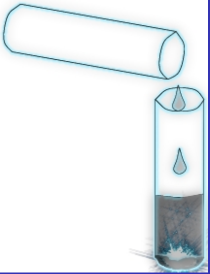
Qualitative Chemical Analysis



István Szalai

Institute of Chemistry, Eötvös University

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Topics

- Acid-base theories; reduction-oxidation reactions: reducing and oxidizing agents, balancing redox equations; complex equilibria; precipitation reactions, principles of solubility equilibria; factors influencing solubility equilibria
- Classification and reactions of ions; group reagents for qualitative analysis of cations and anions; identifications reactions for cations and anions
- pH calculations; solubility of precipitates; effect of pH and other complexing agents on the solubility equilibria

Schedule

Major Tests during the semester:

- Test Paper I on 5^{th} of March
- Test Paper II on 16^{th} of April
- Final Test on 7^{th} of May
- Retakes 23^{rd} of April and 14^{th} of May

Analytical chemistry

Analytical chemistry is the study of the separation, identification, and quantification of the chemical components of natural and artificial materials. Qualitative analysis gives an indication of the identity of the chemical species in the sample and quantitative analysis determines the amount of these components.

		(mg/L)
Sodium	Na^+	6.5
Potassium	K^+	1
Calcium	Ca^{2+}	80
Magnesium	Mg^{2+}	26
Chlorides	Cl^-	6.8
Nitrates	NO_3^-	3.7
Bicarbonates	HCO_3^-	360
Sulfates	SO_4^{2-}	12.6
pH	pH	7.2
Silica	SiO_2	15
Fluoride		0.07

Analytical chemistry & pharmaceutical industry

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"If a pharmaceutical substance may contain residues of metal elements, used as catalyst(s) or reagent(s) in the synthesis, for each of these residual elements an acceptance criterion should be set... For the determination of each of the specified elements an appropriate and validated method should be used in relation to the limit to be applied...
General semi-quantitative heavy metal limit tests based on the precipitation at pH 3.5 of coloured metal sulfides are described in several publications (e.g. Ph. Eur.)."

(Guidline on the specifications limits for residues of metal catalyst- European Medicines Agency)

Reactions

Classical qualitative inorganic analysis is a method of analytical chemistry which seeks to find elemental composition of inorganic compounds. It is mainly focused on detecting ions in an aqueous solution. The solution is treated with various reagents to test for reactions characteristic of certain ions:

- reactions which form insoluble products, e. g. precipitates,
- reactions which give a characteristic color, e. g. colored complex ions,
- reactions which liberate gases, e. g. ammonia, carbon-dioxide.

Reactions

- **Specific** reaction are reactions which under certain conditions make it possible **to detect some ions in the presence of others** by the specific change in color, the formation of characteristic precipitate etc.
- A reaction is **selective** if it reacts in a **similar way** with **only few ions**.
- A reaction is **sensitive** if just a very small amount of ion gives an easily observable change.

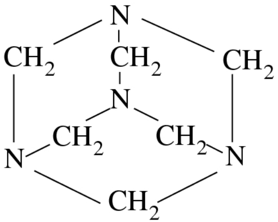
Sensitivity of reactions

Limiting concentration:
The smallest amount of ion (usually in μg) in 1 ml of solution that still gives a positive reaction in a particular test (ppm).

Detection limit:
The smallest amount of the ions (μg or ng) that can be detected by the method concerned.

Group reagents

- Hydrolysis:
  - CH_3COONa-NaCl *(pH$\sim 7-8$, acid-base reactions, ppt formation)*
  - hexametilenetetramine $(CH_2)_6N_4$ *(pH~ 5, acid-base reactions, ppt formation)*



$$C_6H_{12}N_4 + 6\,H_2O \rightleftharpoons 6HCHO + 4\,NH_3$$

Group reagents

Group reagents:

- HCl *(acid-base reactions, ppt formation)*
- Alkali hydroxides (OH^-) *(acid-base reactions, ppt formation, complex formation)*
- NH_3 *(acid-base reactions, ppt formation, complex formation)*
- H_2S *(ppt formation, complex formation, redox reactions)*
- $(NH_4)_2S$ and $(NH_4)_2S_x$ *(ppt formation, complex formation, redox reactions)*

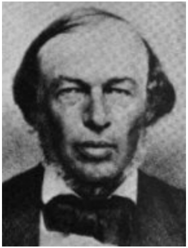
Group reagents

Group reagents:

- KI *(ppt formation, complex formation, redox reactions)*
- H_2SO_4 *(ppt formation, acid-base reactions)*
- Zn *(redox reactions)*
- $KMnO_4$ *(redox reactions)*
- I_2 sol. (I_3^-) *(redox reactions, ppt formation, complex formation)*

Classification of cations

Karl Remigius FRESENIUS (1818 - 1897)



Classification of cations

Group I

Cations which can be precipitated as sulfides from acidic solution (pH∼2) by H_2S; the precipitates are insoluble in $(NH_4)_2S$ and KOH.

Cu^{2+}, Ag^{+}, Cd^{2+}, Hg_2^{2+}, Hg^{2+}, Pb^{2+}, Bi^{3+}

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Group II

Cations which can be precipitated in acidic media with H_2S but the sulfides of are soluble in $(NH_4)_2S_x$ and KOH with formation of thiocomplexes.

As(III), As(V), Sb(III), Sb(V), Sn(II), Sn(IV)
{*Se(IV), V(V), Mo(VI), W(VI), Au(I,III), Pt(IV)*}

Classification of cations

Group III

Cations which can be precipitated with $(NH_4)_2S$ in neutral or slightly alkaline solutions, but cannot be precipitated with H_2S in acidic solutions.

Ni^{2+}, Co^{2+}, Fe^{2+}, Fe^{3+}, Mn^{2+}, Zn^{2+}, Cr^{3+}, Al^{3+}
{*Be^{2+}, TiO^{2+}, Tl^{+}, Ce(III,IV), UO_2^{2+}*}

Classification of cations

Group IV

The cations of Group IV cannot be precipitated with H_2S or $(NH_4)_2S$, but they form precipitate with $(NH_4)_2CO_3$ in neutral or slightly alkaline solutions, in the presence of NH_4Cl.

Ca^{2+}, Sr^{2+}, Ba^{2+}

Group V

The cations of Group V cannot be precipitated with any of above reagents.

Mg^{2+}, Na^{+}, K^{+}, NH_4^{+}
$\{Li^{+}\}$

Sulfide precipitates

$$2\ Ag^+ + S^{2-} \underset{dissolution}{\overset{precipitation}{\rightleftharpoons}} \underline{Ag_2S}$$

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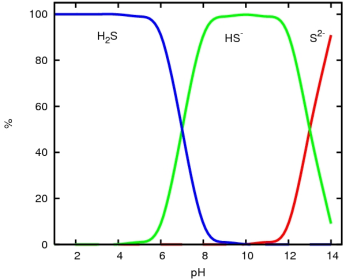
- Common ion effect: more reactants → precipitation
- pH effect: decrease of pH → dissolution
  $[S^{2-}]_t = [H_2S] + [HS^{-}] + [S^{2-}]$
  $([H_2S]_t = 0{,}1\ mol/dm^3$ and $pH = 2 \Rightarrow [S^{2-}] \approx 10^{-17} M)$



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$$K_{so} = [Ag^{+}]^2[S^{2-}]$$

- Complex formation: increase of ligand conc. $\rightarrow$ dissolution
  $[Ag^{+}]_t = [Ag^{+}] + [Ag(NH_3)^{+}] + [Ag(NH_3)_2^{+}]$

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- Complex formation: increase of ligand conc. $\rightarrow$ dissolution
  $[Ag^+]_t = [Ag^+] + [Ag(NH_3)^+] + [Ag(NH_3)_2^+]$
- Redox reactions: oxidation of sulfide ions $\rightarrow$ dissolution
  $H_2S + 2\ NO_3^- + 2\ H^+ \longrightarrow 3\ \underline{S} + 2\ NO + 4\ H_2O$
  (5 M HNO_3 $[S^{2-}] \approx 10^{-45}$M (! $N_A = 6 \times 10^{23}$))

Group I cations

Cation which can be precipitated as sulfides from acidic solution (pH∼2) by H_2S; the precipitates are insoluble in $(NH_4)_2S$ and KOH.

Ions	E_0/V (Ion/Metal)	Electronic config.	Pearson	Oxidation states
Cu^{2+}	0,34	$3d^9$	borderline	+2, +1, 0
Ag^+	0,80	$4d^{10}$	soft acid	+1, 0
Cd^{2+}	-0,40	$4d^{10}$	soft acid	+2, 0
Hg^{2+}	0,91	$5d^{10}$	soft acid	+2, +1, 0
Hg_2^{2+}	0,80	$5d^{10}6s^1$	soft acid	+2, +1, 0
Pb^{2+}	-0,13	$5d^{10}6s^2$	borderline	+4, +2, 0
Bi^{3+}	0,23	$5d^{10}6s^2$	borderline	+5, +3, 0

Group I cations

H_2S		+cc HNO_3
$\underline{CuS}$	brownish black	dissolves (redox reaction)
$\underline{Ag_2S}$	black	dissolves (redox reaction)
$\underline{PbS}$	black	dissolves (redox reaction)
$\underline{Bi_2S_3}$	black	dissolves (redox reaction)

$$3\ \underline{CuS} + 2\,NO_3{}^- + 8\,H^+ = 3\,Cu^{2+} + 3\ \underline{S} + 2\,NO + 4\,H_2O$$

Group I cations

H_2S		+cc HNO_3
$\underline{CdS}$	yellow	dissolves, but it dissolves even if the conc. of strong acid >0.5M in acid-base reaction)

$\underline{CdS} + 2\,H^+ = Cd^{2+} + 2\,H_2S$

Group I cations

H_2S		+cc HNO_3
Hg_2S (Hg + HgS)	black	does not dissolve, but dissolves in Br_2/HCl (redox+complex formation reaction)
HgS	black	does not dissolve, but Br_2/HCl, dissolves in Br_2/HCl (redox+complex formation reaction)

$$HgS + 4\,Br_2 + 4\,H_2O = HgBr_4{}^{2-} + SO_4{}^{2-} + 4\,Br^- + 8\,H^+$$

Group I cations

Group Ia:

Ag^{+}, Pb^{2+}, Hg_2^{2+}

White ppt with chloride ions (HCl, NaCl. . .):

$\underline{AgCl}$, $\underline{PbCl_2}$, $\underline{Hg_2Cl_2}$

Group I cations

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White ppt with chloride ions (HCl, NaCl...):

$\underline{AgCl}$, $\underline{PbCl_2}$, $\underline{Hg_2Cl_2}$

$$\underline{AgCl} \xrightarrow{NH_3} Ag(NH_3)_2^{+}$$
$$\underline{Hg_2Cl_2} \xrightarrow{NH_3} \underline{HgNH_2Cl} + \underline{Hg}$$
$$\underline{PbCl_2} \xrightarrow{NH_3} \text{no reaction}$$

Group I cations

	KI		$+I^-$
Cu^{2+}	$\underline{CuI} + I_2$	yellowish white	CuI_2^- ($KI_{(s)}$)

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Ag^+	$\underline{AgI}$	yellow	AgI_2^- $(KI_{(s)})$
Cd^{2+}	–		CdI_4^{2-}

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Cd^{2+}	–		CdI_4^{2-}
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Cd^{2+}	–		CdI_4^{2-}	
Hg_2^{2+}	$\underline{Hg_2I_2}$	greenish yellow	$HgI_4^{2-} + \underline{Hg}$	
Hg^{2+}	$\underline{HgI_2}$	red	HgI_4^{2-}	yellow

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Cd^{2+}	–		CdI_4^{2-}	
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Hg^{2+}	$\underline{HgI_2}$	red	HgI_4^{2-}	yellow
Pb^{2+}	$\underline{PbI_2}$	yellow	PbI_4^{2-} ($KI_{(s)}$)	

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Hg^{2+}	$\underline{HgI_2}$	red	HgI_4^{2-}	yellow
Pb^{2+}	$\underline{PbI_2}$	yellow	PbI_4^{2-} ($KI_{(s)}$)	
Bi^{3+}	$\underline{BiI_3}$ ($\underline{BiOI}$)	black	BiI_4^-	orange

Group I cations

	NaOH		$+OH^-$
Cu^{2+}	$\underline{Cu(OH)_2}$	light blue	–

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Hg_2^{2+}	$\underline{Hg_2O}$ ($\underline{Hg}$, $\underline{HgO}$)	black	–

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Hg^{2+}	$\underline{HgO}$	yellow	–

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Pb^{2+}	$\underline{Pb(OH)_2}$	white	$Pb(OH)_4^{2-}$

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Hg_2^{2+}	$\underline{Hg_2O}$ ($\underline{Hg}$, $\underline{HgO}$)	black	–
Hg^{2+}	$\underline{HgO}$	yellow	–
Pb^{2+}	$\underline{Pb(OH)_2}$	white	$Pb(OH)_4^{2-}$
Bi^{3+}	$\underline{Bi(OH)_3}$	white	–

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Hg_2^{2+}	$\underline{Hg(NH_2)Cl} + \underline{Hg}$	–
Hg^{2+}	$\underline{Hg(NH_2)Cl}$	–
	$\underline{HgO}\cdot\underline{Hg(NH_2)NO_3}$	

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Pb^{2+}	$\underline{Pb(OH)_2}$	–
Bi^{3+}	$\underline{Bi(OH)_3}$	–

Group I cations

Redox reactions

Ion	Oxidation	Reduction
Cu^{2+}	–	$Cu^{2+} \xrightarrow{Fe,Zn} \underline{Cu}$, $Cu^{2+} \xrightarrow{I^-} \underline{CuI} + I_2$ $Cu^{2+} \xrightarrow{CN^-} \underline{CuCN} + (CN)_2$

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Ag^{+}	–	$Ag^{+} \xrightarrow{Cu} \underline{Ag}$, $Ag(NH_3)_2^{+} \xrightarrow{formaldehide} \underline{Ag}$

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Cd^{2+}	–	$Cd^{2+} \xrightarrow{Zn} \underline{Cd}$

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Cd^{2+}	–	$Cd^{2+} \xrightarrow{Zn} \underline{Cd}$
Hg^{2+}	–	$Hg^{2+} \xrightarrow{Cu} \underline{Hg}$
		$HgCl_2 \xrightarrow{SnCl_4^{2-}} \underline{Hg_2Cl_2} \xrightarrow{SnCl_4^{2-}} \underline{Hg}$

Group I cations

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Ag^+	–	$Ag^+ \xrightarrow{Cu} \underline{Ag}$, $Ag(NH_3)_2^+ \xrightarrow{formaldehide} \underline{Ag}$
Cd^{2+}	–	$Cd^{2+} \xrightarrow{Zn} \underline{Cd}$
Hg^{2+}	–	$Hg^{2+} \xrightarrow{Cu} \underline{Hg}$
		$HgCl_2 \xrightarrow{SnCl_4^{2-}} \underline{Hg_2Cl_2} \xrightarrow{SnCl_4^{2-}} \underline{Hg}$
Hg_2^{2+}	$\underline{Hg_2Cl_2} \xrightarrow{Cl_2} HgCl_2$	
	$Hg_2^{2+} \xrightarrow{MnO_4^-} Hg^{2+}$	

Group I cations

Redox reactions

Ion	Oxidation	Reduction
Pb^{2+}	$\underline{Pb(OH)_2} \xrightarrow{OCl^-} \underline{PbO_2}$	$Pb^{2+} \xrightarrow{Zn} \underline{Pb}$

Group I cations

Redox reactions

Ion	Oxidation	Reduction
Pb^{2+}	$\underline{Pb(OH)_2} \xrightarrow{OCl^-} \underline{PbO_2}$	$Pb^{2+} \xrightarrow{Zn} \underline{Pb}$
Bi^{3+}	$\underline{Bi(OH)_3} \xrightarrow{OCl^-} \underline{BiO_2OH}$	$\underline{Bi(OH)_3} \xrightarrow{Sn(OH)_4^{2-}} \underline{Bi}$

Group I cations, analysis

Group reagents	Observation	Conclusions
Color	blue	Cu^{2+} and all the colourless ions

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+ heating	no ppt	no Ag^{+} and Hg_2^{2+} only Pb^{2+}

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	ppt does not dissolve	Ag^{+} and Hg_2^{2+}

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Hydrolysis	ppt	Bi^{3+}

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+ heating	no ppt	no Ag^{+} and Hg_2^{2+} only Pb^{2+}
	ppt does not dissolve	Ag^{+} and Hg_2^{2+}
Hydrolysis	ppt	Bi^{3+}
	no ppt	no Bi^{3+}

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NH_3	ppt	can be Bi^{3+}, Pb^{2+}, Hg^{2+}
		amine complexes ?!

Group I cations, analysis

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NH_3	ppt	can be Bi^{3+}, Pb^{2+}, Hg^{2+}
		amine complexes ?!
	no ppt	only Cu^{2+}, Ag^{+}, Cd^{2+}
		no Bi^{3+}, Pb^{2+}, Hg^{2+}

Group I cations, analysis

Group reagents	Observation	Conclusions
NH_3	ppt	can be Bi^{3+}, Pb^{2+}, Hg^{2+}
		amine complexes ?!
	no ppt	only Cu^{2+}, Ag^{+}, Cd^{2+}
		no Bi^{3+}, Pb^{2+}, Hg^{2+}
NaOH	ppt	can be Cu^{2+}, Bi^{3+}, Cd^{2+}, Hg^{2+}, Ag^{+}

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NaOH	ppt	can be Cu^{2+}, Bi^{3+}, Cd^{2+},
		Hg^{2+}, Ag^{+}
	no ppt	only Pb^{2+}

Group I cations, analysis

Group reagents	Observation	Conclusions
KI	colored ppt	BiI_3 black, HgI_2 red
	complexes	PbI_2 yellow, BiI_4^- orange
	no ppt	only Cd^{2+}

Group I cations, analysis

	Reagent, observation	products
Cu^{2+}	NH_3, blue	$Cu(NH_3)_4^{2+}$

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Ag^{+}	HCl white ppt can be dissolved in NH_3	$\underline{AgCl}\xrightarrow{NH_3}Ag(NH_3)_2^{+}$

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Cu^{2+}	NH_3, blue	$Cu(NH_3)_4^{2+}$
Ag^{+}	HCl white ppt can be dissolved in NH_3	$\underline{AgCl} \xrightarrow{NH_3} Ag(NH_3)_2^{+}$
Hg_2^{2+}	HCl white ppt, $+NH_3$ ppt become black	$\underline{Hg_2Cl_2} \xrightarrow{NH_3} HgNH_2Cl +$ $+ \underline{Hg}$

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Ag^+	HCl white ppt can be dissolved in NH_3	$\underline{AgCl} \xrightarrow{NH_3} Ag(NH_3)_2^+$
Hg_2^{2+}	HCl white ppt, $+NH_3$ ppt become black	$\underline{Hg_2Cl_2} \xrightarrow{NH_3} HgNH_2Cl +$ $+ \underline{Hg}$
Hg^{2+}	$SnCl_4^{2-}$ white ppt, in excess gray	$\underline{Hg_2Cl_2} \xrightarrow{SnCl_4^{2-}} \underline{Hg}$
	KI red ppt, that dissolves in excess	$\underline{HgI_2} \xrightarrow{I^-} HgI_4^{2-}$

Group I cations, analysis

	Reagent, observation	products
Pb^{2+}	H_2SO_4 white ppt	$\underline{PbSO_4}$
	KI yellow ppt.	$\underline{PbI_2}$

Group I cations, analysis

	Reagent, observation	products
Pb^{2+}	H_2SO_4 white ppt	$\underline{PbSO_4}$
	KI yellow ppt.	$\underline{PbI_2}$
Bi^{3+}	KI black ppt., in excess orange solution	$\underline{BiI_3} \xrightarrow{I^-} BiI_4^-$
	$Sn(OH)_4^{2-}$ black ppt	$\underline{Bi(OH)_3} \xrightarrow{Sn(OH)_4^{2-}} \underline{Bi}$
	hidrolysis, white ppt	$\underline{BiOCl}$

Group I cations, analysis

	Reagent, observation	products
Pb^{2+}	H_2SO_4 white ppt	$\underline{PbSO_4}$
	KI yellow ppt.	$\underline{PbI_2}$
Bi^{3+}	KI black ppt., in excess orange solution	$\underline{BiI_3} \xrightarrow{I^-} BiI_4^-$
	$Sn(OH)_4^{2-}$ black ppt	$\underline{Bi(OH)_3} \xrightarrow{Sn(OH)_4^{2-}} \underline{Bi}$
	hidrolysis, white ppt	$\underline{BiOCl}$
Cd^{2+}	(a) heating with Fe powder filtrate $+HCl+H_2S$ yellow ppt (b) NH_3, filtration + CN^- $+(NH_4)_2S$ yellow ppt	$\underline{CdS}$

Group I cations, analysis

Cd^{2+} and Cu^{2+} in presence of each other

1. $NH_3 \Rightarrow [Cu(NH_3)_4]^{2+}$ and $[Cd(NH_3)_4]^{2+}$
2. $KCN \Rightarrow [Cu(CN)_4]^{3-}$ and $[Cd(CN)_4]^{2-}$
3. $(NH_4)_2S \Rightarrow \underline{CdS}$

Group I cations, analysis

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2. $KCN \Rightarrow [Cu(CN)_4]^{3-}$ and $[Cd(CN)_4]^{2-}$
3. $(NH_4)_2S \Rightarrow \underline{CdS}$

1. iron powder $\Rightarrow \underline{Cu}$ and Cd^{2+}
2. $H_2S \Rightarrow \underline{CdS}$

Group I cations, analysis

Hg^{2+} and Bi^{3+} in presence of each other

1. CH_3COONa-NaCl or hexametilenetetramine ⇒ Hg^{2+}, $\underline{BiOCl}$
2. filtration
3. ppt + HOCl ⇒ $\underline{BiO_2(OH)}$
4. solution + $SnCl_4^{2-}$ ⇒ $\underline{Hg_2Cl_2}$ + $SnCl_4^{2-}$ ⇒ $\underline{Hg}$

Group II cations

The cations of Group II can be precipitated in acidic media with H_2S but the sulfides of are soluble in $(NH_4)_2S_x$ and KOH with formation of thiocomplexes.

Ion	Elektronic config.	Pearson	Oxidation number
As(III) H_3AsO_3, AsO_3^{3-}	$3d^{10}4s^2$	hard acid	+5, +3, 0, (-3)

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As(III) H_3AsO_3, AsO_3^{3-}	$3d^{10}4s^2$	hard acid	+5, +3, 0, (-3)
As(V) H_3AsO_4, AsO_4^{3-}	$3d^{10}$	hard acid	

Group II cations

Ion	Elektronic config.	Pearson	Oxidation number
Sb(III) $SbCl_4^-$	$4d^{10}4s^2$	borderline	+5, +3, 0, (-3)

Group II cations

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Sb(III)	$4d^{10}4s^2$	borderline	+5, +3, 0, (-3)
$SbCl_4^-$			
Sb(V)	$4d^{10}$	hard acid	
$SbCl_6^-$			

Group II cations

Ion	Elektronic config.	Pearson	Oxidation number
Sb(III)	$4d^{10}4s^2$	borderline	+5, +3, 0, (-3)
$SbCl_4^-$			
Sb(V)	$4d^{10}$	hard acid	
$SbCl_6^-$			
Sn(II)	$4d^{10}4s^2$	borderline	+4, +2, 0, (-4)
$SnCl_4^{2-}$			

Group II cations

Ion	Elektronic config.	Pearson	Oxidation number
Sb(III) $SbCl_4^-$	$4d^{10}4s^2$	borderline	+5, +3, 0, (-3)
Sb(V) $SbCl_6^-$	$4d^{10}$	hard acid	
Sn(II) $SnCl_4^{2-}$	$4d^{10}4s^2$	borderline	+4, +2, 0, (-4)
Sn(IV) $SnCl_6^{2-}$	$4d^{10}$	hard acid	

Group II cations

Sulfide precipitates

		$(NH_4)_2S$	$(NH_4)_2S_x$	KOH	cc HCl
As(V)	$\underline{As_2S_3}$+ $\underline{S}$ ($\underline{As_2S_5}$)	AsS_3^{3-}	AsS_4^{3-}	AsO_3^{3-} + AsS_3^{3-}	–

Group II cations

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		$(NH_4)_2S$	$(NH_4)_2S_x$	KOH	cc HCl
As(V)	$\underline{As_2S_3}$+ $\underline{S}$ ($\underline{As_2S_5}$)	AsS_3^{3-}	AsS_4^{3-}	AsO_3^{3-} + AsS_3^{3-}	–
As(III)	$\underline{As_2S_3}$	AsS_3^{3-}	AsS_4^{3-}	AsO_3^{3-} + AsS_3^{3-}	–

Group II cations

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		$(NH_4)_2S$	$(NH_4)_2S_x$	KOH	cc HCl
As(V)	$\underline{As_2S_3}$+ $\underline{S}$ ($\underline{As_2S_5}$)	AsS_3^{3-}	AsS_4^{3-}	AsO_3^{3-} + AsS_3^{3-}	–
As(III)	$\underline{As_2S_3}$	AsS_3^{3-}	AsS_4^{3-}	AsO_3^{3-} + AsS_3^{3-}	–
Sb(V)	$\underline{Sb_2S_3}$+ $\underline{S}$ $\underline{Sb_2S_5}$	SbS_3^{3-}	SbS_4^{3-}	$Sb(OH)_4^-$ + SbS_3^{3-} $Sb(OH)_6^-$	$Sb(Cl)_4^-$ $Sb(Cl)_6^-$

Group II cations

Sulfide precipitates

		$(NH_4)_2S$	$(NH_4)_2S_x$	KOH	cc HCl
As(V)	$\underline{As_2S_3}$+ $\underline{S}$ ($\underline{As_2S_5}$)	AsS_3^{3-}	AsS_4^{3-}	AsO_3^{3-} + AsS_3^{3-}	–
As(III)	$\underline{As_2S_3}$	AsS_3^{3-}	AsS_4^{3-}	AsO_3^{3-} + AsS_3^{3-}	–
Sb(V)	$\underline{Sb_2S_3}$+ $\underline{S}$ $\underline{Sb_2S_5}$	SbS_3^{3-}	SbS_4^{3-}	$Sb(OH)_4^-$ + SbS_3^{3-} $Sb(OH)_6^-$	$Sb(Cl)_4^-$ $Sb(Cl)_6^-$
Sb(III)	$\underline{Sb_2S_3}$	SbS_3^{3-}	SbS_4^{3-}	$Sb(OH)_4^-$ + SbS_3^{3-}	$Sb(Cl)_4^-$

Group II cations

Sulfide precipitates

		$(NH_4)_2S$	$(NH_4)_2S_x$	KOH	cc HCl
As(V)	$\underline{As_2S_3}$+ $\underline{S}$	AsS_3^{3-}	AsS_4^{3-}	AsO_3^{3-} + AsS_3^{3-}	–
	$(\underline{As_2S_5})$				
As(III)	$\underline{As_2S_3}$	AsS_3^{3-}	AsS_4^{3-}	AsO_3^{3-} + AsS_3^{3-}	–
Sb(V)	$\underline{Sb_2S_3}$+ $\underline{S}$	SbS_3^{3-}	SbS_4^{3-}	$Sb(OH)_4^-$ + SbS_3^{3-}	$Sb(Cl)_4^-$
	$\underline{Sb_2S_5}$			$Sb(OH)_6^-$	$Sb(Cl)_6^-$
Sb(III)	$\underline{Sb_2S_3}$	SbS_3^{3-}	SbS_4^{3-}	$Sb(OH)_4^-$ + SbS_3^{3-}	$Sb(Cl)_4^-$
Sn(IV)	$\underline{SnS_2}$	SnS_3^{2-}	SnS_3^{2-}	$Sn(OH)_6^{2-}$ + S^{2-}	$Sn(Cl)_6^{2-}$

Group II cations

Sulfide precipitates

		$(NH_4)_2S$	$(NH_4)_2S_x$	KOH	cc HCl
As(V)	$\underline{As_2S_3}$ + $\underline{S}$ ($\underline{As_2S_5}$)	AsS_3^{3-}	AsS_4^{3-}	AsO_3^{3-} + AsS_3^{3-}	–
As(III)	$\underline{As_2S_3}$	AsS_3^{3-}	AsS_4^{3-}	AsO_3^{3-} + AsS_3^{3-}	–
Sb(V)	$\underline{Sb_2S_3}$ + $\underline{S}$ $\underline{Sb_2S_5}$	SbS_3^{3-}	SbS_4^{3-}	$Sb(OH)_4^-$ + SbS_3^{3-} $Sb(OH)_6^-$	$Sb(Cl)_4^-$ $Sb(Cl)_6^-$
Sb(III)	$\underline{Sb_2S_3}$	SbS_3^{3-}	SbS_4^{3-}	$Sb(OH)_4^-$ + SbS_3^{3-}	$Sb(Cl)_4^-$
Sn(IV)	$\underline{SnS_2}$	SnS_3^{2-}	SnS_3^{2-}	$Sn(OH)_6^{2-}$ + S^{2-}	$Sn(Cl)_6^{2-}$
Sn(II)	$\underline{SnS}$	–	SnS_3^{2-}	$Sn(OH)_4^{2-}$ + S^{2-}	$Sn(Cl)_4^{2-}$