SWAMI DAYANANDA COLLEGE OF ARTS & SCIENCE

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DEPARTMENT OF CHEMISTRY

I M.Sc.,CHEMISTRY

Core Practical-II, Inorganic Chemistry Practical-I

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SEMI-MICRO QUALITATIVE ANALYSIS FOR CATIONS (TWO COMMON AND TWO RARE)

Systematic semi-micro qualitative analysis for cations

1. In semi micro analysis the quantity of the sample taken for analysis is very small usually about 50mg, the volume of the solutions used varies from a few drops to 2 to 3 ml.
2. The noble metals Pt, Pd and Au are not usually given for analysis because of their precious nature and high cost.
3. Interfering anions which interfere with systematic cation analysis are not provided for analysis.

Preparation of solution for cation analysis

All reactions are carried out in solution and hence this is the most important part in the analysis of any mixture. The preparation of a solution for cation analysis involves the choice of a suitable solvent. An unknown mixture completely soluble in water would be very rare indeed. One is invariably driven to use one of the three mineral acids.The great majority of substances soluble in dilute hydrochloric acid are salts of the weaker acids, such as carbonates, sulphides, sulphites, phosphates, arsenites, arsenates, borates, nitrites and the like. With a few exceptions, the salts of the strong acids, HCl, HNO_3 and H_2SO_4 are water soluble and a little acid may

have to be added to prevent hydrolysis. Dil. HCl is the most suitable solvent and should always be used unless ruled out by special reasons. Most substances dissolve in dil. HCl; if necessary, con. HCl may be used to bring the unknown into solution which is then suitably diluted.

Table – 1 Classification of Cations into groups

Group No.	Group reagents	Cations	Precipitate
I	Cold dil, HCl	$Pb^{2+}, Hg_2^{2+}, Ag^{+}$ Tl^{+}, WO_4^{2-}	$PbCl_2$ Hg_2Cl_2 AgCl TlCl } White WO_3 yellow
IA	NH_2 NH_2 HCl	SeO_3^{2-}, SeO_4^{2-} TeO_3^{2-}, TeO_4^{2-}	As metals Se Red brown Te blue black
II	Cold dil. HCl and H_2S	$Hg^{2+}, Cu^{2+}, Pb^{2+}$ Cd^{2+}, Bi^{3+}	HgS Black CuS Black PbS Black Bi_2S_3 Dark brown CdS Yellow

		Sb^{3+}, Sb^{5+} $As^{3+}, As^{5+}, Sn^{2+}$ Sn^{4+}, MoO_4^{2-}	As_2S_3 Yellow Sb_2S_3 Red orange SnS Brown SnS_2 Yellow MoS_3 Brown
III	NH_4Cl and Aq NH_3	$Al^{3+}, Fe^{3+}, Cr^{3+}$ $Be^{2+}, Tl^{3+}, Ce^{3+}$ $Tl^{4+}, VO_3^-, VO^{++}, UO_2^{++}$ Th^{4+}, Zn^{4+}	$Al(OH)_3$ White $Fe(OH)_3$ Red brown $Cr(OH)_3$ Bluish green $Be(OH)_2$ $Tl(OH)_3$ $Ce(OH)_3$ White $Ti(OH)_4$ $Zr(OH)_4$ $Th(OH)_4$ $Ce(OH)_4$ $(NH_4)_2U_2O_7$ Yellow $VO(OH)_2$ or $Fe(VO_3)_3$ Grey
IV	NH_4Cl, aq. NH_3 and H_2S	Mn^{2+}, Zn^{2+} Co^{2+}, Ni^{2+}	MnS Plate Brown ZnS White CoS Black NiS Black
V	Aq. NH_3 and $(NH_4)_2CO_3$	$Ca^{2+}, Sr^{2+}, Ba^{2+}$	$CaCO_3$ $SrCO_3$ White $BaCO_3$
VI	None	Mg^{2+} and Li^+	

Table – 2 Separations of Cations into Groups

<table>
<tr><td colspan="6">To a part of the mixture add 3 to 5 drops of conc. HCl, boil and then dilute it with water. Centrifuge.</td></tr>
<tr><td rowspan="6">Residue:

Examine residue for Group I cations</td><td colspan="5">Centrifugate: Add a small crystal or two of hydrazine hydrochloride (1) and heat on the block. Centrifuge.</td></tr>
<tr><td rowspan="5">Residue: Examine residue for Group IA cations</td><td colspan="4">Centrifugate: Add 2 drops of 6% (20 volumes) H_2O_2 (2) solution. Adjust the acidity of the solution to about 0.5N. Heat nearly to boiling and pass H_2S gas and warm. Digest for a minute and centrifuge.</td></tr>
<tr><td rowspan="4">Residue: Examine residue for Group II cations</td><td colspan="3">Centrifugate: Boil off H_2S, add a drop of con. HNO_3, (3) and boil to oxidise any metal ion in a lower oxidation state due to reduction by H_2S. Test a drop of the solution for the presence of Fe^{3+} with KCNS. Add two drops of $FeCl_3$ (4) drops of a saturated NH_4Cl solution and then dil. Aq. NH_3 to neutralise the acid completely and to slight excess. Boil the solution and then centrifuge.</td></tr>
<tr><td rowspan="3">Residue: Examine residue for Group III cations</td><td colspan="2">Centrifugate: Pass H_2S through the solution till precipitation, if any, is complete, Boil and centrifuge.</td></tr>
<tr><td rowspan="2">Residue: Examine residue for Group IV cations</td><td>Centrifugate: Neutralise with dil. HNO_3 and evaporate to dryness (5). Heat cautiously to remove ammonium salts by volatalisation. Cool and dissolve the residue in the minimum amount of dil. HCl. Add 3 drops of it in excess and neutralize with aq. NH_3. (6) Add 2 drops of it in excess and then a solution of $(NH_3)_2CO_3$ dropwise, to precipitate completely any ion which may get precipitated. Digest and centrifuge.</td></tr>
<tr><td>Residue: Examine residue for Group V cations</td><td>Centrifugate: Examine for Group VI cations</td></tr>
</table>

Table – 3 Analysis of Group I

<table>
<tr><td colspan="4">Residue: Boil the I group residue with 3 cc. water, centrifuge the hot solution rapidly and remove the clear solution immediately (1).</td></tr>
<tr><td colspan="2">Residue: Hg_2Cl_2, AgCl, WO_3; wash twice with hot water to remove any Pb^{++} and Tl^{+} chlorides. Add ½ cc. of dil. aq. NH_3 warm and centrifuge.</td><td colspan="2">Centrifugate: $PbCl_2$ and TlCl. Add 2 drops of con. H_2SO_4. Heat to fumes. Cautiously add 1 cc. water. Stir and centrifuge.</td></tr>
<tr><td rowspan="2">Residue: Black colour Add three drops of con. HCl and a drop of con. HNO_3. Heat and centrifuge. To the clear centrifugate add 3 drops of $SnCl_2$. White precipitate turns grey.

MERCURY</td><td colspan="2">Centrifugate: $[Ag(NH_3)_2]Cl$ and ammonium tungstate. Add drops of dil. HCl till a precipitate begins to form. Redissolve with drops of aq. NH_3. Add 2 drops of Kl (2). Centrifuge.</td><td rowspan="2">Residue: White $PbSO_4$. Add 5 drops of NH_4OAc and warm. Add 2 drops of dil. HOAc and 2 drops K_2CrO_4. Yellow precipitate

LEAD</td><td rowspan="2">Centrifugate: Tl_2SO_4 (4) Just neutralize with aq. NH_3 and add 2 drops of Kl and 2 drops of $Na_2S_2O_3$ (5). Yellow precipitate Tl.

THALLIUM</td></tr>
<tr><td>Residue: Yellow AgI insoluble in aq. NH_3

SILVER</td><td>Centrifugate: Evaporate to half the bulk, add 2 drops of $SnCl_2$ and 2 drops con HCl. Warm; blue precipitate (3).

TUNGSTEN</td></tr>
</table>

Table – 4
Analysis of Group IA

Residue: To the IA group residue add two drops of con. HCl and an equal amount of bromine water (1). Then add a few crystals of $NH_2OH.HCl$(2). Warm and centrifuge.	
Residue: Red crystalline powder shows **SELENIUM**	**Centrifugate:** Add a crystal of N_2H_4. 2HCl and boil. A blue-black crystalline precipitate shows **TELLURIUM**

Table – 5 Separations of II A and II B Group Cations

Residue: Boil the II group residue with 1-2 cc. of 2N NaOH (1). Heat and centrifuge	
Residue: Examine the residue for II A group cations	**Centrifugate:** Neutralise with dil. HCl (2) Heat and centrifuge. Wash the precipitate. Discard centrifugate and washings. Examine the residue for IIB Group.

Table – 6 Analysis of Group IIA

<table>
<tr><td colspan="4">Residue: Wash the precipitate with 1 cc of water to remove alkali. Discard washings. Add 1.5 cc dil. HNO_3 to residue and boil (1) Add 2 drops of dil. H_2SO_4 (2). Centrifuge.</td></tr>
<tr><td colspan="2">Residue: HgS and $PbSO_4$. Wash with 1 cc water. Centrifuge and discard washings. Add 5 drops saturated NH_4OAc and heat. Centrifuge.</td><td colspan="2">Centrifugate: Nitrates of Cu^{2+}, Cd^{2+} and Bi^{3+}, Add ammonia in drops to slight excess (3) (smell). Heat and centrifuge.</td></tr>
<tr><td>Residue: Add 3 drops con. HCl and 1 drop con. HNO_3. Heat. Dilute to ½ cc with water and add 2 drops $SnCl_2$. White or grey precipitate.

MERCURY</td><td>Centrifugate: Add 1 drop dil. HOAc and 2 drops K_2CrO_4. Yellow precipitate.

LEAD</td><td>Residue: Add dil. HCl in drops till dissolved and add 3 drops of stannite solution.

Black and white precipitate (4) shows

BISMUTH</td><td>Centrifugate: Deep blue (5) if Cu is present. Divide into two portions.

(i) Add dil. HOAc in drops till pale blue and then 2 drops of $K_4[Fe(CN)_6]$. Reddish brown precipitate shows

COPPER

(ii) To another part add drops of KCN till colourless. Dilute with equal volume of water, Pass H_2S. Yellow precipitate (6) shows

CADMIUM</td></tr>
</table>

Table – 7 Analysis of Group IIB

<table>
<tr><td colspan="3">Residue: Wash the precipitate with NH_4Cl solution. Add 10 drops con. HCl, stir and heat for a minute on the block. Add 10 drops of water. Stir and centrifuge.</td></tr>
<tr><td colspan="2">Residue: As_2S_3 and MoS_3. Add 5 drops of saturated $(NH_4)_2CO_3$ solution. Stir well. Centrifuge.</td><td rowspan="2">Centrifugate: Divide into two portions
(i) To 5 drops of the centrifugate, add a small quantity of iron fillings or Zn dust. Warm to dissolve the metal. Add 3 drops of $HgCl_2$. White Hg_2Cl_2 or grey Hg (2) shows

TIN

(ii) To 5 drops of centrifugate add crystals of oxalic acid to saturation. Dilute and pass H_2S. Orange precipitate (3) shows

ANTIMONY</td></tr>
<tr><td>Residue: Dark brown MoS_3 Add 3 drops of con. HCl and 2 drops of bromine water. Boil to expel excess bromine. Dilute and add 5 drops 10% KCNS, 3 drops $SnCl_2$, and 10 drops amyl alcohol. Shake. Red alcohol layer (1)

MOLYBDENUM</td><td>Centrifugate:
acidify, Yellow precipitate

ARSENIC</td></tr>
</table>

Table – 8 Analysis of Group III

<table>
<tr><td colspan="5">Residue: Dissolve the III group residue in the minimum amount of dil. HCl, add about 50 mg of oxalic acid crystals, digest hot, and centrifuge (1)</td></tr>
<tr><td colspan="2">Residue: Oxalates of Th and Ce. Add 1 cc of saturated $(NH_4)_2$ C_2O_4, boil and centrifuge.</td><td colspan="3">Centrifugate: Neutralise with aqueous NH_3 and digest hot for a few minutes. Centrifuge and discard the solution. Wash residue will dil. NH_4Cl solution and discard washings. Suspend in 1 cc of water in a boiling tube and add about 50 mg Na_2O_2 (4). Boil till effervescence ceases. Centrifuge, wash residue with water and combine washings with centrifugate.</td></tr>
<tr><td>Residue: Cerium oxalate. Add 3 drops 2N NaOH, boil, centrifuge, and dissolve residue in dil. HNO_3
To 2 drops of the solution, add 2 drops dil. aq. NH_3. 2 drops 6% H_2O_2</td><td>Centrifugate: Oxalato complex of Th. Add 5 drops of dil. HCl. White precipitate(3) $Th(C_2O_4)_2$. Boil with 5 drops of 2N NaOH, centrifuge, and dissolve the $Th(OH)_4$ residue in dil. HCl. Just neutralize with aq. NH_3, and add 5 drops m-nitrobenzoic acid reagent. Heat to 80°. White precipitate shows
THORIUM</td><td>Residue: Hydrated oxides of Tl, Fe, Ti, Zr, and Mn. Redissolve in dil. HCl, boil and divide into several test portions.</td><td colspan="2">Centrifugate: Chromate, aluminate, uranate, vanadate, and beryllate. Acidify with dil. HNO_3, Add 5 drops of $Pb(NO_3)$ and then about 200 mg of NH_4OAc (8) crystals. Stir well and centrifuge.</td></tr>
<tr><td colspan="2"></td><td>1. Add 2 drops KI and then $Na_2S_2O_3$ in drops. (5) Yellow precipitate of TlI shows
THALLIUM</td><td>Residue: $PbCrO_4$ and $Pb(VO_3)_2$. Dissolve in 10 drops of hot dil. HNO_3 and cool. Add 10 drops amyl alcohol and 3 drops 6% H_2O_2. (9) Shake. Blue alcohol layer:
CHROMIUM</td><td>Centrifugate: Nitrates of Pb^{2+}, Al^{3+}, Be^{2+}, UO_2^{2+}.
Add 3 drops dil. HCl and pass H_2S. Centrifuge and reject the precipitated PbS. Transfer solution to boiling tube and boil to expel H_2S. Cool and add carefully 5 drops of saturated $(NH_4)_2CO_3$ (11) Boil for a minute and centrifuge.</td></tr>
</table>

<table>
<tr>
<td rowspan="3">and heat. Yellowish brown CeO_2 (2) shows
CERIUM</td>
<td rowspan="3"></td>
<td colspan="2">2. Add syrupy phosphoric acid in drops just to decolourise iron. Add 2 drops of 6% H_2O_2 and 2 drops dil. H_2SO_4. Orange colour (6) shows titanium. Precipitate shows zirconium. Centrifuge.</td>
<td rowspan="3">Reddish brown aqueous layer shows vanadium (10). To the aqueous solution add 3 drops aq. NH_3 and pass H_2S Red colour shows
VANADIUM</td>
<td colspan="2">Residue: Basic carbonates and hydroxides of Al and Be. Dissolve in the minimum volume of dil. HCl. Add 2 drops of $Na_2S_2O_3$. Warm and centrifuge (12).</td>
<td>Centrifuge: Complex uranyl carbonate. Evaporate to small volume, remove any precipitate, and acidify with dil HCl. Add 2 drops of $K_4[Fe(CN)_6]$ and drops of aq. NH_3. Brown precipitate turns yellow on adding NaOH.(13)
URANIUM</td>
</tr>
<tr>
<td>Residue: White zirconium phosphate:
ZIRCONIUM</td>
<td>Centrifugate: Add about 20 mg Na_2SO_3, and heat. White precipitate (7) of $Ti(OH)PO_4$
TITANIUM</td>
<td>Residue: White $Al(OH)_3$
ALUMINIUM</td>
<td>Centrifugate: Add 1 drop of quinalizarin. Blue colour confirms
BERYLLIUM</td>
<td></td>
</tr>
<tr>
<td colspan="2">3. Evaporate with a drop of con. H_2SO_4 to remove HCl. Add 5 drops of dil. HNO_3 and about 50 mg of $NaBiO_3$. Stir and left stand. Purple colour of $HMnO_4$ shows
MANGANESE</td>
<td colspan="2"></td>
<td></td>
</tr>
</table>

Table – 9 Analysis of Group IV

<table>
<tr><td colspan="4">Residue: Stir the IV Group residue with 1 cc water and add 5 drops dil, HCl (I) Centrifuge.</td></tr>
<tr><td colspan="2">Residue: CoS and NiS. Add 5 to 10 drops. con. HCl. Transfer to crucible or beaker. Add a small crystal of $KClO_3$(2). Boil and evaporate just to dryness. Dissolve in 1 cc water and divide into two portions.</td><td colspan="2">Centrifugate: Zn^{2+}, Mn^{2+}. Boil off H_2S. Add NaOH to slight excess (5) Centrifuge.</td></tr>
<tr><td>To 5 drops of solution add a few crystals of NH_4CNS and 10 drops of amyl alcohol. Shake. Blue alcohol layer (3) shows
COBALT</td><td>To 5 drops of solution add 3 drops of dimethylglyoxime reagent followed by aq. NH_3. Scarlet precipitate (4) shows
NICKEL</td><td>Residue:
$Mn(OH)_2$ turns brown in air. Add 10 drops of dil. HNO_3 and about 50 mg of $NaBiO_3$. Stir well. Centrifuge. Pink coloured centrifugate (6) shows
MANGANESE</td><td>Centrifugate:
(i) Through part of the solution pass H_2S. White (7) or dirty white precipitate.
(ii) Acidify a part of the solution with HOAc and add $K_4[Fe(CN_6)]$.
White precipitate (8) shows
ZINC</td></tr>
</table>

Table – 10 Analysis of Group V

<table>
<tr><td colspan="2">Residue: Dissolve the V Group residue in the minimum amount of dil. HOAc. (1) Add 3 drops of K_2CrO_4 solution. Centrifuge.</td></tr>
<tr><td>Residue: Yellow $BaCrO_4$

BARIUM</td><td>Centrifugate: Ca^{2+}, Sr^{2+} Neutralise with aq. NH_3. Reprecipitate carbonates (2) with $(NH_4)_2CO_3$. Centrifuge and reject solutions. Redissolve residue in dil. HOAc and test as described below:

(i) Test for Sr^{2+}: To 3 drops of solution add 3 drops of $CaSO_4$ solution. Boil and let stand. White precipitate of $SrSO_4$. (3)

STRONTIUM

(ii) Test for Ca^{2+}: To 5 drops of the solution add 5 drops saturated $(NH_4)_2SO_4$ solution. Boil cool and centrifuge (4). To one half of the centrifugate add 3 drops 3% ammonium oxalate solution followed by aq. NH_3. White precipitate (5).

To other half of centrifugate add 3 drops of saturated NH_4Cl and 3 drops of $K_4[Fe(CN)_6]$. Let stand. Pale yellow precipitate shows

CALCIUM</td></tr>
</table>

Table – 11 Analysis of Group VI

This group includes Mg^{2+} and Li^{+} since many ammonium salts are added during the course of the analysis, the ion has to be tested in the unknown before proceeding to the systematic cation analysis.

Evaporate the centrifugate from group V to dryness. Add 5 drops of con. HNO_3 and evaporate cautiously. Ignite till there are no more fumes. Extract residue with water. Divide into two portions.

Test for Magnesium

1. To 3 drops of the solution, add 2 drops of NH_4Cl, 2 drops of aqueous NH_3 and 3 drops of Na_2HPO_4. Scratch the sides of the tube with a glass rod. White crystalline precipitate of $MgNH_4PO_4$ shows MAGNESIUM.

Test for Lithium

2. To 3 drops of the solution add ferric periodate reagent white precipitate shows lithium.