Classification of the Cations and Anions

Having become familiar with the characteristic reactions of cations and anions, one may be able to identify an unknown material using simple chemical tests and separations. In this process, called inorganic qualitative analysis, one deals with the detection and identification of the elements that are present in a sample of material. Frequently this is accomplished by making an aqueous solution of the sample and then determining which cations and anions are present on the basis of chemical and physical properties.

If a sample contains only a single cation and anion, their identification is a fairly simple and straightforward process, although to distinguish between two cations (or anions) that have similar chemical properties is not easy and in this instance additional confirmatory tests are required. The detection of a particular ion in a sample that contains several ions is somewhat more difficult, because the presence of the other ions may interfere with the test. This problem can be circumvented by precipitating, thereby removing, the disturbing ions from solution prior to testing for the particular ion. The successful analysis of a mixture containing large number of ions centres upon the systematic separation of the ions into groups containing only a few ion. It is much simpler task to work with 2 or 3 ions than with 10 or more. Ultimately, the separation of cations depends upon the difference in their tendencies to form precipitates, or to form complex ions.

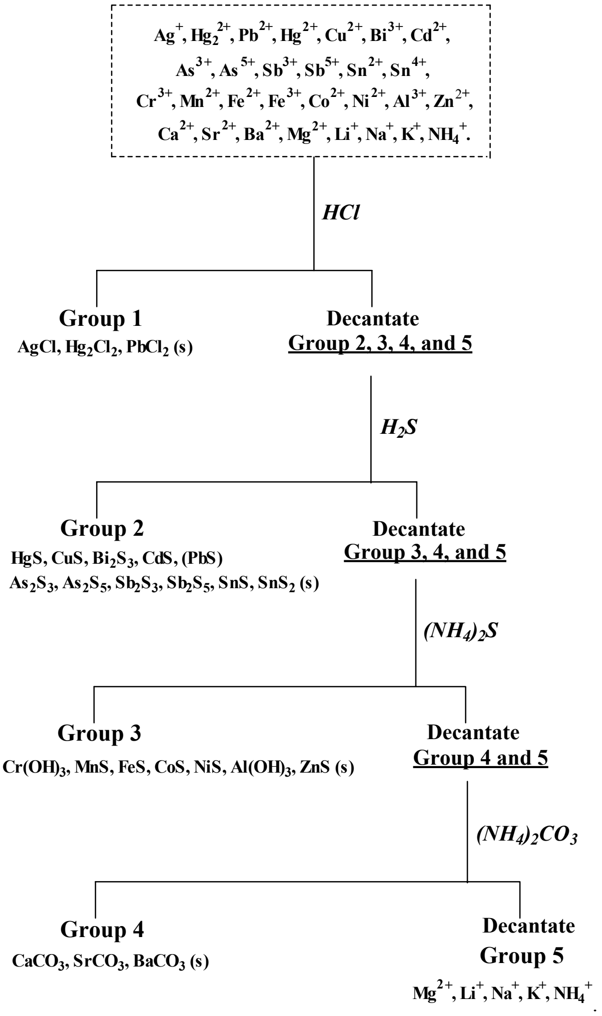
One of the best and well known separation scheme, outlined below, was first described by R. Fresenius in 1841, though in the course of time modifications were introduced. In this system cations are classified into five groups on the basis of their behaviour against some reagents, called group-reagents. By the systematic use of these reagents one can decide about the presence or absence of groups of cations, and can also separate these groups for further examination. The group reagents used for the classification of most common cations are hydrochloric acid, hydrogen sulphide, ammonium sulphide, and ammonium carbonate. Classification is based on whether a cation reacts with these reagents by the formation of precipitates or not. It can therefore be said that classification of the most common cations is based on the differences of solubilities of their chlorides, sulphides, and carbonates.

The **<u>five groups of cations</u>** and the characteristics of these groups are as follows:

Group 1 Cations of this group form precipitates with dilute hydrochloric acid. Ions of this group are **lead(II)**, **mercury(I)**, and **silver(I)**.

Group 2 The cations of this group do not react with hydrochloric acid, but form precipitates with hydrogen sulphide in dilute mineral acid medium. Ions of this group are ***mercury(II), copper(II), bismuth(III), cadmium (II),*** **tin(II)**, **tin(IV)**, **arsenic(III)**, **arsenic(V)**, **antimony(III),** and **antimony(V)**. The first four form the sub-group 2/a and the last six the sub-group 2/b. While sulphides of cations in Group 2/a are insoluble in ammonium polysulphide, those of cations in Group 2/b are soluble.

Group 3 Cations of this group do not react either with dilute hydrochloric acid, or with hydrogen sulphide in dilute mineral acid medium. However they form precipitates with ammonium sulphide in neutral or ammoniacal medium. Cations of this group are **iron(II), iron(III), cobalt(II), nickel(II), manganese(II), chromium(III), aluminium(III),** and **zinc(II)**.



Group 4 Cations of this group do not react with the reagents of Groups 1, 2, and 3. They form precipitates with ammonium carbonate in the presence of ammonium chloride in neutral medium. Cations of this group are **calcium(II), strontium(II),** and **barium(II)**.

Group 5 Common cations, which do not react with reagents of the previous groups, form the last group of cations, which includes **magnesium(II), lithium(I), sodium(I), potassium(I),** and **ammonium(I)** ions.

The methods available for the detection of anions are not as systematic as those which have been described above for cations. No really satisfactory scheme has yet been proposed which permits the separation of the common anions into major groups, and the subsequent unequivocal separation of each group into its independent constituents; however, it is possible to detect anions individually in most cases, after perhaps a 1-2 stage separation. It is advantageous to remove all heavy metals from the sample by extracting the anions through boiling with sodium carbonate solution; heavy metal ions are precipitated out in the form of carbonates, while the anions remain in solution accompanied by sodium ions.

The following scheme of classification of anions has been found to work well in practice; anions are divided into four groups on the basis of their reactions with dilute hydrochloric acid and of the differences of solubilities of their barium and silver salts.

The **four groups of anions** and the characteristics of these groups are as follows:

Group 1 Visible change, gas evolution and/or formation of a precipitate, with dilute hydrochloric acid. Ions of this group are **carbonate, silicate, sulphide, sulphite,** and **thiosulphate**.

Group 2 The anions of this group do not react with hydrochloric acid, but form precipitates with barium ions in neutral medium. Ions of this group are **sulphate, phosphate, fluoride,** and **borate**.

Group 3 Anions of this group do not react either with dilute hydrochloric acid, or with barium ions in neutral medium. However, they form precipitates with silver ions in dilute nitric acid medium. Anions of this group are **chloride, bromide, iodide,** and **thiocyanate**.

Group 4 Common anions, which do not react with reagents of the previous groups, form the last group of anions, which includes **nitrite**, **nitrate** and **chlorate** ions.

Classification of the anions

	I. group		**II. group**	**III. group**	**IV. group**
	reacts with HCl gas liberation or precipitate		**Ba^{2+}** **pH= 7**	**$AgNO_3$** $+ HNO_3$	------
	precipitate with Ag^+	precipitate with Ba^{2+}			
no reaction with KI or I_2 soln.	**CO_3^{2-}** **SiO_3^{2-}**	**CO_3^{2-}** **SiO_3^{2-}**	**SO_4^{2-}** **PO_4^{3-}** **F^-** **BO_3^{3-}**	**Cl^-** **Br^-** **I^-** **SCN^-**	**NO_3^-**
decolourise I_2 soln.	**S^{2-}** **SO_3^{2-}** **$S_2O_3^{2-}$**	**SO_3^{2-}** **$S_2O_3^{2-}$**			
liberate I_2 from KI soln.	**(NO_2^-)**				**NO_2^-** **ClO_3^-**

TESTING FOR A SINGLE CATION IN SOLUTION

The identification of a single cation in solution is a fairly simple and straightforward process, although without a good identification scheme it may require so many experiments as the number of potential cations, if we know at least one specific reaction for each cation. In order to reduce the number of tests required for the identification, it is important to develop a good identification scheme, which reduces the number of potential cations step by step placing them into groups. There are several possibilities and anyone could develop his/her own identification scheme. The scheme you find below follows the classification of cations into groups, as described in the Fresenius' system. In case of a solid sample it is assumed that the sample is soluble in water or dilute nitric acid.

Once the cation is found, its presence should be verified by other, characteristic reactions.

(1) Group I cations

Add to the solution an excess of dilute HCl. If there is no change, follow **(2a)**.
A white precipitate may contain Pb^{2+}, Hg_2^{2+} or Ag^+.
Filter and wash the precipitate and then add NH_3 solution to the precipitate.
If the precipitate

does not change: Pb^{2+} present
turns black: Hg_2^{2+} present
dissolves: Ag^+ present

(2a) Group IIA cations

Acidify the solution and add H_2S in excess. If there is no change follow **(3)**.
A precipitate may result if Hg^{2+}, Bi^{3+}, Cu^{2+}, Cd^{2+}, As^{3+}, As^{5+}, Sb^{3+}, Sb^{5+}, Sn^{2+}, Sn^{4+} were originally present. (Check the colour of the precipitate !)
Filter the precipitate, wash with dilute HCl, and treat with an excess of $(NH_4)_2S_x$. If the precipitate dissolves, follow **(2b)**.

If the remaining precipitate is

yellow: Cd^{2+} present

Take a fresh sample and add dilute NaOH. If the precipitate is

blue: Cu^{2+} present
yellow: Hg^{2+} present
white: Bi^{3+} present

(2b) Group IIB cations

Add dilute HCl to the $(NH_4)_2S_x$ filtrate in excess, when the precipitate reappears. Take a fresh sample, acidify, and precipitate the sulphide.
Examine its colour:

brown precipitate: Sn^{2+} present

An orange precipitate indicates Sb. To identify its oxidation state, take a fresh sample, acidify with 1:1 HCl and add KI:

no colouration: Sb^{3+} present
brown colouration Sb^{5+} present

A yellow precipitate indicates As or Sn^{4+}. Add $(NH_4)_2CO_3$ in excess.
If the precipitate remains undissolved: Sn^{4+} present
Perform the luminescence test for identifying Sn^{4+} ions.

If the precipitate dissoves: As^{3+} or As^{5+} present.
To identify the oxidation state of As present in the solution, take a fresh sample, acidify with 1:1 HCl and add KI:

no coloration: As^{3+} present
brown coloration: As^{5+} present

(3) Group III cations

Neutralise the solution with NH_3 solution and add $(NH_4)_2S$ in excess. If there is no change, follow **(4)**. Examine the precipitate.

A green precipitate indicates Cr^{3+}. To a fresh sample, add NaOH:

green precipitate which dissolves in an excess of the reagent: Cr^{3+} present

A pink (flesh-like) precipitate indicates Mn^{2+}. To a fresh sample, add NaOH:

white precipitate, which turns darker on standing: Mn^{2+} present

A white precipitate may be caused by Al^{3+} or Zn^{2+}. To a fresh sample add NH_3, first in moderate amounts, then in excess:

white precipitate, which dissolves in excess NH_3 soln.: Zn^{2+} present
white precipitate, which remaines unchanged if excess NH_3 is added: Al^{3+} present

A black precipitate occurs if Co^{2+}, Ni^{2+}, Fe^{2+} or Fe^{3+} were present originally. Filter, wash and mix the precipitate with 1:1 HCl. The precipitate dissolves if Fe^{2+} or Fe^{3+} were present, otherwise it remains unchanged.

To a fresh sample add NaOH in excess:

green precipitate, turning dark on standing: Fe^{2+} present
dark brown precipitate: Fe^{3+} present
blue precipitate, turning pink if excess NaOH is added: Co^{2+} present
green precipitate, which remains unchanged on standing: Ni^{2+} present

(4) Group IV cations

To the solution add $(NH_4)_2CO_3$ in excess, in the presence of NH_4Cl. If there is no precipitation, follow **(5)**.
A white precipitate indicates the presence of Ba^{2+}, Sr^{2+} or Ca^{2+}.

To a fresh sample add a four fold (in volume) of saturated $CaSO_4$ solution:
immediate white precipitate: Ba^{2+} present
a white precipitate is slowly formed: Sr^{2+} present
no precipitation occurs: Ca^{2+} present

(5) Group V cations

Heat a fresh sample gently with some dilute NaOH:
characteristic odour of ammonia: NH_4^+ present

Carry out a flame test with the original sample:
red coloration: Li^+ present
yellow coloration: Na^+ present
pale violet coloration: K^+ present

To the solution add NaOH in excess:
white precipitate, which turns red by adding
a few drops of titan yellow reagent: Mg^{2+} present

TESTING FOR A SINGLE ANION IN SOLUTION

The identification of a single anion in solution is a fairly simple and straightforward process, and anyone could develop his/her own identification scheme. The scheme below follows the classification of anions into four groups, as described on page 131. It is assumed that the heavy metals are removed from the solution. In case of a solid sample it is assumed that the sample is soluble in water.

Once the anion is found, its presence should be verified by other, characteristic reactions.

(1) Group I anions

Add to the solution an excess of dilute HCl. If there is no change, follow **(2)**. If a white precipitate or/and gas liberation is observed, one of the following anions may present: CO_3^{2-}, SiO_3^{2-}, S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$.

White, gelatinous precipitate without the liberation of any gas: SiO_3^{2-} present

White precipitate with the liberation of SO_2. The gas is tested with a filter paper moistened with potassium iodate and starch solution.

blue coloration: $S_2O_3^{2-}$ present

No precipitate, only gas liberation is observed.

Test the gas with filter paper moistened with lead acetate solution.

black coloration: S^{2-} present

Test the gas with filter paper moistened with potassium iodate and starch solution.

blue coloration: SO_3^{2-} present

Introduce the gas into baryta or lime water:

white precipitate: CO_3^{2-} present

(2) Group II anions

Neutralise the solution and add $BaCl_2$ solution. If there is no change follow **(3)**.

A white precipitate may result if SO_4^{2-}, PO_4^{3-}, F^-, or BO_3^{3-} was originally present.

Filter the precipitate, and add HCl solution.

precipitate is not soluble: SO_4^{2-} present

Add concentrated sulphuric acid to the precipitate or to the original solid sample, and warm the test tube:

test-tube acquires a greasy appearance: F^- present

Add concentrated sulphuric acid and ethanol to the precipitate or to the original sample in a porcelain basin and ignite the alcohol:

green-edged flame: BO_3^{3-} present

Take a fresh sample and add ammonium molybdate reagent.

yellow, crystalline precipitate: PO_4^{3-} present

(3) Group III anions

Acidify the solution with dilute nitric acid and add $AgNO_3$ solution. If there is no change, follow **(4)**.

Examine the precipitate.
A yellow and yellowish white precipitate indicates I^- and Br^-, respectively.
To a fresh sample, add 1-2 ml carbon tetrachloride and chlorine water dropweise, and shake it intensively:

violet organic layer, which turns colourless with excess chlorine water: I^- present
reddish-brown organic layer, which turns yellow with excess chlorine water: Br^- present

A white precipitate may be caused by Cl^- or SCN^-.
To a fresh sample add $FeCl_3$ solution:

blood-red coloration: SCN^- present

Apply the chromyl chloride test:

positive test: Cl^- present

(4) Group IV anions

One of the following ions may present: NO_2^-, NO_3^-, or ClO_3^-.

Acidify a fresh sample with acetic acid, add sulphanilic acid and α-naphthylamine reagents:

red coloration: NO_2^- present

Acidify a fresh sample with acetic acid, add sulphanilic acid and α-naphthylamine reagents and zinc chips:

red coloration: NO_3^- present

Add zinc chips to a fresh sample, filter the solution after a couple of minutes, acidify with dilute nitric or sulphuric acid and add $AgNO_3$ solution to the filtrate:

white precipitate: ClO_3^- present

Separating and Identifying the Cations

The separation scheme outlined below was first described by R. Fresenuis. Separation of the cations can be done by following the procedure outlined on pages 139-145. *It is important to verify the presence of a given cation by further tests.*
In case of a solid sample it is assumed that it is soluble in water or dilute nitric acid.

<u>Consequences of applying the Fresenius' system for the separation of cations:</u>

1. Ammonium ions, NH_4^+, must be tested in the <u>original sample</u>.
During the course of analysis most of the group reagents are added in the form of ammonium compounds, thus by the time Group V is reached, a considerable amount of ammonium ions will be built up in the test solution.

2. The oxidation state of As, Sb, Sn, and Fe can not be decided during the analysis. It may be tested in the original sample.

$$As^{5+} \xrightarrow{H_2S} As^{3+}$$

$$\begin{tikzcd}
As^{3+} \arrow[r, "H_2S"] & As_2S_3 \arrow[r, "(NH_4)_2S_2"] & AsS_4^{3-} \arrow[r, "HCl"] & As_2S_5 \\
As^{5+} \arrow[r, "H_2S"] & As_2S_5 \arrow[r, "(NH_4)_2S_2"] & AsS_4^{3-} \arrow[ur, "HCl"] &
\end{tikzcd}$$

$$\begin{tikzcd}
Sb^{3+} \arrow[r, "H_2S"] & Sb_2S_3 \arrow[r, "(NH_4)_2S_2"] & SbS_4^{3-} \arrow[r, "HCl"] & Sb_2S_5 \\
Sb^{5+} \arrow[r, "H_2S"] & Sb_2S_5 \arrow[r, "(NH_4)_2S_2"] & SbS_4^{3-} \arrow[ur, "HCl"] &
\end{tikzcd}$$

$$\begin{tikzcd}
Sn^{2+} \arrow[r, "H_2S"] & SnS \arrow[r, "(NH_4)_2S_2"] & SnS_3^{2-} \arrow[r, "HCl"] & SnS_2 \\
Sn^{4+} \arrow[r, "H_2S"] & SnS_2 \arrow[r, "(NH_4)_2S_2"] & SnS_3^{2-} \arrow[ur, "HCl"] &
\end{tikzcd}$$

$$\begin{tikzcd}
Fe^{3+} \arrow[r, "H_2S"] & Fe^{2+} & Fe^{2+} \arrow[r, "(NH_4)_2S"] & FeS \\
 & & Fe^{3+} \arrow[ur, "(NH_4)_2S"] &
\end{tikzcd}$$

Group I

……

Cations of this group form precipitates with dilute (2 M) HCl.

Precipitate: $AgCl$, $PbCl_2$, Hg_2Cl_2 **Filtrate**: cations of groups II-V

The precipitate is separated, and washed with hydrochloric acidic water. Transfer the precipitate to a small beaker, and boil with 5-10 ml water. Filter hot.

Residue: $AgCl, Hg_2Cl_2$ Wash the ppt. with hot water. Add NH_4OH to the precipitate and filter.	Filtrate: $PbCl_2$

Residue: black precipitate $HgNH_2Cl + Hg$	Solution: Ag^+ complex $[Ag(NH_3)_2]^+$	Cool a portion of the solution: a white crystalline ppt. of $PbCl_2$ is obtained if Pb is present in any quantity.
Hg_2^{2+}	Ag^+	Pb^{2+}

Additional reactions for identification:

	Divide the filtrate into two parts: a.) Acidify with dilute HNO_3. White ppt. of AgCl. b.) Add a few drops of KI solution. Pale yellow ppt. of AgI. Ag^+ present.	Divide the hot filtrate into three parts: a.) Add K_2CrO_4 solution. Yellow ppt. of $PbCrO_4$, insoluble in dilute acetic acid. b.) Add KI solution. Yellow ppt. of PbI_2, soluble in hot water to a colourless solution, which deposites brilliant yellow crystals upon cooling. c.) Add dilute H_2SO_4. White ppt. of $PbSO_4$, soluble in ammonium tartrate solution. Pb^{2+} present.

Group II

……

Cations of this group form precipitates with H_2S in dilute mineral acid medium.
(They do not react with hydrochloric acid.)

Precipitate: PbS, HgS, CuS, Bi_2S_3, CdS, As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5, SnS, SnS_2
Filtrate: cations of Groups III-V

Transfer the precipitate to a porcelain dish, add about 5 ml yellow $(NH_4)_2S_x$ solution, heat to 50-60 ^oC, and maintain at this temperature for 3-4 minutes with constant stirring. Filter.

Residue: Group IIA	**Filtrate**: Group IIB
May contain HgS, PbS, Bi_2S_3, CuS, and CdS. Wash with small volumes of dilute (1:100) ammonium sulphide.	May contain solutions of the thio-salts $(NH_4)_2AsS_4$, $(NH_4)_2SbS_4$, and $(NH_4)_2SnS_3$. Just acidify by adding concentrated HCl dropwise, and warm gently. A yellow or orange precipitate, which may contain As_2S_5, Sb_2S_5, and SnS_2, indicates Group IIB present.

Group IIA

....

The precipitate may contain HgS, PbS, Bi_2S_3, CuS, and CdS.
Transfer to a beaker or porcelain basin, add 5-10 ml dilute HNO_3, boil gently for 2-3 minutes, filter and wash with a little water.

<table>
<tr>
<td rowspan="3">**Residue**
Black. HgS

Dissolve in a mixture of M NaOCl and dilute HCl solutios Add dilute HCl, boil off excess Cl_2 and cool.
or
Dissolve in aqua regia (add also a little solid KCl). Evaporate the solvent, dissolve the residue in dilute HCl. Add $SnCl_2$ solution. White ppt. turning grey or black.

Hg^{2+}present.</td>
<td colspan="3">**Filtrate**
May contain nitrates of Pb, Bi, Cu, and Cd. Test a small portion for Pb by adding dilute H_2SO_4. A white precipitate of $PbSO_4$ indicates Pb present. If Pb present, add dilute H_2SO_4 to the remainder of the solution, concentrate in the fume cupboard until white fumes (from the dissociation of H_2SO_4) appear.
Cool, add 10 ml of water, stir, allow to stand 2-3 minutes, filter and wash with a little water.</td>
</tr>
<tr>
<td rowspan="2">Residue
White $PbSO_4$

Pour 2 ml of 10% ammonium acetate through the ppt. on the filter paper several times, add to the filtrate a few drops of dilute acetic acid and then K_2CrO_4 solution. Yellow ppt. of $PbCrO_4$.

Pb^{2+} present.</td>
<td colspan="2">Filtrate
May contain nitrates and sulphates of Bi, Cu and Cd. Add concentrated NH_4OH solution until solution is distinctly alkaline. Filter.</td>
</tr>
<tr>
<td>Residue
White: may be $Bi(OH)_3$.

Wash.
Dissolve in the minimum volume of dilute HCl and pour into cold sodium tetrahydroxo-stannate(II).
Black ppt.

Bi^{3+} present.</td>
<td>Filtrate
May contain $[Cu(NH_3)_4]^{2+}$ and $[Cd(NH_3)_4]^{2+}$.

If deep blue in colour, Cu is present in quantity. Confirm Cu by acidifying a portion of the filtrate with dilute acetic acid and add $K_4[Fe(CN)_6]$ solution.
Reddish-brown ppt.
Cu^{2+} present.

To the remainder of the filtrate, add KCN solution dropwise until the colour disappears, and add a further ml in excess. Pass H_2S for 20-30 seconds.
Yellow ppt., sometimes discoloured, of CdS.
Cd^{2+} present.</td>
</tr>
<tr>
<td>Hg</td>
<td>Pb</td>
<td>Bi</td>
<td>Cu Cd</td>
</tr>
</table>

Group IIB

……

Treat the yellow ammonium polysulphide extract of the Group II ppt. with dilute HCl, with constant stirring, until it is slightly acidic, warm and shake or stir for 1-2 minutes.

A fine white (or yellow) ppt. is sulphur only.

A yellow or orange flocculant ppt. indicates As, Sb, and/or Sn present.

Filter and wash the ppt., which may contain As_2S_5, (As_2S_3), Sb_2S_5, (Sb_2S_3), SnS_2 , with a little H_2S water.

Transfer the precipitate to a beaker or porcelain dish, add 5-10 ml dilute HCl (1:1) and boil gently for 5 minutes. Filter.

Residue: may contain (As_2S_3), As_2S_5, and S. Dissolve the ppt. in warm dilute NH_3 solution, add 3% H_2O_2 solution and warm for a few minutes.	**Filtrate**: may contain Sb^{3+}, or/and Sn^{4+} Boil to expel H_2S, partially neutralize the solution, add iron wire or nail, warm on water bath for 10 minutes. After cooling, filter the liquid	
	Precipitate: Sb (Fe)	Filtrate: Sn^{2+} (Fe^{2+})
As	Sb	Sn

Identification

Add a few ml $Mg(NO_3)_2$ reagent, stir and allow to stand. White precipitate of $Mg(NH_4)AsO_4$. Filter off ppt., and pour $AgNO_3$ solution containing a few drops of 2M acetic acid on to residue on filter. Brownish-red residue of Ag_3AsO_4. As^{5+} present May also try Bettendorff's reaction.	Dissolve in a mixture of tartaric acid and dilute HNO_3, or in aqua regia. Render the solution less acidic by adding NH_3 soln (add NH_3 soln. until white ppt. appears). Pass H_2S into the solution. Orange precipitate of Sb_2S_3. Sb^{3+} present.	Add the filtrate to a solution of $HgCl_2$. White precipitate of Hg_2Cl_2 or grey ppt. of Hg. Sn^{2+} present. May also try luminescence test.

Group III

Neutralize the solution with NH_3 solution and add $(NH_4)_2S$ in excess.

Precipitate: CoS, NiS, FeS, MnS, $Cr(OH)_3$, $Al(OH)_3$, ZnS

Wash the precipitated sulphides with a small amount of dilute $(NH_4)_2S$ solution. Transfer the precipitate to a small beaker, add 1 M HCl, stir well, allow to stand for 2-3 minutes and filter.

Residue: CoS, NiS	**Filtrate**: Fe^{2+}, Mn^{2+}, Cr^{3+}, Al^{3+}, Zn^{2+} After removing H_2S by boiling, 30% NaOH and 3% H_2O_2 (1:1) are added to the soln.		
Dissolve the precipitate in a mixture of CH_3COOH and a few drops of 30% H_2O_2. The precipitate is also soluble in dilute nitric acid by heating.	Residue: $Fe(OH)_3$, $MnO(OH)_2$	Filtrate: $Al(OH)_4^-$, $Zn(OH)_4^-$, CrO_4^{2-} The solution is boiled with solid NH_4Cl	
		Precipitate: $Al(OH)_3$	Filtrate: $Zn(NH_3)_6^{2+}$, CrO_4^{2-}
Co Ni	**Fe Mn**	**Al**	**Zn Cr**
	Identification		
Divide the solution into two equal parts. a) Add 1 ml amyl alcohol, 2 g solid NH_4SCN and shake well. Amyl alcohol layer coloured blue. Co^{2+} present. b) Add 2 ml NH_4Cl soln., NH_4OH soln. until alkaline, and then excess of dimethyl-glyoxime reagent. Red ppt. Ni^{2+} present.	Divide the precipitate into two parts. a) Dissolve the ppt. in dilute HCl (filter, if necessary). Either - add a few drops of KSCN soln. Deep red coloration. Or - add $K_4Fe(CN)_6$ soln. Blue ppt. Fe^{3+} present. b) Dissolve the ppt. in cc HNO_3, add PbO_2 to the soln., heat, allow to settle. Purple soln. of MnO_4^-. Mn^{2+} present.	Dissolve the precipitate in acetic acid, and add morin reagent. Characteristic fluorescence. Al^{3+} present.	If the soln. is yellow, Cr^{3+} is indicated. Divide the liquid into two portions. a) Acidify with acetic acid and add lead acetate soln. Yellow ppt. of $PbCrO_4$. Cr^{3+} present. (May also try chromium pentoxide test.) b.) Acidify with acetic acid and pass H_2S. White precipitate of ZnS. Zn^{2+} present. (Try also dithizone test.)

Group IV

Treat the filtrate of the Group III ppt. with concentrated HCl; boil the solution to remove sulphide, S^{2-}. Neutralize the solution with NH_3 soln., boil, and add $(NH_4)_2CO_3$ in excess.

White precipitate may contain $BaCO_3$, $SrCO_3$, and $CaCO_3$.

Wash ppt. with a little hot water and reject the washings. Dissolve the ppt. in 2 M acetic acid.

Add CH_3COONa to soln., heat the solution, and add a slight excess of $K_2Cr_2O_7$ solution (i.e. until the solution assumes a slight yellow colour and precipitation is complete).

Precipitate: yellow $BaCrO_4$	**Filtrate**: Ca^{2+}, Sr^{2+}
Wash the ppt. with hot water. Dissolve the ppt. in a little concentrated HCl, evaporate almost to dryness and apply the flame test. Green (or yellowish-green) flame. Ba^{2+} present.	Add a four fold (in volume) of saturated $CaSO_4$ solution: a white ppt. slowly formed: Sr^{2+} indicated. Render the soln. alkali with NH_3 soln., and add $(NH_4)_2(COO)_2$: white precipitate: Ca^{2+} indicated. Render the solution neutral, and then add $K_2[Fe(CN)_6]$ solution and a little NH_4Cl: white ppt., Ca^{2+} indicated. If only one of the two ions present, apply the flame test. Crimson flame: Sr^{2+} present. Brick-red flame: Ca^{2+} present.

Group V

The residue from Group IV contains the Group V cations, Na^+, K^+, Mg^{2+}, NH_4^+(added during the process of separation of different cations in the form of e.g. $(NH_4)_2S$ and $(NH_4)_2CO_3$. Do not test for NH_4^+ from this solution !!!!!!!), and a very small amount of unprecipitated Ca^{2+}.

Test for Na^+: use the flame test. Persistent yellow flame: Na^+ present.

Test for Mg^{2+}: add NaOH solution until alkaline. If white precipitate forms, divide it into two portions, and add titan yellow and magnezon to the different portions of ppt.: red colouration of ppt. with titan yellow and blue colouration of ppt. with magnezon: Mg^{2+} present.

Test for K^+: add NaOH and boil the solution until NH_3 completely disappears (test NH_3 with wet pH paper). Filter the solution if necessary. Add concentrated $HClO_4$ solution: white, crystalline precipitate (of $KClO_4$): K^+ present.

Test for NH_4^+: use the original solution. Add NaOH and boil the solution, test the gas evolved using wet indicator paper or filter paper moistened with mercury(I) nitrate.