

TITRIMETRY

Titration Setup

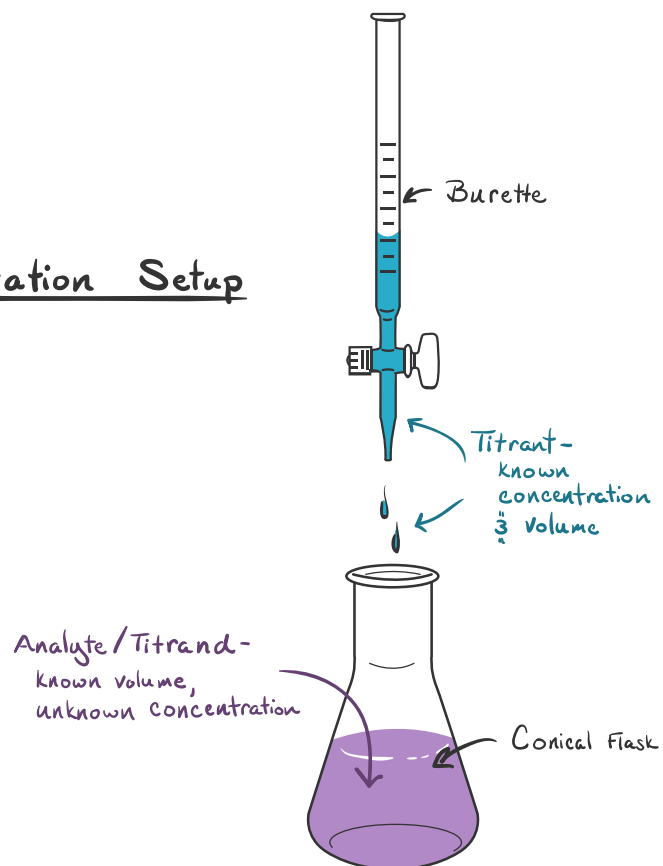


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PROCEDURES

Chloride determination

Aim: Chloride determination with Mohr's method

Method group: Precipitation titration

Reagents:

- **analyte:** Cl^-
- **titrant:** AgNO_3
- **indicator:** K_2CrO_4

Conditions: pH 6.5-10

Chemical Reactions:

- **titrant:** $\text{Ag}^+ + \text{Cl}^- \rightarrow \text{AgCl}$
- **indicator:** $2\text{Ag}^+ + \text{CrO}_4^{2-} \rightarrow \text{Ag}_2\text{CrO}_4$

Instructions:

1. Transfer quantitatively the content of the ampoule to a 100 mL volumetric flask.
Warning! Use a towel to break the ampoule and be careful when handling broken glass to avoid cutting your hand.
3. Bring to mark with deionized water.
4. Take out 4 aliquots of 10.00 ml with a transfer pipette and transfer them in four 250 ml Erlenmeyer flasks.
5. Dilute the solutions by adding 40 ml deionized water in each flask.
You can measure the first 40 ml with a graduated cylinder, and fill the next three flasks to the same level approximately.
7. Add 1 ml of 5% K_2CrO_4 indicator using a plastic syringe to each flask.
8. Start the titration with AgNO_3 titrant.
When approaching the endpoint, stop shaking the flask from time to time to allow the precipitate to settle down. This helps to catch the exact endpoint.
10. Stop the titration when the first trace of red-brown color is observed.
Use 1:1 ammonia to clean the precipitate from the flask.
12. Repeat the titration to obtain 4 results.
13. Calculate the quantity of Cl^- in the unknown sample (mg/ampoule).

Bromide determination

Aim: Bromide determination with Volhard's method

Method group: Precipitation titration

Reagents:

- **analyte:** Br^-
- **titrant:** NH_4SCN and AgNO_3
- **indicator:** $\text{Fe}(\text{NO}_3)_3$

Conditions: pH < 6.5

Chemical Reactions:

- **auxiliary_titrant:** $\text{Ag}^+ + \text{Br}^- \rightarrow \text{AgBr}$
- **titrant:** $\text{Ag}^+ + \text{SCN}^- \rightarrow \text{AgSCN}$
- **indicator:** $\text{Fe}^{3+} + \text{SCN}^- \rightarrow [\text{FeSCN}]^{2+}$

Instructions:

1. Transfer quantitatively the content of the ampoule to a 100 mL volumetric flask.
Warning! Use a towel to break the ampoule and be careful when handling broken glass to avoid cutting your hand.
3. Bring to mark with deionized water.
4. Take out 4 aliquots of 10.00 ml with a transfer pipette and transfer them in four 250 ml Erlenmeyer flasks.
5. Add 20.00 ml of 0.1 M AgNO_3 auxiliary titrant to the samples. Yellowish AgBr precipitate appears.
6. Add 5 ml 10% nitric acid to adjust the acidity of the solution.
7. Add 1 ml Fe(III) indicator using a plastic syringe to each flask.
8. Start the titration with NH_4SCN titrant.
Vigorously shake the sample near the equivalence point to desorb the silver ions from the surface of the precipitate.
10. Stop the titration when the solution above the precipitate becomes reddish brown.
11. Repeat the titration to obtain 4 results.
12. Calculate the quantity of Br^- in the unknown sample (mg/ampoule).

Lead determination

Aim: Lead determination

Method group: Complexometric titration

Reagents:

- **analyte:** Pb^{2+}
- **titrant:** EDTA
- **indicator:** xylenol orange

Conditions: slightly acidic pH (pH < 6)

Chemical Reactions:

- **titrant:** $\text{Pb}^{2+} + \text{Y}^{4-} \rightarrow \text{PbY}^{2-}$
- **indicator:** $\text{PbInd} + \text{Y}^{4-} \rightarrow \text{PbY}^{2-} + \text{Ind}$

Instructions:

1. Transfer quantitatively the content of the ampoule to a 100 mL volumetric flask.
Warning! Use a towel to break the ampoule and be careful when handling broken glass to avoid cutting your hand.
3. Bring to mark with deionized water.
4. Take out 4 aliquots of 10.00 ml with a transfer pipette and transfer them in four 250 ml Erlenmeyer flasks.
5. Add 1 ml of 2 M nitric acid using a plastic syringe to each flask.
6. Dilute the solutions by adding 40 ml deionized water in each flask.
7. Add 2-3 drops of the xylenol orange indicator (0.1 wt% aq. solution).
The yellow color is the free indicator in strong acidic medium.
9. Adjust the pH by adding small aliquots of hexamethylenetetramine powder until the color of the solution becomes violet.
We adjust the pH toward neutral with hexamethylenetetramine until a pH is reached where the indicator can form a stable complex (violet) with the lead ions. In even more basic medium the free indicator would also be violet in color.
11. Start the titration with 0.05 M EDTA titrant.
12. Stop the titration when the color of the solution becomes constant yellow.
If the yellow color does not stabilize within 2-3 drops around the equivalence point, add more hexamethylenetetramine and continue the titration until a stable yellow color is reached.
14. Repeat the titration to obtain 4 results.
15. Calculate the quantity of Pb^{2+} in the unknown sample (mg/ampoule).

Carbonate and bicarbonate determination

Aim: Side-by-side determination of carbonate and bicarbonate with Warder's method

Method group: Acid-base titration

Reagents:

- **analyte:** HCO_3^- and CO_3^{2-}
- **titrant:** HCl
- **indicator:** phenolphthalein and methyl red

Conditions: boiled and cooled down DI water, boil sample before endpoint

Chemical Reactions:

- **titrant:** $\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^-$
- **titrant:** $\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{CO}_3 \rightarrow \text{H}_2\text{O} + \text{CO}_2 \#$

Instructions:

1. Transfer quantitatively the content of the ampoule to a 100 mL volumetric flask.
Warning! Use a towel to break the ampoule and be careful when handling broken glass to avoid cutting your hand.
3. Bring to mark with previously boiled and cooled down deionized water.
4. Take out 1 aliquot of 10.00 ml with a transfer pipette and transfer it in a 250 ml round-bottomed flask.
Do not take out all four aliquots at once, because carbon-dioxide can dissolve into the solutions while standing.
6. Add ~4 g of solid NaCl and stir.
7. Dilute the solution by adding 10 ml boiled and cooled down deionized water.
8. Add 5-6 drops of phenolphthalein indicator.
9. Start the titration with 0.1 M HCl titrant.
10. Stop the titration when when you reach a faint pink solution. Make note of the consumption, from which you will calculate the amount of carbonate ions.
Prepare and display a solution for color matching by dissolving ~0.1 g NaHCO_3 and ~4 g NaCl in 20 ml deionized water containing 5-6 drops of phenolphthalein.
12. Refill the burette with 0.1 M HCl and continue titrating the sample until the pink color completely disappears.
This is not an endpoint, we add the second indicator with some delay to avoid confusion by mixing the different colors.
14. Add 2-3 drops of methyl red indicator and continue the titration until it is faint red.
15. Heat the solution with constant stirring until it becomes yellow again to drive out the carbon-dioxide.
16. Cool down the solution under running water. Be careful not to let the tap water enter the flask.
17. Continue the titration until an onion color is reached. If the color change is obtained within 2-3 drops of titrant, make note of the consumption, from which you will calculate the combined amount of carbonate and bicarbonate ions. If the color change takes more than 2-3 drops of titrant, then continue until red, and repeat from the heating step, until you obtain the red color within 2-3 drops.
18. Repeat the entire titration 3 more times to obtain 4 results.

19. Calculate the quantity of CO_3^{2-} and HCO_3^- in the unknown sample (mg/ampoule).

Copper determination

Aim: Copper(II) determination by iodometry

Method group: Redox titration

Reagents:

- **analyte:** Cu^{2+}
- **titrant:** $\text{Na}_2\text{S}_2\text{O}_3$
- **indicator:** starch

Conditions: slightly acidic pH (AcH)

Chemical Reactions:

- **titrant:** $\text{Cu}^{2+} + 4\text{I}^- \rightarrow 2\text{CuI} + \text{I}_2$
- **titrant:** $\text{I}_2 + 2\text{S}_2\text{O}_3^{2-} \rightarrow 2\text{I}^- + \text{S}_4\text{O}_6^{2-}$

Instructions:

1. Transfer quantitatively the content of the ampoule to a 100 mL volumetric flask.
Warning! Use a towel to break the ampoule and be careful when handling broken glass to avoid cutting your hand.
3. Bring to mark with deionized water.
4. Take out 4 aliquots of 10.00 ml with a transfer pipette and transfer them in a 250 ml Erlenmeyer flask with a stopper.
5. Add 5 ml of 5% acetic acid to the samples.
6. Dilute the solutions to ~50 ml by adding deionized water.
7. One by one, add ~1 g of solid KI to the flasks and quickly close them.
8. After waiting 5 min, wash the iodine on the stopper and the flask neck with a small amount of DI water.
9. Start the titration with 0.1 M thiosulphate titrant.
10. When the solution becomes faint yellow, add 1 ml starch indicator and continue the titration until the color disappears.
Vigorously shake the sample near the endpoint to desorb the iodine from the surface of the precipitate.
12. Repeat the titration to obtain 4 results.
13. Calculate the quantity of copper in the unknown sample (mg/ampoule).

SUMMARY

Analyte	Method	Titrant	Indicator	Conditions	Reactions
Cl ⁻	Precipitation titration	AgNO ₃	K ₂ CrO ₄	pH 6.5-10	$Ag^+ + Cl^- \rightarrow AgCl$ $2Ag^+ + CrO_4^{2-} \rightarrow Ag_2CrO_4$
Br ⁻	Precipitation titration	NH ₄ SCN and AgNO ₃	Fe(NO ₃) ₃	pH < 6.5	$Ag^+ + Br^- \rightarrow AgBr$ $Ag^+ + SCN^- \rightarrow AgSCN$ $Fe^{3+} + SCN^- \rightarrow [FeSCN]^{2+}$
Pb ²⁺	Complexometric titration	EDTA	xylene orange	slightly acidic pH (pH < 6)	$Pb^{2+} + Y^{4-} \rightarrow PbY^{2-}$ $PbInd + Y^{4-} \rightarrow PbY^{2-} + Ind$
HCO ₃ ⁻ and CO ₃ ²⁻	Acid-base titration	HCl	phenolphthalein and methyl red	boiled and cooled down DI water, boil sample before endpoint	$CO_3^{2-} + H^+ \rightarrow HCO_3^-$ $HCO_3^- + H^+ \rightarrow H_2CO_3 \rightarrow H_2O + CO_2 \#$
Cu ²⁺	Redox titration	Na ₂ S ₂ O ₃	starch	slightly acidic pH (ACh)	$Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$ $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$

TEST QUESTIONS

Precipitation titration

1. What methods of indication can you use in precipitation titrations?
Mohr's method: chromate indicator forms red-brown precipitate with the excess of Ag^+ titrant. Volhard's method: Fe^{3+} indicator forms red-brown complex with the excess of thiocyanate auxiliary titrant.
2. What is argentometry?
Argentometry is the most important group of precipitation titrations, which are based on reactions of silver ions with halogenide or pseudohalogenide ions.
3. Why is neutral pH needed to execute Mohr's method?
At $\text{pH} < 6.5$, silver chromate dissolves as dichromate. At $\text{pH} > 10$, the titrant precipitates as silver oxide hydrate.
4. Why is a strong acid added to the sample in Volhard's method?
Acidic medium is required, since the Fe(III) indicator hydrolyzes in basic medium.

Complexometric titration

5. Why do we need to adjust the pH in chelatometric titrations?
The EDTA ligand is (partially) protonated at low pH values, but it only forms a stable complex with metal ions in its fully deprotonated form.

Acid-base titration

6. What is the transition range of an acid-base indicator?
The pH interval where color change is visible to the naked eye. The width of the transition range is usually about 2 pH units.
7. What is the transition point of an acid-base indicator?
The pH where the protonated and deprotonated forms are present in equal concentration. In this point, the transition color is observed.
8. Can we use acetic acid as titrant?
It can be used if the analyte is a strong base, but not if it is a weak base. Weak acid-weak base titrations are uncommon as they have a very small pH change at the equivalence point, which is difficult to detect.

Redox titration

9. What indication method do you use in iodometry?

Starch forms a dark blue clathrate with iodine. It should only be added to the sample near the endpoint, to prevent irreversible chemical bonding between the starch and the iodine.