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The chemistry of each element is inexhaustible.

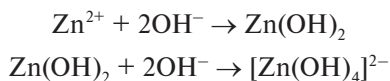
*Academician I.I. Chernyaev (1893–1966)*

## Chapter 15

# ANALYTICAL REACTIONS OF THE FOURTH, FIFTH, AND SIXTH ANALYTICAL GROUP CATIONS

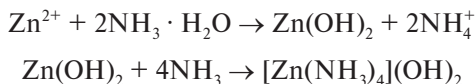
### 15.1. ANALYTICAL REACTIONS OF THE FOURTH ANALYTICAL GROUP CATIONS ACCORDING TO ACID-BASE CLASSIFICATION: $Zn^{2+}$ , $Al^{3+}$ , $Sn^{2+}$ , $Sn^{4+}$ , $As^{3+}$ , $As^{5+}$ , $Cr^{3+}$

**Analytical reactions of zinc  $Zn^{2+}$  cation.** *Reaction with alkalis.*  $Zn^{2+}$  react with alkali metal hydroxides forming white zinc hydroxide  $Zn(OH)_2$  precipitate, which is soluble in excess alkali with the formation of colorless hydroxo-complex  $[Zn(OH)_4]^{2-}$ :



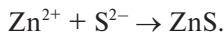
*Procedure.* Zinc chloride  $ZnCl_2$  solution (5–6 drops) is placed in a test tube, and NaOH solution (1–2 drops) is added to it. A white precipitate of zinc hydroxide is formed. NaOH solution is continued to be added by drops while stirring the test tube contents. The precipitate dissolves.

*Reaction with ammonia solution.* Ammonia, similar to alkalis, initially reacts with  $Zn^{2+}$  cations forming white zinc hydroxide precipitate, which, during further addition of ammonia solution, is dissolved with the formation of colorless zinc ammonia complex  $[Zn(NH_3)_4]^{2+}$ :



The *procedure* is similar to the previous one.

*Reaction with sulfide ions (pharmacopeial).*  $\text{Zn}^{2+}$  cations react with sulfide ions  $\text{S}^{2-}$  in neutral, slightly acidic, or slightly alkaline medium ( $2 \leq \text{pH} \leq 9$ ) forming white zinc sulfide  $\text{ZnS}$  precipitate:



The precipitate is insoluble in acetic acid, but soluble in  $\text{HCl}$  solutions and other mineral acids. The reaction is often performed in acetic acid medium, since under these conditions the remaining cations of the fourth analytical group, except for tin(II), do not interfere with  $\text{Zn}^{2+}$  detection.

*Procedure.* 1–2 drops of freshly prepared ammonium sulfide  $(\text{NH}_4)_2\text{S}$  solution are added to 2–3 drops of  $\text{ZnCl}_2$  solution. A white precipitate of zinc sulfide is formed.

*Reaction with potassium hexacyanoferrate(II) (pharmacopeial).*  $\text{Zn}^{2+}$  cations react with  $\text{K}_4[\text{Fe}(\text{CN})_6]$  in neutral or slightly acidic medium (reaction rate is higher with heating) forming a white precipitate of mixed potassium and zinc hexacyanoferrate (II)  $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$ :

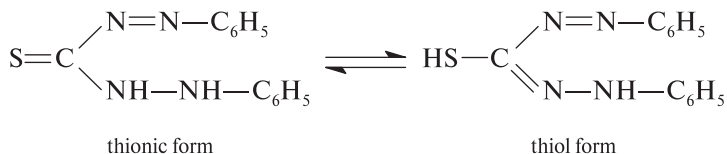


The precipitate is insoluble in diluted  $\text{HCl}$ , but soluble in alkalis, so the reaction cannot be performed in alkaline medium. All cations, which form slightly soluble ferrocyanides, interfere with detection.  $\text{Al}^{3+}$  and  $\text{Cr}^{3+}$  cations do not interfere with detection. Limit concentration of detectable zinc cations is equal to  $\sim 1 \mu\text{g}/\text{ml} = 10^{-6} \text{g}/\text{ml}$ .

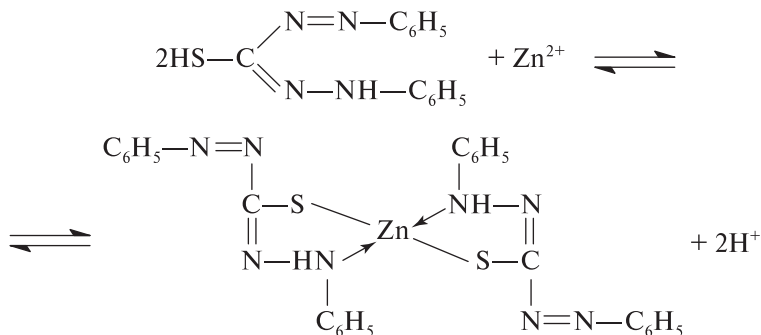
*Procedure.* 5–6 drops of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  solution are added to a test tube containing 5–10 drops of  $\text{ZnCl}_2$  solution. The mixture is heated to boiling. A white precipitate of potassium and zinc hexacyanoferrate(II) is formed.

*Reaction with dithizone (diphenylthiocarbazone).* Mixing of chloroform dithizone solution (extraction reagent) with an aqueous alkaline solution comprising  $\text{Zn}^{2+}$  cations leads to the formation of red dithizonate complex, which is extracted from the aqueous phase into the organic one. The chloroform layer turns more intense red than the aqueous one.

Reaction behavior can be *presumably* described by the following scheme. Tautomeric equilibrium between thionic and thiol forms is established in dithizone solutions:



The thiol form is a weak dibasic acid capable of losing hydrogen ions, primarily from its SH group, and of forming complexes with metal complexing ions. If only one proton is lost, then the reaction with zinc cations leads to the formation of intracomplex compound comprising two dithizonate anions.

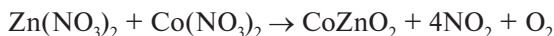


The presence of alkali facilitates a shift in equilibrium to the right due to the binding of the released hydrogen ions to water molecules.

The reaction is highly sensitive: detection limit is equal to 0.025  $\mu\text{g}$ . Allows detecting zinc cations at very low concentrations. Cations which also form dithizonate complexes ( $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Sn(II)}$ , etc.), interfere with detection.

*Procedure.*  $\text{ZnCl}_2$  solution (5–10 drops) is placed in a test tube, and several drops of  $\text{NaOH}$  solution are gradually added until the dissolution of the formed white zinc hydroxide precipitate, and  $\sim 5$  drops of chloroform dithizone solution is added to it. The test tube is shaken several times. The chloroform layer turns red after separation of a mixture.

“*Rinman’s green*” formation reaction. Heating a mixture of zinc nitrate  $\text{Zn(NO}_3)_2$  and cobalt nitrate  $\text{Co(NO}_3)_2$  leads to the formation of mixed cobalt and zinc oxide  $\text{CoZnO}_2$  (green color), which is so-called “*Rinman’s green*”:

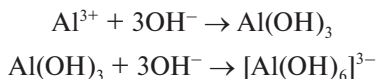


*Procedure.*  $\sim 5$  drops of  $\text{Zn(NO}_3)_2$  solution and  $\sim 5$  drops of  $\text{Co(NO}_3)_2$  solution are mixed in a test tube or a porcelain crucible. The mixture is heated to boiling and boiled for about a minute. A filter paper strip is moistened with the hot solution, dried, and ignited in a porcelain crucible on a gas burner. Green ash is formed.

*Other reactions of zinc cations.*  $\text{Zn}^{2+}$  cations form precipitates of various composition during the following reactions in solutions: white zinc tetraiodanomercurate(II)  $\text{Zn[Hg(SCN)}_4]$  in reaction with ammonium tetraiodanomercurate(II)  $(\text{NH}_4)_2[\text{Hg(SCN)}_4]$ ; light blue  $\text{ZnCo[Hg(SCN)}_4]$

in reaction with cobalt chloride  $\text{CoCl}_2$  and  $(\text{NH}_4)_2[\text{Hg}(\text{SCN})_4]$ ; white  $\text{Zn}_3(\text{PO}_4)_2$  (soluble in acids and ammonia) in reaction with  $\text{Na}_2\text{HPO}_4$ , and less soluble white  $\text{NH}_4\text{ZnPO}_4$  (soluble in acids, alkalis, and ammonia) during the same reaction in the presence of ammonia; a white basic salt precipitate of variable composition in reaction with sodium or potassium carbonate; yellow  $\text{ZnCrO}_4$  (soluble in acids and alkalis) in reaction with  $\text{K}_2\text{CrO}_4$ . Zinc cations also form precipitates of complex compounds with various organic reagents.

**Analytical reactions of aluminum  $\text{Al}^{3+}$  cation.** *Reaction with alkalis.*  $\text{Al}^{3+}$  cations react with alkalis in solutions forming white aluminum hydroxide  $\text{Al}(\text{OH})_3$  precipitate, which is soluble in excess of alkali with the formation of hydroxocomplex  $[\text{Al}(\text{OH})_6]^{3-}$  (sometimes,  $[\text{Al}(\text{OH})_4]^-$  composition is attributed to aluminum hydroxocomplexes in solution):



The most complete precipitation of aluminum hydroxide occurs at  $\text{pH} \approx 5-6$ .  $\text{Al}(\text{OH})_3$  precipitate is soluble in acids but insoluble in ammonia.

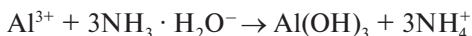
If ammonium salts are added to an alkaline solution (especially with heating) obtained after aluminum hydroxide dissolution, then aluminum hydroxocomplexes are decomposed, and aluminum hydroxide is precipitated again:



*Procedure.* Aluminum chloride  $\text{AlCl}_3$  solution (3–5 drops) is placed in a test tube, and  $\text{NaOH}$  solution is added by drops. A white precipitate of aluminum hydroxide is formed.  $\text{NaOH}$  solution is continued to be added by drops. The precipitate dissolves.

A few crystals of ammonium chloride are added to the solution, and the mixture is heated. Aluminum hydroxide is precipitated again.

*Reaction with ammonia.*  $\text{Al}^{3+}$  cations form a white amorphous precipitate of aluminum hydroxide in reaction with ammonia or alkalis:



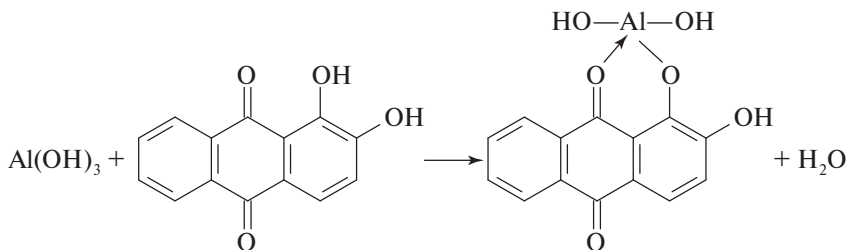
The precipitate is insoluble in excess of ammonia solution (contrary to alkalis). The *procedure* is similar to the previous one.

*Reaction with cobalt nitrate — formation of Thenard's blue (pharmacoceial).* During ignition of aluminum salt moistened with a *diluted* cobalt nitrate  $\text{Co}(\text{NO}_3)_2$  solution, mixed aluminum and cobalt oxide (cobalt aluminate)  $\text{Co}(\text{AlO}_2)_2$  is formed (blue color), which is so-called "Thenard's blue":



*Procedure.* Initially, a filter paper strip is moistened with 1–2 drops of aluminum sulfate  $\text{Al}_2(\text{SO}_4)_3$  solution, and then with 1–2 drops of *diluted* cobalt nitrate solution. The paper is dried, placed in a porcelain crucible, and ignited on a gas burner. Blue ash (“Thenard’s blue”) is formed.

*Reaction with alizarin.* Alizarin (1,2-dioxoanthraquinone) as well as some of its derivatives, during reactions with  $\text{Al}^{3+}$  cations in ammonia medium form slightly soluble complexes, so-called “aluminum lacquers” (bright red color). The reaction with alizarin proceeds according to the following scheme:



The complex is stable in acetic acid medium. The reaction is highly sensitive: detection limit is equal to 0.5  $\mu\text{g}$ . Cations which also form complexes with alizarin ( $\text{Zn}^{2+}$ ,  $\text{Sn(II)}$ ,  $\text{Cr}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{3+}$ , etc.), interfere with detection.

The reaction can be performed by drop method on a filter paper.

*Procedure.* 1–2 drops of aluminum salt solution is applied to a filter paper sheet. The paper is held in ammonia vapors (over a flask with concentrated ammonia solution). Contact of ammonia vapors with a wet spot leads to formation of aluminum hydroxide on paper.

A drop of alizarin solution is applied to a spot, and the paper is held again in ammonia vapors. Initially, the spot turns purple (alizarin background color). The paper is slightly dried, 1–2 drops of acetic acid solution is applied to it, and the paper is dried again. The spot turns pinkish-red.

If other cations, which also produce complexes with alizarin, are present in the solution simultaneously with aluminum cations, then drop reaction with alizarin is performed on a filter paper impregnated with potassium ferrocyanide  $\text{K}_4[\text{Fe}(\text{CN})_6]$  solution. When a drop of the solution is applied to such paper, slightly soluble ferrocyanides of interfering cations, which form a dark spot, are formed, while  $\text{Al}^{3+}$  cations, which do not form ferrocyanide precipitate, pass to spot periphery with the solvent after addition of a water drop, and form aluminum alizarin complex after treatment with ammonia vapors. As the paper dries, the violet alizarin background disappears, while aluminum lacquer remains red (also refer to Chapter 13, section 13.2.4 “Detection of aluminum cations”).

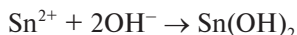
*Reaction with aluminon.*  $\text{Al}^{3+}$  cation reacts with aluminon (ammonium salt of aurintricarboxylic acid, which is denoted  $\text{NH}_4\text{L}$  for brevity) forming red complex (apparently, of composition  $\text{Al}(\text{OH})_2\text{L}$ ) in acetic acid or ammonia medium. The exact structure of the complex in solution is unknown.

The reaction is highly sensitive.  $\text{Ca}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$  cations, which also form colored complexes with aluminon, interfere with detection.

*Procedure.* Aluminum salt solution (3–4 drops), acetic acid solution (2–3 drops), and 0.01% aluminon solution (3–5 drops) are placed in a test tube. The mixture is heated on a water bath, a few drops of ammonia solution are added until the alkaline reaction (litmus paper test), and 2–3 drops of ammonium carbonate solution are added. A red flocculent precipitate is formed.

*Other reactions of aluminum cations.*  $\text{Al}^{3+}$  cations also form precipitates during the following reactions in solutions: white  $\text{AlPO}_4$  in reaction with  $\text{Na}_2\text{HPO}_4$ , white  $\text{CH}_3\text{COOAl}(\text{OH})_2$  in reaction with  $\text{CH}_3\text{COONa}$ , yellow-green  $[\text{Al}(\text{Ox})_3]$  in reaction with oxyquinoline (short designation is  $\text{HOx}$ ), and also react with other inorganic and organic reagents.

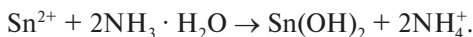
**Analytical reactions of tin(II) cation.** *Reaction with alkalis.* Tin(II) compounds react with alkalis forming white tin(II) hydroxide  $\text{Sn}(\text{OH})_2$  precipitate from solutions, which is soluble in excess of the reagent with the formation of hydroxocomplex  $[\text{Sn}(\text{OH})_4]^{2-}$ :



$\text{Sn}(\text{OH})_2$  precipitate is soluble in acids.

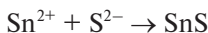
*Procedure.* A few drops of tin(II) salt solution (usually in hydrochloric acid) is placed in a test tube, and  $\text{NaOH}$  solution is added by drops: initially until the formation of white  $\text{Sn}(\text{OH})_2$  precipitate, and then until its dissolution.

*Reaction with ammonia.* Addition of ammonia solution to a solution containing tin (II) leads to the formation of white tin hydroxide  $\text{Sn}(\text{OH})_2$  precipitate, which is insoluble in excess ammonia:



The reaction *procedure* is similar to the previous one.

*Reaction with sulfide ions.* The reaction between tin(II) and sulfide ions  $\text{S}^{2-}$  leads to precipitation of dark-brown tin(II) sulfide  $\text{SnS}$  from the solution:



The precipitate is insoluble in alkalis, as well as in excess of sodium sulfide solution.

*Procedure.* A few drops of sodium sulfide  $\text{Na}_2\text{S}$  solution (or ammonium sulfide  $(\text{NH}_4)_2\text{S}$  solution, or hydrogen sulfide water) are added to a few drops of tin(II) salt solution. A brown precipitate of tin(II) sulfide  $\text{SnS}$  is formed.

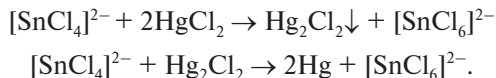
*Reaction with bismuth(III) salts.* Tin(II) is a good reducing agent. Thus, it reacts with bismuth(III) in alkaline medium reducing bismuth(III) to metallic bismuth and oxidizing itself to tin(IV):



Metallic bismuth is released in a finely dispersed state, forming a black precipitate.

*Procedure.* Tin(II) salt solution (3–5 drops) is placed in a test tube, and  $\text{NaOH}$  solution is added by drops. A white precipitate  $\text{Sn}(\text{OH})_2$  is initially formed, which is dissolved during further addition of  $\text{NaOH}$ . 1–2 drops of bismuth(III) nitrate solution are added to the resulting alkaline solution. As the mixture is stirred, the black precipitate of metallic bismuth is formed.

*Reaction with mercury(II) chloride.* Tin(II) reduces mercury(II) compounds to metallic mercury, which is released, similar to metallic bismuth, in the form of a black precipitate. The reaction proceeds in two stages. Initially, mercury(II) is reduced to mercury(I), and then to metallic mercury:



*Procedure.* Hydrochloric tin(II) chloride solution (3–5 drops) is placed in a test tube, and 2–3 drops of mercury(II) chloride solution (sublimite  $\text{HgCl}_2$ ) are added to it. A white precipitate of calomel  $\text{Hg}_2\text{Cl}_2$  is formed, which is gradually blackens due to released metallic mercury.

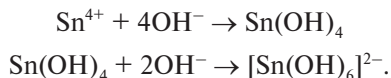
*Other reactions of tin(II).* Tin(II) compounds react with ammonium molybdate forming so-called “molybdenum blue” (the solution turns blue); with  $\text{Na}_2\text{HPO}_4$  forming white  $\text{Sn}_3(\text{PO}_4)_2$  precipitate (soluble in acids and alkalis); with  $\text{FeCl}_3$ , reducing iron(III) to iron(II), and in the presence of potassium hexacyanoferrate(III)  $\text{K}_3[\text{Fe}(\text{CN})_6]$ , the solution immediately turns blue due to the formation of Turnbull’s blue. Other reactions of tin(II) with inorganic and organic reagents are known.

**Analytical reactions of tin(IV) cation.** Tin(IV) is usually detected after preliminarily reduction to tin(II) by metallic iron, magnesium, aluminum, etc. Then, reactions, which are specific for tin(II), are performed, as described in the previous section.

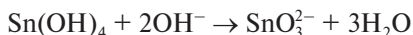
*Reaction of tin(IV) with alkalis.* As the alkali solution is slowly added (by drops) to the solution containing tin(IV), a white  $\text{Sn}(\text{OH})_4$  precipitate



is initially formed, which is called  $\alpha$ -stannic acid — composition of the precipitate can also be represented by formula  $\text{H}_2\text{SnO}_3 \cdot \text{H}_2\text{O}$ . The *freshly formed precipitate* is dissolved in excess of alkali solution forming tin(IV) hydroxo-complexes of composition  $[\text{Sn}(\text{OH})_6]^{2-}$ . The reaction can be described by the following conditional scheme:



Sometimes (especially in “old” guidelines) the latter reaction is represented as

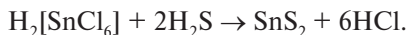


with the formation of stannate ions  $\text{SnO}_3^{2-}$ . Both schemes are equivalent, since formula  $\text{SnO}_3^{2-} \cdot 3\text{H}_2\text{O}$  also corresponds to hydroxocomplex.

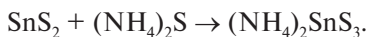
As the solution with  $\alpha$ -stannic acid precipitate stands, the latter gradually “ages” and transforms into  $\beta$ -stannic acid  $\text{H}_2\text{SnO}_3$ , which is poorly soluble in alkalis and hydrochloric acid.

*Procedure.* Tin(IV) salt solution (3–4 drops) is placed in a test tube, and NaOH solution is added by drops. Initially, a white precipitate is formed, which is dissolved after the addition of alkali solution excess.

*Reaction with sulfide ions.* Passing hydrogen sulfide  $\text{H}_2\text{S}$  through acidic solutions containing tin(IV), or adding hydrogen sulfide water to them, leads to the formation of yellow tin(IV) sulfide  $\text{SnS}_2$  precipitate:



Tin(IV) sulfide precipitate, *contrary to tin(II) sulfide*, is soluble in excess of ammonium sulfide  $(\text{NH}_4)_2\text{S}$  or sodium sulfide  $\text{Na}_2\text{S}$  with the formation of thiosalts:



Therefore, the addition of ammonium or sodium sulfides solutions to acidic solutions of tin(IV) salts does not lead to precipitation of tin(IV) sulfide.

*Procedure.* Hydrochloric tin(IV) salt solution (3–4 drops) is placed in a test tube, and hydrogen sulfide water is added by drops. A yellow precipitate of tin(IV) sulfide is formed.

The precipitate is dissolved after addition of sodium or ammonium sulfide solution to the mixture.

*Reaction of tin(IV) reduction to tin(II).* Various reducing agents can be used to reduce tin(IV) to tin(II). The reaction of tin(IV) reduction by metal-

lic iron in hydrochloric acid medium proceeds according to the following scheme:



Tin(II), obtained after tin(IV) reduction, is detected by reactions with bismuth (III) salts, mercury (II) chloride, etc.

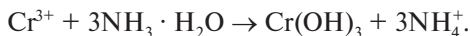
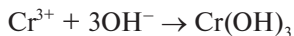
*Procedure.* Tin(IV) salt solution (8–10 drops) and concentrated HCl (2–3 drops) are placed in a test tube, some iron powder or iron filings are added, and the mixture is heated to boiling. After 3–5 minutes, the remaining metallic iron is filtered, and tin(II) is detected in the filtrate, as described above in the previous section.

*Other reactions of tin(IV).* Tin(IV) forms colored or slightly soluble complexes with various organic reagents. Thus, tin(IV) reacts with cupferron  $\text{C}_6\text{H}_5\text{N}(\text{NO})\text{ONH}_4$  in acidic medium forming a slightly soluble precipitate of tin(IV) cupferronate, whose composition, apparently, corresponds to the formula  $[\text{Sn}\{\text{C}_6\text{H}_5\text{N}(\text{NO})\text{O}\}_4]$ .

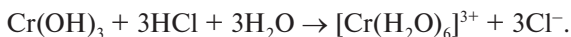
Tin(IV) react with rubidium and cesium chlorides forming slightly soluble salts of composition  $\text{Rb}_2[\text{SnCl}_6]$  and  $\text{Cs}_2[\text{SnCl}_6]$ . The reaction is performed as microcrystalloscopic.

**Analytical reactions of arsenic(III) and arsenic(V).** Arsenic(III) and arsenic(V) are usually detected in the form of arsenite ions  $\text{AsO}_3^{3-}$  ( $\text{AsO}_2^-$ ) and arsenate ions  $\text{AsO}_4^{3-}$ , respectively, i.e., in the form of *anions*, but not in the form of cations. Therefore, the reactions of these cations are described below in Chapter 16, which is dedicated to the consideration of analytical reactions of anions.

**Analytical reactions of chromium  $\text{Cr}^{3+}$  cation.** *Reactions with alkalis and ammonia.*  $\text{Cr}^{3+}$  cations react with alkali or ammonia solutions forming grey-green or blue-violet chromium(III) hydroxide  $\text{Cr}(\text{OH})_3$  precipitate.



$\text{Cr}(\text{OH})_3$  precipitate, which exhibits amphoteric properties, is soluble in both alkalis and acids:



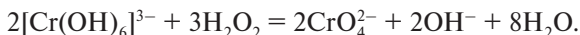
Chromium(III) hydroxide is only partially soluble in ammonia solution forming purple complex  $[\text{Cr}(\text{NH}_3)_6]^{3+}$ :



*Procedure.* A few drops of chromium(III) salt are placed in each of two test tubes. The following reagents are added by drops to the test tubes: NaOH solution is added to the first test tube, ammonia solution is added to the second one until the formation of grey-green (or blue-purple) precipitate. If NaOH solution is added (by drops) to the first test tube and mixed, then the precipitate is dissolved forming green solution. Addition (by drops) of ammonia solution to the second test tube leads only to partial dissolution of the precipitate. The solution above the precipitate turns purple.

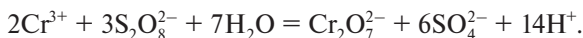
*Oxidation reactions of chromium(III) cations to chromate ions and dichromate ions.*  $\text{Cr}^{3+}$  cations react with oxidizing agents (hydrogen peroxide, potassium permanganate, etc.), oxidizing to chromate anions  $\text{CrO}_4^{2-}$  or dichromate anions  $\text{Cr}_2\text{O}_7^{2-}$ , which color the solution yellow (due to chromate ions), or yellowish-orange (due to dichromate ions).

a) *Oxidation with hydrogen peroxide.* Oxidation with hydrogen peroxide  $\text{H}_2\text{O}_2$  is usually performed in alkaline medium with heating:



*Procedure.* Chromium(III) salt solution (2–3 drops) is placed in a test tube, 2 mol/L NaOH solution (4–5 drops) and 3%  $\text{H}_2\text{O}_2$  solution (2–3 drops) are added, and the tube is heated until a green solution (due to aquacomplexes  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ ) turns yellow (due to chromate ions  $2\text{CrO}_4^{2-}$ ). The solution is preserved to perform the reaction of perchromic acid formation (see below).

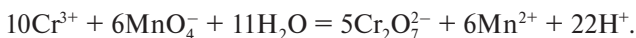
b) *Oxidation with ammonium persulfate.*  $\text{Cr}^{3+}$  cation in acidic medium is oxidized with persulfate ion  $\text{S}_2\text{O}_8^{2-}$  to dichromate ion  $\text{Cr}_2\text{O}_7^{2-}$ , which colors the solution yellow-orange:



The reaction is accelerated in the presence of silver(I) salts traces, which act as a catalyst.

*Procedure.* Ammonium persulfate  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  solution (5–6 drops), 1 mol/L sulfuric acid  $\text{H}_2\text{SO}_4$  solution (1 drop), one drop of silver nitrate  $\text{AgNO}_3$  solution, and 2–3 drops of chromium(III) sulfate or nitrate solution (but not chloride, since chloride ions are also oxidized!) are sequentially placed in a test tube. The solution turns yellow-orange (due to dichromate ions  $\text{Cr}_2\text{O}_7^{2-}$ ).

c) *Oxidation with potassium permanganate.* Potassium permanganate  $\text{KMnO}_4$  oxidizes  $\text{Cr}^{3+}$  cation to dichromate ion with heating in sulfuric acid medium, which can be described by the following scheme:



The solution turns yellow-orange.

Addition of excess potassium permanganate solution leads to oxidation of manganese(II) cation  $\text{Mn}^{2+}$  and formation of brown  $\text{MnO}(\text{OH})_2$  precipitate:

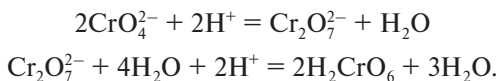


Increase of medium acidity prevents the formation of  $\text{MnO}(\text{OH})_2$  precipitate.

*Procedure.* 3–4 drops of chromium(III) sulfate or nitrate (but not chloride!) solution are placed in a test tube, 3–4 drops of sulfuric acid solution are added, the mixture is heated, and  $\text{KMnO}_4$  solution is added by drops to it until the solution turns yellow-orange. Further addition of  $\text{KMnO}_4$  solution leads to the formation of brown  $\text{MnO}(\text{OH})_2$  precipitate.

*Reaction of perchromic acid formation.* Oxidation of  $\text{Cr}^{3+}$  cations to chromate or dichromate ions is confirmed, in addition to solution color identification, by the reaction of perchromic acid  $\text{H}_2\text{CrO}_6$  formation.

Addition of hydrogen peroxide  $\text{H}_2\text{O}_2$  to the solution containing chromate ion (which is formed, for example, during oxidation of  $\text{Cr}^{3+}$  cations by hydrogen peroxide, as described above) in *sulfuric acid medium* leads to the formation of blue perchromic acid  $\text{H}_2\text{CrO}_6$ :



Perchromic acid in aqueous solutions is unstable and decomposes to chromium(III) compounds, which color the solution green. However, it is relatively stable in solutions of organic solvents. Therefore, it is usually extracted from aqueous solution with an organic extractant (diethyl ether, isoamyl alcohol, etc.), which turns intense blue.

The reaction is specific for chromium compounds and highly sensitive: detection limit is equal to 2.5  $\mu\text{g}$ .

*Procedure.* The yellow solution obtained during oxidation of chromium(III) with hydrogen peroxide (see above), is heated to boiling, cooled under a stream of cold water, and then hydrogen peroxide (5 drops), amyl alcohol and diethyl ether mixture (~0.5 ml) are added and mixed thoroughly, after which  $\text{H}_2\text{SO}_4$  (1 mol/L) solution is added by drops. The upper organic layer turns intense blue.

*Other reactions of chromium(III) cations.*  $\text{Cr}^{3+}$  cation reacts with sodium hydrogen phosphate  $\text{Na}_2\text{HPO}_4$  forming green chromium phosphate  $\text{CrPO}_4$  precipitate, which is soluble in acids and alkalis; with arsenites and arsenates forming slightly soluble arsenite  $\text{CrAsO}_3$  and arsenate  $\text{CrAsO}_4$  precipitates, respectively.

Some analytical reaction products of the fourth analytical group cations are described in table 15.1.

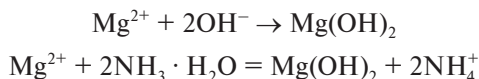
Table 15.1. Some analytical reaction products of the fourth analytical group cations according to acid-base classification

Reagents	Analytical reaction products					
	Zn <sup>2+</sup>	Al <sup>3+</sup>	Sn(II)	As(III)	As(V)	Cr <sup>3+</sup>
NaOH, KOH	White precipitate Zn(OH) <sub>2</sub>	White precipitate Al(OH) <sub>3</sub>	White precipitate Sn(OH) <sub>2</sub>	AsO <sub>3</sub> <sup>3-</sup> In solution	AsO <sub>4</sub> <sup>3-</sup> In solution	Grey-Green precipitate Cr(OH) <sub>3</sub>
Soluble in excess of alkali solutions						
NaOH + H <sub>2</sub> O <sub>2</sub>	[Zn(OH) <sub>4</sub> ] <sup>2-</sup> In solution	[Al(OH) <sub>4</sub> ] <sup>-</sup> , [Al(OH) <sub>6</sub> ] <sup>3-</sup> In solution	[Sn(OH) <sub>6</sub> ] <sup>2-</sup> In solution	AsO <sub>3</sub> <sup>3-</sup> In solution	AsO <sub>4</sub> <sup>3-</sup> In solution	Yellow solution CrO <sub>4</sub> <sup>2-</sup>
Solution NH <sub>3</sub>	White precipitate Zn(OH) <sub>2</sub>	White precipitate Al(OH) <sub>3</sub>	White precipitate Sn(OH) <sub>2</sub>	AsO <sub>3</sub> <sup>3-</sup> In solution	AsO <sub>4</sub> <sup>3-</sup> In solution	Grey-Green precipitate Cr(OH) <sub>3</sub>
Na <sub>2</sub> CO <sub>3</sub> , K <sub>2</sub> CO <sub>3</sub>	White precipitate (ZnOH) <sub>2</sub> CO <sub>3</sub>	White precipitate Al(OH) <sub>3</sub>	White precipitate Sn(OH) <sub>2</sub>	AsO <sub>3</sub> <sup>3-</sup> In solution	AsO <sub>4</sub> <sup>3-</sup> In solution	Grey-Green precipitate Cr(OH) <sub>3</sub>
Na <sub>2</sub> HPO <sub>4</sub>	White precipitate Zn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> . Soluble in alkalis, ammonia, in acetic acid	White precipitate AlPO <sub>4</sub> . Soluble in alkalis. Insoluble in acetic acid	White precipitate SnHPO <sub>4</sub> . Sn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	AsO <sub>3</sub> <sup>3-</sup> In solution	AsO <sub>4</sub> <sup>3-</sup> In solution	Green precipitate CrPO <sub>4</sub> . Soluble in alkalis. Insoluble in acetic acid
(NH <sub>4</sub> ) <sub>2</sub> S	White precipitate ZnS	White precipitate Al(OH) <sub>3</sub>	Brown-black precipitate SnS	Yellow precipitate As <sub>2</sub> S <sub>3</sub> . Soluble in excess (NH <sub>4</sub> ) <sub>2</sub> S	Yellow precipitate As <sub>2</sub> S <sub>3</sub> . Soluble in excess (NH <sub>4</sub> ) <sub>2</sub> S	Grey-green (grey-purple) precipitate Cr(OH) <sub>3</sub>
H <sub>2</sub> S + HCl	White precipitate ZnS		Brown-black precipitate SnS	Yellow precipitate As <sub>2</sub> S <sub>3</sub> . Soluble in excess of reagent	Yellow precipitate As <sub>2</sub> S <sub>3</sub> . Soluble in excess of reagent	Not colored
Flame color	Not colored	Not colored	Blue	Pale-blue	Pale-blue	Not colored

## 15.2. ANALYTICAL REACTIONS OF THE FIFTH ANALYTICAL GROUP CATIONS ACCORDING TO ACID-BASE

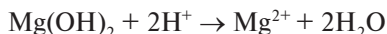
**CLASSIFICATION:**  $\text{Mg}^{2+}$ ,  $\text{Sb}^{3+}$ ,  $\text{Sb}^{5+}$ ,  $\text{Bi}^{3+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$

**Analytical reactions of magnesium  $\text{Mg}^{2+}$  cation.** *Reactions with alkalis and ammonia.* Under the action of alkalis and ammonia,  $\text{Mg}^{2+}$  cations form white amorphous magnesium hydroxide  $\text{Mg}(\text{OH})_2$  precipitate:



In the reaction with ammonia,  $\text{Mg}^{2+}$  cations are partially precipitated in the form of  $\text{Mg}(\text{OH})_2$ , since magnesium hydroxide is partially dissolved in ammonium salts solutions (especially in concentrated) due to shift of the latter equilibrium to the left with an increase in the concentration of ammonium cations.

$\text{Mg}(\text{OH})_2$  is insoluble in alkalis, but soluble in acids:



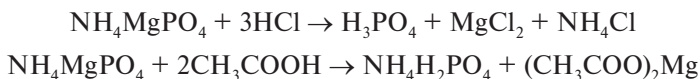
*Procedure.* Magnesium salt solution (5–6 drops to each test tube) is added, and  $\text{NaOH}$  solution is added by drops to one test tube (ammonia solution — to another test tube) until the formation of a white amorphous precipitate.

*Reaction with sodium hydrogen phosphate (pharmacopeial).*  $\text{Mg}^{2+}$  cations react with sodium hydrogen phosphate in the presence of ammonium cations and ammonia (ammonia buffer) forming a white finely crystalline precipitate of magnesium ammonium phosphate  $\text{NH}_4\text{MgPO}_4$ :



The reaction between  $\text{Mg}^{2+}$  cations and sodium hydrogen phosphate in the *absence* of ammonium cations and ammonia leads to the formation of a white amorphous precipitate of magnesium hydrogen phosphate  $\text{MgHPO}_4$ .

Magnesium ammonium phosphate precipitate is soluble in mineral acids and acetic acid:



The reaction of  $\text{NH}_4\text{MgPO}_4$  formation is rather sensitive: detection limit is approximately  $0.010 \mu\text{g}$  ( $\sim 10 \mu\text{g}$  according to other data), limit dilution is  $8.3 \cdot 10^4 \text{ ml/g}$ .  $\text{Li}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$  and other cations, which form slightly soluble phosphates, interfere with detection.

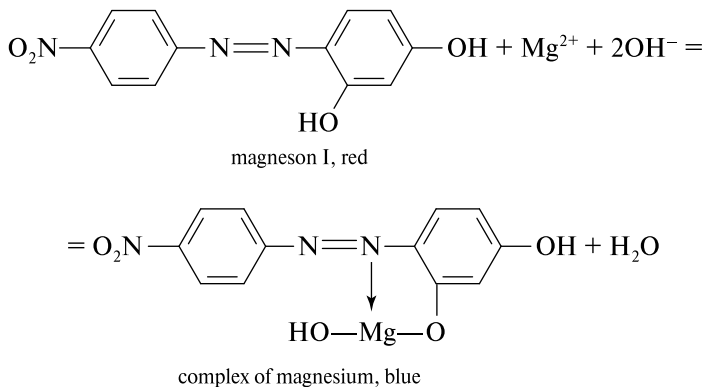
The reaction can be performed as microcrystalloscopic.

*Procedure.*

*Option one.* Magnesium salt solution (2–3 drops) is placed in a test tube;  $\text{NH}_4\text{Cl}$ , ammonia, and  $\text{Na}_2\text{HPO}_4$  solutions (1–2 drops of each solution) are added to it. The solution becomes turbid, and white  $\text{NH}_4\text{MgPO}_4$  precipitate is formed.

*Option two.* Magnesium salt,  $\text{NH}_4\text{Cl}$ , and concentrated ammonia solutions (one drop of each solution) are placed in a test tube. A drop of the mixture is applied to a glass slide, and a drop of  $\text{Na}_2\text{HPO}_4$  solution is placed nearby. The drops are brought in contact, and after 1–3 minutes, the formation of colorless transparent crystals of magnesium ammonium phosphate is observed under a microscope.

*Reaction with magneson I — *n*-nitrobenzoazoresorcinol.* Magneson I (red color) react with  $\text{Mg}^{2+}$  cations in alkaline medium forming a blue complex, which is absorbed on magnesium hydroxide precipitate. The reaction can be presumably described by the following scheme:

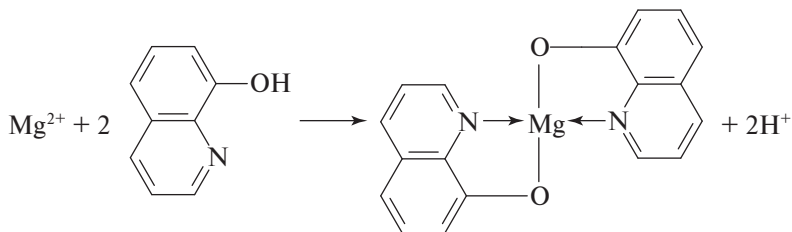


This scheme demonstrates the structure of the resulting complex *fragment*. Apparently, other ligands (for example, water molecules) are also bound to magnesium(II) atom, since coordination number 3 is uncharacteristic for magnesium(II).

The reaction is highly sensitive: detection limit is equal to 0.5  $\mu\text{g}$ . Numerous cations ( $\text{Cd}^{2+}$ ,  $\text{Sn}^{2+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , etc.), which form colored complexes with magneson, interfere with detection.

*Procedure.* A drop of magnesium salt solution is applied to a glass slide, and a drop of magneson alkaline solution is added to it. A blue precipitate is formed. In the case of low magnesium cations concentrations, the precipitate is not formed, and the solution turns blue.

*Reaction with 8-oxyquinoline.*  $Mg^{2+}$  cations react with 8-oxyquinoline in ammonia medium at  $pH \approx 8-13$  (better with heating) forming a yellow-green crystalline precipitate of intracomplex compound (magnesium oxyquinolate):

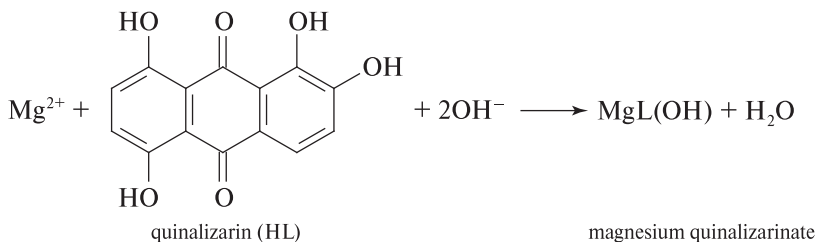


Magnesium oxyquinolate precipitate is soluble in mineral acids and acetic acid.

The reaction is highly sensitive: detection limit is equal to 0.25  $\mu\text{g}$ . Cations ( $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Fe}^{3+}$ , etc.), which also form complexes with 8-oxyquinoline, interfere with detection.

*Procedure.* Magnesium chloride solution (2–3 drops) and ammonia solution (2 drops) are placed in a test tube; ammonia chloride solution is added by drops until the dissolution of initially formed white magnesium hydroxide  $\text{Mg}(\text{OH})_2$  precipitate. 8-Oxyquinolate solution is added by drops to the solution until the formation of yellow-green magnesium oxyquinolate precipitate.

*Reaction with quinalizarin.*  $Mg^{2+}$  cation reacts with quinalizarin in alkaline medium forming a blue precipitate of a complex compound — magnesium quinalizarinate of composition  $\text{MgL}(\text{OH})$ , where HL is designation of a quinalizarin molecule:



The exact structure of the complex is unknown. The solution of quinalizarin itself in alkaline medium is purple.

If the concentration of magnesium cations in the solution is low, then precipitate does not form, and the solution turns cornflower-blue.



The reaction is highly sensitive: detection limit is equal to 0.25  $\mu\text{g}$ . Aluminum cations interfere with detection.

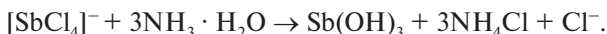
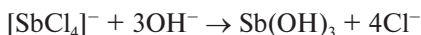
*Procedure.*  $\text{MgCl}_2$  solution (3–4 drops), alcohol quinalizarin solution (2–3 drops), and  $\text{NaOH}$  solution (2–3 drops) are placed in a test tube. A blue precipitate of magnesium quinalizarinate is formed, and the solution turns cornflower-blue.

*Other reactions of magnesium cations.*  $\text{Mg}^{2+}$  react with ammonium oxalate  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  forming a white precipitate of magnesium oxalate  $\text{MgC}_2\text{O}_4$ , with diphenylcarbazide  $(\text{C}_6\text{H}_5\text{NHNH})_2\text{CO}$  forming red-purple complex. Freshly precipitated  $\text{Mg}(\text{OH})_2$  in the reaction with potassium hypoiodite  $\text{KIO}$  (or sodium hypoiodite  $\text{NaIO}$ ) turns reddish-brown due to iodine sorption on magnesium hydroxide surface. Magnesium cations also react with other reagents forming products of various composition.

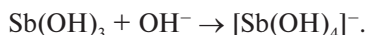
**Analytical reactions of antimony(III) and antimony(V).** Antimony(III) and antimony(V) salts undergo hydrolysis in aqueous solutions forming precipitates of slightly soluble basic salts of antimony. Therefore, acidic solutions of antimony(III) and antimony(V) are used, in which hydrolysis is suppressed, and corresponding acidocomplexes are formed. Thus, concentrated  $\text{HCl}$  solutions comprise acidocomplexes  $[\text{SbCl}_4]^-$  or  $[\text{SbCl}_6]^-$ .

Antimony compounds color gas burner flame light blue.

**Analytical reactions of antimony(III).** *Reactions with alkalis and ammonia solution.* When alkali solution or ammonia is added to the solution comprising antimony(III), a white precipitate of antimony(III) hydroxide  $\text{Sb}(\text{OH})_3$  is formed (which can also be represented as antimonous acid  $\text{H}_3\text{SbO}_3$  or  $\text{HSbO}_2 \cdot \text{H}_2\text{O}$ ):



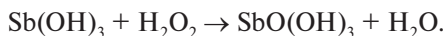
Freshly precipitated  $\text{Sb}(\text{OH})_3$  is soluble in excess of alkali with the formation of hydroxocomplexes  $[\text{Sb}(\text{OH})_4]^-$ :



$\text{Sb}(\text{OH})_3$  precipitate is also soluble in acids with the formation of acidocomplexes:



Alkali in the presence of hydrogen peroxide  $\text{H}_2\text{O}_2$  oxidize antimony(III) to antimony(V) with the formation of white  $\text{SbO}(\text{OH})_3$  precipitate:

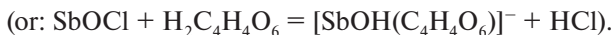


*Procedure.* 3–4 drops of hydrochloric acid solution of antimony(III) are placed in a test tube, 3–4 drops of distilled water are added, and then NaOH solution is added by drops until white precipitation of  $\text{Sb}(\text{OH})_3$ . NaOH solution is continued to be added by drops while stirring the test tube contents until the dissolution of the formed precipitate.

*Hydrolysis reaction.* Dilution of solutions comprising antimony(III) with water leads to its hydrolysis. Thus, the addition of water to antimony(III) solution in hydrochloric acid leads to hydrolysis (at  $\text{pH} \approx 3\text{--}4$ ) with precipitation of slightly soluble antimony(III) oxochloride  $\text{SbOCl}$  (white color):

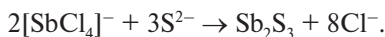


Freshly precipitated antimony oxochloride is soluble (better with heating) in HCl solutions, tartaric acid  $\text{H}_2\text{C}_4\text{H}_4\text{O}_6$  and its salts:

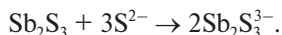


*Procedure.* 2–3 drops of hydrochloric acid solution of antimony(III) chloride are placed in a test tube, and distilled water is added by drops until the formation of white flocculent  $\text{SbOCl}$  precipitate.

*Reaction with sulfide ions.* Sulfide ions  $\text{S}^{2-}$  in acidic medium precipitate orange antimony(III) sulfide  $\text{Sb}_2\text{S}_3$  from antimony(III) solutions:



If sulfide ions are present in excess, the precipitate is dissolved with the formation of thiosalt comprising  $\text{SbS}_3^{3-}$  anion:

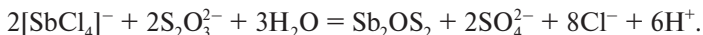


Antimony(III) sulfide precipitate is also soluble in concentrated HCl with heating, and in alkaline solutions:



*Procedure.* 3 drops of hydrochloric acid solution of antimony(III) chloride are placed in a test tube, 2 drops of concentrated HCl is added, and ammonium sulfide  $(\text{NH}_4)_2\text{S}$  (or sodium sulfide  $\text{Na}_2\text{S}$ ) solution or hydrogen sulfide water is added by drops. An orange precipitate of antimony(III) sulfide is formed.

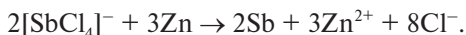
*Reaction with sodium thiosulfate.* Addition of sodium thiosulfate solution  $\text{Na}_2\text{S}_2\text{O}_3$  to acidic solution of antimony(III) leads to precipitation of “antimony cinnabar”  $\text{Sb}_2\text{OS}_2$  (red color):



It was previously thought that this precipitate is a mixture of  $\text{Sb}_2\text{S}_3$  and  $\text{Sb}_2\text{O}_3$ . Bismuth (III), which forms a black precipitate, interferes with detection.

*Procedure.* Hydrochloric solution of antimony(III) chloride (3–4 drops) is placed in a test tube, and sodium thiosulfate solution (2–3 drops) is added to it. A red precipitate is formed.

*Reaction of antimony(III) reduction to antimony(0).* Antimony(III) is reduced to metallic antimony in acidic medium by metallic magnesium, aluminum, zinc, tin, iron, for example:



Metallic antimony is released in the form of black precipitate on a metal surface.

*Procedure.* A few drops of hydrochloric acid solution of antimony(III) chloride, and a bit of metallic aluminum, or zinc, or iron are placed in a test tube. Metal surface turns black due to formation of a flocculent precipitate of free antimony.

*Other reactions of antimony(III).* Antimony(III) reacts with phosphoromolybdenum heteropolyacid forming a blue reaction product (“molybdenum blue”), which is extracted with amyl alcohol.

Antimony(III) reacts with methylfluorone  $\text{C}_{13}\text{H}_4\text{O}_2(\text{OH})_3\text{CH}_3$  in the presence of  $\text{H}_2\text{O}_2$  and  $\text{HCl}$  forming a red product (a drop reaction on filter paper); the reaction is specific for antimony(III).

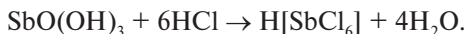
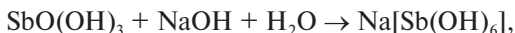
Such oxidizing agents, as  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{KBrO}_3$  and others, oxidize antimony(III) to antimony(V) in solutions.

Numerous other reactions of antimony(III) are known.

**Analytical reactions of antimony(V).** *Reaction with alkalis and ammonia.* Antimony(V) react with alkali metal hydroxides and ammonia forming a white precipitate of composition  $\text{SbO}(\text{OH})_3$ :



Freshly precipitated  $\text{SbO}(\text{OH})_3$  is soluble in alkali excess and strong acids:



*Procedure.* A few drops of hydrochloric acid solution of antimony(V) are placed in a test tube, and NaOH solution is added by drops until white precipitation of  $\text{Sb}(\text{OH})_3$ . Further addition of alkali solution leads to dissolution of the precipitate.

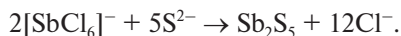
*Hydrolysis reaction.* When antimony(V) solutions are diluted with water, antimony(V) undergoes hydrolysis forming basic salts. Thus, if water is added to hydrochloric acid solution of antimony(V), hydrolysis proceeds until the formation of white antimony(V) oxochloride precipitate of composition  $\text{SbO}_2\text{Cl}$ :



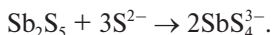
$\text{SbO}_2\text{Cl}$  precipitate is soluble in excess HCl (opposite reaction) and solutions of tartaric acid and its salts.

*Procedure.* 2–3 drops of hydrochloric acid solution of antimony(V) are placed in a test tube, and distilled water is added by drops until the formation of white  $\text{SbO}_2\text{Cl}$  precipitate.

*Reaction with sulfide ions.* The reaction between antimony(V) and sulfide ions in acidic medium leads to the formation of orange antimony(V) sulfide  $\text{Sb}_2\text{S}_5$  precipitate:



In excess of sulfide ions, the precipitate is dissolved with the formation of thiosalts:



$\text{Sb}_2\text{S}_5$  precipitate is soluble in alkalis:



Antimony(V) sulfide is dissolved in concentrated HCl with heating leading to release of free sulfur and reduction of antimony(V) to antimony(III):

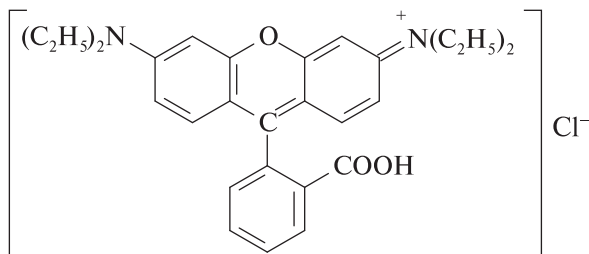


*Procedure.* Approximately 3 drops of hydrochloric solution of antimony(V) and 2 drops of concentrated HCl are placed in a test tube, and ammonium sulfide  $(\text{NH}_4)_2\text{S}$  (or sodium sulfide  $\text{Na}_2\text{S}$ ) solution or hydrogen sulfide water is added by drops. Orange  $\text{Sb}_2\text{S}_5$  precipitate is formed. Addition of reagent excess leads to the dissolution of the precipitate.

*Reaction of antimony(V) reduction to antimony(0).* Antimony(V), similarly to antimony(III), is reduced to free antimony(0) in acidic medium by metallic magnesium, zinc, aluminum, tin, and iron. Conditions for reactions

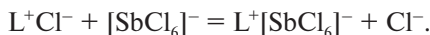
of antimony(V) reduction are similar to the conditions for reactions of antimony(III) reduction (see above).

*Reaction with rhodamine B.* In hydrochloric acid solutions, antimony(V) reacts with an organic reagent — rhodamine B (which is designated as  $L^+Cl^-$ )



Rhodamine B ( $L^+Cl^-$ )

forming purple or bluish-purple compound (ionic associate) of composition  $L^+[SbCl_6]^-$ :



The formed ionic associate is extracted from an aqueous phase with benzene or isopropanol; in this case, the organic layer turns bluish-purple.

If antimony(III) is present in the solution instead of antimony(V), then antimony(III) is preliminarily oxidized by sodium nitrite  $NaNO_2$  to antimony(V), after which antimony(V) is detected by reaction with rhodamine B.

*Procedure.* 3–4 drops of hydrochloric acid solution of antimony(V) are placed in a test tube, 2–3 drops of concentrated HCl, ~1 ml of distilled water, 3–4 drops of rhodamine B (usually 0.06%) and 5–6 drops of benzene are added. The mixture is shaken. Organic (benzene) layer turns purple-blue.

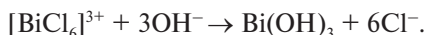
If antimony(III) is present in the solution, the reaction is performed similarly, except that additional 2–3 drops of sodium nitrite solution are added to the test tube after addition of concentrated HCl.

*Other reactions of antimony(V).* Antimony(V) in hydrochloric acid solutions (in the form of  $[SbCl_6]^-$ ) reacts with organic reagent methyl violet, iodides, and some other compounds. Thin suspension of a slightly soluble blue compound is formed in the reaction with methyl violet. Antimony(V) is reduced by iodides to antimony(III). In this case, the reaction mixture turns brown due to the release of iodine  $I_2$ .

**Analytical reactions of bismuth(III).** Bismuth(III) salts undergo hydrolysis in aqueous solutions forming precipitates of slightly soluble oxocom-

pounds — bismuthyl salts formally containing the bismuthyl cation  $\text{BiO}^+$  (for example,  $\text{BiOCl}$ ,  $\text{BiONO}_3$ , etc.), interfere with detection of lead cations in the form of lead sulfate. If bismuth(III) salt is dissolved in water, then cloudy solution is obtained due to the formation of hydrolysis products particles. In order to suppress hydrolysis and obtain clear solutions, bismuth(III) salt is dissolved not in pure water, but in acid solutions, most often in  $\text{HCl}$  solution, in which bismuth(III) is present in the form of chloride complexes  $[\text{BiCl}_6]^{3-}$ . In practice, hydrochloric solutions of bismuth(III) chloride are usually used.

*Reactions with alkalis and ammonia.* Addition of alkali solutions or ammonia to bismuth(III) salt solution leads to the formation of white  $\text{Bi}(\text{OH})_3$  hydroxide precipitate:



The precipitate is soluble in mineral acids. When heated, white  $\text{Bi}(\text{OH})_3$  precipitate turns yellow due to the formation of bismuth(III) oxohydroxide  $\text{BiO}(\text{OH})$  (bismuthyl hydroxide):



*Procedure.* A few drops of hydrochloric acid solution of bismuth (III) chloride are placed in a test tube,  $\text{NaOH}$  solution is added by drops, and  $\text{NaOH}$  solution is added by drops until white precipitation of  $\text{Bi}(\text{OH})_3$ .

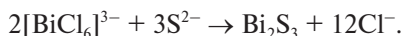
*Hydrolysis reaction.* Dilution of bismuth(III) salts solutions with water leads to their hydrolysis forming a white precipitate of bismuth oxochloride  $\text{BiOCl}$  (bismuthyl chloride):



If  $\text{HCl}$  solution is added with heating, the precipitate is dissolved (opposite reaction). In contrast to antimony oxochlorides, bismuth(III) oxochloride precipitate is insoluble in solutions of tartaric acid and its salts.

*Procedure.* Water is added by drops to 2–3 drops of hydrochloric acid solution of bismuth(III) chloride in a test tube until the formation of white  $\text{BiOCl}$  precipitate.

*Reaction with sulfide ions (pharmacopeial).* Bismuth(III) reacts with sulfide ions in acidic medium forming a blackish-brown precipitate of bismuth(III) sulfide  $\text{Bi}_2\text{S}_3$ :



The precipitate is insoluble in diluted mineral acids, except for diluted  $\text{HNO}_3$ , in which it is dissolved with the release of free sulfur:

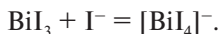
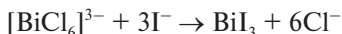


Bismuth sulfide precipitate is dissolved in the presence of iron chloride  $\text{FeCl}_3$ , also with release of free sulfur:



*Procedure.* 3–4 drops of hydrochloric acid solution of bismuth(III) chloride are placed in a test tube, and  $(\text{NH}_4)_2\text{S}$ , or  $\text{Na}_2\text{S}$  solution, or hydrogen sulfide water is added by drops. A blackish-brown precipitate of bismuth sulfide  $\text{Bi}_2\text{S}_3$  is formed.

*Reaction with iodides (pharmacopeial).* If iodide solutions are added to acidic solutions of bismuth(III), black bismuth(III) iodide  $\text{BiI}_3$  precipitate is formed, which is soluble in excess of the reagent forming a yellow-orange solution comprising tetraiodobismuthate(III) ions  $[\text{BiI}_4]^-$ :

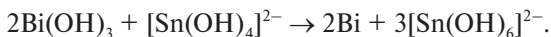


Dilution of the resulting solution with water leads to precipitation of  $\text{BiI}_3$ , followed by its hydrolysis and the formation of yellow-orange bismuth oxoiodide  $\text{BiOI}$  (bismuthyl iodide). Overall hydrolysis reaction can be described by the following scheme:



*Procedure.* Approximately 5 drops of hydrochloric acid solution of bismuth(III) chloride are placed in a test tube, and KI solution is added by drops until black precipitation of bismuth iodide(III). Further addition of KI solution excess leads to the dissolution of the precipitate and formation of orange solution. Addition of water to this solution with heating leads to formation of orange bismuthyl iodide  $\text{BiOI}$  precipitate.

*Reaction of bismuth(III) reduction to bismuth(0) by tin compounds(II).* In an alkaline medium ( $\text{pH} \approx 10$ ) tin(II) reduce bismuth(III) to metallic bismuth(0), which is released in the form of a black precipitate. In this case, tin(II) is oxidized to tin(IV):



A large excess of alkali with heating leads to the formation of black metallic tin precipitate due to disproportionation reaction:

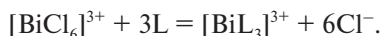


Lack of alkali can lead to the formation of black tin(II) oxide  $\text{SnO}$  precipitate:



*Procedure.* 2 drops of hydrochloric acid solution of tin(II) chloride are placed in a test tube, 8–10 drops of 2 mol/L NaOH solution are added until the dissolution of initially formed  $\text{Sn}(\text{OH})_2$  precipitate, and 1–2 drops of bismuth(III) salt solution is added. A black precipitate (metallic bismuth) is formed.

*Reaction with thiocarbamide (thiourea).* Bismuth(III) reacts with thiocarbamide  $\text{SC}(\text{NH}_2)_2$  in acidic medium forming a yellow soluble complex of composition  $[\text{BiL}_3]^{2+}$ , where L is a designation of thiocarbamide molecule:



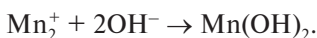
Cations  $\text{Hg}^{2+}$ ,  $\text{Fe}^{3+}$  interfere with detection.

*Procedure.* A drop of hydrochloric solution of bismuth(III) chloride is applied to a glass slide, and one small thiocarbamide crystal is added. The drop turns orange.

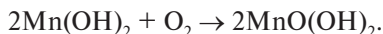
*Other reactions of bismuth(III).* A large number (several tens) of bismuth(III) reactions, which may have analytical value, are known. Thus, bismuth(III) reacts with sodium thiosulfate with heating forming bismuth sulfide  $\text{Bi}_2\text{S}_3$  precipitate; with sodium hydrogen phosphate  $\text{Na}_2\text{HPO}_4$  forming white bismuth phosphate  $\text{BiPO}_4$  precipitate; with dichromates forming yellow bismuthil dichromate  $(\text{BiO})_2\text{Cr}_2\text{O}_7$  precipitate; with 8-oxyquinoline and KI forming an orange-red precipitate of a complex compound, etc.

**Analytical reactions of manganese(II)  $\text{Mn}^{2+}$  cation.** Nickel(II) aqua-complexes  $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$  are pale pink, therefore, aqueous solutions of manganese(II) salts at rather high concentrations are pale pink. Strongly diluted aqueous solutions of manganese(II) salts are almost colorless.

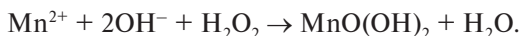
*Reactions with alkalis and ammonia.* Addition of alkali solutions or ammonia to solutions comprising  $\text{Mn}^{2+}$  cations leads to white manganese(II) hydroxide precipitate of composition  $\text{Mn}(\text{OH})_2$ :



The precipitate turns brown if left to stand due to oxidation by ambient oxygen to blackish-brown manganese(IV) oxohydroxide of composition  $\text{MnO}(\text{OH})_2$  ( $\text{H}_2\text{MnO}_3$ ):

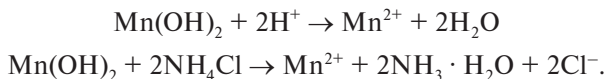


Under the action of alkalis on manganese(II) salts solutions in the presence of hydrogen peroxide, initially formed manganese (II) hydroxide  $\text{Mn}(\text{OH})_2$  is oxidized by hydrogen peroxide to blackish-brown  $\text{MnO}(\text{OH})_2$ :





$\text{Mn(OH)}_2$  precipitate is soluble in diluted strong acids solutions and saturated ammonium chloride solution:



$\text{MnO(OH)}_2$  precipitate does not dissolve under the action of these reagents.

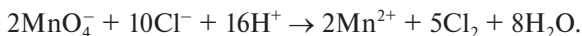
*Procedure.*

a) 3–4 drops of manganese(II) salt solution are placed in a test tube, and NaOH solution is added by drops until the end of white  $\text{Mn(OH)}_2$  precipitation. The precipitate darkens if left to stand due to the formation of  $\text{MnO(OH)}_2$ .

b) 3–4 drops of NaOH solution and 3–4 drops of  $\text{H}_2\text{O}_2$  solution are added to freshly precipitated  $\text{Mn(OH)}_2$ , which has been obtained, as described above. White  $\text{Mn(OH)}_2$  precipitate transforms into blackish-brown  $\text{MnO(OH)}_2$ .

*Oxidation reactions of  $\text{Mn}^{2+}$  cations to permanganate ions.* Under an action of various oxidizing agents,  $\text{Mn}^{2+}$  cations are oxidized to permanganate ions  $\text{MnO}_4^-$ , which color the solution crimson-purple. Sodium bismuthate  $\text{NaBiO}_3$ , ammonium persulfate  $(\text{NH}_4)_2\text{S}_2\text{O}_8$ , lead dioxide  $\text{PbO}_2$  and other compounds are used as oxidizing agents. Sodium bismuthate is most commonly used. The oxidation reaction of  $\text{Mn}^{2+}$  cations to  $\text{MnO}_4^-$  is used to detect these ions in solution.

Oxidation reactions are performed in the absence of chloride ions  $\text{Cl}^-$ , since they are reduced by permanganate ions to chlorine  $\text{Cl}_2$ :



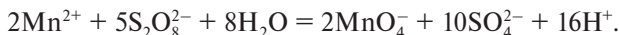
a) *Oxidation of sodium bismuthate in acidic medium* proceeds according to the following scheme:



Excess of sodium bismuthate can mask solution color.

*Procedure.* Approximately 5 drops of concentrated  $\text{HNO}_3$  and several bits of sodium bismuthate are placed in a test tube. The mixture is stirred, and 1–2 drops of manganese(II) sulfate  $\text{MnSO}_4$  or nitrate  $\text{Mn(NO}_3)_2$  solution (but not chloride  $\text{MnCl}_2$ !) are added to it. The solution turns crimson-purple.

b) *Oxidation by ammonium persulfate.* The reaction is performed in an acidic medium in the presence of catalyst — silver salts ( $\text{AgNO}_3$ ) with heating:

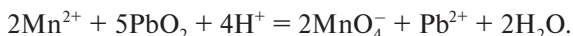


Cobalt and copper salts are also used as a catalyst.

Decomposition of permanganate ions is possible in hot solution, which is suppressed in the presence of phosphoric acid  $\text{H}_3\text{PO}_4$ .

*Procedure.* A few crystals of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (or  $\sim 0.5$  ml of saturated  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  solution) are placed in a test tube,  $\sim 2$  ml of  $\text{HNO}_3$  (or  $\text{H}_2\text{SO}_4$ ) solution, 2–3 drops of  $\text{AgNO}_3$  solution, and 1–2 drops of concentrated  $\text{H}_3\text{PO}_4$  solution are added to it. The mixture is heated to boiling, and a drop of manganese(II) salt is added to it. The solution turns crimson.

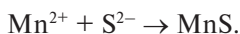
c) *Oxidation of lead dioxide in acidic medium with heating:*



In excess of manganese(II) salt,  $\text{MnO}(\text{OH})_2$ , instead of permanganate ion, is formed.

*Procedure.* A small amount of  $\text{PbO}_2$  is placed in a test tube, and  $\sim 1$  ml of  $\text{HNO}_3$  solution is added to it. The mixture is heated to boiling, a drop of manganese (II) sulfate or nitrate solution is added, and the mixture is again heated to boiling. The solution turns crimson.

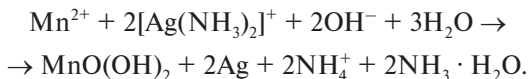
*Reaction with sulfide ions.*  $\text{Mn}^{2+}$  cations react with sulfide ions  $\text{S}^{2-}$  forming manganese(II) sulfide  $\text{MnS}$  fleshy pink precipitate:



The precipitate is soluble in diluted acids.

*Procedure.* Manganese(II) salt solution (3–4 drops) is placed in a test tube, and 1–2 drops of ammonium sulfide  $(\text{NH}_4)_2\text{S}$  (or sodium sulfide  $\text{Na}_2\text{S}$ ) solution or hydrogen sulfide water are added to it. Fleshy pink manganese(II) sulfide is precipitated.

*Other reactions of manganese(II).*  $\text{Mn}^{2+}$  cations react with silver ammoniate  $[\text{Ag}(\text{NH}_3)_2]^+$  forming brownish-black mixture of  $\text{MnO}(\text{OH})_2$  and metallic silver:

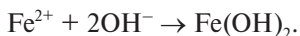


The reaction can be performed by drop method on filter paper (a blackish-brown spot is formed).

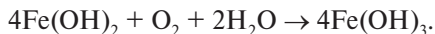
$\text{Mn}^{2+}$  cations undergo a number of other reactions of less analytical value.

**Analytical reactions of iron(II) cation  $\text{Fe}^{2+}$ .** Aqua ions of iron(II)  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  are almost colorless, therefore, iron(II) salts solutions are usually colorless.

*Reactions with alkalis and ammonia.*  $\text{Fe}^{2+}$  cations react with alkalis and ammonia forming white iron(II) hydroxide  $\text{Fe}(\text{OH})_2$  precipitate:



$\text{Fe}(\text{OH})_2$  hydroxide is soluble in acids, but insoluble in alkalis. Iron(II) hydroxide  $\text{Fe}(\text{OH})_2$  gradually darkens if left to stand with access to air due to oxidation of iron(II) to iron(III) by ambient oxygen and formation of reddish-brown iron(III) hydroxide  $\text{Fe}(\text{OH})_3$ :



Under the action of alkalis on iron(II) salts solutions in the presence of hydrogen peroxide, reddish-brown precipitate of iron(III) hydroxide  $\text{Fe}(\text{OH})_3$  is immediately formed:

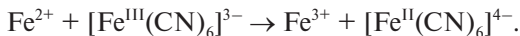


*Procedure.*

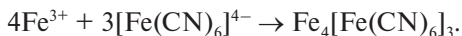
a) Iron(II) salt solution (5–6 drops) is placed in a test tube, and NaOH solution is added by drops until the end of white  $\text{Fe}(\text{OH})_2$  precipitation. The precipitate gradually darkens if left to stand with access to air.

b) 2–3 drops of NaOH solution and 2–3 drops of  $\text{H}_2\text{O}_2$  solution are added to freshly prepared white precipitate  $\text{Fe}(\text{OH})_2$ , as described above. The precipitate turns reddish-brown.

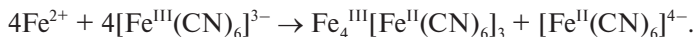
*Reaction with potassium hexacyanoferrate(III) — potassium ferricyanide (pharmacopeial).*  $\text{Fe}^{2+}$  cations react with potassium ferricyanide  $\text{K}_3[\text{Fe}(\text{CN})_6]$  in acidic medium forming a black-blue precipitate of Turnbull's blue. It was previously thought that composition of this precipitate corresponds to formula  $\text{Fe}_3[\text{Fe}(\text{CN})_6] \cdot x\text{H}_2\text{O}$  with a variable number of water molecules; moreover, depending on precipitation conditions, the composition of the precipitate changes and can correspond, for example, to formula  $\text{KFe}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6] \cdot x\text{H}_2\text{O}$  with an excess of potassium cations in solution. However, it was later shown that even during precipitation, redox process occurs with electron transfer from “outer sphere” iron(II) to “inner sphere” iron(III):



Formed  $\text{Fe}^{3+}$  cations and  $[\text{Fe}^{\text{II}}(\text{CN})_6]^{4-}$  anions form a dark-blue precipitate of the final product of composition  $\text{Fe}_4^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$  which is called Turnbull's blue:



Overall reaction equation:



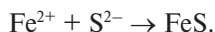
In terms of composition, structure and properties, Turnbull's blue precipitate is identical to Berlin blue precipitate obtained by adding potassium

ferrocyanide  $K_4[Fe(CN)_6]$  solution to iron(III) salts solutions (refer to “Analytical reactions of iron(III)  $Fe^{3+}$  cations” below).

The reaction is highly sensitive: detection limit is equal to 0.05  $\mu g$ . Turnbull’s blue precipitate is insoluble in acids, but decomposes in alkaline medium.

*Procedure.* Iron(II) salt solution (2–3 drops) is placed in a test tube, 1–2 drops of HCl solution and 2–3 drops of potassium ferricyanide  $K_3[Fe(CN)_6]$  solution are added. The solution turns blue, and Turnbull’s blue precipitate is formed.

*Reaction with sulfide ions (pharmacopeial).*  $Fe^{2+}$  cations react with sulfide ions in neutral or ammonia medium forming a black precipitate of iron(II) sulfide  $FeS$ :



The precipitate is soluble in diluted mineral acids and acetic acid.

*Procedure.* Iron(II) salt solution (3–4 drops) is placed in a test tube, and ammonium sulfide  $(NH_4)_2S$  (or sodium sulfide) solution (2–3 drops) is added to it. A black precipitate of iron(II) sulfide is formed.

*Other reactions of iron(II) cations.*  $Fe^{2+}$  cations react with many reagents. Some of these reactions have analytical value.

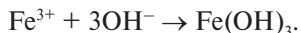
Dimethyl glyoxime  $(CH_3CNOH)_2$  react with  $Fe^{2+}$  cations forming pinkish-red iron(II) dimethyl glyoximate complex of composition  $FeL_2$ , where HL is a designation of dimethyl glyoxime molecule. The reaction is highly sensitive (detection limit is approximately 0.4  $\mu g$ ), however, other cations (especially  $Ni^{2+}$ ), which also form dimethyl glyoximate complexes, interfere with detection.

$Fe^{2+}$  cations react with 2,2'-dipyridyl, *o*-phenanthroline in acidic medium forming pinkish-red complex compounds.

A number of other reactions of  $Fe^{3+}$  cations, which have analytical value, is described.

**Analytical reactions of iron(III) cations  $Fe^{3+}$ .** Iron(III) aqua ions  $[Fe(H_2O)_6]^{3+}$  are yellow in aqueous solutions, and partially hydrolyzed to soluble hydroxo-aqua complexes  $[Fe(OH)_n(H_2O)_{6-n}]^{3-n}$ , which are also yellow-brown. Therefore aqueous iron(III) salts solutions are yellow or reddish-brown.

*Reaction with alkalis and ammonia.*  $Fe^{3+}$  cations react with alkalis and ammonia in aqueous solutions forming reddish-brown iron(III) hydroxide precipitate:

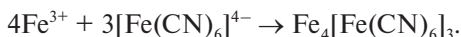


The precipitate is soluble in diluted acids and insoluble in saturated ammonium chloride solution (contrary to white iron(II) hydroxide  $Fe(OH)_2$  precipitate), as well as in alkali solutions.

*Procedure.* 3–4 drops of iron(III) salt solution are placed in a test tube, and 3–4 drops of NaOH solution are added to it. A reddish-brown precipitate of iron(III) hydroxide  $\text{Fe}(\text{OH})_3$  is formed.

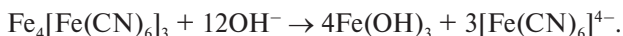
*Reaction with potassium hexacyanoferrate(II) — with potassium ferrocyanide (pharmacoceial).*  $\text{Fe}^{3+}$  cations react with potassium ferrocyanide in acidic medium ( $\text{pH} \approx 2\text{--}3$ ) forming a dark-blue precipitate of Berlin blue. Composition of pure Berlin blue precipitate is described by formula  $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \cdot x\text{H}_2\text{O}$  with a variable number of water molecules. However, it was shown that, depending on precipitation conditions, Berlin blue precipitate, as well as Turnbull's blue precipitate (see above), entrains other cations from the solution, so that its composition varies somewhat and may correspond, for example, formula  $\text{KFe}^{\text{III}}[\text{Fe}^{\text{II}}(\text{CN})_6]$ . Therefore, all compounds of this type are called Berlin blue.

Berlin blue precipitate is unstable in alkaline medium, but stable in acidic solution, therefore, the reaction is performed in an acidic medium at  $\text{pH} \approx 2\text{--}3$ . Reaction of pure Berlin blue formation proceeds according to the following scheme:



The reaction is highly sensitive: detected minimum is approximately 0.05  $\mu\text{g}$ , limit dilution is  $\sim 10^6$  ml/g. Oxidizing and reducing agents interfere with reaction (as well as Turnbull's blue precipitation). Oxidizing agents oxidize ferrocyanide to ferricyanide, and reducing agents reduce iron(III) to iron(II).

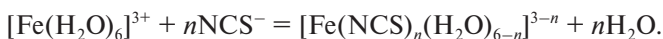
As in the case of Turnbull's blue, Berlin blue precipitate is not dissolved in acids, and decomposes by adding alkali solution:



*Procedure.* Iron(III) salt solution (2–3 drops) is placed in a test tube, 1–2 drops of HCl solution and 2 drops of  $\text{K}_4[\text{Fe}(\text{CN})_6]$  solution are added. The solution turns blue, and dark-blue precipitate of Berlin blue is formed.

*Reaction with thiocyanate ions (pharmacoceial).*  $\text{Fe}^{3+}$  cations react with thiocyanate ions  $\text{NCS}^-$  (better in an acidic medium at  $\text{pH} \approx 3$ ) forming red iron(III) thicyanate complexes. Depending on the ratio of reagent concentrations, complexes of various composition  $[\text{Fe}(\text{NCS})_n(\text{H}_2\text{O})_{6-n}]^{3-n}$  can dominate, where  $n = 1, 2, 3, \dots, 6$ . All of them are red and are in equilibrium. In order to suppress the formation of hydroxocomplexes containing hydroxyl groups  $\text{OH}^-$ , the reaction is performed in an acidic medium at  $\text{pH} \approx 3$ .

The reaction proceeds according to the following scheme:

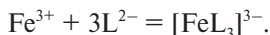


The reaction is highly sensitive: detection limit of iron(III) cations is equal to 0.25  $\mu\text{g}$ . A number of substances interfere with detection: oxidizing agents, reducing agents, mercury(II), fluorides, iodides, phosphates, citrates, tartrates, and other compounds. Iron(II) cations  $\text{Fe}^{2+}$  do not interfere with detection.

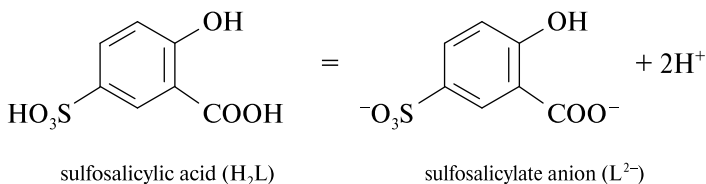
*Procedure.* Iron(III) salt solution (3–4 drops) is placed in a test tube, and ammonium thiocyanate  $\text{NH}_4\text{NCS}$  or potassium thiocyanate  $\text{KNCS}$  solution (2–3 drops) is added to it. The solution turns red.

*Reaction with sulfosalicylic acid (pharmacopeial).*  $\text{Fe}^{3+}$  cations react with sul sulfosalicylic acid in aqueous solutions forming colored complexes. Depending on medium pH and ratio of reagents, the resulting complexes may vary in composition and color. Thus, red complexes dominate at pH 2–2.5, brown complexes dominate at pH  $\approx$  4–8, and yellow complexes dominate at pH  $\approx$  9–11.5. The most stable is yellow complex, which comprises iron(III) and anions of sulfosalicylic acid in a molar ratio of iron(III): sulfosalicylate anion equal to 1:3, i.e., three sulfosalicylate ligands per iron atom. This complex dominates in ammonia solution. The exact structure of complexes in the solution is unknown.

It is assumed that at pH  $\approx$  9–11.5 the reaction proceeds with the formation of trisulfosalicylate ferrate(III) ions  $[\text{FeL}_3]^{3-}$  according to the scheme:



where  $\text{H}_2\text{L}$  is designation of a molecule of sulfosalicylic acid, and  $\text{L}^{2-}$  is designation of sulfosalicylate anion formed from sulfosalicylic acid after losing two protons, *apparently*, by groups  $\text{COOH}$  and  $\text{SO}_3\text{H}$ :



Apparently, at pH 2–2.5, the resulting red-complex contains iron(III) and sulfosalicylate ligand in a molar ratio of 1:1, at pH 4–8, the brown complex contains them in a molar ratio of 1:2.

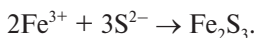
In the case of  $\text{Fe}^{3+}$  cations detection by reaction with sulfosalicylic acid, iron(III) limit concentration is 0.05  $\mu\text{g}/\text{ml}$ , i.e., the reaction is highly sensitive.

$\text{Fe}^{3+}$  cations undergo similar reactions with salicylic acid (*ortho*-oxybenzoic acid  $\text{HOC}_6\text{H}_4\text{COOH}$ ).

*Procedure.* Iron(III) salt solution (~5 drops) is placed in a test tube, sulfosalicylic acid solution (~10 drops) and concentrated ammonia solution (~0.5 ml) are added to it. The solution turns yellow.

If ~1 ml of HCl solution (1:1) is added instead of the ammonia solution, then a red solution is obtained instead of yellow.

*Reaction with sulfide ions (pharmacopeial).*  $\text{Fe}^{3+}$  cations react with sulfide ions  $\text{S}^{2-}$  in neutral or slightly ammonia solutions forming black iron(III) sulfide  $\text{Fe}_2\text{S}_3$  precipitate:



The precipitate is soluble in mineral acids.

*Procedure.* Iron(III) salt solution (3–4 drops) is placed in a test tube, and 2–3 drops of ammonium sulfide  $(\text{NH}_4)_2\text{S}$  (or  $\text{Na}_2\text{S}$ ) solution or hydrogen sulfide water are added to it. A black precipitate of iron(III) sulfide is formed.

Other reactions of  $\text{Fe}^{3+}$  cations. A number of reactions having analytical value for iron(III) cations, especially with organic reagents, are described. Thus,  $\text{Fe}^{3+}$  cations react with ferron (7-iodine-8-oxyquinoline-5-sulfonic acid) in acidic medium ( $\text{pH} \approx 2.6$ ) forming green complexes (the reaction is highly sensitive: detection limit is equal to 0.5  $\mu\text{g}$ ); with tyron (1,2-dioxy-3,5-disulfobenzene) forming blue complexes turning red in alkaline medium (detection limit is ~0.05  $\mu\text{g}$ ); with cupferon forming red iron(III) cupferonate precipitate; with salicylic acid-forming violet or red-violet salicylate complexes, etc.

Some analytical reaction products of the fifth analytical group cations are described in table 15.2.

### 15.3. ANALYTICAL REACTIONS OF THE SIXTH ANALYTICAL GROUP CATIONS ACCORDING TO ACID-BASE CLASSIFICATION: $\text{Cu}^{2+}$ , $\text{Cd}^{2+}$ , $\text{Hg}^{2+}$ , $\text{Co}^{2+}$ , $\text{Ni}^{2+}$

**Analytical reactions of copper(II)  $\text{Cu}^{2+}$  cation.** Copper(II) aqua ions  $[\text{Cu}(\text{H}_2\text{O})_n]^{2+}$  are blue, therefore, copper(II) salts solutions are blue with various shades (from light blue to bluish-green). In aqueous solutions, copper(II) aqua ions undergo partial hydrolysis forming soluble hydroxo-aqua complexes of composition  $[\text{Cu}(\text{H}_2\text{O})_{n-m}(\text{OH})_m]^{2-m}$  according to the scheme:

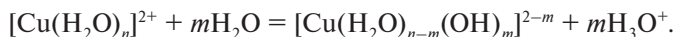
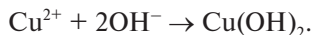


Table 15.2. Some analytical reaction products of the fifth analytical group cations according to acid-base classification

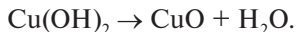
Reagents	Analytical reaction products						
	Mg <sup>2+</sup>	Sb(III)	Sb(V)	Bi(III)	Mn <sup>2+</sup>	Fe <sup>2+</sup>	Fe <sup>3+</sup>
NaOH, KOH, NH <sub>3</sub> solution	White precipitate of Mg(OH) <sub>2</sub>	White precipitate of Sb(OH) <sub>3</sub>	White precipitate of SbO(OH) <sub>3</sub>	White precipitate of Bi(OH) <sub>3</sub>	White precipitate of Mn(OH) <sub>2</sub>	White precipitate of Fe(OH) <sub>2</sub>	Reddish-brown precipitate of Fe(OH) <sub>3</sub>
NaOH (excess) + H <sub>2</sub> O <sub>2</sub>	White precipitate of Mg(OH) <sub>2</sub>	[Sb(OH) <sub>6</sub> ] <sup>-</sup> in solution	[Sb(OH) <sub>6</sub> ] <sup>-</sup> in solution	White precipitate of Bi(OH) <sub>3</sub>	Dark-brown precipitate of MnO(OH) <sub>2</sub>	Reddish-brown precipitate of Fe(OH) <sub>3</sub>	Reddish-brown precipitate of Fe(OH) <sub>3</sub>
Na <sub>2</sub> CO <sub>3</sub>	White precipitate of (MgOH) <sub>2</sub> CO <sub>3</sub>	White precipitate of Sb(OH) <sub>3</sub>	White precipitate of Sb(OH) <sub>3</sub>	White precipitate of BiO <sub>2</sub> CO <sub>3</sub>	White precipitate of (MnOH) <sub>2</sub> CO <sub>3</sub>	White precipitate of FeCO <sub>3</sub>	Reddish-brown precipitate of FeO <sub>2</sub> CO <sub>3</sub>
Na <sub>2</sub> HPO <sub>4</sub>	White precipitate of MgHPO <sub>4</sub> , Mg <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> ; in the presence of NH <sub>3</sub> , white precipitate of NH <sub>4</sub> MgPO <sub>4</sub>	White precipitate of (SbO) <sub>3</sub> PO <sub>4</sub>	White precipitate of SbO(OH) <sub>3</sub>	White precipitate of BiPO <sub>4</sub>	White precipitate of MnH <sub>2</sub> PO <sub>4</sub> , Mn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	Green precipitate of FeHPO <sub>4</sub> , Fe <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	Yellow precipitate of FePO <sub>4</sub>
(NH <sub>4</sub> ) <sub>2</sub> S	White precipitate of Mg(OH) <sub>2</sub> from concentrated solutions; in complete precipitation	Orange precipitate of Sb <sub>2</sub> S <sub>3</sub>	Orange precipitate of Sb <sub>2</sub> S <sub>3</sub>	Black precipitate of Bi <sub>2</sub> S <sub>3</sub>	Flesh precipitate of MnS	Black precipitate of FeS	Black precipitate of FeS+S
Dilution with water (hydrolysis of chloride solutions)		White precipitate of SbOCl	White precipitate of SbO <sub>2</sub> Cl	White precipitate of BiOCl			
Gas burner flame	Not colored	Blue	Blue	Green	Not colored	Not colored	Not colored



*Reaction with alkalis.* Addition of alkali solution to copper(II) salt solution leads to precipitation of copper(II) hydroxide  $\text{Cu}(\text{OH})_2$  (from bluish-green to light blue):



If the mixture of solution and precipitate is boiled, copper (II) hydroxide decomposes, losing water, to black copper(II) oxide  $\text{CuO}$ :

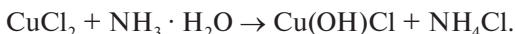


$\text{Cu}(\text{OH})_2$  precipitate is soluble in acids, ammonia solutions (forming blue complex  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ , complexing organic acids (citric, tartaric), partially soluble in concentrated alkalis forming copper(II) hydroxocomplexes.

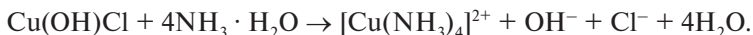
*Procedure.* Copper(II) salt solution (3–4 drops) is placed in a test tube, and  $\text{NaOH}$  solution (1–2 drops) is added to it. A light blue or bluish-green precipitate of copper(II) hydroxide is formed.

The mixture is *carefully* heated to boiling and boiled until the precipitate darkens due to the formation of black copper(II) oxide.

*Reaction with ammonia (pharmacopeial).* If ammonia a solution is added to solution containing copper(II) salt, initially a blue-green precipitate of basic copper salt is formed, which is dissolved in excess ammonia forming bright blue complex cation  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ . Thus, ammonia precipitates copper(II) oxychloride  $\text{Cu}(\text{OH})\text{Cl}$  from copper(II) chloride solution  $\text{CuCl}_2$ :

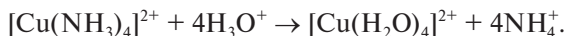


The precipitate is insoluble in excess ammonia:



The solution turns bright blue.

In acidic medium, complex tetramine copper (II) cation is decomposed:



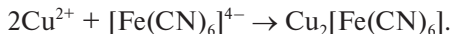
and the bright blue solution turns light blue (due to copper(II) aquacomplex).

$\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , tin(II) cations interfere with detection.

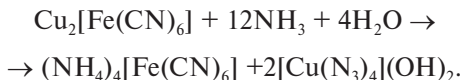
*Procedure.* Copper(II) salt solution (3–5 drops) is placed in a test tube, and diluted ammonia solution is added to the mixture by drops with stirring. The initially formed blue (or bluish-greenish) precipitate of basic copper(II) salt is then dissolved forming a bright blue solution.

Diluted  $\text{HCl}$ ,  $\text{HNO}_3$ , or  $\text{H}_2\text{SO}_4$  solution is added by drops. The bright blue solution turns light blue.

*Reaction with potassium hexacyanoferrate(II).*  $\text{Cu}^{2+}$  cations react with potassium ferrocyanide  $\text{K}_4[\text{Fe}(\text{CN})_6]$  in slightly acidic medium forming a red-brown precipitate of copper(II) hexacyanoferrate  $\text{Cu}_2[\text{Fe}(\text{CN})_6]$ .



The precipitate is insoluble in diluted acids, but soluble in 25% aqueous ammonia:



Cations that also form colored ferrocyanide precipitates ( $\text{Fe}^{3+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ), interfere with detection.

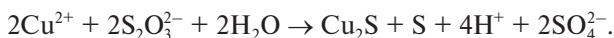
The reaction between copper(II) cations and potassium ferrocyanide can be performed by drop method on filter paper.

*Procedure.*

a) Copper(II) salt solution (3–4 drops) is placed in a test tube, and  $\text{K}_4[\text{Fe}(\text{CN})_6]$  solution (2–3 drops) is added to it. A reddish-brown precipitate of copper(II) ferrocyanide is formed.

b) A drop of copper(II) salt solution is applied to a filter paper sheet moistened with potassium ferrocyanide solution. A reddish-brown spot is formed on paper.

*Reaction with sodium thiosulfate.* During boiling a mixture of acidified copper(II) salt solution with sodium thiosulfate  $\text{Na}_2\text{S}_2\text{O}_3$  excess, copper(II) is reduced to copper(I) forming copper(I) sulfide  $\text{Cu}_2\text{S}$ . As a result, a dark brown precipitate is formed, which is a mixture of copper(I) sulfide  $\text{Cu}_2\text{S}$  and free sulfide. Apparently, the reaction proceeds according to the following scheme:

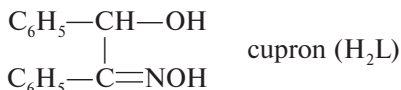


Other schemes describing this reaction are also mentioned in the literature.

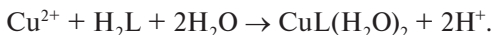
*Procedure.* Copper(II) salt solution (3–4 drops) is placed in a test tube, 2–3 drops of diluted  $\text{H}_2\text{SO}_4$  solution and several crystals of sodium thiosulfate are added to it. The test tube is carefully heated to boiling. A dark precipitate comprising a mixture of  $\text{Cu}_2\text{S}$  and S is formed.

*Reaction with cupron (1-benzoin oxime).*  $\text{Cu}^{2+}$  cations react with organic reagent (cupron), usually in ammonia medium, forming green flocculent precipitate of intracomplex compound of composition  $\text{CuL} \cdot 2\text{H}_2\text{O}$ , where  $\text{H}_2\text{L}$

is designation of cupron (1-benzoin oxime):



The reaction proceeds according to the following scheme:



Apparently, protons are released from both hydroxyl groups of cupron molecule. The precipitate is insoluble in excess ammonia.

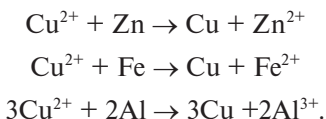
The reaction can be performed by the drop method on filter paper. The detection limit is approximately 0.1  $\mu\text{g}$ .

*Procedure.*

a) Copper(II) salt acidic solution (2–3 drops) is placed in a test tube, 1–2 drops of alcohol cupron solution and 2–3 drops of ammonia solution are added to it. A green precipitate of copper(II) cupron complex is formed.

b) A drop of acidified copper(II) salt solution, a drop of alcohol cupron solution, and a drop of ammonia solution are applied to a filter paper sheet. A green spot is formed on paper.

*Reaction of copper(II) reduction to metallic copper with metals (pharmaco-peial).* Metals located in reactivity series to the left of copper reduce copper(II)  $\text{Cu}^{2+}$  cations to metallic copper. For this purpose, metallic aluminum, zinc, and iron are most commonly used. If these metals are added to copper(II) salts solutions, the metal surface is covered with a thin layer of reddish metallic copper:



*Procedure.* A bit of metallic aluminum, or zinc, or iron is immersed in a test tube with acidified copper(II) salt solution. The metal surface is gradually covered with red metallic copper layer.

*Gas burner flame coloration.* Copper salts color gas burner flame emerald-green.

*Procedure.* Platinum or nichrome wire is immersed in concentrated hydrochloric acid and then in dry copper salt, and placed in a gas burner flame, which turns green.

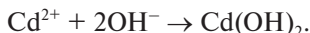
*Other reactions of copper(II) cations.*  $\text{Cu}^{2+}$  cations undergo a number of reactions which have analytical value. Thus, reactions with thiocyanates

lead to the formation of black  $\text{Cu}(\text{SCN})_2$  precipitate, which is gradually transformed into white  $\text{CuSCN}$ ; reactions with sulfide ions lead to black precipitate of copper sulfide  $\text{CuS}$ ; reactions with phosphates lead to light blue  $\text{Cu}_3(\text{PO}_4)_2$ , etc. Copper(II) complexation reactions with various organic reagents (cuproin, cupferon, dithiooxamide, etc.) are known.

A rather sensitive (limit dilution is  $\sim 10^4$  g/ml) microcrystalloscopic reaction leading to the formation of yellow-green  $\text{Cu}[\text{Hg}(\text{SCN})_4]$  crystals is also used.

**Analytical reactions of cadmium cation  $\text{Cd}^{2+}$ .** Cadmium aqua ions  $[\text{Cd}(\text{H}_2\text{O})_n]^{2+}$  in aqueous solutions are colorless.

*Reaction with alkalis and ammonia.* Addition of alkali or ammonia solution to cadmium salt solution leads to the formation of white cadmium hydroxide precipitate:



The precipitate is insoluble in excess alkali, but soluble in excess ammonia forming a colorless ammonia complex  $[\text{Cd}(\text{NH}_3)_4]^{2+}$ :



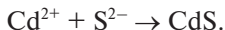
Cadmium hydroxide precipitate is soluble in acids:



*Procedure.* 3–4 drops of cadmium salt solution are placed in each of two test tubes. 1–2 drops of  $\text{NaOH}$  or  $\text{KOH}$  solution are added to the first test tube. A white precipitate of cadmium hydroxide  $\text{Cd}(\text{OH})_2$  is formed.

Ammonia solution is added by drops to the second test tube. Initially formed white precipitate of cadmium hydroxide is dissolved in excess ammonia.

*Reaction with sulfide ions.*  $\text{Cd}^{2+}$  cations react with sulfide ions  $\text{S}^{2-}$  in slightly acidic or alkaline solutions forming a yellow precipitate of cadmium sulfide  $\text{CdS}$ :



The precipitate is insoluble in alkalis and sodium sulfide solution, partially soluble in saturated sodium chloride solution forming cadmium chloride complex  $[\text{CdCl}_4]^{2-}$ :



Cadmium sulfide is insoluble in acids, except for  $\text{HCl}$ , in which it is dissolved with the formation of cadmium chloride complex:

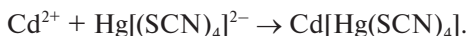


*Procedure.* Cadmium nitrate solution (2–3 drops) is placed in a test tube, and 2 drops of sodium sulfide  $\text{Na}_2\text{S}$  solution are added to it. A yellowish-brown precipitate of cadmium sulfide  $\text{CdS}$  is formed.

Saturated sodium chloride  $\text{NaCl}$  solution is added by drops to the precipitate while stirring the mixture until the precipitate is dissolved.

Reaction to cadmium cations can also be performed with hydrogen sulfide water at  $\text{pH} \approx 0.5$ .

*Reaction with ammonium tetraiodomercurate(II).* Cadmium cations react with ammonium tetraiodomercurate(II)  $(\text{NH}_4)_2[\text{Hg}(\text{SCN})_4]$  forming a white crystalline precipitate of cadmium tetraiodomercurate(II)  $\text{Cd}[\text{Hg}(\text{SCN})_4]$ :

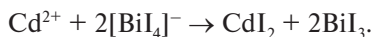


The reaction is highly sensitive: detection limit is approximately  $1 \mu\text{g}$ , limit dilution is  $\sim 10^3 \text{ ml/g}$ .

*Procedure.* 2–3 drops of cadmium salt solution are placed in a test tube, and approximately the same amount of  $(\text{NH}_4)_2[\text{Hg}(\text{SCN})_4]$  solution is added to it. Colorless (or white, depending on size of precipitate particles) cadmium tetraiodomercurate(II)  $\text{Cd}[\text{Hg}(\text{SCN})_4]$  crystals are formed.

The reaction can be performed as microcrystalloscopic. For this purpose, a drop of cadmium salt solution and a drop of ammonium tetraiodomercurate(II) are applied to a glass slide. The formed colorless oblong crystals of cadmium tetraiodomercurate  $\text{Cd}[\text{Hg}(\text{SCN})_4]$  can be observed with a microscope.

*Reaction with potassium tetraiodobismuthate(III).* Cadmium cations react with potassium tetraiodobismuthate(III)  $\text{K}[\text{BiI}_4]$  forming black precipitate of bismuth(III) iodide  $\text{BiI}_3$ :



Bismuth(III) iodide precipitate is dissolved after adding an excess of potassium iodide  $\text{KI}$  or sodium thiosulfate  $\text{Na}_2\text{S}_2\text{O}_3$  solutions.

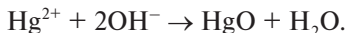
*Procedure.* A drop of potassium tetraiodobismuthate(III)  $\text{K}[\text{BiI}_4]$  and a drop of cadmium salt are added to a filter paper sheet. A black spot is formed on paper. If potassium iodide or sodium thiosulfate solution is added by drops, the spot disappears.

*Other reactions of cadmium cations.* A number of analytical reactions for cadmium cations are known, especially with complexing organic reagents: dithione, cadione, mercaptobenzothiazole, mercaptobenzimidazole,  $\beta$ -naphthoquinoline, quinaldic acid, a mixture of potassium iodide with tris- $\alpha$ -dipyridyl iron (II), etc.

**Analytical reactions of mercury(II)  $\text{Hg}^{2+}$  cation.** Mercury(II) aqua ions  $[\text{Hg}(\text{H}_2\text{O})_n]^{2+}$  in aqueous solutions are colorless.

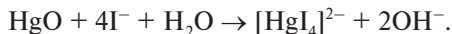
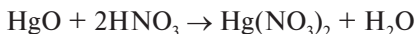
**All mercury(II) compounds are highly toxic, therefore, precautionary measures should be taken when handling!**

*Reactions with alkalis and ammonia.* Addition of aqueous alkali solution to aqueous solution containing  $\text{Hg}^{2+}$  cation leads to the formation of yellow mercury(II) oxide  $\text{HgO}$  precipitate:



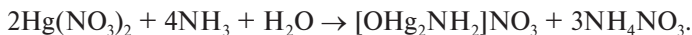
*The reaction is pharmacopoeial.*

$\text{HgO}$  precipitate is soluble in nitric acid, alkali metal chlorides and iodides solutions with the formation of  $\text{Hg}(\text{NO}_3)_2$ ,  $\text{HgCl}_2$ , and complex  $[\text{HgI}_4]^{2-}$ , respectively:

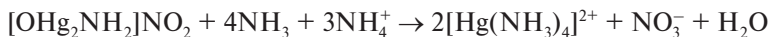


*Procedure.* Aqueous solution of mercury(II) salt (3–4 drops) is placed in a test tube, and aqueous  $\text{NaOH}$  or  $\text{KOH}$  solution is added by drops. A yellow precipitate of mercury(II) oxide  $\text{HgO}$  is formed.

$\text{Hg}^{2+}$  cations react with aqueous ammonia solution forming white precipitates. White  $\text{HgNH}_2\text{Cl}$  precipitate is formed from aqueous solutions of mercury(II) chloride  $\text{HgCl}_2$ , and white  $[\text{OHg}_2\text{NH}_2]\text{NO}_3$  precipitate is formed from aqueous solutions of mercury(II) nitrate  $\text{Hg}(\text{NO}_3)_2$  :



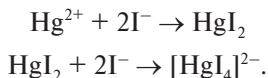
The precipitates are dissolved (better with heating) in excess ammonia, but only in the presence of ammonia salts, with the formation of colorless complex tetraamminmercury(II) cation  $[\text{Hg}(\text{NH}_3)_4]^{2+}$ :



*Procedure.* Aqueous solution of mercury(II) chloride  $\text{HgCl}_2$  (3–4 drops) is placed in one test tube, and aqueous solution of mercury(II) nitrate  $\text{Hg}(\text{NO}_3)_2$  (the same amount) is placed in another test tube. Aqueous ammonia solution is added by drops to each test tube until the formation of white precipitates. Then, 3–4 drops of aqueous ammonium salt ( $\text{NH}_4\text{Cl}$  or  $\text{NH}_4\text{NO}_3$ ) solution

are added to each test tube, and aqueous ammonia solution is added by drops with stirring until completely dissolution of precipitates.

*Reaction with potassium iodide (pharmacopeial).*  $\text{Hg}^{2+}$  cations react with iodide ions  $\text{I}^-$  in an aqueous solution forming a red precipitate of mercury(II) iodide  $\text{HgI}_2$ , which is dissolved in excess of iodide ions forming colorless tetraiodomercurate(II) ion  $[\text{HgI}_4]^{2-}$ :



$\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Ag}^+$ , bismuth(III) and some other cations, and also oxidizing agents interfere with detection.

*Procedure.* 2–3 drops of mercury(II) salt solution is placed in a test tube, and a drop of diluted (5%) potassium iodide solution is added to it. A red precipitate of mercury(II) iodide  $\text{HgI}_2$  is formed.

During further addition by drops (with shaking) of potassium iodide solution, the precipitate is dissolved forming a colorless solution.

The reaction can also be performed by drop method on filter paper — a reddish-orange spot is formed, which disappears after addition of excess potassium iodide solution.

*Procedure.* A drop of diluted aqueous solution of potassium iodide is applied to a filter paper sheet, then a drop of mercury(II) salt solution is applied. A reddish-orange spot is formed. During further addition by drops of potassium iodide solution, the spot is discolored.

This procedure is recommended for the detection of  $\text{Hg}^{2+}$  cations even in the presence of interfering cations.

*Reaction with sulfide ions (pharmacopeial).*  $\text{Hg}^{2+}$  cations are precipitated from aqueous solutions by sulfide ions  $\text{S}^{2-}$  in the form of blackish-brown mercury(II) sulfide  $\text{HgS}$  precipitate. The reaction proceeds in several stages. Initially, a white precipitate is formed, which gradually turns yellowish-red, brown and then brownish-black in excess of sulfide ions.

Thus, under the action of hydrogen sulfide  $\text{H}_2\text{S}$  on aqueous mercury(II) chloride  $\text{HgCl}_2$  solution, a white precipitate of composition  $2\text{HgS} \cdot \text{HgCl}_2$  is initially formed:



In excess of  $\text{H}_2\text{S}$ , white precipitate transforms into brownish-black  $\text{HgS}$ :



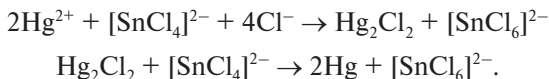
The reaction between  $\text{HgCl}_2$  and sodium sulfide  $\text{Na}_2\text{S}$  proceeds similarly.

Mercury(II) sulfide  $\text{HgS}$  is insoluble in diluted nitric acid, but soluble in aqua regia (mixture of  $\text{HCl} + \text{HNO}_3$ ):



*Procedure.* Mercury(II) chloride  $\text{HgCl}_2$  solution (2–3 drops) is placed in a test tube and sodium sulfide  $\text{Na}_2\text{S}$  or hydrogen sulfide solution is added by drops. A white precipitate is formed, which blackens with the further addition of  $\text{Na}_2\text{S}$  solution or hydrogen sulfide water.

*Reaction with tin(II) chloride.*  $\text{Hg}^{2+}$  cations are reduced with tin(II) to  $\text{Hg}_2^{2+}$  cations, and then to metallic mercury  $\text{Hg}$ . Thus, during a reaction of mercury(II) chloride  $\text{HgCl}_2$  with tin(II) chloride, a white precipitate of calgomel  $\text{Hg}_2\text{Cl}_2$ , which darkens due to the release of finely dispersed metallic mercury, is formed:



Cations  $\text{Ag}^+$ ,  $\text{Hg}^{2+}$ ,  $\text{Sb(III)}$ ,  $\text{Bi(III)}$  interfere with detection.

*Procedure.* Aqueous solution of mercury(II) chloride  $\text{HgCl}_2$  (2–3 drops) is placed in a test tube, and hydrochloric solution of tin(II) chloride is added by drops to it. White  $\text{Hg}_2\text{Cl}_2$  precipitate is formed, which gradually darkens.

The reaction can be performed by drop method on filter paper: if one drop of tin(II) chloride solution and one drop of mercury(II) chloride solution are applied to the paper, a dark spot is formed.

The reactions of mercury(II) salts with some other reducing agents, for example, metallic copper, proceed similarly. In order to perform this reaction, a drop of mercury(II) salt solution is applied to the copper surface. A dark (blackish-gray) spot appears on the surface, which, when wiped with filter paper, turns silvery-shiny.

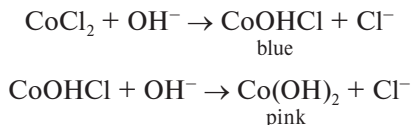
*Other reactions of mercury(II) cations.* Qualitative reactions to mercury(II) are known with a number of other inorganic and organic reagents — with chromate ions (yellow  $\text{HgCrO}_4$  is formed), with orthophosphate ions (white  $\text{Hg}_3(\text{PO}_4)_2$ ), with diphenylcarbazine and diphenylcarbazone (bluish-violet complexes), with dithizone (yellowish-orange or red complexes, depending on reaction conditions), etc.

**Analytical reactions of cobalt(II) cation  $\text{Co}^{2+}$ .** Cobalt(II) aqua ion with octahedral configuration  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  are pink, therefore, diluted aqueous cobalt(II) salt solutions are also pink. However, during evaporation of aqueous cobalt(II) salts solutions, the violet color of solutions turn blue characteristic for cobalt(II) complexes with tetrahedral structure.

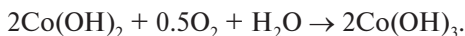


Cobalt(II) compounds are relatively easily oxidized to cobalt(III) compounds, and in some cases with ambient oxygen (dissolved in water), which must be taken into account when performing qualitative reactions to cobalt(II). In aqueous solutions, cobalt(II) and cobalt(III) exist exclusively in the form of complex compounds. Cobalt(III) complexes are more stable than cobalt(II) complexes, although stable cobalt (II) complexes are also known.

*Reaction with alkalis.*  $\text{Co}^{2+}$  cations in the reaction with alkalis initially form a blue precipitate of cobalt(II) hydroxosalt (for example,  $\text{CoOHCl}$ ), which then transforms into pink cobalt(II) hydroxide  $\text{Co}(\text{OH})_2$  precipitate. Thus, the reaction between cobalt(II) chloride and alkali proceeds according to the following scheme:



Pink cobalt(II) hydroxide  $\text{Co}(\text{OH})_2$  gradually turns brown due to oxidation with ambient oxygen forming blackish-brown cobalt(III) hydroxide of composition  $\text{Co}(\text{OH})_3$ :



If hydrogen peroxide  $\text{H}_2\text{O}_2$  is added to pink  $\text{Co}(\text{OH})_2$  precipitate, then  $\text{Co}(\text{OH})_2$  is almost immediately oxidized to blackish-brown  $\text{Co}(\text{OH})_3$ :

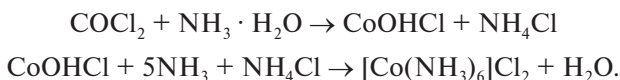


The action of a mixture of  $\text{H}_2\text{O}_2$  and alkali on cobalt(II) salt solution immediately leads to the formation of a blackish-brown  $\text{Co}(\text{OH})_3$  precipitate.

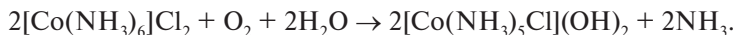


*Procedure.* Cobalt(II) salt solution (3 drops), for example,  $\text{CoCl}_2$ , is placed in a test tube, and aqueous  $\text{NaOH}$  or  $\text{KOH}$  solution is slowly added by drops with continuous stirring of the mixture until a blue  $\text{CoOHCl}$  precipitate is formed, which further transforms into a pink  $\text{Co}(\text{OH})_2$  precipitate after adding alkali and gradually darkens after a while due to  $\text{Co}(\text{OH})_3$  oxidation.

*Reaction with ammonia.* In the reaction between  $\text{Co}^{2+}$  cations and ammonia, a light blue precipitate of basic salt is also initially formed. Further addition of ammonia solution leads to precipitate dissolution forming dirty-yellow hexamminecobalt(II) cations  $[\text{Co}(\text{NH}_3)_6]^{2+}$  (yellow solution):



If left to stand with access to air, the solution gradually turns cherry red due to the oxidation of cobalt(II) to cobalt(III) with the formation of cherry red chloropentammincobalt(III) anions  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2-}$ :



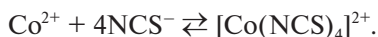
In the presence of hydrogen peroxide and ammonium salts, oxidation reaction of  $[\text{Co}(\text{NH}_3)_6]^{2+}$  to  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$  proceeds almost immediately:



*Procedure.* Cobalt(II) chloride solution (3 drops) is placed in a test tube and ammonia solution is slowly added by drops until a blue  $\text{CoOHCl}$  precipitate is formed. A few crystals of ammonium chloride are added, and the ammonia solution is continued to be added while the mixture is stirred until the precipitate is completely dissolved, and a yellow solution is formed. The solution gradually turns cherry red, if left to stand with access to air.

Cobalt(II) chloride solution (3 drops) is placed in a test tube, 2 drops of hydrogen peroxide solution is added, and then ammonia solution is added by drops until the formation of blackish-brown cobalt(III) hydroxide precipitate. Concentrated ammonia solution is added by drops until the dissolution of the precipitate and formation of a cherry red solution containing complexes  $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ .

*Reaction with thiocyanate ions.*  $\text{Co}^{2+}$  cations in slightly soluble medium react with thiocyanate ions  $\text{NCS}^-$  forming a blue complex of tetrathiocyanatocobaltate(II) ion  $[\text{Co}(\text{NCS})_4]^{2+}$ :



The complex is unstable in aqueous solutions, and the complexation equilibrium is shifted to the left towards the formation of pink cobalt(II) aqua complex. Therefore, the reaction is performed in excess of thiocyanate ions to shift the equilibrium to the right.

The equilibrium also shifts to the right in water-acetone solutions, therefore, the reaction is sometimes performed in water-acetone medium (acetone is well miscible with water).

Stability of the complex increases in solutions of organic solvents (isoamyl alcohol, ether). Therefore, during this reaction, an aqueous solution containing  $\text{Co}^{2+}$  cations is mixed with a small amount of organic solvent (usually a mixture of isoamyl alcohol and diethyl ether). In this case, cobalt(II) tetrathiocyanate complex transfers into the organic phase and colors it blue.

The detection limit of cobalt(II) ions by this reaction is equal to 0.5  $\mu\text{g}$ .

Iron(III)  $\text{Fe}^{3+}$ , copper(II)  $\text{Cu}^{2+}$  cations, which also form colored compounds with thiocyanate ions (yellowish-brown copper(I) complex and red iron(III) complexes), interfere with the reaction. The interfering effect of these ions can be eliminated by reducing them with tin(II) chloride to iron(II) and copper(I).

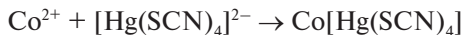
The interfering effect of  $\text{Fe}^{3+}$  cations is also eliminated by binding them in stable colorless complexes with such masking agents as fluoride and tartrate anions, adding sodium fluoride  $\text{NaF}$  or sodium potassium tartrate  $\text{NaKC}_4\text{H}_4\text{O}_6$ , respectively. Oxalate ions  $\text{C}_2\text{O}_4^{2-}$  and orthophosphate ions  $\text{PO}_4^{3-}$  are also used as masking agents.

*Procedure.* Cobalt(II) salt solution (2–3 drops) is placed in a test tube, 8–10 drops of saturated potassium thiocyanate  $\text{KNCS}$  or ammonium  $\text{NH}_4\text{NCS}$  solution (or several crystals of these salts), 5–6 drops of an organic solvent (isoamyl alcohol or a mixture of isoamyl alcohol with diethyl ether) are added, and the mixture is shaken. The upper layer of the organic phase turns blue.

Cobalt(II) salt solution (2–3 drops), iron(III) salt solution (2–3 drops) are placed in another test tube and a saturated solution of potassium or ammonium thiocyanate (5–6 drops) is added. The solution turns red (the color of iron(III) thiocyanate complexes), which masks the blue color of cobalt(II) thiocyanate complexes. Powdered  $\text{NaF}$  or  $\text{NaKC}_4\text{H}_4\text{O}_6$  is added to the mixture until red color disappears. Then, organic solvent (5–6 drops) is added and the tube is shaken. The upper liquid organic phase turns blue.

The reaction can also be performed by drop method on filter paper. For this purpose, a drop of concentrated potassium or ammonium thiocyanate solution, a drop of cobalt(II) salt solution are applied to the filter paper sheet, and the paper is dried in air. A blue spot is formed.

*Reaction with ammonium tetrathiocyanatomercurate(II) (ammonium tetrarodanomercurate(II)).*  $\text{Co}^{2+}$  cations react with ammonium tetrathiocyanatomercurate(II)  $(\text{NH}_4)_2[\text{Hg}(\text{SCN})_4]$  forming complex  $\text{Co}[\text{Hg}(\text{SCN})_4]$ , which is precipitated from the solution in the form of dark blue crystals:



Crystals precipitate slowly from diluted solutions. If  $\text{Zn}^{2+}$  zinc cations are present in the solution, then during the reaction, a light blue precipitate of a mixed thiocyanate complex of zinc and cobalt(II)  $\text{Zn}_x\text{Co}_y[\text{Hg}(\text{SCN})_4]_{x+y}$  is formed:

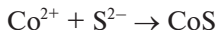


The addition of even small amounts of a zinc salt leads to almost complete precipitation of cobalt(II).

$\text{Cd}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ni}^{2+}$  cations interfere with reaction.

*Procedure.* Cobalt(II) salt solution (4–5 drops) is placed in a test tube, zinc salt solution (for example,  $\text{ZnSO}_4$ ) (one drop) and  $(\text{NH}_4)_2[\text{Hg}(\text{SCN})_4]$  solution (3–4 drops) are added. A blue mixed thiocyanate complex precipitate of zinc and cobalt(II) is formed.

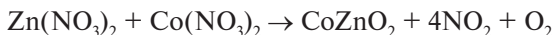
*Reaction with sulfide ions.*  $\text{Co}^{2+}$  cations react with sulfide ions forming a black precipitate of cobalt(II) sulfide  $\text{CoS}$ :



Freshly precipitated  $\text{CoS}$  is soluble in mineral acids, however, it transforms into sparingly soluble form in diluted  $\text{HCl}$ , and soluble form in acids in the presence of oxidizing agents, if left to stand.

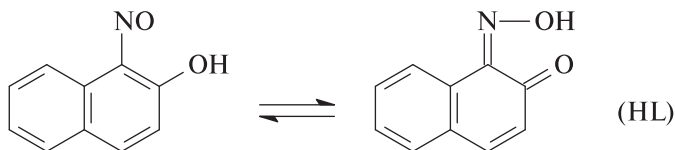
*Procedure.* Cobalt(II) salt solution (2–3 drops) is placed in a test tube and ammonium sulfide  $(\text{NH}_4)_2\text{S}$  solution (2–3 drops) is added. A black precipitate of cobalt sulfide  $\text{CoS}$  is formed.

*Reaction with zinc salts — “Rinman’s green” formation.* If a few drops of zinc nitrate  $\text{Zn}(\text{NO}_3)_2$  solution and a few drops of cobalt nitrate  $\text{Co}(\text{NO}_3)_2$  solution are added to a filter paper sheet, after which the sheet is dried and ignited (for example, placed in a porcelain crucible and held in a gas burner flame), then green ash (“Rinman’s green”) of composition  $\text{CoZnO}_2$  is formed:



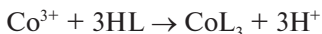
(refer to section “Analytical reactions of zinc cations  $\text{Zn}^{2+}$ ” above).

*Reaction with 1-nitroso-2-naphthol (Ilinski reagent).* In this reaction, cobalt(II) is initially oxidized to cobalt(III), which react with 1-nitroso-2-naphthol leading to intracomplex compound in the form of purple red precipitate. If 1-nitroso-2-naphthol, which can apparently exist in solution in two tautomeric forms, is designated as HL



1-nitroso-2-naphthol or  $\alpha$ -nitroso- $\beta$ -naphthol

then the reaction can be described by the scheme (after oxidation of cobalt(II) to cobalt(III)):

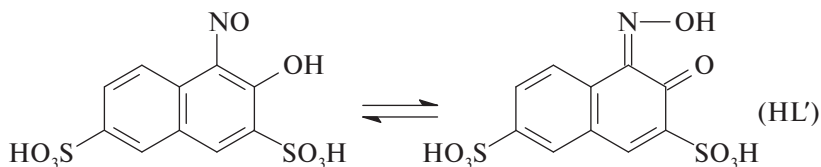


The reaction is performed in neutral or slightly acidic medium. Copper(II) cations  $\text{Cu}^{2+}$  interfere with detection.

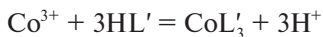
*Procedure.* Cobalt(II) salt solution (2–3 drops), acetic acid (1–2 drops), 1% solution of 1-nitroso-2-naphthol (2–3 drops) are placed in a test tube. A purplish-red precipitate of the intracomplex compound is formed with careful heating.

The reaction can also be performed by the drop method on a filter paper. For this purpose, cobalt(II) salt solution (one drop) and 1% solution of 1-nitroso-2-naphthol (one drop) in acetic acid are applied to a filter paper sheet. A reddish-brown spot is formed on paper.

*Reaction with nitroso-R-salt (pharmacocepal).* Nitroso-R-salt, which can be presented (similar to the Ilinski reagent) in two tautomeric forms



react with cobalt(III), which is released in the acidic medium due to oxidation of cobalt(II) to cobalt(III), forming red intracomplex compound of composition  $\text{CoL}'_3$  ( $\text{HL}'$  is a designation of nitroso-R-salt molecule, as mentioned in the scheme above):



The reaction is performed in an acidic medium with heating. The solution turns red. At sufficiently high concentrations, red intracomplex compound is precipitated from the solution.

The reaction is quite sensitive: detection limit is equal to 0.05  $\mu\text{g}$ .

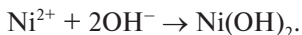
*Procedure.* Cobalt(II) salt solution (3–4 drops), diluted HCl solution (3–4 drops) are placed in a test tube. The solution in the test tube is heated to boiling, 3–4 drops of freshly prepared solution of nitroso-R salt in 50% acetic acid are added and heated to boiling. The solution turns red and a red precipitate is formed.

*Other reactions of cobalt(II) cations.* Cobalt(II) cations react with potassium nitrite  $\text{KNO}_2$  in an acetic acid medium forming (after oxidation to cobalt(III)) a yellow crystalline precipitate of potassium hexanitrocobaltate(III)  $\text{K}_3[\text{Co}(\text{NO}_2)_6]$ ; by this reaction, cobalt cations can be detected in the presence of nickel cations.

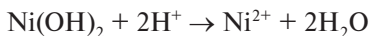
Cobalt compounds react with borax  $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$  forming blue beads, with rubehydroic acid  $\text{NH}_2\text{CSCSNH}_2$  (the formula of which can also be represented as  $\text{NH}=\text{C}(\text{SH})-\text{C}(\text{SH})=\text{NH}$ ) forming a yellowish-brown precipitate of complex compound.

**Analytical reactions of nickel(II)  $\text{Ni}^{2+}$  cations.** Nickel(II) aquacomplexes  $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$  are colored green, therefore, aqueous solutions of nickel(II) salts are green. In solutions, nickel(II) is present only in the form of complex compounds.

*Reaction with alkalis.* Nickel(II) cations  $\text{Ni}^{2+}$  are precipitated with alkali from aqueous solutions in the form of slightly soluble green nickel(II) hydroxide  $\text{Ni}(\text{OH})_2$  :

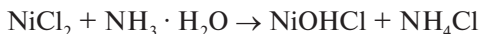
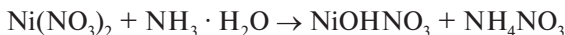


The precipitate is soluble in acids and ammonia solutions:



*Procedure.* Nickel(II) salt solution (2–3 drops) is placed in a test tube and alkali solution is added by drops with stirring. A light green precipitate is formed.

*Reaction with ammonia.* Ammonia precipitates light green nickel(II) oxy-salts from nickel(II) salt solutions, for example:



Nickel(II) oxy-salt precipitates are dissolved in excess ammonia forming blue complex hexaamminnickel(II) cations, for example:



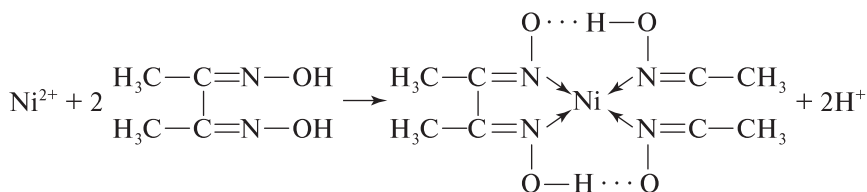
Hexaamminnickel(II) chloride  $[\text{Ni}(\text{NH}_3)_6]\text{Cl}_2$ , hexaamminnickel(II) nitrate  $[\text{Ni}(\text{NH}_3)_6](\text{NO}_3)_2$ , hexaamminnickel(II) sulfate  $[\text{Ni}(\text{NH}_3)_6]\text{SO}_4$  are well soluble in water. Some other hexaamminnickel(II) compounds, such as violet hexaamminnickel (II) bromide  $[\text{Ni}(\text{NH}_3)_6]\text{Br}$ , light blue hexaamminnickel(II) perchlorate  $[\text{Ni}(\text{NH}_3)_6](\text{ClO}_4)_2$  are slightly soluble in water.

*Procedure.* 2–3 drops of nickel(II) chloride  $\text{NiCl}_2$  (or nitrate  $\text{Ni}(\text{NO}_3)_2$ , or sulfate  $\text{NiSO}_4$ ) solution are placed in a test tube, and *diluted* ammonia solution is added by drops with stirring until the formation of green  $\text{NiOHCl}$  precipi-

tate. A *concentrated* (25%) ammonia solution is added by drops while stirring until the precipitate is completely dissolved and a blue solution forms.

The mixture is carefully heated, and concentrated potassium bromide KBr is added by drops until the formation of violet precipitate  $[\text{Ni}(\text{NH}_3)_6]\text{Br}_2$ .

*Reaction with dimethyl glyoxime (Chugaev reagent).*  $\text{Ni}^{2+}$  cations react with dimethyl glyoxime (Chugaev reagent) at  $\text{pH} \approx 6-9$  forming pinkish-red intracomplex compound bis-(dimethylglyoximato)nickel(II) (previously called “nickel dimethylglyoxime”), which is slightly soluble in water:



(in this case, points are the designation of hydrogen bonds  $\text{O} \cdots \text{N}$ ).

Usually, the reaction is performed in the ammonia medium.

The precipitate is soluble in strong acids and alkalis, insoluble in ammonia solutions.

Cobalt(II) cations *at low concentrations* do not interfere with nickel determination. Cations  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  interfere with detection. Methods for eliminating their interfering effect have been developed.

This reaction, which was first proposed by L.A. Chugaev, is the most specific to nickel(II) cations and highly sensitive: detection limit is equal to  $0.16 \mu\text{g}$ , limit dilution is  $3 \cdot 10^5 \text{ ml/g}$ . The sensitivity of the reaction increases in the presence of *small amounts* of oxidizing agents (bromine, iodine, etc.), which transform nickel(II) into nickel(III), whose complex with dimethylglyoxime is more intensive colored.

*Procedure.* Nickel(II) salt solution (3–4 drops) is placed in a test tube, concentrated ammonia solution (3–4 drops) and an alcoholic solution of dimethyl glyoxime (1 drop) are added. A pink-red precipitate of the complex is formed.

The reaction can be performed by the drop method on filter paper. For this purpose, nickel(II) salt solution (one drop) is applied to a filter paper sheet, and then an alcoholic solution of dimethylglyoxime (one drop) is applied. The paper is held over a flask with a concentrated ammonia solution (in ammonia vapors) until a pink-red spot appears.

*Other reactions of nickel(II) cations.*  $\text{Ni}^{2+}$  cations react with sulfide ions  $\text{S}^{2-}$  in a neutral medium forming a black precipitate of nickel(II) sul-

fide NiS; with a mixture of alkali and chlorine water forming blackish-brown nickel(III) hydroxide  $\text{Ni}(\text{OH})_3$  precipitate; with potassium thiocyanate KNCS and pyridine (Py) forming a blue complex precipitate of the composition  $[\text{NiPy}_4](\text{NCS})_2$ ; with rubyenohydric acid forming a bluish-violet precipitate of nickel rubeanate, slightly soluble in acids and ammonia. Other reactions of  $\text{Ni}^{2+}$  cations are also described.

Some analytical reaction products of the sixth analytical group cations are described in table 15.3.

**Table 15.3.** Some analytical reaction products of the sixth analytical group cations according to the acid-base classification

Reagents	Analytical reaction products				
	$\text{Cu}^{2+}$	$\text{Cd}^{2+}$	$\text{Hg}^{2+}$	$\text{Co}^{2+}$	$\text{Ni}^{2+}$
NaOH, KOH	Bluish-green $\text{CuOHCl}$ precipitate (from chloride solutions)	White precipitate $\text{Cd}(\text{OH})_2$	Yellow precipitate $\text{HgO}$	Light blue precipitate $\text{Co}(\text{OH})\text{Cl}$ (from chloride solutions)	Green precipitate $\text{Ni}(\text{OH})\text{Cl}$ (from chloride solutions)
$\text{NH}_3$ solution in excess	Blue $[\text{Cu}(\text{NH}_3)_4]^{2+}$ in solution	Colorless $[\text{Cd}(\text{NH}_3)_4]^{2+}$ in solution	Colorless $[\text{Hg}(\text{NH}_3)_4]^{2+}$ in solution	Yellow $[\text{Co}(\text{NH}_3)_6]^{2+}$ in solution	Bluish-violet $[\text{Ni}(\text{NH}_3)_6]^{2+}$ in solution
$\text{Na}_2\text{CO}_3$	Light blue precipitate of $(\text{CuOH})_2\text{CO}_3$	White precipitate of $(\text{CdOH})_2\text{CO}_3$	Reddish-brown precipitate $\text{HgCO}_3$ or $(\text{HgOH})_2\text{CO}_3$	Pinkish-violet precipitate $(\text{CoOH})_2\text{CO}_3$	Green precipitate of $(\text{NiOH})_2\text{CO}_3$
$\text{Na}_2\text{HPO}_4$	Light blue precipitate of $\text{CuHPO}_4$ , $\text{Cu}_3(\text{PO}_4)_2$	White precipitate of $\text{CdHPO}_4$ , $\text{Cd}_3(\text{PO}_4)_2$	White precipitate of $\text{HgHPO}_4$ , $\text{Hg}_3(\text{PO}_4)_2$	Violet precipitate of $\text{CoHPO}_4$ , $\text{Co}_3(\text{PO}_4)_2$	Green precipitate of $\text{NiHPO}_4$ , $\text{Ni}_3(\text{PO}_4)_2$
$(\text{NH}_4)_2\text{S}$ , $\text{H}_2\text{S}$	Black precipitate of $\text{CuS}$	Yellow precipitate of $\text{CdS}$	Black precipitate of $\text{HgS}$	Black precipitate of $\text{CoS}$	Black precipitate of $\text{NiS}$
Dithizone $\text{H}_2\text{Dz}$	Brown $\text{CuDz}$	Red $\text{CdDz}$	Orange $\text{HgDz}$	Violet $\text{CoDz}$	Violet $\text{NiDz}$
	Dithizonate complexes are extracted from the aqueous phase organic solvents				