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SEMESTR-VI

CHEMISTRY (Core – XIII)

INORGANIC CHEMISTRY – IV

THEORETICAL PRINCIPLES IN QUANTITATIVE ANALYSIS (H₂S Scheme)

Test for Fluoride, Borate, Oxalate and Phosphate-

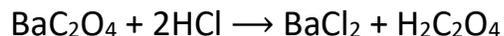
These are known as Interfering radicals

What are the interfering radicals? How do they interfere in systematic separation of cationic radicals? Why is it necessary to remove them before 3rd analysis? Why don't they interfere in 1st or 2nd group analysis? Interfering radicals are oxalate, tartrate, fluoride, borate and phosphate and they are anionic radicals. They form complex with 3rd group reagent ammonium chloride and ammonium hydroxide. This leads to incomplete precipitation of 3rd group cations and causes immature precipitation of 4th and 5th group cations in alkaline medium.

Oxalate, tartrate, fluoride, borate, silicate and phosphate of the metals are soluble in acidic medium.

For 1st and 2nd group analysis medium remain acidic (dilute HCl) that's why they do not interfere then. But for 3rd group analysis the medium becomes alkaline by group reagents ammonium chloride and ammonium sulphide. Here interfering radicals come into action and disturb the solubility product of cations which causes their premature or incomplete precipitation.

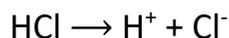
In acidic medium these salts produce their corresponding acids like oxalic acid, phosphoric acid, hydrofluoric acid, boric acid and tartaric acid. For example, barium oxalate reacts with HCl and produces oxalic acid.



These interfering acids are weak acids so they do not dissociate completely and remain in solution in their unionised form. Equilibrium is developed between dissociated and un-dissociated acid.



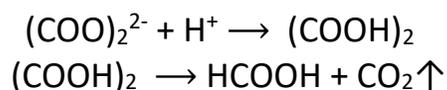
Hydrochloric acid is a strong acid and is ionised completely.



Hydrogen ions acts as common ion among them and higher concentration of H^+ suppresses the ionization of interfering acid. Therefore, ionic product of $\text{C}_2\text{O}_4^{2-}$ and Ba^{2+} doesn't exceed the solubility product of barium oxalate which is why Ba^{2+} remains in the solution as barium oxalate. That's how interfering radicals do not interfere as long as the medium remains acidic enough. But when we make the medium alkaline by adding 3rd group reagent ammonium hydroxide NH_4OH , OH^- ions combine with H^+ and neutralise them. This decreases the concentration of H^+ ions which Shift the equilibrium of dissociation of interfering acid forward and increases the concentration of $\text{C}_2\text{O}_4^{2-}$. Thus the ionic product of $\text{C}_2\text{O}_4^{2-}$ and Ba^{2+} exceeds the solubility product of barium oxalate and Ba^{2+} gets precipitated in the 3rd group, which actually belongs to the 4th group.

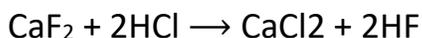
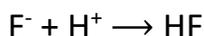
To test the presence of interfering radicals we need to prepare sodium carbonate extract and then test them separately.

Procedure for the removal of oxalate: Oxalate of metals are soluble in acid and they decompose on heating. We have take the filtrate of 2nd group and boil off H_2S gas from it. Then added 4-5ml concentrated nitric acid HNO_3 and heat it till it is almost dry. Repeat this treatment for 2-3 times.

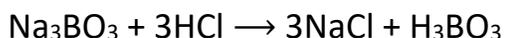
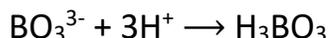




Procedure for the removal of borate and fluoride: We have take the filtrate and evaporate it to dryness. Add concentrated HCl and again evaporate to dryness.

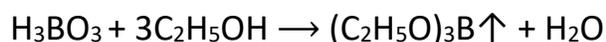
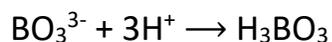


On heating with HCl fluoride forms hydrofluoric acid and Borate forms orthoboric acid which evaporate on heating.

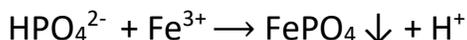


Extract the residue with dilute HCl and filter. Use this filtrate for analysis of 3rd group or use for removal of other interfering radicals.

If fluoride is absent and borate is present then residue use a mixture of 5ml ethyl alcohol and 10ml conc. HCl and evaporate to dryness.

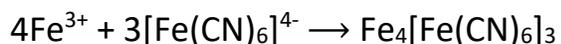


Procedure for the removal of phosphate: Ferric chloride is generally used for the removal of phosphate. Fe(III) combines with phosphate and removes all phosphate as insoluble FePO₄. Fe(III) is also a member of 3rd group so first we have to test its presence in the filtrate of 2nd group then we can proceed for the removal of phosphate.



Test for Fe: To the filtrate of 2nd group add ammonium chloride NH₄Cl and a slight excess of ammonia NH₃ solution. If precipitate appears, it indicates the presence of 3rd group. It may contain hydroxides Fe(OH)₃, Cr(OH)₃, Al(OH)₃, MnO₂.xH₂O,

traces of CaF_2 and phosphates of Mg and IIIA, IIIB and IV group metals. Dissolve the precipitate in minimum volume of 2M HCl. Take 0.5ml solution and add potassium hexacyanoferrate (II) $\text{K}_4[\text{Fe}(\text{CN})_6]$ solution. If iron is present, you will get prussian blue coloured precipitate of iron(III) hexacyanoferrate.



Removal of phosphate: To the main solution add 2M ammonia NH_3 solution drop wise, with stirring, until a faint permanent precipitate is just obtained. Then add 2-3ml 9M acetic acid and 5ml 6M ammonium acetate solution. Discard any precipitate if obtained at this stage. If the solution is red or brownish red, sufficient iron Fe(III) is present here to

combine with phosphate. If the solution is not red or brownish red in colour then add ferric chloride FeCl_3 solution drop wise with stirring, until the solution gets a deep brownish red coloured. Dilute the solution to about 150ml with hot water, boil gently for 1-2min, filter hot and wash the residue with a little boiling water. Residue may contain phosphate of Fe, Al and Cr. Keep the filtrate for test of IIIB group. Rinse the residue in porcelain dish with 10ml cold water, add 1-1.5g sodium peroxoborate and boil gently until the evolution of O_2 ceases (2-3min). Filter and wash with hot water. Reject the residue to remove phosphate in the form of FePO_4 . Keep the filtrate and test for IIIA group.