	4.5	6.74
11	5	6.72
12	5.5	6.68
13	6	6.66
14	6.5	6.62
15	7	6.58
16	7.5	6.55
17	8	6.52
18	8.5	6.48
19	9	6.45
20	9.5	6.42
21	10	6.39
22	10.5	6.35
23	11	6.32
24	11.5	6.29
25	12	6.25
26	12.5	6.76
27	13	7.08
28	13.5	7.44
29	14	7.82
30	14.5	8.37
31	15	8.96

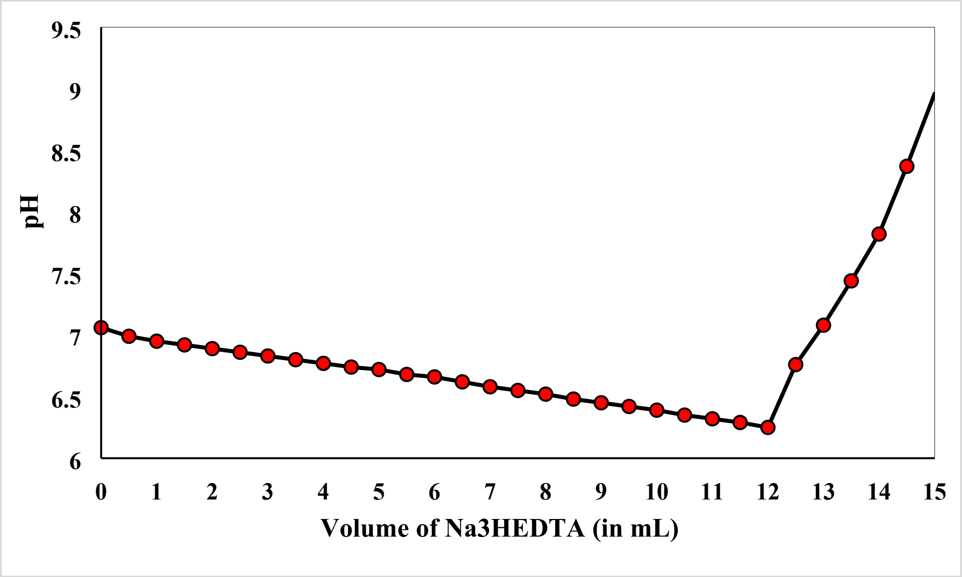


Figure 15: Effect of Aq.Na_3HEDTA Addition on pH of (Ca^{+2} + Sr^{+2}) Solution

Observations: During this titration, formation of Ca- and Sr-EDTA complexes and release of one H^+ ion was taking place and hence decrease in pH from 7.06 to 6.25 was observed. At equivalence point, release of H^+ ion was stopped and sharp increase in pH was observed from 6.25 to 6.76 with further 0.5 mL addition of Na_3HEDTA (pH 11). Upon subsequent addition of Na_3HEDTA solution, pH value of solution significantly jumped to 7.08, 7.44 and 7.82. **So sharp equivalence point for the titration was observed at 12.0 mL.**

Theoretical Calculations:

Solution B contains 7.5 mg of $CaCO_3$ (Theoretical Amount)

Solution B contains 11.0 mg of $SrCl_2$ (Theoretical Amount)

1.0 mL 0.01M Na_3HEDTA ≡ 1.0 mg $CaCO_3$ ≡ 2.66 mg $SrCl_2.6H_2O$

Expected equivalence point is (7.5 + 4.1) mL = 11.6 mL Na_3HEDTA (Theoretical)

Solution A contains (18.5 x 5) = 92.5 mg of Total (Ca^{+2} + Sr^{+2}) content (Theoretical Amount)

Experimental Calculations:

1000.0 mL 1M Na_3HEDTA ≡ 100.0 g $CaCO_3$ ≡ 40.0 g Ca^{+2}

1000.0 mL 1M Na_3HEDTA ≡ 266.62 g $SrCl_2.6H_2O$ ≡ 87.62 g Sr^{+2}

1000.0 mL 0.01M Na_3HEDTA ≡ 1.0 g $CaCO_3$ ≡ 2.66 g $SrCl_2.6H_2O$

1.0 mL 0.01M Na_3HEDTA ≡ 1.0 mg $CaCO_3$ ≡ 2.66 mg $SrCl_2.6H_2O$

Experimental equivalence point: 12.0 mL, which was utilized to form complexes with 7.5 mg $CaCO_3$ and 11.0 mg of $SrCl_2.6H_2O$

Percentage Deviation: (11.6-12.0)/11.6 X 100 = 3.44%

Simulated Titration Curve

To derive simulated titration curve, we need K_f (formation constant for Ca-EDTA complex) and α_3 (fraction of EDTA exist in Na_3HEDTA form) values. K_f value for Ca-EDTA complex is 5×10^{10}. To derive α_3 value of Na_3HEDTA, we need to use following formula.[2]

$$\alpha_3 = \frac{Ka_1 . Ka_2 . Ka_3}{[H^+]^3 + Ka_1 . [H^+]^2 + Ka_1 . Ka_2 . [H+] + Ka_1 . Ka_2 . Ka_3}$$

Ka_1 for EDTA = 1.0×10^{-2}

Ka_2 for EDTA = 2.2×10^{-3}

Ka_3 for EDTA = 6.9×10^{-7}

pH-metric titration performed in experiment 02 is considered for this calculations.

Sr. No.	Volume of 0.01M Na_3HEDTA (in mL)	pH	$[H^+]$
1	0.0	7.06	8.7×10^{-8}

2	0.5	6.99	1.02 x 10 -7
3	1.0	6.94	1.14 x 10^{-7}
4	1.5	6.86	1.38 x 10^{-7}
5	2.0	6.79	1.62 x 10^{-7}
6	2.5	6.73	1.86 x 10^{-7}
7	3.0	6.68	2.09 x 10^{-7}
8	3.5	6.62	2.39 x 10^{-7}
9	4.0	6.56	2.75 x 10^{-7}
10	4.5	6.50	3.16 x 10^{-7}
11	5.0	6.44	3.63 x 10^{-7}
12	5.5	6.39	4.07 x 10^{-7}
13	6.0	6.34	4.57 x 10^{-7}
14	6.5	6.31	4.89 x 10^{-7}
15	7.0	6.28	5.24 x 10^{-7}
16	7.5	6.24	5.75 x 10^{-7}
17	8.0	7.15	7.07 x 10^{-8}
18	8.5	7.79	1.62 x 10^{-8}
19	9.0	8.39	4.07 x 10^{-9}
20	9.5	9.39	4.07 x 10^{-10}
21	10.0	9.70	1.99 x 10^{-10}

By using above data for [H^+] and Ka_1, Ka_2, Ka_3, α_3 value of Na_3HEDTA is calculated.

Note: Value of $\boldsymbol{\alpha_3}$ (fraction of free HEDTA^{3-} ions) value will be zero at the beginning of titration.

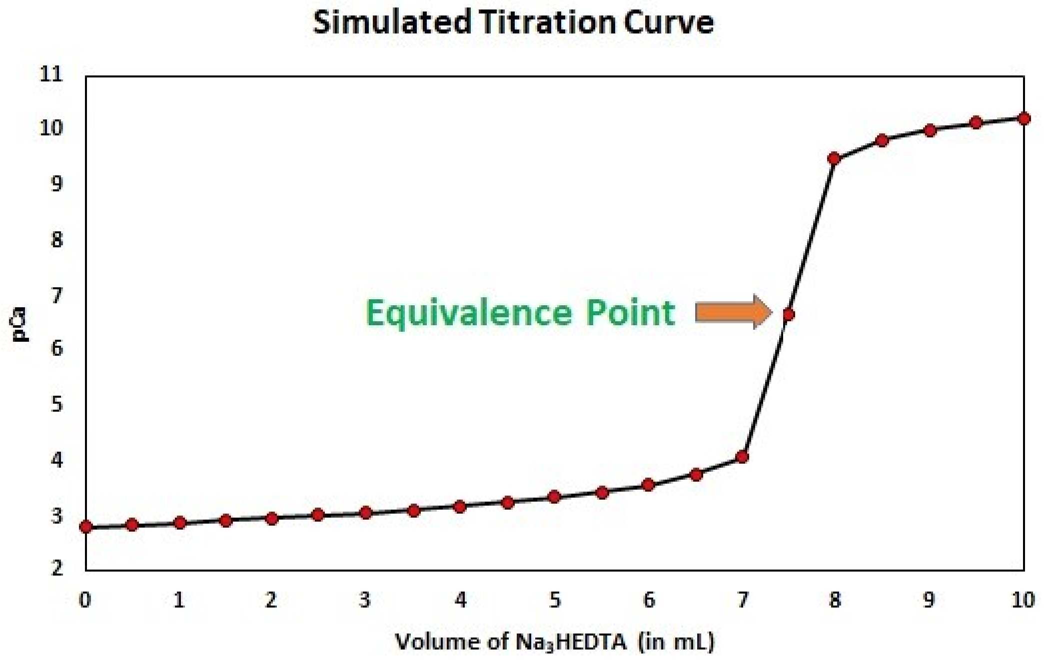
Volume of Na_3HEDTA (in mL)	**$[H^+]$**	**$[H^+]^3$**	**$Ka_1.[H^+]^2$**	**$Ka_1.Ka_2.[H^+]$**	**$Ka_1.Ka_2.Ka_3$**	**α_3**
0.0	8.7×10^{-8}	6.58503E-22	7.569E-17	1.914E-12	1.518E-11	0.888026956
0.5	1.02 x 10 -7	1.06121E-21	1.0404E-16	2.244E-12	1.518E-11	0.871206919
1.0	1.14×10^{-7}	1.48154E-21	1.2996E-16	2.508E-12	1.518E-11	0.85820265
1.5	1.38×10^{-7}	2.62807E-21	1.9044E-16	3.036E-12	1.518E-11	0.833324621
2.0	1.62×10^{-7}	4.25153E-21	2.6244E-16	3.564E-12	1.518E-11	0.809847816
2.5	1.86×10^{-7}	6.43486E-21	3.4596E-16	4.092E-12	1.518E-11	0.787657093
3.0	2.09×10^{-7}	9.12933E-21	4.3681E-16	4.598E-12	1.518E-11	0.767502515
3.5	2.39×10^{-7}	1.36519E-20	5.7121E-16	5.258E-12	1.518E-11	0.742713365
4.0	2.75×10^{-7}	2.07969E-20	7.5625E-16	6.05E-12	1.518E-11	0.715000436
4.5	3.16×10^{-7}	3.15545E-20	9.9856E-16	6.952E-12	1.518E-11	0.685853746
5.0	3.63×10^{-7}	4.78321E-20	1.31769E-15	7.986E-12	1.518E-11	0.655233384
5.5	4.07×10^{-7}	6.74191E-20	1.65649E-15	8.954E-12	1.518E-11	0.628944979
6.0	4.57×10^{-7}	9.5444E-20	2.08849E-15	1.0054E-11	1.518E-11	0.601519524
6.5	4.89×10^{-7}	1.1693E-19	2.39121E-15	1.0758E-11	1.518E-11	0.58518778
7.0	5.24×10^{-7}	1.43878E-19	2.74576E-15	1.1528E-11	1.518E-11	0.568310599
7.5	5.75×10^{-7}	1.90109E-19	3.30625E-15	1.265E-11	1.518E-11	0.545389749
8.0	7.07×10^{-8}	3.53393E-22	4.99849E-17	1.5554E-12	1.518E-11	0.907056578
8.5	1.62×10^{-8}	4.25153E-24	2.6244E-18	3.564E-13	1.518E-11	0.977060158
9.0	4.07×10^{-9}	6.74191E-26	1.65649E-19	8.954E-14	1.518E-11	0.994136027
9.5	4.07×10^{-10}	6.74191E-29	1.65649E-21	8.954E-15	1.518E-11	0.999410493
10.0	1.99×10^{-10}	7.8806E-30	3.9601E-22	4.378E-15	1.518E-11	0.999711677

Now, we have to find out [Ca^{+2}] ions considering three situations i.e. 1) Before equivalence point, 2) At equivalence point, 3) After equivalence point (For all detailed calculations, please follow reference 1

Initially, we have taken 50.0 mL 0.0015M $CaCO_3$. It contains total 0.075 mmoles of $CaCO_3$. To this, 0.5 mL 0.01M Na_3HEDTA was added. It contains 0.005 mmoles of Na_3HEDTA. It will react with 0.005 mmoles of $CaCO_3$ and will form complex.

Sr. No.	**Volume of Na_3HEDTA Added (in mL)**	**Total Volume (in mL)**	**[Ca^{+2}] (M)**	**pCa**
1	0.0	50.0	0.00150	2.823908741
2	0.5	50.5	0.00138	2.860120914
3	0.5	51.0	0.001269	2.896196279
4	0.5	51.5	0.001159	2.935542011
5	0.5	52.0	0.001051	2.978810701
6	0.5	52.5	0.000946	3.024108864
7	0.5	53.0	0.000843	3.074172425
8	0.5	53.5	0.000741	3.130181792
9	0.5	54.0	0.0006424	3.192464972
10	0.5	54.5	0.0005447	3.2644011
11	0.5	55.0	0.0004489	3.348721986
12	0.5	55.5	0.0003547	3.450996738

13	0.5	56.0	0.0002623	3.581698709
14	0.5	56.5	0.0001715	3.76700389
15	0.5	57.0	0.00008228	4.084705717
16	0.5	57.5	2.18 x 10^{-7}	6.661543506
17	0.5	58.0	3.31 x 10^{-10}	9.480172006
18	0.5	58.5	1.541 x 10^{-10}	9.812479279
19	0.5	59.0	1.008 x 10^{-10}	9.996539468
20	0.5	59.5	7.505 x 10^{-11}	10.12465509
21	0.5	60.0	6.003 x 10^{-11}	10.22163889



Uncertainty Calculation for pH-Metric Analysis

Sr. No.	Name of Equipment/Glassware	Uncertainty Involved	No. of Times Equipment/Glassware Used in Experiment
01	Digital balance	0.00005 g	Three
02	Burette (25.0 mL)	0.05 mL	One
03	Pipette (25.0 mL)	0.03 mL	Three
04	Measuring Cyllinder (250.0 mL)	1.0 mL	One
05	SMF (250.0 mL)	0.1 mL	Two

Uncertainty involved with pH measurement: 0.01

Uncertainty Calculation for Entries in the Table 1 of Manuscript

Entry No.	Uncertainty arise from digital balance	Uncertainty arise from burette	Uncertainty arise from pipette	Uncertainty arise from measuring cylinder	Uncertainty arise from SMF	Total % Uncertainty
1	0.16 %	1.33 %	0.36 %	0.40 %	0.08 %	2.33 %
2	0.10 %	0.66 %	0.36 %	0.40 %	0.08 %	1.60 %
3	0.07 %	0.44 %	0.36 %	0.40 %	0.08 %	1.35 %

Uncertainty Calculation for Entries in the Table 2 of Manuscript

Entry No.	Uncertainty arise from digital balance	Uncertainty arise from burette	Uncertainty arise from pipette	Uncertainty arise from measuring cylinder	Uncertainty arise from SMF	Total % Uncertainty
1	0.14 %	1.11 %	0.36 %	0.40 %	0.08 %	2.09 %
2	0.13 %	1.00 %	0.36 %	0.40 %	0.08 %	1.97 %
3	0.15 %	1.17 %	0.36 %	0.40 %	0.08 %	2.16 %
4	0.13 %	1.00 %	0.36 %	0.40 %	0.08 %	1.97 %

Uncertainty Calculation for Entries in the Table 3 of Manuscript

Entry No.	Uncertainty arise from digital balance	Uncertainty arise from burette	Uncertainty arise from pipette	Uncertainty arise from measuring cylinder	Uncertainty arise from SMF	Total % Uncertainty
1	0.13 %	0.93 %	0.36 %	0.40 %	0.08 %	1.90 %
2	0.15 %	1.08 %	0.36 %	0.40 %	0.08 %	2.07 %
3	0.13 %	0.95 %	0.36 %	0.40 %	0.08 %	1.92 %
4	0.15 %	1.12 %	0.36 %	0.40 %	0.08 %	2.11 %

References:

1) G. H. Jeffery, J. Bassett, J. Mendham, R.C. Denney, *Vogel's Textbook of Quantitative Chemical Analysis (Fifth Edition)*, Longan Scientific and Technical Publisher, New York, **1989**, Page No. 551-553
2) G. D. Christian, P. K. Dasgupta, K. A. Schug, *Analytical Chemistry (Seventh Edition)*, John Wiley & Sons, River Street, Hoboken, **2014**, Page No. 326-333