EXPERIMENT 8

COLUMN CHROMATOGRAPHIC SEPARATION AND ESTIMATION OF INORGANIC SUBSTANCES:

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8.1 INTRODUCTION

In the last experiment you have leart how to separate pigment by column chromatography. In this experiment we will use column Chromatography for the separation of inorganic substance.

Column chromatography with an adsorbent in the column can be used to separate inorganic ions analogous to separate organic compounds. An aqueous solution of salts is introduced to a column of an adsorbent and the column is eluted with water, or dilute acid, or any other suitable eluent. The separated substances (ions) can be eluted out of the column and determined by suitable methods.

In this experiment you have to separate a given mixture containing potassium permanganate and potassium dichromate on a column of alumina. The two components are eluted out of the column and their amounts are then determined titrimetrically.

Objective

After studying and performing this experiment you should be able to:

- prepare a column,
- separate $KMnO_4$ and $K_2Cr_2O_7$ by column chromatography,
- determine the strength of $KMnO_4$,
- determine the amount of $K_2Cr_2O_7$ in the sample.

8.2 REQUIREMENTS

Apparatus		Chemicals
Chromatography column	1	Alumina
Cotton wool/glass wool	1	0.5 *M* HNO_3
Beaker	2	1*M* H_2SO_4
Conical flask	1	0.05 *M* $KMnO_4$

Burette (50 cm^3)	1	0.05 M $K_2Cr_2O_7$
Pipette (10 cm^3)	1	0.05 M Ferrous ammonium sulphate

Solutions provided

1. 0.5 M Nitric acid solution; Prepare 0.5M HNO_3 solution O_3 solution from a stock HNO_3 solution of known specific gravity and percentage.
2. 1M sulphuric acid solution: Prepare 1M solution from a stock H_2SO_4 solution of known specific gravity and percentage.

   Remember:- never add water to the acid; always acid is added to water for dilution.
3. Prepare by weighing 0.05 M $KMnO_4$ and 0.05M $K_2Cr_2O_7$ solution in water.
4. Prepare 0.05 M ferrous ammonium sulphate solution by weighing the required amount and transferring to the standard flask containing some dil H_2SO_4 solution to check the hydrolysis, make it to the mark water.

8.5 PROCEDURE

1. **Preparation of column:** Take a glass column or a burette of about 20 cm long and 1-2 cm in diameter. Place some cotton wool into the bottom of the column. Pour nearly 10 cm^3 of hot water and remove air from the wool. Allow to flow some water, opening pinch clamp. Take about 20 g of alumina in a beaker containing 100 cm^3 of water. Heat the beaker to boiling of water to remove the dissolved air. Now transfer a small quantity of alumina slurry to the glass column with the help of a funnel and a glass rod. Tap the column with a glass rod covered with 5 cm rubber tubing. The process of pouring slurry and tapping is continued till a column of about 15 cm deep is formed. Drain off the excess water leaving a water layer of about 5 mm thick above the alumina surface. Wash the column with 10 cm^3 of 0.5 M HNO_3 solution. Now cut out a small disc of filter paper (diameter equal to that of glass column) and place it into the column at the top surface of alumina to ensure that the column packing is not disturbed when more liquid is added to the column. The column can now be used for separation. The column is treated with HNO_3 before the chromatography of anions.

   Remove the alumina of the column immediately after chromatography.
2. Take alumina column and clamp it vertically.
3. Pipette accurately 5 cm^3 of the mixture, drip into the column in the form of thin layer of solution at alumina surface, keeping the stopcock closed.
4. Allow to run the mixture evenly into the adsorbent until the liquid level is just above the top of alumina.
5. Add 1 cm^3 of 0.5 M HNO_3 and again run the column until the liquid meniscus is just above the top of the column.
6. Develop the column first with 0.5 M HNO_3 to elute $KMnO_4$. Collect the fraction of effluent, which is pink, in a conical flask marked as number 1.
7. Next develop the column with 1M H_2SO_4 to elute $K_2Cr_2O_7$. Collect the fraction of effluent containing dichromate (light yellow) in a second conical flask (No. 2).
8. Fill in a burette the supplied $KMnO_4$ solution and find its concentration by titrating with the standard (0.05 M) ferrous ammonium sulphate solution.
9. Add 10 cm^3 of 0.05 M ferrous ammonium sulphate solution to each of the conical flasks 1 and 2. Titrate both solutions separately with standardized $KMnO_4$ and note the readings.

8.6 OBSERVATIONS

The two components are separated in the form of different coloured zones and are collected in different fractions.

For estimation the results are tabulated in the following manner.

Observation Table-I
Standard Ferrous Ammonium Sulphate Vs Potassium Permanganate

Sl. No.	Volume of ferrous ammonium sulphate in cm^3	Burette Reading		Volume of $KMnO_4$ in cm^3 V_2 (Final–Initial)
		Initial	Final	
1.				
2.				
3.				

Observation Table-II
Effluent Fractions Vs Potassium Permanganate

Flask No.	Volume of FeSo$_4$ $(NH_4)_2SO_4$ added in cm^3 to the flask V_3	Burette Reading		Volume of $KMnO_4$ in cm^3
		Initial	Final	
1..				V_4
2.				V_5

8.6 CALCULATIONS

(a) **Determination of the strength of $KMnO_4$ solution**

Molarity of ferrous ammonium sulphate = M_1 ......

Volume of ferrous ammonium sulphate = V_1 ......

Volume of $KMnO_4$ used = V_2 = ...

Molarity of $KMnO_4$ = M_2 = ?

The redox equation is:

$$5Fe^{2+} + MnO_4^- + 8H^+ \longrightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

$$M_1 V_1 = 5 M_2 V_2$$

$$\frac{M_1V_1}{M_2V_2} = \frac{5}{1}$$

$$M_2 = \frac{M_1 V_1}{5 V_2} = ...M$$

(b) **Determination of the amount of $KMnO_4$ in the sample**

No. of millimoles = Molarity × volume in cm^3.

Millimoles of ferrous ammonium sulphate added = 5 × millimoles of $KMnO_4$ in effluent + 5 × millimoles of $KMnO_4$ used in titration

M_1V_3 = 5 (millimoles of $KMnO_4$ in effluent + $M_2 V_4$)

millimoles of $KMnO_4$ in effluent $= \frac{M_1 V_3}{5} - M_2 V_2$

$= x$

Amount of $KMnO_4$ in sample $= x \times 158$ mg

$= .....$ mg

(c) Determination of the amount of $K_2Cr_2O_7$ in the sample

The redox reaction of ferrous ammonium sulphate and $K_2Cr_2O_7$ is:

$$6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \longrightarrow 2Cr^{3+} + 7H_2O$$

Millimoles of ferrous ammounium sulphate added + 6 × millimoles of $K_2Cr_2O_7$ in effluent + 5 Millimoles of $KMnO_4$ used in titration

$M_1V_3 = 6 \times$ millimoles of $K_2Cr_2O_7$ in effluent $+ 5\ M_2\ V_5$

millimoles of $K_2Cr_2O_7$ in effluent $= M_1V_3 - 5M_2\frac{V_5}{6}$

$= y$

Amount of $K_2Cr_2O_7$ in sample $= y \times 294$ mg.

$=$ .... mg.

8.7 Result and Discussion

Amount of $KMnO_4$ in the sample = ... mg

Amount of $K_2Cr_2O_7$ in the sample = ... mg

In column chromatography of inorganic substances, most commonly used adsorbent is alumina. It is used in neutral, acidic and basic forms. On technical alumina the cations show greater adsorptivity, whereas the anions have lower adsorptivity and travel faster and moved out of the column shortly. The trivalent cations, usually have higher adsorptivity than the divalent and monovalent cations.

If the alumina is treated with HCl or HNO_3 prior to the separation process the anions show greater adsorptivity than the cations. On acidified alumina the anions have been found to be retained in the following order:

$$PO_4^{3-} > Fe(CN)_6^{4-} > Cr_2O_7^{2-} > Cl^- > NO_3^- > MnO_4^- > S^{2-}$$

Though the mechanism of separation on alumina is not completely understood, it may be as follows:

For cations it may be regarded in terms of surface buffering and the interaction of alumina, cations and water. The hydrated cations are attracted to the negative oxygen ends of alumina molecules. Further, the adsorptivity of different cations depends on the size, valency and dipole moment of the aquo cations.

When the acid treated alumina is taken, the exchange of anions with chloride, nitrate or sulphate is responsible for the separation of anions.

For quantitative estimation of the eluted oxidants ($KMnO_4/K_2Cr_2O_7$) with an excess of a standard reducing agent (e.g. $FeSO_4(NH_4)_2SO_46H_2O$) solution. The unreacted reducing agent is then titrated with a standardized oxidizing agent.