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MINISTRY OF EDUCATION,
YOUTH AND SPORTS

Practical Inorganic Chemistry

Vojtěch Kubíček

Department of Inorganic Chemistry
Faculty of Science
Charles University

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1. Safety rules for chemical laboratories

Safety rules for chemical laboratories

Chemical laboratory is a potentially dangerous place. Each student is strongly asked to overcome any dangerous situation. Therefore, it is obligatory to know and follow the following rules:

1. Do not eat and drink in the laboratory.
2. Do not smoke in all the building.
3. If you are pregnant, you are not allowed to attend the laboratory training.
4. Have a convenient dress, the best is laboratory overall.
5. During your stay in the laboratory, you have to wear glasses. Corrective eye-glasses are acceptable too.
6. Wear protection gloves when operating with caustics (strong acids and hydroxides).
7. Using a face shield is recommended when operating with vacuum.
8. Any working apparatus must be under your control all the time.
9. Mercury vapour is very toxic. Call your teacher immediately in the case of breakage of thermometer or manometer.
10. Open fire must be excluded during all the operations with flammable liquids. Use fume hood in this case.
11. Operations with toxic or poignant chemicals must be also done in a fume hood.
12. Put all broken glass to the special container.
13. Do not put anything in front of the door. The door must be free all the time.
14. Do not operate with electric devices when your hands are wet.
15. In the case of fire, first try to extinguish it immediately. When it is impossible, call the teacher and leave the laboratory.
16. When your skin or eye are in the contact with any chemicals, wash it immediately with strong stream of water. Then call the teacher.
17. Any injury must be announced and put on record.

2. Report template

Sodium chloride (NaCl) preparation

Introduction:
Sodium chloride is a white, crystalline solid, well soluble in water and poorly soluble in organic solvents prepared in a neutralization reaction from hydrochloric acid and sodium hydroxide.

$NaOH + HCl \rightarrow NaCl + H_2O$

Experiment:
Sodium hydroxide (10 g, 0.25 mol) was dissolved in water (100 ml) in a beaker placed in an ice bath on a magnetic stirrer. Concentrated hydrochloric acid (36%, $\rho = 1.2$ g/cm^3, 21.2 ml, 0.25 mol) was added dropwise, under vigorous stirring and continuously cooling for 5 min. The resulting solution was transferred to a dish and evaporated to crystallization on a water bath. The mixture was cooled in a fridge (30 min). The crystalline solid was filtered on a fritt (S2), briefly washed with cold water (0 °C, 10 ml) and dried in a desiccator over P_2O_5. The yield was 8.2 g (56 %).

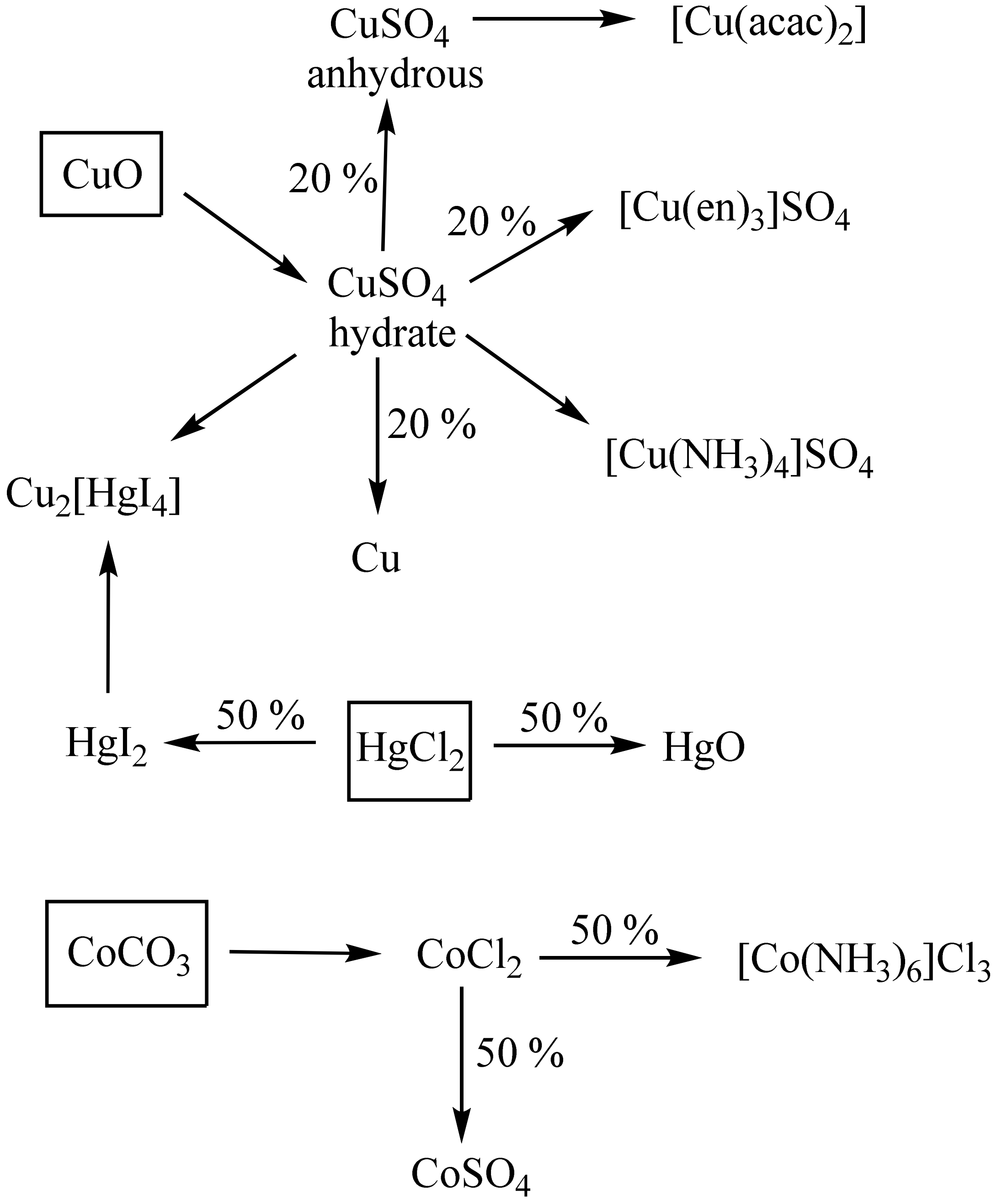
Calculations:
The preparation of sodium chloride started with 10 g of NaOH.

Volume of 36% HCl:
$m = 36.5 \times 10 / 40 = 9.13$ g of pure HCl
$m = 9.13 / 0.36 = 25.4$ g of 36% HCl
$V = 25.4 / 1.2 = 21.2$ mL
Yield:
Theoretical yield $m = 58.5 \times 10 / 40 = 14.6$ g
Percentage yield $p = 100 \times 8.2 / 14.6 = 56$ %

Conclusions and remarks:
Sodium chloride was prepared as a white crystalline solid in 56% yield. The low yield resulted from the high solubility of the product in water, but a higher yield could have been reached after a workup of the mother liquor – repeated evaporation and crystallization. The reaction of sodium hydroxide solution with concentrated hydrochloric acid is highly exothermic, thereby overheating the reaction mixture. For this reason, I recommend using a diluted HCl solution.

3. Schemes, tables

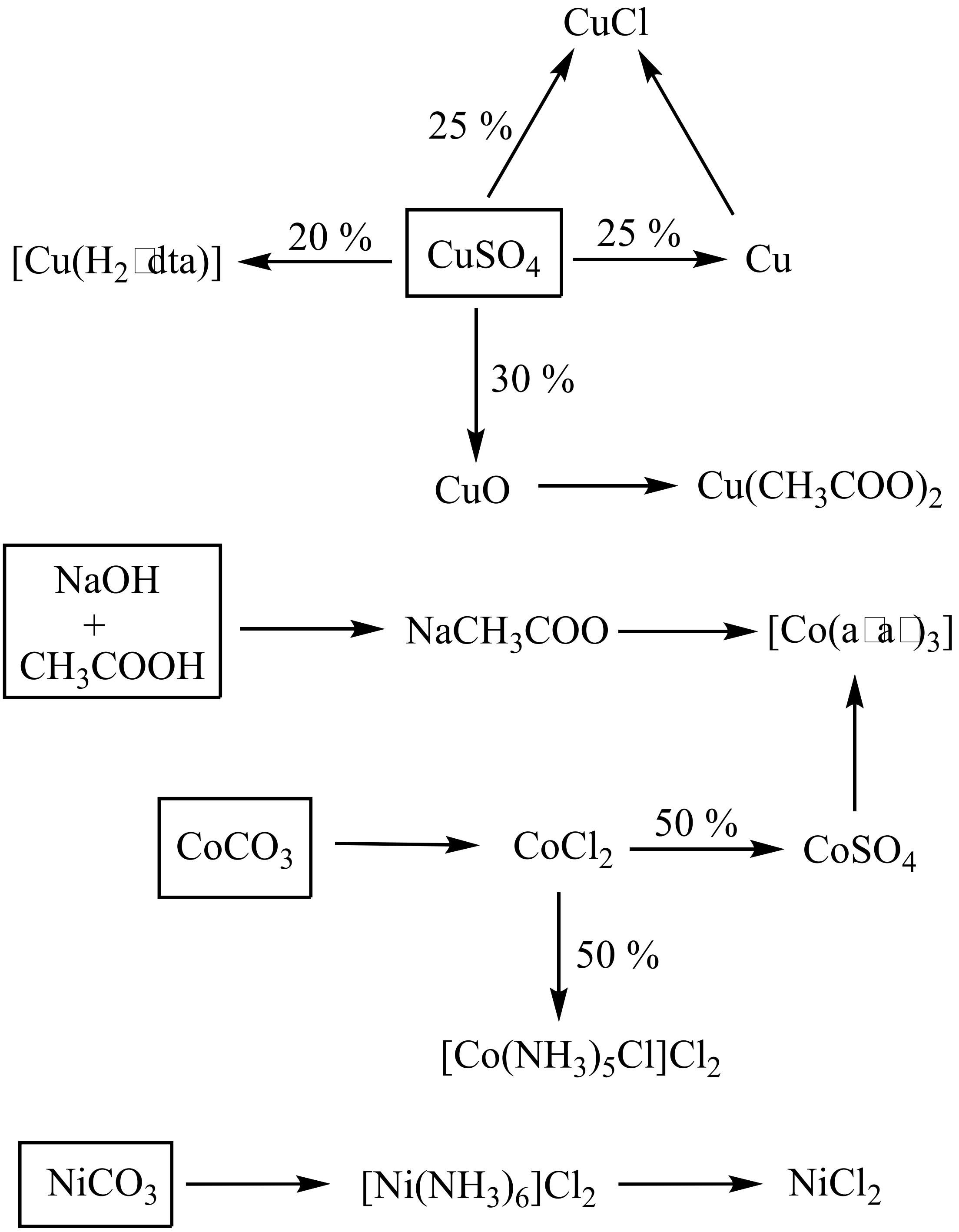
Scheme A1



Scheme A1

	Weight	Yield
$CuSO_4 \cdot 5H_2O$		
$CuSO_4$ anhydrous		
$[Cu(en)_3]SO_4$		
$[Cu(NH_3)_4]SO_4 \cdot H_2O$		
Cu		
$Cu_2[HgI_4]$		
$[Cu(acac)_2]$		
$CoSO_4 \cdot 6H_2O$		
$[Co(NH_3)_6]Cl_3$		
$CoCl_2 \cdot 6H_2O$		
HgO		
HgI_2		
Chromatography	$c([Co(acac)_3])$ [mM]	$c(K[Co(edta)])$ [mM]
Analysis: $CuSO_4 \cdot 5H_2O$	Metal content [%]	Water content [%]

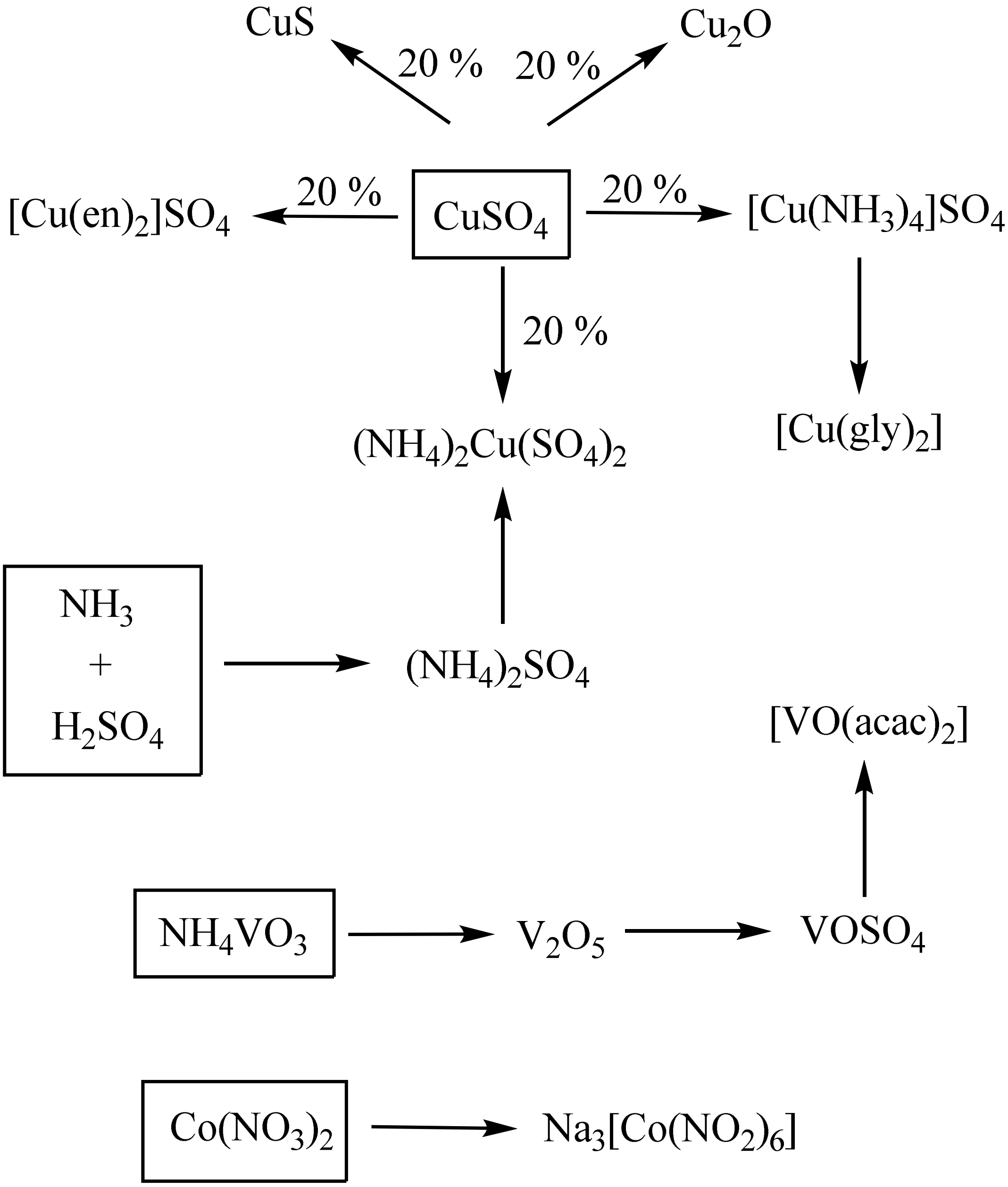
Scheme A2


CuCl
25 %
20 %
CuSO4
25 %
[Cu(H2□dta)]
Cu
30 %
CuO
Cu(CH3COO)2
NaOH
+
CH3COOH
NaCH3COO
[Co(a□a□)3]
CoCO3
CoCl2
50 %
CoSO4
50 %
[Co(NH3)5Cl]Cl2
NiCO3
[Ni(NH3)6]Cl2
NiCl2

Scheme A2

	Weight	Yield
Cu		
[Cu(H_2edta)]·H_2O		
CuCl		
Cu($CH_3COO)_2$·H_2O		
CH_3COONa·3H_2O		
[Ni($NH_3)_6$]Cl_2		
CuO		
[Co($NH_3)_5$Cl]Cl_2		
$CoCl_2$·6H_2O		
$NiCl_2$		
$CoSO_4$·6H_2O		
[Co(acac)$_3$]		
Chromatography	*c*([Co(acac)$_3$]) [mM]	*c*(K[Co(edta)]) [mM]
Analysis: $CoSO_4$·6H_2O	Metal content [%]	Water content [%]

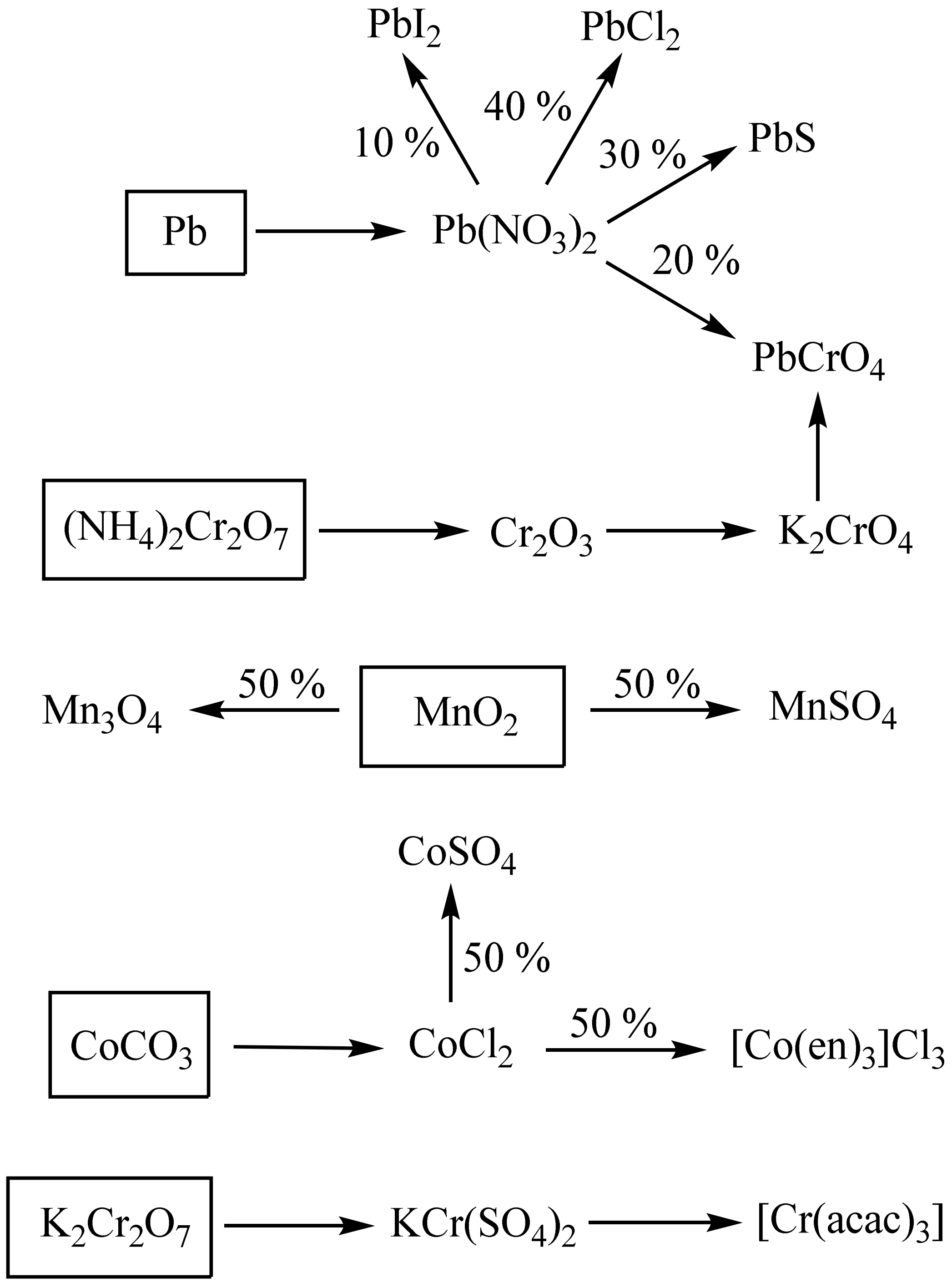
Scheme A3


CuS
20 %
20 %
Cu_2O
$[Cu(en)_2]SO_4$
20 %
$CuSO_4$
20 %
$[Cu(NH_3)_4]SO_4$
20 %
$(NH_4)_2Cu(SO_4)_2$
$[Cu(gly)_2]$
NH_3
+
H_2SO_4
$(NH_4)_2SO_4$
$[VO(acac)_2]$
NH_4VO_3
V_2O_5
$VOSO_4$
$Co(NO_3)_2$
$Na_3[Co(NO_2)_6]$

Scheme A3

	Weight	Yield
$[Cu(gly)_2]$		
CuS		
Cu_2O		
$[Cu(en)_2]SO_4$		
$(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$		
$(NH_4)_2SO_4$		
$[Cu(NH_3)_4]SO_4 \cdot H_2O$		
V_2O_5		
$[VO(acac)_2]$		
$VOSO_4 \cdot 3H_2O$		
$Na_3[Co(NO_2)_6] \cdot H_2O$		
Chromatography	$c([Co(acac)_3])$ [mᴍ]	$c(K[Co(edta)])$ [mᴍ]
Analysis: $(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$	Metal content [%]	Water content [%]

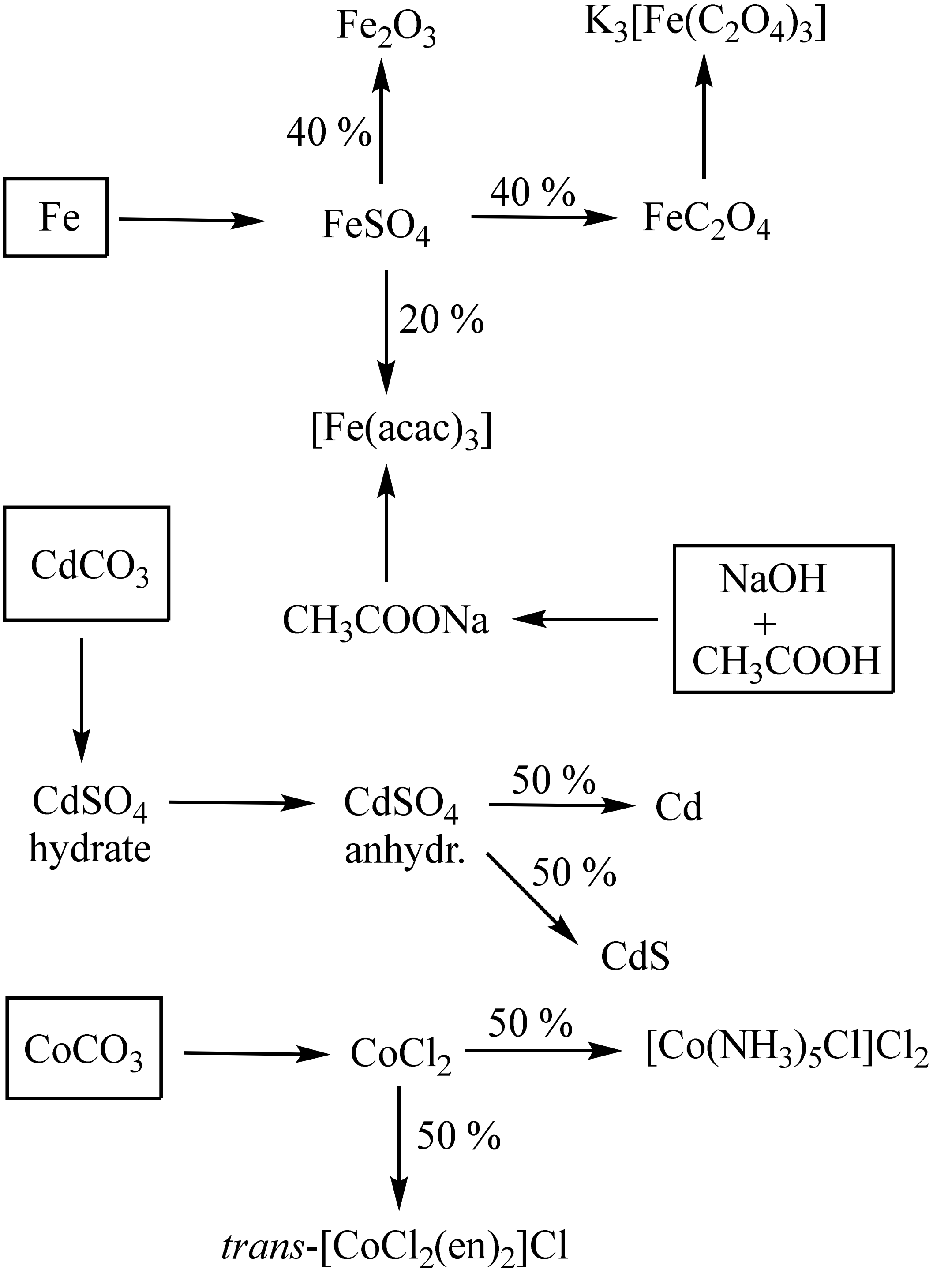
Scheme A4


PbI2
PbCl2
10 %
40 %
30 %
PbS
Pb
Pb(NO3)2
20 %
PbCrO4
(NH4)2Cr2O7
Cr2O3
K2CrO4
Mn3O4
50 %
MnO2
50 %
MnSO4
CoSO4
50 %
CoCO3
CoCl2
50 %
[Co(en)3]Cl3
K2Cr2O7
KCr(SO4)2
[Cr(acac)3]

Scheme A4

	Weight	Yield
$Pb(NO_3)_2$		
PbI_2		
$PbCl_2$		
PbS		
$PbCrO_4$		
Cr_2O_3		
K_2CrO_4		
Mn_3O_4		
$MnSO_4 \cdot H_2O$		
$CoCl_2 \cdot 6H_2O$		
$CoSO_4 \cdot 6H_2O$		
$[Co(en)_3]Cl_3$		
$KCr(SO_4)_2 \cdot 12H_2O$		
$[Cr(acac)_3]$		
Chromatography	$c([Co(acac)_3])$ [mM]	$c(K[Co(edta)])$ [mM]
Analysis: $CoSO_4 \cdot 6H_2O$	Metal content [%]	Water content [%]

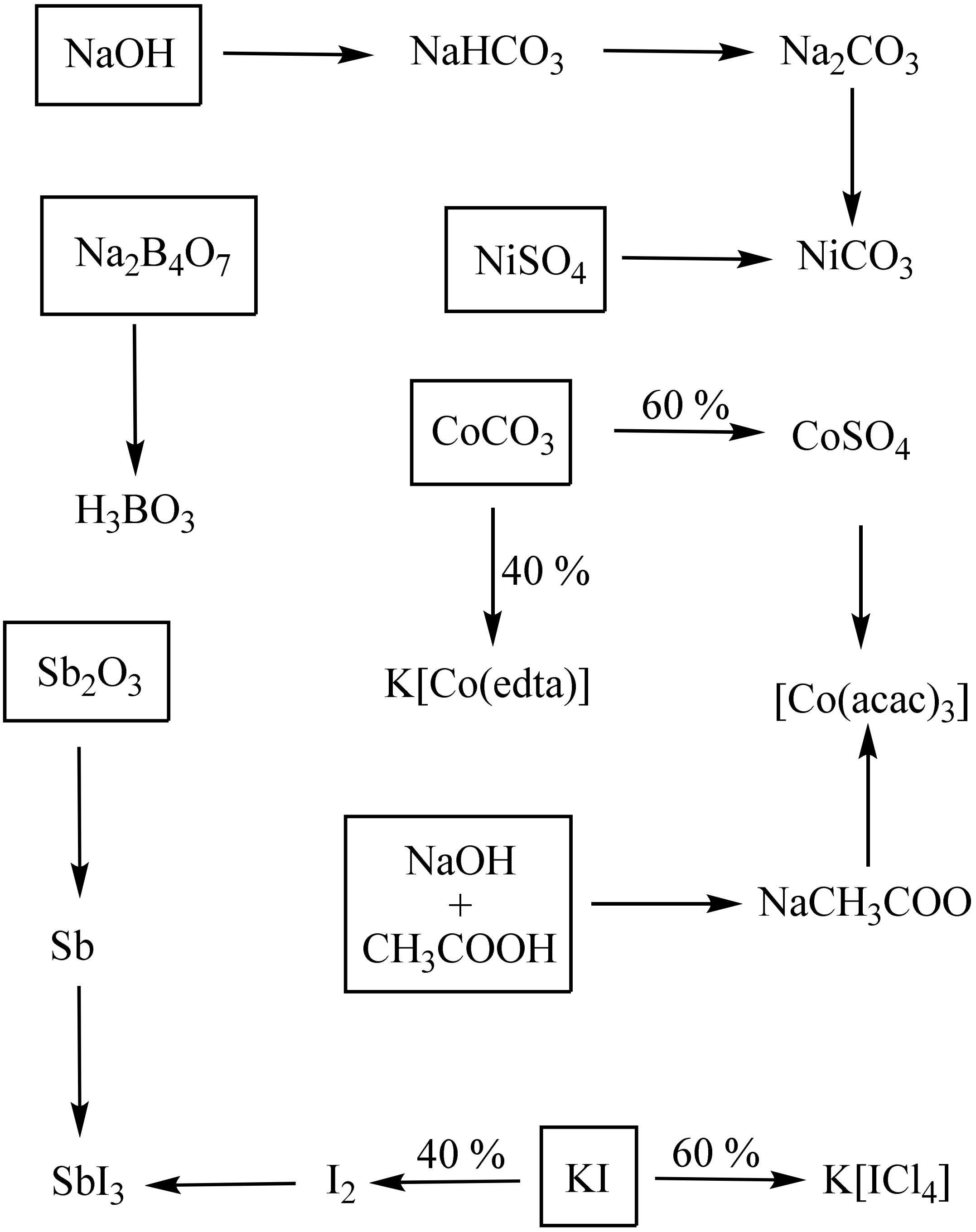
Scheme A5


Fe_2O_3
$K_3[Fe(C_2O_4)_3]$
40 %
Fe
$FeSO_4$
40 %
FeC_2O_4
20 %
$[Fe(acac)_3]$
$CdCO_3$
CH_3COONa
NaOH + CH_3COOH
$CdSO_4$ hydrate
$CdSO_4$ anhydr.
50 %
Cd
50 %
CdS
$CoCO_3$
$CoCl_2$
50 %
$[Co(NH_3)_5Cl]Cl_2$
50 %
trans-$[CoCl_2(en)_2]Cl$

Scheme A5

	Weight	Yield
$FeSO_4 \cdot 7H_2O$		
$FeC_2O_4 \cdot 2H_2O$		
$K_3[Fe(C_2O_4)_3] \cdot 3H_2O$		
Fe_2O_3		
$CdSO_4 \cdot 8/3H_2O$		
$CdSO_4$ anhydrous		
CdS		
Cd		
$[Fe(acac)_3]$		
$CH_3COONa \cdot 3H_2O$		
$CoCl_2 \cdot 6H_2O$		
$[Co(NH_3)_5Cl]Cl_2$		
trans-$[CoCl_2(en)_2]Cl$		
Chromatography	*c*($[Co(acac)_3]$) [mM]	*c*(K[Co(edta)]) [mM]
Analysis: $CdSO_4 \cdot 8/3H_2O$	Metal content [%]	Water content [%]

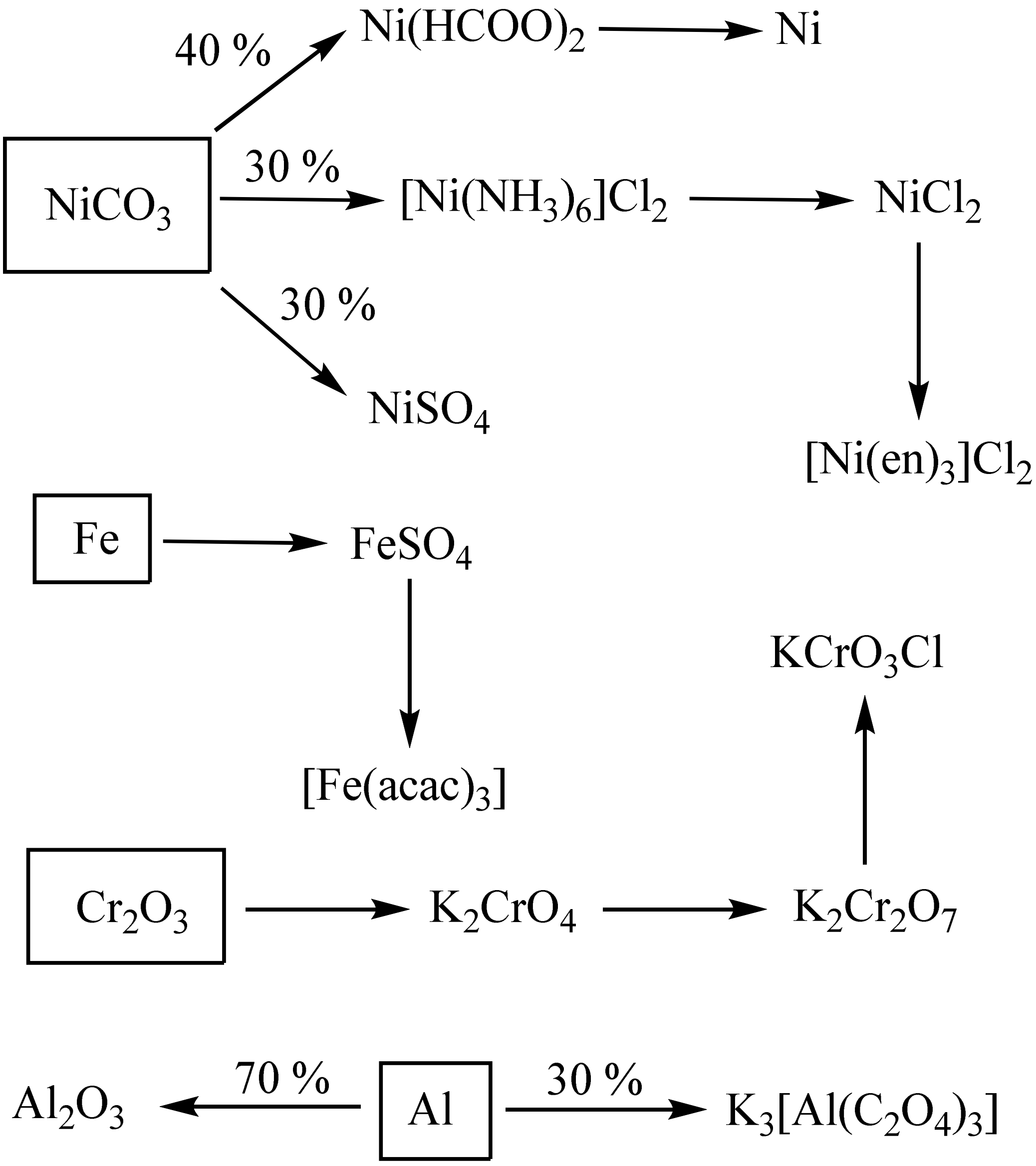
Scheme A6


$NaOH$
$NaHCO_3$
Na_2CO_3
$Na_2B_4O_7$
$NiSO_4$
$NiCO_3$
$CoCO_3$
60 %
$CoSO_4$
H_3BO_3
40 %
$K[Co(edta)]$
Sb_2O_3
$[Co(acac)_3]$
$NaOH$
+
CH_3COOH
$NaCH_3COO$
Sb
SbI_3
I_2
40 %
KI
60 %
$K[ICl_4]$

Scheme A6

	Weight	Yield
$NaHCO_3$		
Na_2CO_3		
$CoSO_4 \cdot 6H_2O$		
$NiCO_3$		
$[Co(acac)_3]$		
H_3BO_3		
$CH_3COONa \cdot 3H_2O$		
$K[Co(edta)] \cdot 2H_2O$		
I_2		
Sb		
SbI_3		
$K[ICl_4]$		
Chromatography	$c([Co(acac)_3])$ [mм]	$c(K[Co(edta)])$ [mм]
Analysis: $CoSO_4 \cdot 6H_2O$	Metal content [%]	Water content [%]

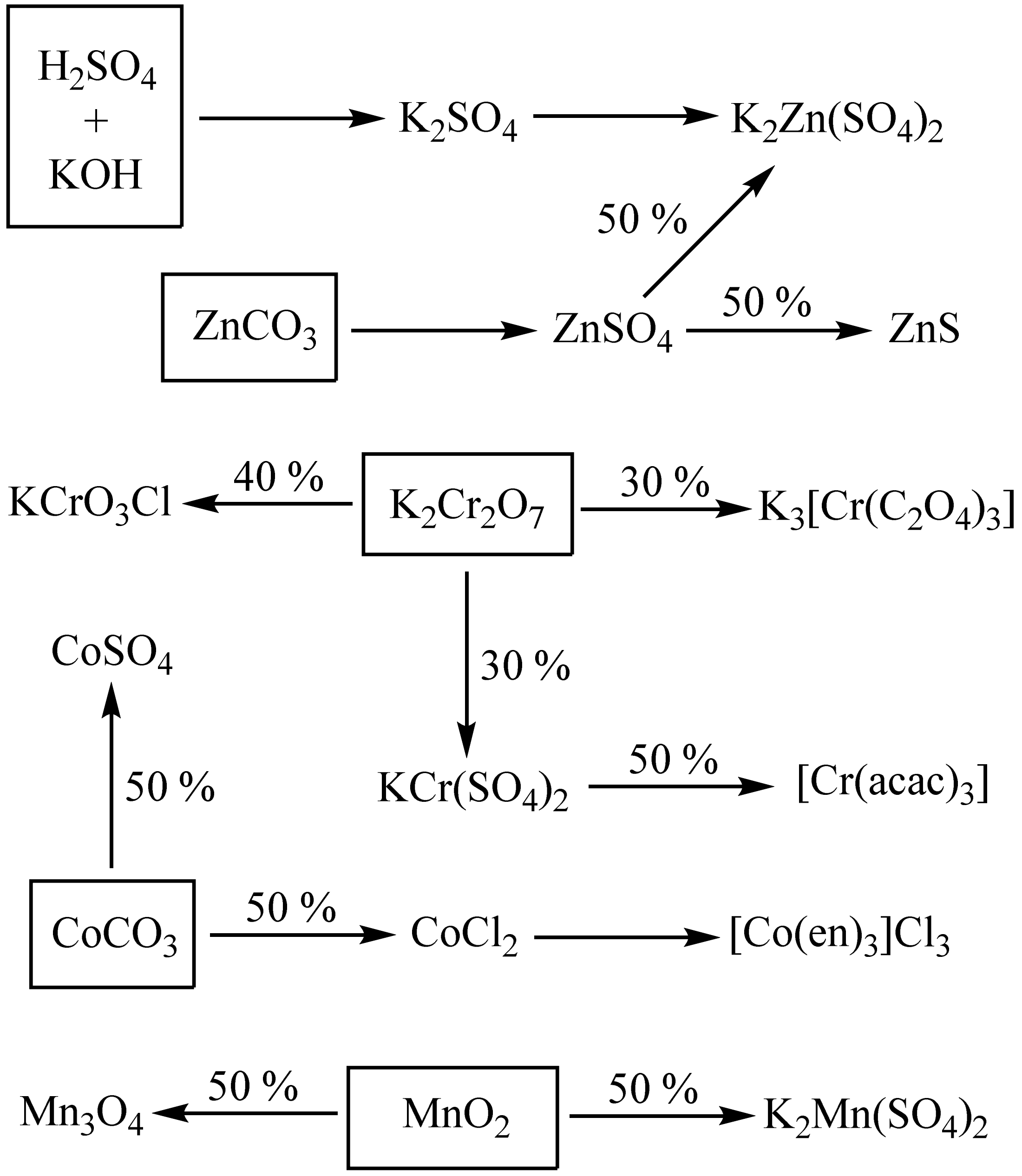
Scheme A7


$NiCO_3$
40 %
$Ni(HCOO)_2$
Ni
30 %
$[Ni(NH_3)_6]Cl_2$
$NiCl_2$
30 %
$NiSO_4$
$[Ni(en)_3]Cl_2$
Fe
$FeSO_4$
$[Fe(acac)_3]$
$KCrO_3Cl$
Cr_2O_3
K_2CrO_4
$K_2Cr_2O_7$
Al_2O_3
70 %
Al
30 %
$K_3[Al(C_2O_4)_3]$

Scheme A7

	Weight	Yield
Al_2O_3		
$Ni(HCOO)_2 \cdot 2H_2O$		
Ni		
$[Ni(NH_3)_6]Cl_2$		
$NiCl_2$		
$NiSO_4 \cdot 6H_2O$		
K_2CrO_4		
$K_2Cr_2O_7$		
K_2CrO_3Cl		
$[Fe(acac)_3]$		
$K_3[Al(C_2O_4)_3] \cdot 3H_2O$		
$FeSO_4 \cdot 7H_2O$		
$[Ni(en)_3]Cl_2 \cdot 2H_2O$		
Chromatography	$c([Co(acac)_3])$ [mM]	$c(K[Co(edta)])$ [mM]
Analysis: $NiSO_4 \cdot 6H_2O$	Metal content [%]	Water content [%]

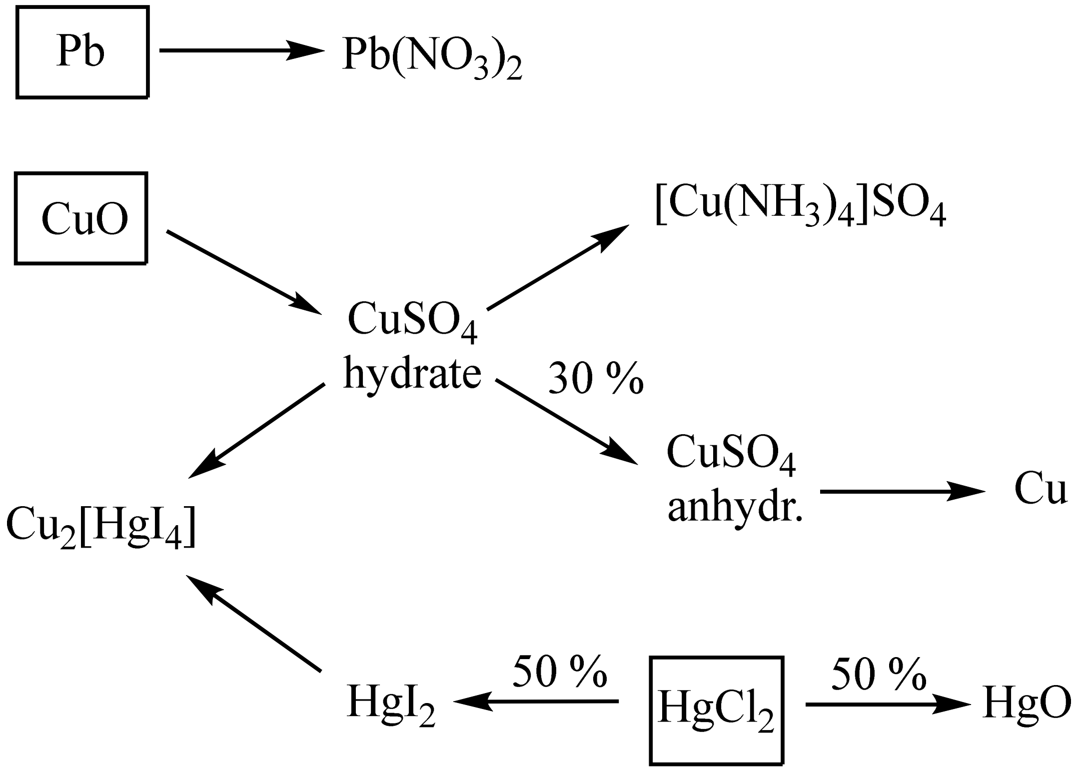
Scheme A8


H_2SO_4 + KOH
K_2SO_4
$K_2Zn(SO_4)_2$
50 %
$ZnCO_3$
$ZnSO_4$
50 %
ZnS
$KCrO_3Cl$
40 %
$K_2Cr_2O_7$
30 %
$K_3[Cr(C_2O_4)_3]$
$CoSO_4$
30 %
50 %
$KCr(SO_4)_2$
50 %
$[Cr(acac)_3]$
$CoCO_3$
50 %
$CoCl_2$
$[Co(en)_3]Cl_3$
Mn_3O_4
50 %
MnO_2
50 %
$K_2Mn(SO_4)_2$

Scheme A8

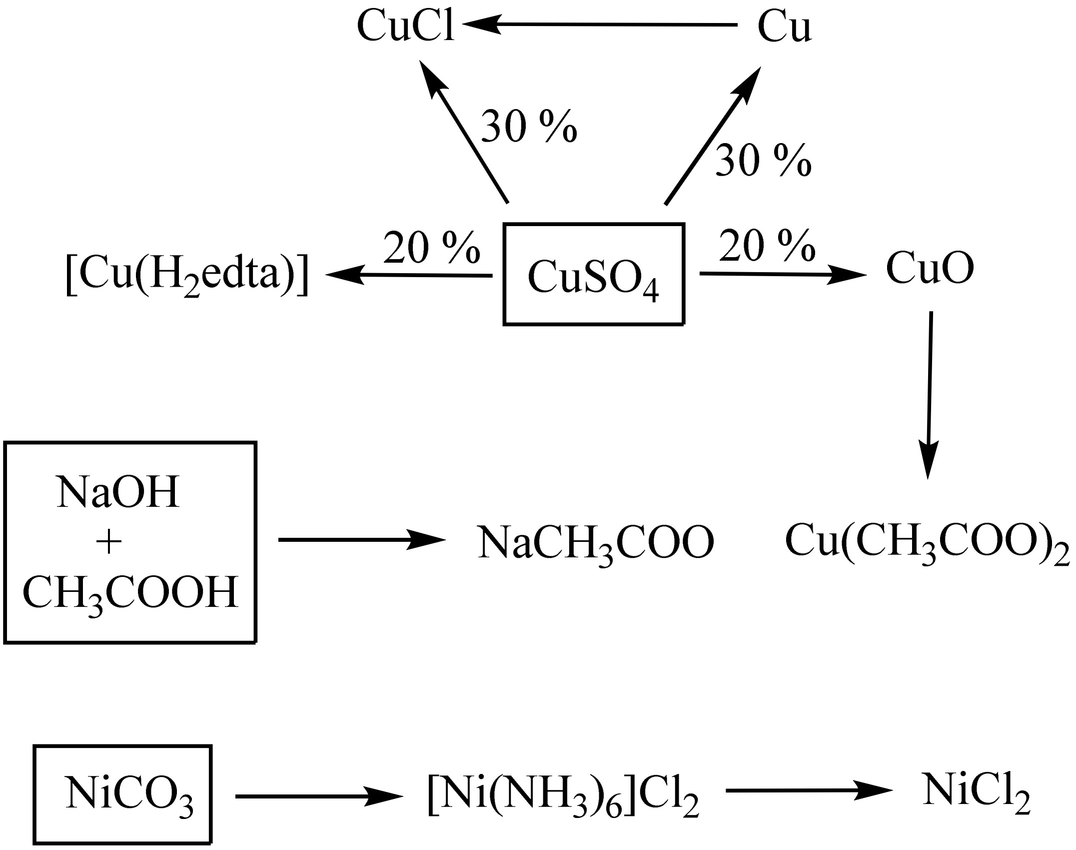
	Weight	Yield
$ZnSO_4 \cdot 7H_2O$		
K_2SO_4		
$K_2Zn(SO_4)_2 \cdot 6H_2O$		
ZnS		
$KCrO_3Cl$		
$K_3[Cr(C_2O_4)_3] \cdot 3H_2O$		
$KCr(SO_4)_2 \cdot 12H_2O$		
Mn_3O_4		
$K_2Mn(SO_4)_2 \cdot 6H_2O$		
$[Cr(acac)_3]$		
$CoSO_4 \cdot 6H_2O$		
$CoCl_2 \cdot 6H_2O$		
$[Co(en)_3]Cl_3$		
Chromatography	*c*($[Co(acac)_3]$) [mM]	*c*($K[Co(edta)]$) [mM]
Analysis: $ZnSO_4 \cdot 7H_2O$	Metal content [%]	Water content [%]

Scheme B1



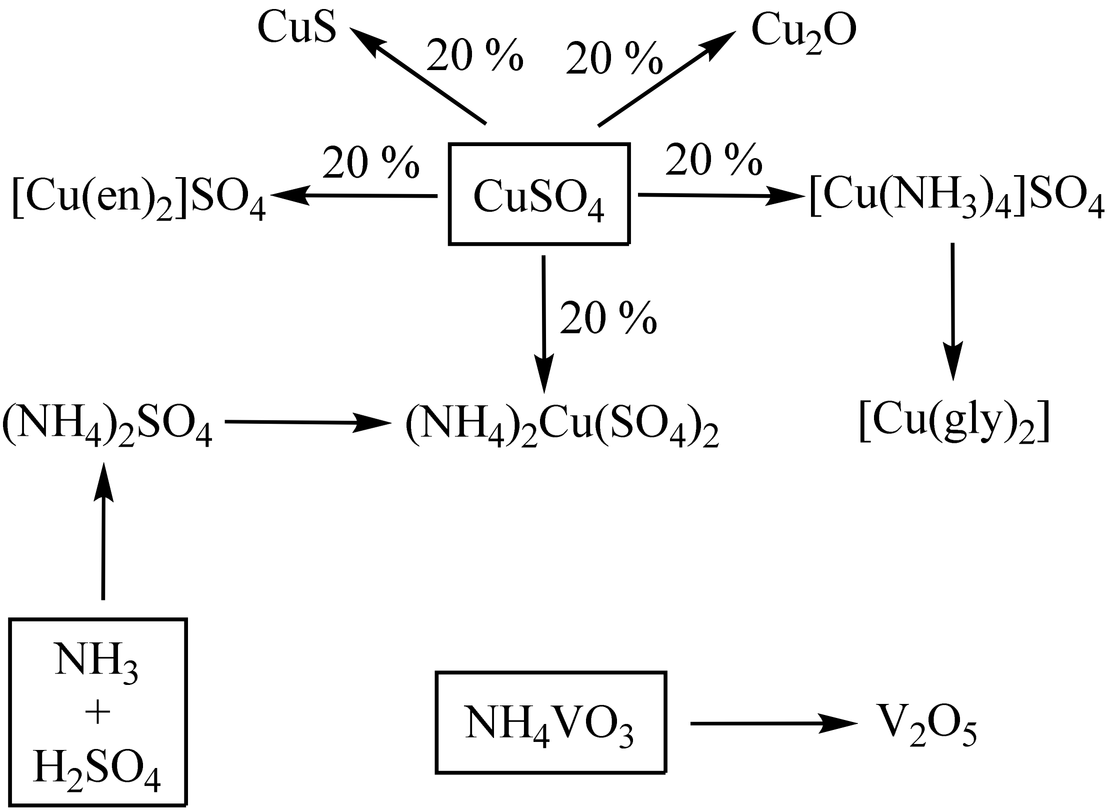
	Weight	Yield
$CuSO_4 \cdot 5H_2O$		
$CuSO_4$ anhydrous		
$[Cu(NH_3)_4]SO_4 \cdot H_2O$		
Cu		
$Cu_2[HgI_4]$		
HgO		
HgI_2		
$Pb(NO_3)_2$		

Scheme B2



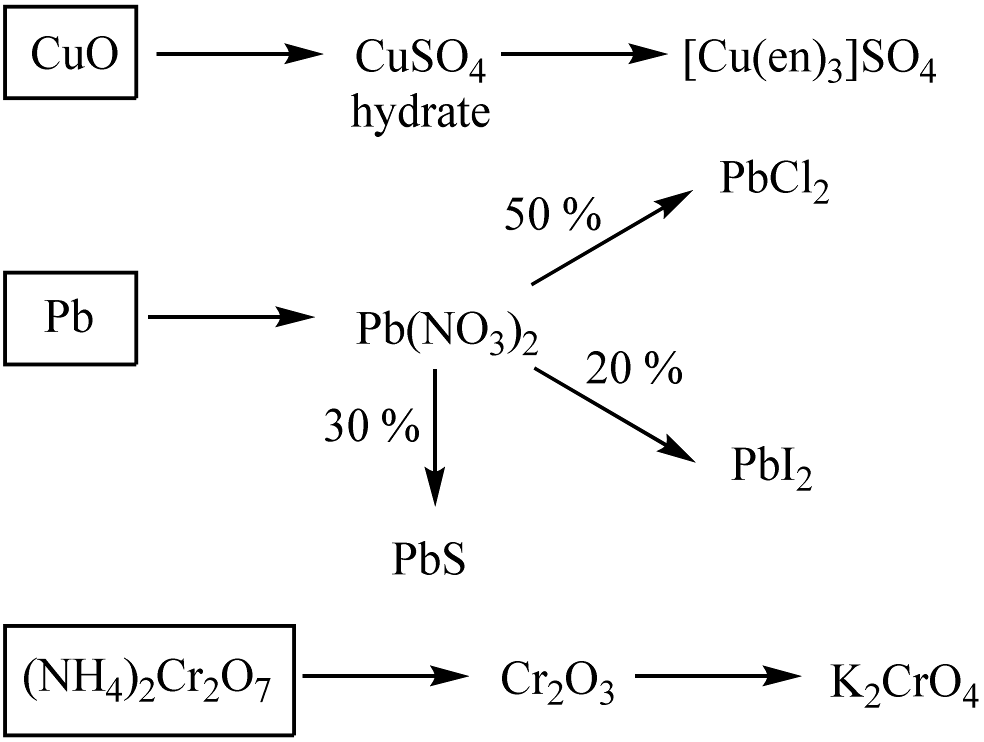
	Weight	Yield
Cu		
$[Cu(H_2edta)]\cdot H_2O$		
CuCl		
$Cu(CH_3COO)_2\cdot H_2O$		
$NaCH_3COO\cdot 3H_2O$		
$[Ni(NH_3)_6]Cl_2$		
CuO		
$NiCl_2$		

Scheme B3



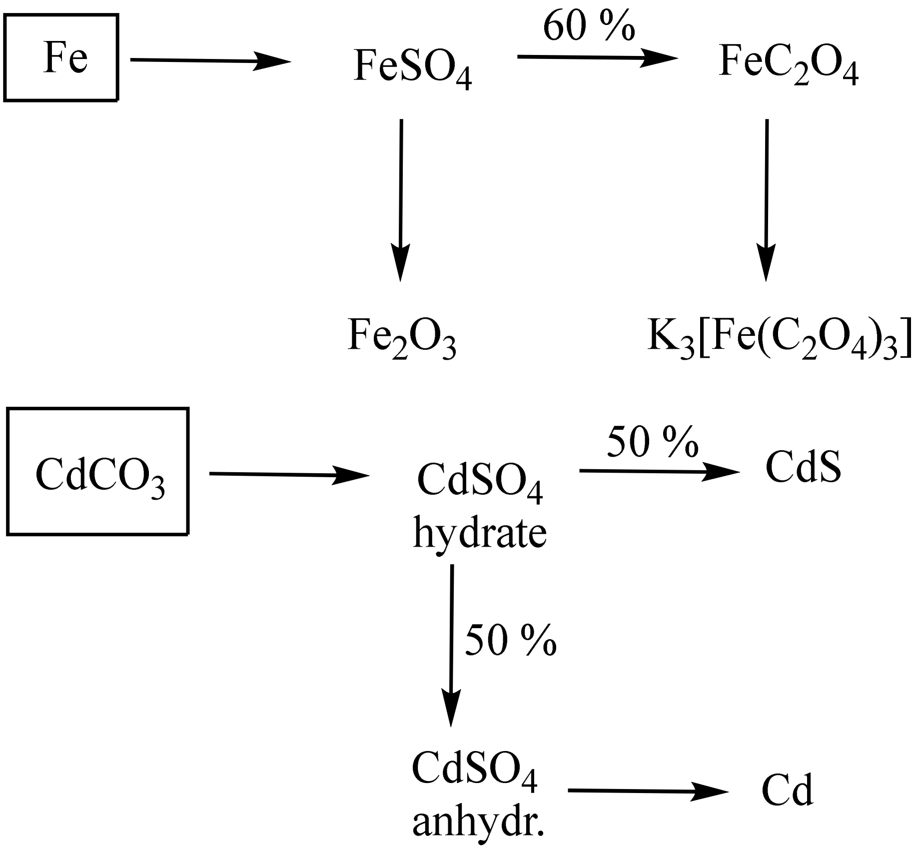
	Weight	Yield
$[Cu(gly)_2]$		
CuS		
Cu_2O		
$[Cu(en)_2]SO_4$		
$(NH_4)_2Cu(SO_4)_2 \cdot 6H_2O$		
$(NH_4)_2SO_4$		
$[Cu(NH_3)_4]SO_4 \cdot H_2O$		
V_2O_5		

Scheme B4



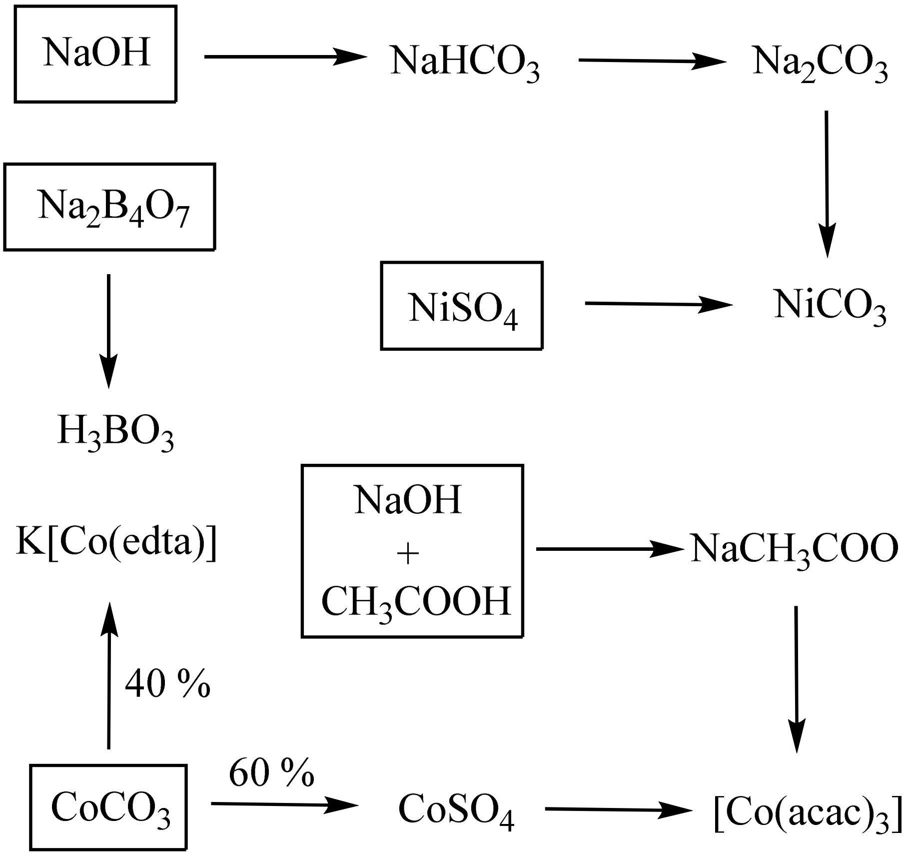
	Weight	Yield
$Pb(NO_3)_2$		
PbI_2		
$PbCl_2$		
PbS		
$CuSO_4 \cdot 5H_2O$		
$[Cu(en)_3]SO_4$		
Cr_2O_3		
K_2CrO_4		

Scheme B5



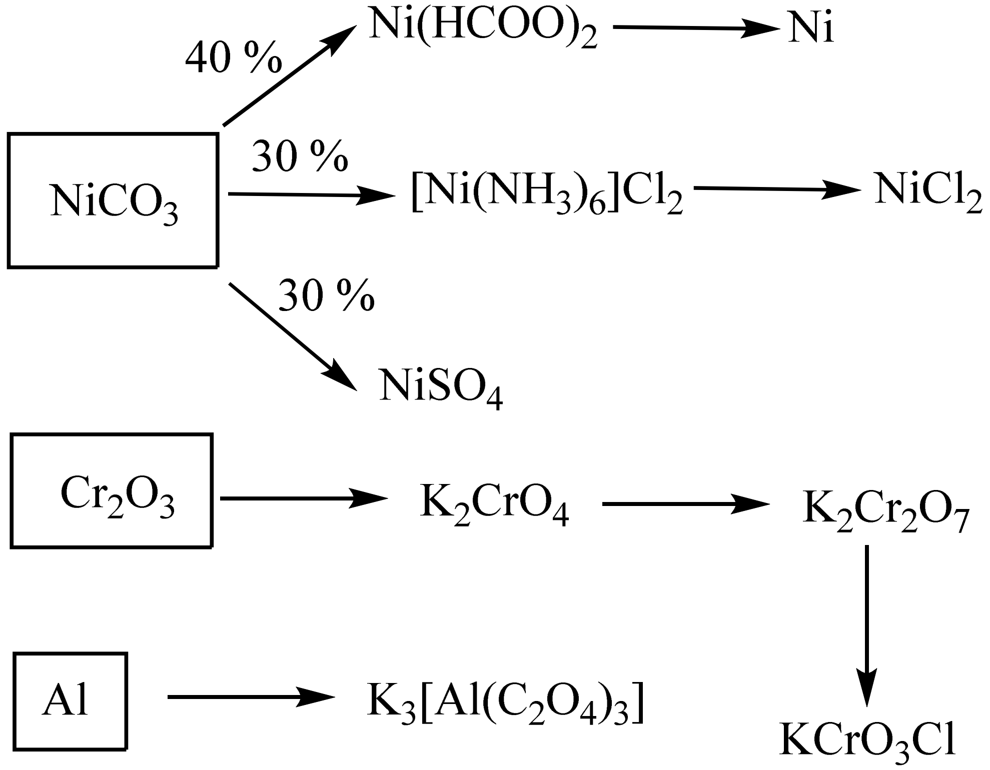
	Weight	Yield
$FeSO_4 \cdot 7H_2O$		
$FeC_2O_4 \cdot 2H_2O$		
$K_3[Fe(C_2O_4)_3] \cdot 3H_2O$		
Fe_2O_3		
$CdSO_4 \cdot 8/3H_2O$		
$CdSO_4$ anhydrous		
CdS		
Cd		

Scheme B6



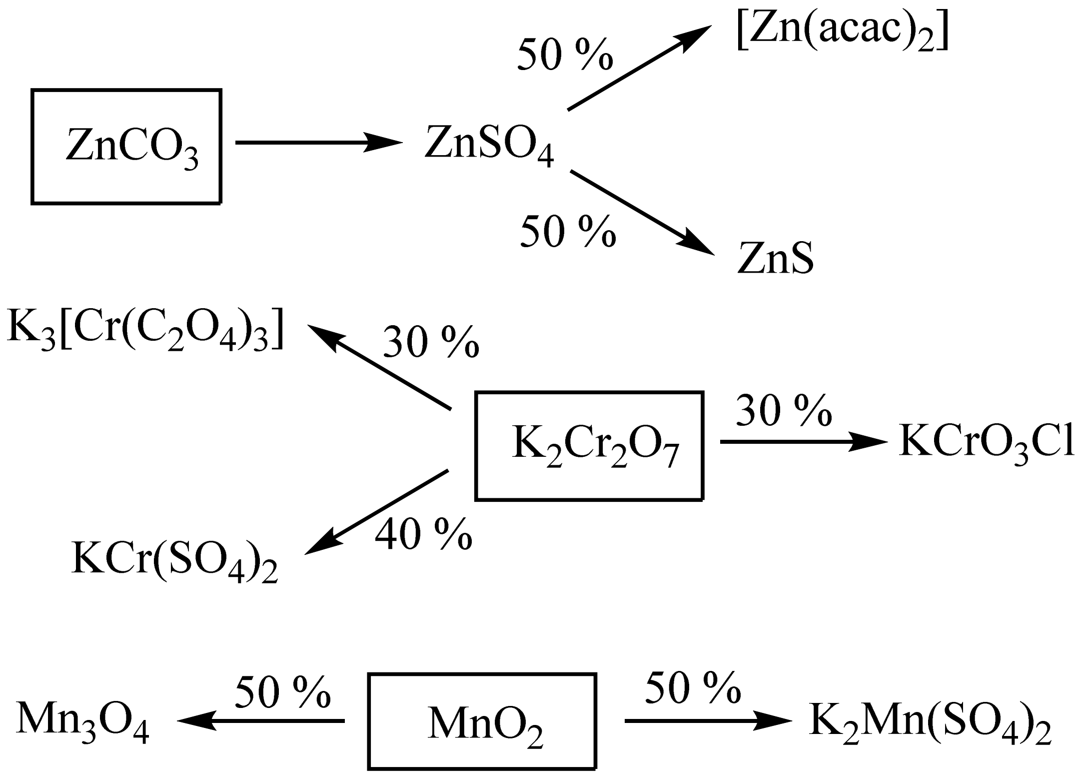
	Weight	Yield
$NaHCO_3$		
Na_2CO_3		
$CoSO_4 \cdot 6H_2O$		
$NiCO_3$		
$[Co(acac)_3]$		
H_3BO_3		
$NaCH_3COO \cdot 3H_2O$		
$K[Co(edta)] \cdot 2H_2O$		

Scheme B7



	Weight	Yield
$K_3[Al(C_2O_4)]\cdot 3H_2O$		
$Ni(HCOO)_2\cdot 2H_2O$		
Ni		
$[Ni(NH_3)_6]Cl_2$		
$NiCl_2$		
$NiSO_4\cdot 6H_2O$		
K_2CrO_4		
$K_2Cr_2O_7$		
K_2CrO_3Cl		

Scheme B8



	Weight	Yield
$ZnSO_4 \cdot 7H_2O$		
[Zn(acac)$_2$]		
ZnS		
$KCrO_3Cl$		
$K_3[Cr(C_2O_4)_3] \cdot 3H_2O$		
$KCr(SO_4)_2 \cdot 12H_2O$		
Mn_3O_4		
$K_2Mn(SO_4)_2 \cdot 6H_2O$		

4. Preparative procedures

4.1. Antimony, Sb

Theory: Antimony is prepared by reduction of antimony(III) chloride with zinc. Antimony(III) chloride is prepared by dissolution of antimony(III) oxide in hydrochloric acid.

$Sb_2O_3 + 6\,HCl \rightarrow 2\,SbCl_3 + 3\,H_2O$
$2\,SbCl_3 + 3\,Zn \rightarrow 3\,ZnCl_2 + 2\,Sb$

Properties: Water-insoluble, air-stable, grey or black powder.

Preparation: Suspend antimony(III) oxide in 15% hydrochloric acid (4-fold stoichiometric excess) in a beaker. Boil the mixture under stirring (magnetic stirrer) until the solid is dissolved. Filtr the solution over a wool scroll in a funnel to a beaker. Add zinc pieces (~4-fold stoichiometric excess) into the solution. Cover the beaker with a watch glass and leave the reaction mixture at room temperature overnight. Separate the solid by decantation and wash the product with 15% HCl, twice with ethanol and finally with ether. The washing liquids are always decanted. Dry the product on air.

4.2. Potassium(I) dichromate, $K_2Cr_2O_7$

Theory: Potassium dichromate is prepared by acidification of potassium(I) chromate solution with sulfuric acid.

$2\,K_2CrO_4 + H_2SO_4 \rightarrow K_2Cr_2O_7 + K_2SO_4 + H_2O$

Properties: Water-soluble orange crystalline solid. Strong oxidation agent.

Preparation: Prepare the saturated aqueous potassium(I) chromate solution (concentration ~40%). Add concentrated sulfuric acid (stoichiometric amount) dropwise. Cool down the resulting solution in an ice bath. Filter the product on a fritt, washed with ice-cold water (10 ml) and dry in an oven at 100 °C.

4.3. Lead(II) nitrate, $Pb(NO_3)_2$

Theory: Lead(III) nitrate is prepared by dissolution of metallic lead in nitric acid.

$3\,Pb + 8\,HNO_3 \rightarrow 3\,Pb(NO_3)_2 + 2\,NO + 4\,H_2O$

Properties: Water and ethanol-soluble, white, crystalline solid.

Preparation: Hammer the lead metal into thin sheets on a solid support. Introduce the metal sheets into a large beaker with 20% nitric acid (5-fold stoichiometric excess), cover the beaker with a watch glass and heated it on a steam bath till the metal dissolves. Transferr the solution into a round-bottom flask and evaporate all volatiles on a rotavap. Dissolve the resulting solid in hot 2% nitric acid to get the saturated solution (solubility is comparable to the solubility in water). Filter the hot solution through a filtr paper and coold it down to room temperature. Add ethanol (equal volume to the solution volume) under stirring and keep the mixture in a fringe for several hours. Filter the product on a fritt and air dry.

4.4. Sodium(I) hexanitrocobaltate(III) monohydrate, $Na_3[Co(NO_2)_6]\cdot H_2O$

Theory: Sodium(I) hexanitrocobaltate(III) monohydrate is prepared by oxidation of cobalt(II) chloride by air in the presence of sodium(I) nitrite.

$4\ Co(NO_3)_2\ +\ 24\ NaNO_2\ +\ 4\ CH_3COOH\ +\ O_2 \rightarrow 4\ Na_3[Co(NO_2)_6]\ +\ 8\ NaNO_3\ +$
$+\ 4\ CH_3COONa\ +\ 2\ H_2O$

Properties: Yellow crystalline powder.

Preparation: Prepare 50% solution of sodium(I) nitrite (2-fold stoichiometric excess) is in warm water. Cool down the solution to room temperature and add cobalt(II) nitrate hexahydrate. Then add 50% acetic acid solution (2,5-fold stoichiometric excess). Transfer the solution into a gas washing bottle. Attach the bottle to the vacuum source (**caution: avoid contamination of the vacuum source with the solution**) and bubble air though the solution for 1 h. Filter the solution through a paper and add ethanol is added (2-times the volume of the treated solution). Keep the mixture for 30 min. Filter the crystals on a fritt, wash with ethanol and air-dry on the fritt by passing air through.

4.5. Sodium(I) hydrogencarbonate, $NaHCO_3$

Theory: Sodium(I) hydrogencarbonate is prepared by neutralization of sodium hydroxide with carbon dioxide.

$NaOH\ +\ CO_2 \rightarrow NaHCO_3$

Properties: Water-soluble, white crystallinic solid.

Preparation: Dissolve sodium hydroxide (5,0 g) in an Erlenmeyer flask to get the 20% solution. Bubble carbon dioxide through the solution until pH drops to 8–9 (precipitate is formed in the course of reaction). If the glass tube is blocked with the precipitate, wash it with hot water. Cool down the reaction mixture in a fridge. Folter the solid on a fritt. Crush the product into a powder, placed on a filtration paper and air-dry overnight.

4.6. Dichlorido-bis(ethylenediamine)cobalt(III) chloride, *trans*-$[CoCl_2(en)_2]Cl$

Theory: Dichlorido-bis(ethylenediamine)cobalt(III) chloride forms two isomers – *cis* a *trans*. The *trans* isomer is prepared by oxidation of cobalt(II) chloride by air in the presence of substoichiometric amount of ethylenediamine.

$4\ CoCl_2 + 4\ HCl + 8\ H_2NCH_2CH_2NH_2 + O_2 \rightarrow 4\ [CoCl_2(en)_2]Cl + 2\ H_2O$

Properties: Green crystalline powder.

Preparation: Prepare 25% cobalt(II) chloride solution in a beaker. Add 10% ethylenediamine solution (1,5-times molar amount of Co(II) salt). Transfer the solution into a gas washing bottle. Attach the bottle to the vacuum source (**caution: avoid contamination of the vacuum source with the solution**) and bubble air though the solution for 1 h. Transfer the solution into a round bottom flask and add concentrated HCl (half volume of the solution). Reduce volume of the solution to half n a rotavap (**caution: the solvent should not be evaporated completely!**) and cool down the mixture in an ice bath. Filter the crystals on a fritt, wash with ethanol and air-dry on the fritt by passing air through. Finish drying in an oven at 100 °C.

4.7. Hexaamminecobalt(III) chloride, $[Co(NH_3)_6]Cl_3$

Theory: Hexaamminecobalt(III) chloride is prepared from cobalt(II) chloride by oxidation with hydrogen peroxide in an ammonium chloride solution. The reaction is catalyzed by charcoal.

$2\ CoCl_2 + 2\ NH_4Cl + 10\ NH_3 + H_2O_2 \rightarrow 2\ [Co(NH_3)_6]Cl_3 + 2\ H_2O$

Properties: Water-soluble, golden-brown-to-orange crystalline powder

Preparation: After preparing a solution of 15% cobalt(II) chloride in an Erlenmeyer flask, add ammonium chloride (3-fold stoichiometric excess), charcoal (1/5 mass of the starting $CoCl_2{\cdot}6H_2O$) and concentrated ammonia (1.5 times the volume of the starting cobalt(II) chloride solution). Cool down the mixture in an ice bath. Fix a thermometer in the solution to monitor the temperature during the following procedure. Slowly add concentrated hydrogen peroxide (4-fold stoichiometric excess) dropwise to keep the temperature of the mixture under 10 ℃. Then, heat the reaction mixture to 60 ℃ in a water bath for 30 min. Cool down the flask in an ice bath. Filter off the solids (mixture of the product with charcoal) on a Büchner funnel. Suspend the solid in 1% HCl (8 times the mass of the starting $CoCl_2{\cdot}6H_2O$) and boil the mixture on a heating plate. Filter the hot mixture through a filter paper. Cool down the filtrate in an ice bath and add 1 ml of concentrated HCl. Filter the solid product on a fritt, wash with small quantity of cold ethanol and air dry.

4.8. Hexaamminenickel(II) chloride, $[Ni(NH_3)_6]Cl_2$

Theory: Hexaamminenickel(II) chloride is prepared ina reaction of nickel(II) chloride solution with gaseous ammonia. The nickel(II) chloride solution is prepared in a reaction of nickel(II) carbonate with hydrochloric acid.

$NiCO_3 + 2\ HCl \rightarrow NiCl_2 + CO_2 + H_2O$

$NiCl_2 + 6\,NH_3 \rightarrow [Ni(NH_3)_6]Cl_2$

Properties: Blue-violet powder which decomposes in hot water. The compound is soluble in diluted ammonia solutions without decomposition. The compound is insoluble in ethanol or in concentrated ammonia solution.

Preparation: Prepare suspension of nickel(II) carbonate in water (3-times wight of nickel(II) carbonate) in a round-bottom flask. Add 20% hydrochloric acid (2-fold stoichiometric excess) under stirring on a magnetic stirrer. **Caution: The reaction is vigorous.** Filter the solution through a filter paper and evaporate the volatiles on a rotavap. Dissolve the remaining solid in water to get 20% solution (considering quantitative yield of the first reaction). Transfer the solution into a large Erlenmeyer flask (more than 3-times volume of the solution). Buuble ammonia through the solution. The solution color changes and, later, precipitate forms and the mixture heats up spontaneously. After the mixture cools down, stop bubbling and add concentrated NH_4Cl in concentrated ammonia (half volume of the solution). Filter the product on a fritt, washed with concentrated ammonia and ethanol and air-dry on the fritt by passing air through.

4.9. Cobalt(II) chloride hexahydrate, $CoCl_2·6H_2O$

Theory: Cobalt(II) chloride hexahydrate is prepared in a reaction of cobalt(II) carbonate with hydrochloric acid.

$CoCO_3 + 2\,HCl \rightarrow CoCl_2 + CO_2 + H_2O$

Properties: Water-soluble red crystals

Preparation: Suspend cobalt(II) carbonate in concentrated hydrochloric acid (5-fold stoichiometric excess) in a beaker. Heat the mixture on a steam bath until all solids dissolve. Filter the solution through a filter paper into a round bottom flask of known mass. Wash the filter with water to minimize losses. Evaporate the volatiles on a rotavap. Dissolve the resulting solid in 30 ml of water and evaporate the volatiles again to reduce the amount of HCl remaining in the solution. Add water (half the mass of the remaining solid), boil the mixture with a heat gun and transfer the solution immediately into a dish. Cover the dish with a paper and leave the solution to crystallize overnight. Filter the product on a fritt and dry between two sheets of filter paper.

4.10. Copper(I) chloride, CuCl

Theory: Copper(I) chloride is prepared in a synproportionation reaction of copper powder with water soluble copper(II) salt in the solution of chloride anions.

$CuSO_4 + Cu + 2\,NaCl \rightarrow 2\,CuCl + Na_2SO_4$

Properties: Poorly water-soluble white powder. Undergoes oxidation and turns green by action of humid air. The compound must be stored in a firmly closed vessels.

Preparation: Prepare 0,5 M copper(II) sulfate solution in a round bottom flask and add few drops of sulfuric acid to reach pH < 2. Add copper powder (stoichiometric amount; freshly prepared by reduction of copper(II) salt with aluminum) and powdered sodium chloride (7-fold stoichiometric excess). Reflux the mixture under stirring in an oil bath until copper dissolves completely. Filter the hot solution through a filter paper and pour the filtrate into 2% sulfuric acid (7-times volume of the solution). Filter the product on a fritt, whashed with acetone and dry in a vacuum desiccator. The product must be stored in a closed vessel.

4.11. Nickel(II) chloride, $NiCl_2$

Theory: The anhydrous nickel(II) chloride is prepared by thermal decomposition of hexaamminenickel(II) chloride.

$$[Ni(NH_3)_6]Cl_2 \rightarrow NiCl_2 + 6\ NH_3$$

Properties: Yellowish powder. Turns green in contanct with moisture.

Preparation: Heat finely powdered hexaamminenickel(II) chloride in an oven at 500 °C until the mass remains constant. Coold down the product in a dessicator. The product must be stored in a closed vessel.

4.12. Lead(II) chloride, $PbCl_2$

Theory: Lead(II) chloride is precipitated with hydrochloric acid from solutions containing lead(II) ions.

$$Pb(NO_3)_2 + 2\ HCl \rightarrow PbCl_2 + 2\ HNO_3$$

Properties: White solid forming silk needles on crystallization, poorly soluble in cold water. Solubility increases with temperature.

Preparation: Prepare 10% solution of lead(II) nitrate in a beaker. Heat the solution at ~90 °C and add add 20% hydrochloric acid (50% stoichiometric excess) dropwise under stiring on a magnetic stirrer. Heat the suspension for 3 hours on a steam bath. Cool down the mixture and filter the precipitate on a fritt. Transfer the crude product into a beaker and dissolve in boiling water (water volume is determined by solubility of the theroretical product amount). Filter the hot solution through a filter paper and cool down the solution. Filter the crystals on a fritt wash with small amount of cold water and dry at 100 °C.

4.13. Pentaammin-chloridocobalt(III) chloride, $[Co(NH_3)_5Cl]Cl_2$

Theory: Pentaammin-chloridocobalt(III) chloride is prepared by cobalt(II) chloride oxidation with hydrogen peroxide in the ammonium chloride solution in aqueous ammonia.

$$2\ CoCl_2 + 2\ NH_4Cl + 8\ NH_3 + H_2O_2 \rightarrow 2\ [Co(NH_3)_5Cl]Cl_2 + 2\ H_2O$$

Properties: Purple crystalline powder.

Preparation: Dissolve ammonium chloride (2,2-times stoichiometric excess) in concentrated aqueous ammonia (6-time weight of ammonium chloride) in an Erlenmeyer flask. Add $CoCl_2.6H_2O$ under stirring on a magnetic stirrer. Then add concentrated H_2O_2 (equal weight to $CoCl_2.6H_2O$) very slowly, because the mixture vigorously bubbles. After finish of the bubbling, add concentrated hydrochloric acid (3-times the volume of used H_2O_2 solution) under stirring. Heat the mixture gently 55–65 ℃ for next 15 min. Cool down the mixture, filter the product on a fritt, whash with mall volume of cold water, with ethanol and dry on air.

4.14. Tris(ethylenediamine)cobalt(III) chloride, $[Co(en)_3]Cl_3$

Theory: Tris(ethylenediamine)cobalt(III) chloride is prepared by cobalt(II) chloride oxidation with hydrogen peroxide in presence of ethylenediamine.

$$2\ CoCl_2 + 2\ HCl + 6\ H_2NCH_2CH_2NH_2 + H_2O_2 \rightarrow 2\ [Co(en)_3]Cl_3 + 2\ H_2O$$

Properties: Gold needles.

Preparation: Prepare 30% ethylenediamine solution (stoichiometry) in a large beaker. Cool down the solution in an ice bath and add 6M HCl (stoichiometric amount) under stirring on a magnetic stirrer. Add 25% cobalt(II) chloride solution. Then add slowly concentrated H_2O_2 (4-fold stoichiometric excess) dropwise under stirring. Evaporate cca half of solven on a steam bath. Add concentrated HCl (volume of the solution) followed by ethanol (2-times volume of the solution). Cool down the solution in an ice bath. Filter the product on a fritt, wash with ethanol and dry on air.

4.15. Tris(ethylenediamine)nickel(II) chloride dihydrate, $[Ni(en)_3]Cl_2{\cdot}2H_2O$

Theory: Tris(ethylenediamine)nickel(II) chloride dehydrate is prepared in a reaction of nickel(II) chloride with ethylenediamine excess.

$$NiCl_2 + 3\ H_2NCH_2CH_2NH_2 \rightarrow [Ni(en)_3]Cl_2$$

Properties: Water-soluble purple crystalline powder, insoluble in acetone and nonpolar organic solvents.

Preparation: Prepare suspension of nickel(II) chloride hydrate in water (5-time weight of the nickel(II) salt). Heat the solution on a steam bath until complete dissolution. Add ethylenediamine (2-fold stoichiometric excess) dropwise under stirring. Filter the solution over a filter paper to a beaker and add slowly acetone (3-times volume of the solution) without stirring. Cover the beaker with a watch glass and leave the solution overnight. Filter the product on a fritt, wash with acetone and dry on air.

4.16. Potassium chlorochromate, $KCrO_3Cl$

Theory: Potassium chlorochromate is prepared in a reaction of potassium dichromate with hydrochloric acid.

$$2\ HCl + K_2Cr_2O_7 \rightarrow 2\ KCrO_3Cl + H_2O$$

Properties: Orange needles. Strong oxidation agent.

Preparation: Mix pulverized potassium dichromate with 20% hydrochloric acid (2-fold stoichiometric excess. Cover the beaker with a watch glass and heat on a steam bath until complete dissolution. Leave the mixture to crystallize for 2 hours. Filter the product on a fritt, and dry on a watch glass in a desiccator filled with sulfuric acid. Avoid contact of the product with fiter paper or organic solvents.

4.17. Potassium chromate, K_2CrO_4

Theory: Poptassium chromate is prepared by chromium(III) oxide oxidation in a melted mixture of potassium nitrate and potassium hydroxide.

$$Cr_2O_3 + 3\ KNO_3 + 4\ KOH \rightarrow 2\ K_2CrO_4 + 3\ KNO_2 + 2\ H_2O$$

Properties: Water soluble yellow crystalline powder, poorly soluble in organic solvents. Strong oxidizing agent.

Preparation: Mix Cr_2O_3 with powdered mixture of KNO_3 and KOH (both compounds in 10% stoichiometric excess). Introduce the mixture in a crucible and heat in a flame for 1 hour. The mixture color turns from green to yellow-orange. Leave the mixture to cool down. Put the crucible into a beaker with water so that the whole crucible is cover with the solution. Boil the mixture for 1 hour. Filter the solution over a filter paper into a round bottom flask. Evaporate water on a rotavap. Dissolve the remaining solid in water (6-times weight of starting Cr_2O_3) and the solution dropp slowly into a beaker with ethanol (volume of the solution) stirred with magnetic stirrer. Filter the product immediately on a fritt, wash with ethanol and dry on air.at room temperature.

If the color is greenish, purify the product by preparation of the saturated solution in 5% aqueous KOH followed by filtration over the filter paper and precipitation in ethanol and isolation as described above.

4.18. Lead(II) chromate, $PbCrO_4$

Theory: Lead(II) chromate is precipitated from lead(II) solts solutions with potassium chromate.

$Pb(NO_3)_2 + K_2CrO_4 \rightarrow PbCrO_4 + 2KNO_3$

Properties: Insoluble yellow powder.

Preparation: Prepare 5% lead(II) nitrate solution in a large beaker. Add 5% potassium chromate solution (stoichiometric amount) dropwise under stirring on a magnetic stirrer. Leave the mixture for 20 minutes. Filter theproduct on a Büchner funnel, wash with water, ethanol and air-dry on the fritt by passing air through. Finish drying at 100 °C. **Do not filter the product on a fritt!**

4.19. Iodine, I_2

Theory: Iodine is in a reaction of iodides with various oxidation agents. The very common oxidation agent is hydrogen peroxide.

$2\ KI + H_2O_2 + 2\ HCl \rightarrow I_2 + 2\ KCl + 2\ H_2O$

Propeeties: Grey-black precipitate or metallic crystals. Iodine is poorly water-soluble and well soluble in organic solvents. The solubility in water significantly increases in the presence of iodide anions due to triiodide anion formation. Iodine sublimates on heating forming purple vapours.

Preparation: Prepare 20% potassium iodide solution. Add concentrated hydrochloric acid (50% stoichiometric excess). Add concentrated hydrogen peroxide (3-fold stoichiometric excess) dropwise and leave the mixture standing for 30 minutes. Filter the product on a fritt, wash with water and dry in desiccator over sulfuric acid.

4.20. Antimony(III) iodide, SbI_3

Theory: Anotimony(III) iodide is prepared in a reaction of antimony with iodine in a high-boiling inert organic solvent.

$2\ Sb + 3\ I_2 \rightarrow 2\ SbI_3$

Properties: Organic solvent-soluble yellow to red powder hydrolyzing in water.

Preparation: Prepare suspension of antimony in toluene (40-times antimony weight). Add iodine (3-times antimony weight) and heat the mixture under reflux under stirring in an oil bath. After complete dissolution of antimony, cool down the mixture to room temperature. Filter the product on a fritt and dry under vacuum in a desiccator. Wash the glass immediately with ethanol. Wash remaining impurities with 20% HCl.

4.21. Lead(II) iodide, PbI_2

Theory: Lead(II) iodide precipitates from lead(II) salts solution by addition of potassium iodide.

$Pb(NO_3)_2 + 2\ KI \rightarrow PbI_2 + 2\ KNO_3$

Properties: Poorly water-soluble yellow crystals. Water solubility significantly increases with increasing temperature. Crystallization from hot solution yields golden plates.

Preparation: Prepare 0,3% potassium iodide solution and add three drops of concentrated nitric acid. Heat the solution on a magnetic stirrer. Add potassium iodide (stoichiometry) into the boiling solution and coll down the solution with cold water. Filter the crystals on a fritt, wash sith water (one volume of the fritt) and dry at 100 °C.

4.22. Mercury(II) iodide, HgI_2

Theory: Mercurry(II) iodide is prepared by precipitating soluble mercury salts with potassium iodide. Iodide must be used in a stoichiometric amount. In excess, iodide dissolves the product, thereby forming tetraiodidomercurate.

$HgCl_2 + 2KI \rightarrow HgI_2 + 2KCl$

Properties: Water-insoluble orange powder

Preparation: Prepare a 5% aqueous solution of mercury(II) chloride. Add 5% aqueous solution of potassium iodide (stoichiometric amount) dropwise. Let the mixture stand for 1 hour. Filter the precipitate on a fritt S4, wash with water and air-dry on the fritt by passing air through. Finally, dry the product at 100 °C. Wash the laboratory equipment contaminated with the product in a mixture of hydrochloric acid and nitric acid (~ 1:1 volume ratio).

4.23. Cadmium, Cd

Theory: Cadmium is prepared by reduction of cadmium(II) salts with zinc metal.

$Cd^{2+} + Zn \rightarrow Cd + Zn^{2+}$

Properties: Silver metal soluble in strong aicds.

Preparation: Zinc peaces (5 to 10-fold stoichiometric excess) wash with 10% nitric acid for 10 seconds and then wash with water. Insert zinc into 10% cadmium(II) sulfate solution. Remove cadmium from the zinc surface every 30 minutes. After the cadmium reduction is complete, remove zinc peaces, wash with water and return for next use. Filter cadmium on a fritt, wash with water and ethanol and dry at 100 °C.

4.24. Bis(acetylacetonate)copper(II) complex, $[Cu(acac)_2]$

Theory: The bis(acetylacetonate)copper(II) complex is prepared in a reaction of acetyacetone with copper sulfate in the presence of aqueous ammonia, which serves as the base that neutralizes acetyacetone.

$$CuSO_4 + 2\ Hacac + 2\ NH_3 \rightarrow [Cu(acac)_2] + (NH_4)_2SO_4$$

Properties: Water-insoluble blue needles, soluble in polar, organic solvents.

Procedure: Prepare a 5% aqueous solution of copper(II) sulfate. Add concentrated aqueous ammonia under vigorous stiring until the light blue precipitate dissolves. Add acetylacetone dropwise (stoichiometric amount) and keep the mixture under stiring for another 15 minutes. Filter the precipitate; wash with water, air-dry on the fritt by passing air through and finish drying in a dessiccator. Dissolve the crude product in a minimum amount of chloroform and filter through cotton wool (placed in a funnel tip) into the crystallization dish. Cover the dish with a paper and leave it in the fume hood. Crystals of the product are formed by solvent evaporation. Caution: The solvent should not evaporate completely. Filter the crystals on a fritt and dry on air. Wash the fritt with nitric acid.

4.25. Bis(acetylacetonate)-oxovanadium(IV) complex, $[VO(acac)_2]$

Theory: 3.25. Bis(acetylacetonate)-oxovanadium(IV) complex, also known as vanadyl acetylacetonate, is prepared in a rection of vanadyl(II) sulfate with acetylacetone in sodium carbonate solution.

$$VOSO_4 + 2\ Hacac + Na_2CO_3 \rightarrow [VO(acac)_2] + Na_2SO_4 + CO_2 + H_2O$$

Properties: Water-insoluble blue-green crystalline powder, soluble in polar organic solvents.

Preparation: Připravte a 5% vanadyl(II) sulfate solution (heat the mixture with aheatgun to accelerate the dissolution). Add acetylacetone (20% stoichiometric excess) and add 15% sodium carbonate solution (2-fold stoichiometric axcess) dropwise under stirring on a magnetic stirrer. Continue stirring for additional 10 minutes. Filter the precipitate on a fritt, wash with water and air-dry on the fritt by passing air through. Finish drying in a desiccator. Dissolve the crude product in minimum volume of acetone, filter the solution through cotton wool (placed in a funnel tip) into the crystallization dish. Cover the dish with a paper and leave it in the fume hood. Crystals of the product are formed by solvent evaporation. Caution: The solvent should not evaporate completely. Filter the crystals on a fritt and air-dry on the fritt by passing air through.

4.26. Bis(acetylacetonate)zinc(II) complex, $[Zn(acac)_2]$

Theory: Bis(acetylacetonate)zinc(II) complex is prepared in a rection of acetylacetone with zinc(II) sulfate in presence of ammonia which serves as a base for acetylacetone deprotonation.

$ZnSO_4 + 2\ Hacac + 2\ NH_3 \rightarrow [Zn(acac)_2] + (NH_4)_2SO_4$

Properties: Cold water-insoluble white crystalline powder, soluble in polar organic soplvents.

Preparation: Prepare a 5 % zinc(II) sulfate solution. Add concentrated ammonia dropwise. Ammonia addition results in precipitation of zinc(II) hydroxide which, consequently, dissiolves in ammonia excess. Add such amount of concentrated ammonia so that the precipitate just dissolves. Add acetylacetone (stoichiometry) dropwise under stirring and continue stirring for additional 15 minutes. Filter the precipitate on a fritt, wash with water and air-dry. Clean the fritt with acetone.

4.27. Bis(glycinate)copper(II) complex, $[Cu(gly)_2]$

Theory: Bis(glycinate)copper(II) complex is prepared in a reaction of copper(II) salts with glycine. Glycine is coordinated as a chelate through both groups, carboxylate and aminogroup. Copper(II) coordination enavironment is square plannar. *Trans* isomer is preferentially formed.

$[Cu(NH_3)_4]SO_4 + 2\ Hgly \rightarrow [Cu(gly)_2] + (NH_4)_2SO_4 + 2NH_3$

Properties: Poorly water-soluble blue crystalline powder.

Preparation: Dossilve tetraammincopper(II) sulfate monohydrate in water (5-times weight of the Cu(II) salt). Add glycine (20% stoichiometric excess) and heat the mixture under reflux (magnetic stirrer, oil bath) for 1 h. Coll down the mixture in a refrigerator, filter the product on a fritt, wash with small amount of cold water and with ethanol and dry on air.

4.28. Tris(acetylacetonate)chromium(III) complex, $[Cr(acac)_3]$

Theory: Tris(acetylacetonate)chromium(III) complex is prepared in a reaction of chromium(III) salt with acetylacetone in an rea containing solution. Urea hydrolysis in the course of reaction yielding ammonia which serves as a base for acetylacetone deprotonation.

$OC(NH_2)_2 + H_2O \rightarrow CO_2 + 2\ NH_3$
$Cr^{3+} + 3\ Hacac + 3\ NH_3 \rightarrow [Cr(acac)_3] + 3\ NH_4^+$

Properties: Cold water-insoluble purple crystals, soluble in less polar organic solvents.

Preparation: Prepare an 0,25 M chromium(III) salt solution in a round bottom flask. Add urea (10-fold stoichiometric excess) and acetylacetone (2,5-fold stoichiometric excess). Heat the mixture in a boiling water bath for 1 h. Coll down the mixture at room temperature. Filter the precipitate on a fritt, wash with water and air-dry on the fritt by passing air through. Finish drying in a desiccator. Dissolve the crude product in minimum volume of acetone, filter the solution through cotton wool (placed in a funnel tip) into the crystallization dish. Cover the dish with a paper and leave it in the fume hood. Crystals of the product are formed by solvent evaporation. Caution: The solvent should not evaporate completely. Filter the crystals on a fritt and air-dry on the fritt by passing air through. Clean the fritt with concentrated nitric acid.

4.29. Tris(acetylacetonate)cobalt(III) complex, [Co(acac)$_3$]

Theory: Tris(acetylacetonate)cobalt(III) complex is prepared by oxidation of cobalt(II) ions with hydrogen peroxide in acetylacetone presence. Sodium acetate is present to maintain optimal pH.

$2\,CoSO_4 + 6\,Hacac + H_2O_2 + 4\,CH_3COONa \rightarrow 2\,[Co(acac)_3] + 2\,Na_2SO_4 +$
$+\ 4\,CH_3COOH + 2\,H_2O$

Properties: Smaragdově zelený krystalický prášek nerozpustný ve studené vodě, rozpustný v organických rozpouštědlech.

Preparation: Prepare a 10% cobalt(II) sulfate solution in a beaker. Add acetylacetone (2-fold stoichiometric excess) and sudium acetate trihydrate (2-times weight of acetylacetone) and stirre the mixture on a magnetic stirrer for 10 minutes. Add ethanol (2-times volume of the suspension) and heat the mixture. Add 10% hydrogen peroxide (3-fold stoichiometric excess) dropwise under stirring during 10 minutes. Cover the beaker with a watch glass and keep the mixture boiling for additional 30 minutes. Cool down the mixture at room temperatu and add water (3-times volume of the mixture). Filter the product on a fritt, wash with water and and air-dry on the fritt by passing air through.

4.30. Tris(acetylacetonate)iron(III) complex, [Fe(acac)$_3$]

Theory: Tris(acetylacetonate)iron(III) complex is prepared by oxidation of iron(II) ions with hydrogen peroxide in acetylacetone presence. Sodium acetate is present to maintain optimal pH.

$2\,FeSO_4 + 6\,Hacac + H_2O_2 + 4\,CH_3COONa \rightarrow 2\,[Fe(acac)_3] + 2\,Na_2SO_4 +$
$+\ 4\,CH_3COOH + 2\,H_2O$

Properties: Wtaer-insoluble red crystalline powder, soluble in organic solvents.

Preparation: Prepare the saturated iron(II) sulfate solution. Add acetylacetone (stoichiometry) and sodium acetate trihydrate (3-times weight of acetylacetone. Heat the mixture at 90 °C and add 10% hyhdrogen peroxide (3-fold stoichiometric excess) dropwise under stirring (magnetic stirrer) during 30 minutes. Continue heating at the same temperature for additional 30 minut. Cool down the mixture in an ice bath. Filter the precipitate on a fritt, wash with water and air-dry on the fritt by passing air through. Finish drying in a desiccator. Dissolve the crude product in minimum volume of acetone, filter the solution through cotton wool (placed in a funnel tip) into the crystallization dish. Cover the dish with a paper and leave it in the fume hood. Crystals of the product are formed by solvent evaporation. Caution: The solvent should not evaporate completely. Filter the crystals on a fritt and air-dry on the fritt by passing air through. Clean the fritt with acetone.

4.31. Potassium-cobalt(III) complexonate dihydrate, $K[Co(edta)]\cdot 2H_2O$

Theory: Ethylenediamintetraacetic acid (H_4edta) is a ligand suitable for complexation of the first-row transition metal ions. Complexes show high stability. Potassium-cobalt(III) complexonate dihydrate is prepared by oxidation of cobalt(II)-edta complex with hydrogen peroxide.

$CoCO_3 + 2\ CH_3COOH \rightarrow Co(CH_3COO)_2 + CO_2 + H_2O$
$2\ Co(CH_3COO)_2 + 2\ H_4edta + 6\ KOH + H_2O_2 \rightarrow 2\ K[Co(edta)] + 4\ CH_3COOK +$
$+\ 8\ H_2O$

Properties: Water-soluble dark-purple crystal, insoluble in organioc solvents.

Preparation: In a large beaker prepare suspension of cobalt(II) carbonate in 20% acetic acid (4-fold stoichiometric excess). Stire the mixture untill solid completely dissolves. Add H_4edta (stoichiometry) and add slowly 30% KOH (50% stoichiometric excess) dropwise. Heat the solution and add 3% hydrogen peroxide (2-fold stoichiometric excess) dropwise under stirring (magnetic stirrer). Overlayer the solution with ethanolu (2-times volume of the solution) and leave the mixture overnight in a refrigerator. To overlayer the solution, add ethanol slowly from a wash bottle on wall of the flask so that the liquids do not mix and two layers are formed. Filter the product on a frit, wash with ethanol and air-dry on the fritt by passing air through. Finish drying on air.

4.32. Copper(II) complexonate monohydrate, $[Cu(H_2edta)]\cdot H_2O$

Theory: Ethylenediamintetraacetic acid (H_4edta) is a ligand suitable for complexation of the first-row transition metal ions. Copper(II) complexonate monohydrate is prepared in a reaction of copper(II) ions with ethylenediamintetraacetic acid.

$CuSO_4 + H_4edta \rightarrow [Cu(H_2dta)] + H_2SO_4$

Properties: Poorly water-soluble mlue crystalline solid.

Preparation: Prepare a 20% copper(II) sulfate solution in a beaker. The mixture can be heated with a heat-gun to accelerate dissolution. Add H_4edta (stoichiometry) cover the beaker with a watch glass. As soon as the mixture becomes boiling, remove the beaker from heat and leave it ar room temperature overnight. Filter the product on a fritt, wash with ethanol and air-dry on the fritt by passing air through. Finish drying between sheets of filter paper.

4.33. Boric acid, H_3BO_3

Theory: Boric acid is prepared in a reaction of borax (sodium tetraborate decahydrate $Na_2B_4O_7 \cdot 10H_2O$) with hydrochloric acid.

$Na_2B_4O_7 + 2\,HCl + 5\,H_2O \rightarrow 4\,H_3BO_3 + 2\,NaCl$

Properties: Poorly cold water-soluble colorless plate crystals, soluble in alcohols.

Preparation: Prepare a sodium tetraborate solution saturated at 100 °C in an Erlenmeyer flask. Keep the solution boiling and add concentrated hydrochloric acid (10% stoichiometric axcess). Cool down the flask with cold water. Filter the product, wash with small volume of cold water and air-dry at room temperature.

4.34. Copper, Cu

Theory: Copper powder is prepared by reducing soluble copper salts with aluminum. The aluminum excess is dissolved by the diluted hydrochloric acid that does not dissolve copper.

$3\,CuSO_4 + 2\,Al \rightarrow 3\,Cu + Al_2(SO_4)_3$

Properties: Red or brown powder insoluble in water or organic solvents. It is soluble only in oxidizing acids.

Procedure: Prepare a 5% aqueous solution of copper(II) sulfate. Add aluminum metal (two-fold stoichiometric excess) and three drops of concentrated hydrochloric acid. Heat the mixture on a steem bath until the solution is no longer blue. Separate the solid by decantation. Add concentrated hydrochloric acid in small portions (30 times the molar amount of aluminum) and leave the mixture stand until no more hydrogen bubbles are formed. Separate the solid by decantation, wash it 3 times with water and 3 times with ethanol and ether. The product is separated by decantation in each washing step. Leave the beaker cover with a paper until the product is dry.

4.35. Nickel(II) formate dihydrate, $Ni(HCOO)_2 \cdot 2H_2O$

Theory: Nickel(II) formate dihydrate is prepared in a reaction of nicke(II) carbonate with hydrochloric acid followed by ethanol-initiated crystallization from formate-containing solution.

$NiCO_3 + 2\,HCl \rightarrow NiCl_2 + CO_2 + H_2O$

$NiCl_2 + 2\,HCOOH + 2\,NaOH \rightarrow Ni(HCOO)_2 + 2\,NaCl + 2\,H_2O$

Properties: Poorly water-soluble green crystals.

Preparation: Prepare suspension of nickel(II) carbonate in water (3-times weight of nickel(II) carbonate). Add concentrated hydrochloric acid (5-fold stoichiometric excess) under stirring (magnetic stirrer). Carefully, the mixture bubbles vigorously. After the solid is dissolved, filter tho solution over a filter paper into a 250ml round-bottom flask. Evaporate the volatiles on a rotavap. Evaporations yields a yellow-green oily residue. Dissolve the residue in 50% formic acid (20% stoichiometric excess). Place the flaks in a cold water bath and add 20% sodium hydroxide solution (stoichiometry) dropwise under stirring (magnetic stirrer). Overlayer the solution with ethanol (2-times volume of the solution) and leave the mixture overnight. To overlayer the solution, add ethanol slowly from a wash bottle on wall of the flask so that the liquids do not mix and two layers are formed. Next day mix the two layers, filre the product on a fritt, wash with ethanol and air-dry at room temperature.

4.36. Nickel, Ni

Theory: Nickel is prepared by thermal decomposition of nickel(II) formate under inert atmosphere.

$$Ni(HCOO)_2 \rightarrow Ni + CO + CO_2 + H_2O$$

Properties: Water-insoluble blask magnetic powder, soluble in strongly acidic solutions.

Preparation: Support a temperature-resistent glass tube with two stands. Place a weighing boat with nickel(II) formate dihydrate in the middle of the glass tube. Close both ends of the tube with stoppers penetrated with a thin glass tube. Connect the nitrogen outlet to a water-filled beaker to control the nitrogen stream. Flush the tube with nitrogen for 5 minutes. Then reduce the nitrogen strem (2–3 bubbles per second) and heat the salt with flame for 1 hour with Mecker burner. After the tube cools down, stop the nitrogen stream and dissemble the apparatus.

4.37. Copper(II) acetate monohydrate, $Cu(CH_3COO)_2{\cdot}H_2O$

Theory: Copper(II) acetate monohydrate is prepared by neutralization of acetic acid with copper(II) oxide.

$$CuO + 2\,CH_3COOH \rightarrow Cu(CH_3COO)_2 + H_2O$$

Properties: Hot water and ethanol-soluble green-blue crystals losing water of crystallization when stored on air.

Preparation: Prepare suspension of copper(II) oxide in 20% acetic acid (5-fold stoichiometric excess) in a round bottom flask. Heat the mixture under reflux (oil bath, stirrer) till the solid completely dissolves. Filter the solution through a filter paper into an evaporation dish. Evaporate the solution on a stem bath until first crystals are formed and cool down the solution at room temperature. Filter the product on a fritt, wash with small volume of cold water and dry between sheets of s filter paper.

4.38. Sodium acetate trihydrate, $CH_3COONa·3H_2O$

Theory: Sodium acetate trihydrate is prepared in a neutralization of sodium hydroxide with acetic acid.

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

Properties: Water-soluble, colorless crystalline solid.

Preparation: Mix acetic acid (10 ml) and water (20 ml) in a 250ml flask. Add 10% sodium hydroxide solution (stoichiometry) dropwise under stirring. Check pH with an indicator paper. Adjust solution pH at 7 with diluted (3–5%) acetic acid or sodium hydroxide. Evaporate all volatiles on a rotavap. Add water (10 ml) and heat breafly the mixture with a heatgun to dissolve the solid. Transfer the solution to a beaker and cool down in a refrigerator. If no crystals are formed after several hours, add a crystallization center – few crystals of the previously prepared product. Filter the product ona fritt and air-dry on the fritt by passing air through. Finish drying on air at room temperature.

4.39. Aluminum(III) oxide, Al_2O_3

Theory: Aluminum(III) oxide is prepared by calcination of aluminum(III) hydroxide which is prepared by precipitation of soluble aluminum(III) salts with aqueous ammonia solution.

$$2\,Al + 6\,HCl \rightarrow 2\,AlCl_3 + 3H_2$$
$$AlCl_3 + 3\,NH_4OH \rightarrow Al(OH)_3 + 3\,NH_4Cl$$
$$2\,Al(OH)_3 \rightarrow Al_2O_3 + 3\,H_2O$$

Properties: Water-inosluble white powder, soluble in acidic and alkaline solutions.

Preparation: Add aluminum portionwise to the beaker with concentrated hydrochloric acid (3-fold stoichiometric excess). **Caution, the mixture bubbles vigorously!** Heat the mixture on a stem bath until all metal dissolves. Filter the solution through a filter paper and evaporate volatiles in a rotavap. Dissolve the dry residue in water to obtain 10% solution (considering $AlCl_3$ quanitative yield). Transfer the solution to a beaker. Boil the solution and add slowly concentrated ammonia (2-fold stoichiometric excess) under stirring (magnetic stirrer). Cover the beaker with a watch glass and continue boiling for additional 1 hour. Separate the solid by centrifugation at maximum speed for 3 minutes. Remove carefully the supernatant, suspend in water and repeat centrifugation. Repeat the washing step twice with water, twice with ethanol and finally with diethylether. Dry the product in the centrifucation tubes in a desiccator under vacuum. Pulverize the resulting aluminum(III) hydroxide, transfer to a crucible and calcinate with a flame till constant weight.

4.40. Chromium(III) oxide, Cr_2O_3

Theory: Chromium(III) oxide is preparen in a thermal decoimposition of ammonium dichromate. The reaction is exothermic and proceeds spontaneously after the initiation.

$$(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + 2\,N_2 + 4\,H_2O$$

Properties: Water-insolble green amorphous powder.

Preparation: **The amminum dichromate thermal decomposition performe in a fumehood under supervision of the course leader!** Pulverize ammonium dichromate and pour the powder to a metallic vessel to form a cone. Dropp few mililitres of ethanol from the washing bottle on the top of the cone and ingnite the mixture. After the exotheric reaction terminates, suspend the resulting powder in water (300 ml) and stirre the mixture for 10 minut. Filter the product on a Bűchner funnel, wash with water until yellow color disappears and dry at 100 °C.

4.41. Manganese(II)-manganese(IV) oxide, Mn_3O_4

Theory: Manganese(II)-manganese(IV) oxide is prepared in a thermal decomposition of manganese(IV) oxide.

$$3\,MnO_2 \rightarrow Mn_3O_4 + O_2$$

Properties: Water-insoluble black powder.

Preparation: Transfer manganese(IV) oxide to a crucible and heat with a flame till constant weight.

4.42. Copper(II) oxide, CuO

Theory: Copper(II) oxide is prepared in a thermal decomposition of copper(II) hydroxide. Copper(II) hydroxide is prepared in situ by precipitation of copper(II) ions with sodium or potassium hydroxide.

$$Cu^{2+} + 2\,OH^{-} \rightarrow Cu(OH)_2$$
$$Cu(OH)_2 \rightarrow CuO + H_2O$$

Properties: Water-insoluble black powder, soluble in acids.

Preparation: Boil 10% copper(II) sulfate solution in a beaker covered with a watch glass. Add 10% potassium hydroxide solution (10% stoichiometric excess) portionwise. If needed, add few more drops of potassium hydroxide solution to adjust the mixture pH > 10. Boil the suspension until the color changes completely to black (cca 1 hour). Cool down the mixture to room temperature. Filter the product on a Büchner funnel, wash with hot water, with ethanol and air-dry on the fritt by passing air through. Finish drying at 100 °C.

4.43. Copper(I) oxide, Cu_2O

Theory: Copper(I) oxide is prepare in a reduction of copper(II) ions with glucose in alkaline solution containing tartarate ions.

$$2\,Cu^{2+} + C_6H_{12}O_6 + 4\,OH^- \rightarrow Cu_2O + C_6H_{12}O_7 + 2\,H_2O$$

Properties: Water-insoluble red powder. Dissolution in acids leads to copper oxidation.

Preparation: Prepare a 10% copper(II) sulfate solution in a round bottom flask. Add potassium tartaarate or potassium-sodium tartarate (6-times molar amount of copper(II) sulfate). Adjust pH to 13 with 10% potassium hydroxide solution. Boil the mixture (oil bath on a magnetic stirrer) and add slowly 10% glucose solution (2-fold stoichiometric excess) under stirring. Heat the mixture under reflux for 1 hour. Filter the product on a S4 fritt, wash with water and ethanol and air-dry on the fritt by passing air through. Finish drying at 100 °C.

4.44. Mercury(II) oxide, HgO

Theory: Mercury(II) oxide is prepared by precipitating soluble mercury salts with alkalimetal hydroxide under heating.

$$HgCl_2 + 2KOH \rightarrow HgO + 2\,KCl + H_2O$$

Properties: Water-insoluble, yellow-to-brown powder.

Preparation: Prepare a 5% aqueous solution of mercury(II) chloride in a beaker. Boil the solution on a magnetic stirrer. Slowly add a 10% aqueous solution of potassium hydroxide (20% stoichiometric excess) dropwise. Cover the beaker with a watch glass and boil the mixture for 1 h. After colling down, filter the product on a Büchner funnel, wash with water, with ethanol and air-dry on the fritt by passing air through. Finish the drying at 100 °C.

4.45. Vanadium(V) oxide, V_2O_5

Theory: Vanadium(V) oxide is prepared in a thermal decomposition of ammonium vanadate.

$$2\,NH_4VO_3 \rightarrow V_2O_5 + 2\,NH_3 + H_2O$$

Properties: Poorly water-soluble yellow to red powder, soluble in alkaline and acidic solutions.

Preparation: Transfer ammonium vanadate to a crucible and heat in an oven at 500 ℃. The reaction is finished when ammonia is not formed any more (test with placing a moisted indicator pH paper above the crucible). **Caution, inhalation of vanadium(V) oxide causes permanent rhinitis. Thus, work always carefully in a fumehood!**

4.46. Iron(III) oxide, Fe_2O_3

Theory: Iron(III) oxide is prepared by precipitation of soluble iron salts with hydroxide solution followe by calcination of the formed mixture of iron hydroxides.

$FeSO_4 + 2\ KOH \rightarrow Fe(OH)_2 + K_2SO_4$
$4\ Fe(OH)_2 + O_2 \rightarrow 2\ Fe_2O_3 + 4\ H_2O$

Properties: Water-insoluble red powder, soluble in acidic solutions.

Preparation: Boil a 5% iron(II) sulfate solution in a beaker and add 10% potassium hydroxide solution dropwise under stirring (magnetic stirrer). Cover the beaker with a watch glass and continue boiling for addition 1 h. Filter the precipitate on a Büchner funnel, wash with water and ethanol and air-dry on the funnel by passing air through. Pulverize the resulting hydroxide mixture, transfer the powder to a crucible and heat with a flame till constant weight.

4.47. Ammonium-copper(II) sulfate hexahydrate, $(NH_4)_2Cu(SO_4)_2{\cdot}6H_2O$

Theory: Ammonium-copper(II) sulfate hexahydrate is a Schönit-type salt. It is prepared by crystallization from solution containing both cations.

$CuSO_4 + (NH_4)_2SO_4 \rightarrow (NH_4)_2Cu(SO_4)_2$

Properties: Poorly water-soluble light-blue large crystals, insoluble in organic solvents.

Preparation: Prepare solutions of amonium sulfate and copper(II) sulfate in water (30% more than the volume corresponding to the saturated solutions at 100 °C). Mix the hot solution in a beaker, close with a watch glass and leave the mixture at room temperature overnigh. Filter the crystals on a frit, wash with small amount of cold water and ethanol and dry between two sheets of a filter paper.

4.48. Ammonium sulfate, $(NH_4)_2SO_4$

Theory: Ammonium sulfate is prepared in a neutralization reaction of sulfuric acid and ammonia solutions.

$H_2SO_4 + 2\ NH_3 \rightarrow (NH_4)_2SO_4$

Properties: Water-soluble white compounds, poorly soluble in organic solvents.

Preparation: Prepare 10% sulfuric acid solution (start with 10 g of concentrated sulfuric acid) in a round bottom flask. Cool down the solution in an ice bat and add 10% ammonia solution (stoichiometry) under cooling and stirring (magnetic stirrer). Finally adjust solution pH with ammonia or sulfuric acid solution to be neutral (use indicator pH paper). Remove the stirring bar and evaporate water partly on a rotavap to obtain a mash. Add ethanol (2-tiomes volume of the mash) under stirrung with a glass rod. Filter the product on a fritt, wash with ethanol and air-dry on the fritt by passing air through. Finish drying between two sheets of a filter paper.

4.49. Bis(ethylenediamine)copper(II) sulfate, $[Cu(en)_2]SO_4$

Theory: Bis(ethylenediamine)copper(II) sulfate is prepared in a reaction of copper(II) sulfate with stoichiometric amount of ethaylenediamine. Ethylenediamine binds as a bidentate ligand forming square-planar coordination copper(II) ion environment.

$$CuSO_4 + 2\ NH_2–CH_2–CH_2–NH_2 \rightarrow [Cu(en)_2]SO_4$$

Properties: Water-soluble dar blue crystalline powder, insoluble in organic solvents.

Preparation: prepare 1 M copper(II) sulfate solution and add ethylenediamine (stoichiometry) dropwise under stirring. Add ethanol (3-times volume of the solution) dropwise under stirring (magnetic stirrer) and leave the mixture for 20 minutes. Filter the product on a fritt, wash with ethanol and air-dry on the fritt by passing air through.

4.50. Potassium-chromium(III) sulfate dodecahydrate, $KCr(SO_4)_2 \cdot 12H_2O$

Theory: Potassium-chromium(III) sulfate dodecahydrate is prepared by reduction of potassium dichromate with ethanol in a sulfuric acid solution.

$$K_2Cr_2O_7 + 4\ H_2SO_4 + 3\ C_2H_5OH \rightarrow 2\ KCr(SO_4)_2 + 3\ CH_3CHO + 7\ H_2O$$

Properties: Water-soluble dark purple crystals.

Preparation: **Aldehyde is formed in in the reaction and, thus, the reaction should be done in a fumehood.** Prepare the saturated potassium dichromate solution in and Erlenmeyer flask. Add concentrated sulfuric acid (50% stoichiometric excess). Cool down the mixture in an ice bath. Add slowly 50% ethanol (2-fold stoichiometric excess) under stirring (magnetic stirrer) and cooling so that the solution temperature keeps under 20 °C (control with a thermometer in the mixture). Continue stirring for 2 hours. Then add ethanol (volume of the solution), close the flask and keep in a refrigerator overnight. Filter the crystals on a fritt, wash with ethanol and air-dry by passing air through the fritt. Finish drying between two sheets of a fiter paper.

4.51. Potassium-manganese(II) sulfate hexahydrate, $K_2Mn(SO_4)_2 \cdot 6H_2O$

Theory: Potassium-manganese(II) sulfate hexahydrate is prepared by crystallization from a solution containing both cations. Manganese(II) sulfate solution is prepared by reduction of manganese(IV) oxide with hydrogen peroxide in a sulfuric acid solution. Hydrogen peroxide must be uxed in a large excess because manganese compounds catalyze its decomposition.

$$MnO_2 + H_2O_2 + H_2SO_4 \rightarrow MnSO_4 + O_2 + 2\,H_2O$$
$$MnSO_4 + H_2SO_4 + 2\,KOH \rightarrow K_2Mn(SO_4)_2 + 2\,H_2O$$

Properties: Water-soluble light pink crystals, insoluble in organic solvents.

Preparation: Prepare a suspension of manganese(IV) oxide in water (5-times weight of the oxide). Odd concentrated sulfuric acid (2-times molar amount of oxide). Add a 10% hydrogen perozide solution (5-fold stoichiometric excess) dropwise under stirring (magnetic stirrer). **Caution, the mixture bubbles vigorously!** If necessary. Add another portion of 10% hydrogen peroxide until all solid dissolves. Fiter the solution over a filter paper to a round bottom flask. Evaporate volatiles on a rotavap. Dissolve the oily residue in a 10% potassium hydroxide solution (90% of stoichiometry). Check pH with a universal indicator paper. If needed, add few drops of 10% sulfuric acid to set pH < 4. If needed, add few drops of concentrated hydrogen peroxide to decolorize the solution. Transfer the solution to a beaker. Overlayer the solution with ethanol (volume of the solution), cover the dish with a watch glass and leave in a refrigerator overnight. To overlayer the solution, add ethanol slowly from a wash bottle on wall of the flask so that the liquids do not mix and two layers are formed. Filter the product on a fritt, wash with ethanol and air-dry by passing air through the fritt. Finish drying between two sheets of a filter paper.

4.52. Potassium-zinc(II) sulfate hexahydrate, $K_2Zn(SO_4)_2 \cdot 6H_2O$

Theory: Potassium-zinc(II) sulfate hexahydrate is prepared by crystallization from a solution containing both cations.

$$ZnSO_4 + K_2SO_4 \rightarrow K_2Zn(SO_4)_2$$

Properties: Water-soluble white crystals, insoluble in organic solvents.

Preparation: Prepare solutions of potassium sulfate in water saturated at 100 °C in a beaker. Add zinc(II) sulfate, cover the beaker with a watch glass and leave the mixture at room temperature overnigh. Filter the crystals on a frit, wash with small amount of cold water and ethanol and dry between two sheets of a filter paper.

4.53. Potassium sulfate, K_2SO_4

Theory: Potassium sulfate is prepared in a neutralization of sulfuric acid with potassium hydroxide.

$$H_2SO_4 + 2\ KOH \rightarrow K_2SO_4 + 2\ H_2O$$

Properties: Partly water-soluble colorless crystalline compound.

Preparation: Prepare a 20% potassium hydroxide solution (use 5 g of KOH) in a beaker. Coold down the solution in an ice bath. Add slowly a 20% sulfuric acid solution dropwise under stirring (magnetic stirrer) and cooling. Filter the crystals on a fritt, wash with ethanol and air-dry by passing air through the fritt. Finish drying at při 100 °C.

4.54. Cadmium(II) sulfate hydrate, $CdSO_4 \cdot 8/3H_2O$

Theory: Cadmium(II) sulfate hydrate is prepared in a rection of cadmium(II) carbonate with sulfuric acid.

$$CdCO_3 + H_2SO_4 \rightarrow CdSO_4 + CO_2 + H_2O$$

Properties: Water-soluble white crystalline compound, insoluble in organic solvents.

Preparation: Prepare cadmium(II) carbonate suspension in a 20% sulfuric acid solution (10% stoichiometric excess) in a beaker. Add 10% nitric acid solution (volume equal to that of the starting suspension) and stire (magnetic stirrer) the solution until solid dissolves. Filter the solution over a filter paper in a round bottom flask and evaporate volatiles on a rotavap. Dissolve the dry residue in minimum amount of water. Transfer the solution to an evaporation dish and heat on a steam bath until crystals are formed on the solution surface. Then overlayer with ethanol (volume of the solution), cover the dish with a watch glass and leave at room temperature overnight. To overlayer the solution, add ethanol slowly from a wash bottle on wall of the flask so that the liquids do not mix and two layers are formed. Filter the product on a fritt, wash with ethanol and air-dry by passing air through the fritt. Finish drying between two sheets of a filter paper.

4.55. Cadmium(II) sulfate anhydrous

Theory: Anhydrous cadmium(II) sulfate is prepared by calcination of correposnding hydrate.

$$CdSO_4 \cdot 8/3H_2O \rightarrow CdSO_4 + 8/3H_2O$$

Properties: White hyroscopic powder.

Preparation: Pulverize cadmium(II) sulfate hydrate and transfer to a crucible. Heat at 500 °C in an oven till constant weight. Cool down the crucible in a desiccator and staore the product in a closed vial or test tube.

4.56. Cobalt(II) sulfate hexahydrate, $CoSO_4 \cdot 6H_2O$

Theory: Cobalt(II) sulfate hexahydrate is prepared by crystallizing cobalt(II) ions in the presence of sulfate anions. When using oxide or carbonate as the starting material, they must be transformed into chloride or another soluble salt.

$$CoCO_3 + 2\,HCl \rightarrow CoCl_2 + CO_2 + H_2O$$
$$CoCl_2 + H_2SO_4 \rightarrow CoSO_4 + 2\,HCl$$

Properties: Coblat(II) sulfate hexahydrate is a pink, water-soluble crystalline solid, insoluble in organic solvents.

Preparation: Suspend cobalt(II) carbonate in concentrated hydrochloric acid (5-fold stoichiometric excess) in a beaker. Heat the mixture on a steam bath until the solid is completely dissolved. Filter the solution through a filter paper into a round bottom flask of known mass and wash the filter with water. Evaporate the solution completely on a rotavap. Dissolve the remaining solid in water (30 ml) and evaporate the solution again to remove traces of hydrochloric acid. Dissolve the remaining solid in water to prepare a 10–20% solution. Add 10% sulfuric acid (10% stoichiometric excess) and evaporate the solution on a rotavap. Dissolve the solution in the minimum amount of water (according to solubility tables) and slowly add ethanol (3 times the amount of water) under stiring. Let the mixture stand for 20 minutes. Filter the product on a fritt, wash with ethanol and air-dry on the fritt by passing air through. Finish drying between two sheets of filter paper.

4.57. Manganese(II) sulfate hydrate, $MnSO_4 \cdot H_2O$

Theory: Manganese(II) sulfate is prepared by reduction of manganese(IV) oxide with hydrogen peroxide in a sulfuric acid solution. Hydrogen peroxide must be uxed in a large excess because manganese compounds catalyze its decomposition.

$$2\,MnO_2 + 2\,H_2O_2 + 2\,H_2SO_4 \rightarrow 2\,MnSO_4 + O_2 + 4\,H_2O$$

Properties: Water-soluble ligh pink crystals, insoluble in organic solvents.

Preparation: Prepare a suspension of manganese(IV) oxide in water (5-times weight of the oxide). Odd concentrated sulfuric acid (2-fold stoichiometric excess). Add a 10% hydrogen perozide solution (5-fold stoichiometric excess) dropwise under stirring (magnetic stirrer). **Caution, the mixture bubbles vigorously!** If necessary. Add another portion of 10% hydrogen peroxide until all solid dissolves. Fiter the solution over a filter paper. Transfer the solution to an evaporation dish and heat on a steam bath until crystals are formed on the solution surface. Then overlayer with ethanol (volume of the solution), cover the dish with a watch glass and leave at room temperature overnight. To overlayer the solution, add ethanol slowly from a wash bottle on wall of the flask so that the liquids do not mix and two layers are formed. Filter the product on a fritt, wash with ethanol and air-dry by passing air through the fritt. Finish drying between two sheets of a filter paper.

4.58. Copper(II) sulfate (hydrate), $CuSO_4 \cdot 5H_2O$

Theory: Copper(II) sulfate pentahydrate is prepared by copper oxide neutralization with sulfuric acid.

$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$

Properties: Copper(II) sulfate pentahydrate is a blue, water-soluble crystalline solid, insoluble in organic solvents. The microcrystalline form is light blue. Slow crystallization leads to large, dark blue crystals.

Preparation: Suspend copper(II) oxide in 10% aqueous sulfuric acid (10% stoichiometric excess) in a beaker. Add concentrated nitric acid (2 ml) and heat the mixture on a steam bath until the silds dissolve completely. Filter the solution through a paper and add slowly ethanol (2 times the volume of the copper sulfate solution) under stiring. Filter the product on a fritt, wash with ethanol and air-dry on the fritt by passing air through. Finish drying between sheets of filter paper.

4.59. Copper(II) sulfate (anhydrous), $CuSO_4$ anhydrous

Theory: Anhydrous copper(II) sulfate is prepared by heating the hydrate at 500 °C.

$CuSO_4 \cdot 5H_2O \rightarrow CuSO_4 + 5H_2O$

Properties: Anhydrous copper(II) sulfate is a white, water-soluble, hygroscopic solid, yielding blue solutions.

Preparation: Pulverize copper(II) sulfate pentahydrate and transfer the powder into a crucible. Heat the crucible at 500 °C in an oven to constat mass. Cool down the crucible in a dessiccator to avoid rehydratation. Close the product in a vial or a test tube.

4.60. Nickel(II) sulfate hexahydrate, $NiSO_4 \cdot 6H_2O$

Theory: Nickel(II) sulfate hexahydrate is prepared in a reaction of nickel(II) carbonate with sulfuric acid.

$NiCO_3 + H_2SO_4 \rightarrow NiSO_4 + CO_2 + H_2O$

Properties: Water-soluble light green crystalline compound, insoluble in organic solvents.

Preparation: Prepare a suspension of nickel(II) carbonate in a 10% sulfuric acid solution (10% stoichiometric axcess) in a beaker. Keep the suspension stirring until solids dissolve. Filter the solution over a filter paper and add ethanol (2-times volume of the solution). Filter the product on a fritt, wash with ethanol and air-dry by passing air through the fritt. Finish drying between two sheets of a filter paper.

4.61. Tetraammincopper(II) sulfate, $[Cu(NH_3)_4]SO_4 \cdot H_2O$

Theory: Tetraammincopper(II) sulfate monohydrate is prepared in a reaction of copper(II) sulfate with aqueous ammonia.

$$CuSO_4 + 4\ NH_3 \rightarrow [Cu(NH_3)_4]SO_4$$

Properties: Water-soluble, dark blue crystals. The compound undergoes slow decomposition on air due to the release of water and ammonia.

Preparation: Pulverize copper(II) sulfate pentahydrate. Dissolve the powder in 20% aqueous ammonia (50% stoichiometric excess). Slowly add ethanol (two times the volume of the solution) and keep the mixture in a fume hood for 1 h. Filter the product on a fritt, wash with a mixture of ethanol and concentrated aqueous ammonia (1:1), with a small amount of ethanol and diethylether and air-dry on the fritt by passing air through.

4.62. Tris(ethylenediamine)copper(II) sulfate, $[Cu(en)_3]SO_4$

Theory: tris(ethylenediamine)copper(II) sulfate is prepared in a reaction of copper(II) sulfate with an excess of ethylenediamine. Ethylenediamine is a bidentate ligand, and copper(II) ion is coordinated in an octahedral environment.

$$CuSO_4 + 3\ NH_2\text{–}CH_2\text{–}CH_2\text{–}NH_2 \rightarrow [Cu(en)_3]SO_4$$

Properties: Blue crystals, poorly soluble in water. Dissolution in water leads to the release of one ethylenediamine molecule, forming a bis(ethylenediamine)copper(II) cation.

Preparation: Prepare 2 M solution of copper(II) sulfate pentahydrate. Slowly add ethylenediammine (4-fold stoichiometric excess) under stiring. Add ethanol (5 times the volume of the solution). Filter the product on a fritt, whash with ethanol and air-dry on the fritt by passing air through.

4.63. Vanadyl sulfate trihydrate, $VOSO_4 \cdot 3H_2O$

Theory: Vanadyl sulfate trihydrate is prepared in a reduction of vanadium(V) oxide with sulfur dioxide in acidic solution. The amount and concentration of the sulfuric acid in the reaction must be strictly controlled.

$$V_2O_5 + H_2SO_4 + SO_2 \rightarrow 2\ VOSO_4 + H_2O$$

Properties: Water-soluble blue crystalinne powder.

Preparation: **Caution, inhalation of vanadium(V) oxide causes permanent rhinitis. Thus, work always carefully in a fumehood!** Transfer vanadium(V) oxide to a flask and add a 70% sulfuric acid solution (8 ml per 10 g of V_2O_5). Mix the components and leave the flask standing overnight for vanadium(V) oxide activation. Then, add water (2-times volume of used sulfuric acid solution), fix the flask to a stand support and heat in a boiling water bath. Bubble sulfur dioxide through the mixture under stirring (magnetic stirrer) until the solid dissolves forming a dark blue solution. Filter the solution through a frfitt and keep bubling sulfur dioxide through the filtrate for addition 5 minut. Evaporate the volatiles on rotavap. Dissolve the residue in water (1,5-times weight of vanadium(V) oxide), add few crystals of the product (which serve as crystallization centers) and leave the solution in a freezer overnight. Remove the flask from the freezer and leave at room temperature. After the mixture melts down, leave it standing for 2 hours to finish crystallization. Filter the product on a fritt, wash with ethanol and air-dry by passing air though the fritt.

Preparation of sulfur dioxide: Sulfur dioxide is a toxic gas with a foul odor. Thus, all manipulations must be done in a fume hood. After ensuring that the apparatus is ready for use in a fume hood and that all joints are well greased pulverize the available sulfite or disulfite (5-fold stoichiometric excess). Add water (2 times the mass of sulfite) and transfer the mixture into a three-neck flask. Fill the dropping funnel with concentrated sulfuric acid. Attach a tubing and seal the last neck and the funnel with stoppers. The funnel must be fixed on a rack to avoid breaking the funnel when the apparatus is overpreassured. Add sulfuric acid dropwise to the sulfite suspension. When all sulfite is exhausted (no more sulfur dioxide is formed when adding sulfuric acid), wash the flask with a large volume of water in a fumehood. Refill the flask with a new portion of sulfite suspension and continue working.

4.64. Zinc(II) sulfate heptahydrate, $ZnSO_4{\cdot}7H_2O$

Theory: Zinc(II) sulfate heptahydrate is prepared in a reaction of zinc(II) carbonate with sulfuric acid.

$$ZnCO_3 + H_2SO_4 \rightarrow ZnSO_4 + CO_2 + H_2O$$

Properties: Water-soluble white crystals, insoluble in organic solvents.

Preparation: Prepare suspension of zinc(II) carbonate in a 10% sulfuric acid solution (10% stoichiometric excess) in a beaker. Stirre the mixture (magnetic stirrer) until solid dissolves. Filter the solution over a filter paper and evaporate on a steam bath until crystals are formed on the solution surface. Then overlayer with ethanol (volume of the solution), cover the dish with a watch glass and leave at room temperature overnight. To overlayer the solution, add ethanol slowly from a wash bottle on wall of the flask so that the liquids do not mix and two layers are formed. Filter the product on a fritt, wash with ethanol and air-dry by passing air through the fritt. Finish drying between two sheets of a filter paper.

4.65. Iron(II) sulfate heptahydrate, $FeSO_4{\cdot}7H_2O$

Theory: Iron(II) sulfate heptahydrate is prepared in a rection of iron with sulfuric acid.

$$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$$

Properties: Water-soluble light green crystals, insoluble in organic solvents.

Preparation: Prepare a 5% sulfuric acid solution (stoichiometry) in a beaker. Add metal iron portionwise. Heat the mixture on a staem bath until the metal almost dissolves. Filter the solution over a filter paper and add ethanol (2-times volume of the solution) under stirring. Filter the product on a fritt, wash with ethanol and air-dry by passing air through the fritt. Finish drying between two sheets of a filter paper.

4.66. Cadmium(II) sulfide, CdS

Theory: Cadmium(II) sulfide is prepared in a precipitation of cadmium(II) salts with sulfane.

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

Properties: Water-insoluble yellow powder.

Preparation: Prepare 5% cadmium(II) sulfate solution in an Erlenmayer flask of appropriate volume (2-times volume of the solution) and add several drops of a 5% sulfuric acid solution to adjust pH = 2. Bubble sulfane from a Kipp apparatus through the solution in the rate of 1 bubble per second. Check regulary presence of cadmium(II) ions in the solution - transfer one solution drop on a filter paper, put one drop of a 10% sodium sulfide solution on the same spot. Yellow color indicates presence of free cadmium(II) ions. After the precipitation is complete, filter the product on a Büchner funnel, wash with water and ethanol and air-dry by passing air through the fritt. Finish drying at 100 °C.

4.67. Copper sulfide, CuS

Theory: Copper(II) sulfide is prepared in a precipitation of copper(II) salts with sulfane.

$Cu^{2+} + H_2S \rightarrow CuS + 2H^+$

Properties: Water-insoluble black powder.

Preparation: Prepare 5% copper(II) sulfate solution in an Erlenmayer flask of appropriate volume (2-times volume of the solution). Bubble sulfane from a Kipp apparatus through the solution in the rate of 1 bubble per second. Check regulary presence of copper(II) ions in the solution - transfer one solution drop on a filter paper, put one drop of concentrated ammonia on the same spot. Blue color of tetraammincopper(II) complex indicates presence of free copper(II) ions. After the precipitation is complete, filter the product on a Büchner funnel, wash with water and ethanol and air-dry by passing air through the fritt. Finish drying at 100 °C.

4.68. Lead(II) sulfide, PbS

Theory: Lead(II) sulfide is prepared in a precipitation of lead(II) salts with sulfane.

$Pb^{2+} + H_2S \rightarrow PbS + 2\,H^+$

Properties: Water-insoluble black powder.

Preparation: Prepare 5% lead(II) nitrate solution in an Erlenmayer flask of appropriate volume (2-times volume of the solution). Bubble sulfane generated in a Kipp apparatus through the solution in the rate of 1 bubble per second. Check regulary presence of lead(II) ions in the solution - transfer one solution drop on a filter paper, put one drop of a 10% potassium iodide solution on the same spot. Yellow color of lead(II) iodide indicates presence of free lead(II) ions. After the precipitation is complete, filter the product on a Büchner funnel, wash with water and ethanol and air-dry by passing air through the fritt. Finish drying at 100 °C.

4.69. Zinc(II) sulfide, ZnS

Theory: Zinc(II) sulfide is prepared in a precipitation of zinc(II) salts with sulfane.

$Zn^{2+} + H_2S \rightarrow ZnS + 2\,H^+$

Properties: Water-insoluble zinc powder.

Preparation: Prepare 1M zinc(II) sulfate solution in 2M ammonium acetate in an Erlenmayer flask of appropriate volume (2-times volume of the solution). Heat the solution at 80-90 °C (buble of steam is formed time to time on the bottom of flask) on a magnetic stirrer. Bubble sulfane generated in a Kipp apparatus through the solution in the rate of 1 bubble per second for 60 minutes. Remove the glass tube and heat the solution under reflux for 1 h. Filter the product on a Büchner funnel, wash with water and ethanol and air-dry by passing air through the fritt. Finish drying at 100 °C.

4.70. Iron(II) oxalate dihydrate, $FeC_2O_4{\cdot}2H_2O$

Theory: Iron(II) oxalate dihydrate is prepared in a precipitation of iron(II) ions with oxalate anions.

$FeSO_4 + H_2C_2O_4 \rightarrow FeC_2O_4 + H_2SO_4$

Properties: Poorly water-soluble yellow powder, insoluble in organic solvents.

Preparation: Prepare a 15% iron(II) sulfate solution and add three drops of a 5% sulfuric acid solution. Add slowly a 10% oxalix acid solution (50% stoichiometric excess) under stirring (magnetic stirrer). Heat the suspension. When the mixture start boiling, stop heating and coold down the mixture. Separate mother liquor by decantation. Spread the precipitate in water (20-times theretical weight of the product), filter on a Büchner funnel, wash with hot water and ethanol and air-dry by passing air through the funnel. Finish drying by standing on air.

4.71. Copper(I) tetraiodidomercurate(II), $Cu_2[HgI_4]$

Theory: Copper(I) tetraiodidomercurate(II) is prepared by reducing copper(II) ions by sulfur dioxide in the presence of tetraiodidomercurate(II) anions. Tetraiodidomercuraet(II) anions are prepared in a reaction of mercury(II) iode with potassium iodide.

$$HgI_2 + 2\ KI \rightarrow K_2[HgI_4]$$

$$K_2[HgI_4] + 2\ CuSO_4 + SO_2 + 2\ H_2O \rightarrow Cu_2[HgI_4] + K_2SO_4 + 2\ H_2SO_4$$

Properties: Red powder, poorly soluble in water, reversibly turns black upon heating.

Preparation: Dissolve mercury(II) iodide in a 10% aqueous solution of potassium iodide (stoichiometric amount). Add 20% aqueous solution of copper(II) sulfate (stoichiometric amount) and bubble sulfur dioxide through the solution until reaching quantitative reduction of Cu(II) ions. The presence of Cu(II) ions is tested by transferring one drop of the rection mixture to filter paper and dropping concentrated ammonia on the same spot. Blue indicates the presence of Cu(II) ions. Filter the precipitate on a fritt, wash with water and with small amount of ethanol and air-dry on the fritt by passing air through. Finish drying on air at room temperature.

Preparation of sulfur dioxide: Sulfur dioxide is a toxic gas with a foul odor. Thus, all manipulations must be done in a fume hood. After ensuring that the apparatus is ready for use in a fume hood and that all joints are well greased pulverize the available sulfite or disulfite (5-fold stoichiometric excess). Add water (2 times the mass of sulfite) and transfer the mixture into a three-neck flask. Fill the dropping funnel with concentrated sulfuric acid. Attach a tubing and seal the last neck and the funnel with stoppers. The funnel must be fixed on a rack to avoid breaking the funnel when the apparatus is overpreassured. Add sulfuric acid dropwise to the sulfite suspension. When all sulfite is exhausted (no more sulfur dioxide is formed when adding sulfuric acid), wash the flask with a large volume of water in a fumehood. Refill the flask with a new portion of sulfite suspension and continue working.

4.72. Potassium tetrachloroiodate(III), $K[ICl_4]$

Theory: Potassium tetrachloroiodate is prepared in areaction of chlorine with potassium iodide solution. Iodide is firstly oxidized to iodine, which is consequently oxidized by another chlorine portion yielding tetrachoroiodate. Chlorine is prepared in a reaction between manganese(IV) oxide and hydrochloric acid.

$$MnO_2 + 4\ HCl \rightarrow Cl_2 + MnCl_2 + 2\ H_2O$$
$$2\ KI + 3\ Cl_2 \rightarrow 2\ K[ICl_4]$$

Properties: Gold-yellow needles. The compound must be stored in a closed vessel to avoid hydrolysis be air moisture.

Preparation: Prepare a saturated potassium iodide solution in a large test tube (3-times volume of the solution or more) and add few drops of concentrated HCl. Fix the test tube on a stand support and bubble chlorine through the solution. Black iodine is firstly formed which consequently dissolves to yield yellow solution. Continue chlorine bubbling until product in the form yellow needles is formed. Filter the product on a fritt and dry in a desiccator with concentrated sulfuric acid.

Preparation of chlorine: Chlorine is a toxic gas with a foul odor. Thus, all manipulations must be done in a fume hood. Prepare a suspension of manganese(IV) oxide (3-fold stoichiometric excess) in concentrated hydrochloric acid (50% stoichiometric excess in respect to oxide) in an Ostwald flask. Attach a tubing and seal the neck with a stopper. Heat the flask in a boiling water bath. When no more chlorine is produced, wash the flask with a large volume of water in a fumehood. Refill the flask with a new portion manganese(IV) oxide and hydrochloric acid of sulfite suspension and continue working.

4.73. Potassium tris(oxalato)aluminate(III) trihydrate, $K_3[Al(C_2O_4)_3]\cdot 3H_2O$

Theory: Potassium tris(oxalato)aluminate trihydrate is prepared in a reaction of aluminum with potassium hydroxide followed by a reaction with oxalic acid.

$$2\,Al + 2\,KOH + 6\,H_2O \rightarrow 2\,K[Al(OH)_4] + 3\,H_2$$
$$K[Al(OH)_4] + 3\,H_2C_2O_4 + 2\,KOH \rightarrow K_3[Al(C_2O_4)_3] + 6\,H_2O$$

Properties: Water-soluble colorless crystals, insoluble in organic solvents.

Preparation: Prepare a suspension of aluminum in water (60-times weight of aluminum) in a large beaker. Add a 20% potassium hydroxide solution (stoichiometry over both reaction steps) dropwise under stirring (magnetic stirrer) in a fumehood. Close the beaker with a watch glass and boil the mixture until the metal dissolves. Add oxalix acid dehydrate (15% stoichiometric excess) portionwise into the hot solution. Aluminum(III) hydroxide precipitate is formed first which consequently dissolves. If needed, add an more oxalix acid to dissolve remaining hydroxide. Filter the hot solution over a Büchner funnel, transfer to a large beaker and cool down at room temperature. Add ethanol until first precipitate forms and cool the mixture in an ice bath for 30 minutes. Filter the product, wash with ethanol and air-dry by passing air through the fritt.

4.74. Potassium tris(oxalato)chromate(III) trihydrate, $K_3[Cr(C_2O_4)_3]\cdot 3H_2O$

Theory: Potassium tris(oxalato)chromate trihydrate is prepared in a reduction of potassium dichromate by oxalic acid in a potassium oxalate solution.

$K_2Cr_2O_7 + 7\ H_2C_2O_4 + 2\ K_2C_2O_4 \rightarrow 2\ K_3[Cr(C_2O_4)_3] + 6\ CO_2 + 7\ H_2O$

Properties: Water-soluble green powder.

Preparation: Prepare a 30% oxalic acid solution in a large beaker. The mixture must be heated for complete solid dissolution. Remove the beaker from heat and add portionwise potassium dichromate (stoichiometry). **Caution, the mixture vigorously bubbles.** Then, boil the solution and add potassium oxalate monohydrate (stoichiometry). Cover the beaker with a watch glass and boil the mixture for additional 20 minutes. Cool the mixture at room temperature and add ethanol (half weight of the starting oxalic acid dihydrate). Cool the mixture in an ice bath for 1 hour. Filter the product on a frit, wash with water/ethanol mixture (1:1) and with ethanol and air-dry by passing air through the frit. Finish drying between two sheets of a filter paper.

4.75. Potassium tris(oxalato)ferrate(III) trihydrate, $K_3[Fe(C_2O_4)_3]\cdot 3H_2O$

Theory: Potassium tris(oxalato)ferrate(III) trihydrate is prepared in an oxidation of iron(II) salts with hydrogen peroxide in the oxalate solution.

$2\ FeC_2O_4 + H_2O_2 + 4\ H_2C_2O_4 + 6\ KOH \rightarrow 2\ K_3[Fe(C_2O_4)_3] + 8H_2O$

Properties: Water-soluble light green crystals, insoluble in organic solvents. Decomposes when stored on light yielding yellow iron(II) oxalate.

Preparation: Prepare a 20% oxalic acid solution (50% stoichiometric excess) and add potassium hydroxide (molar amount of oxaxlic acid). Add iron(II) oxalate dehydrate and heat the suspension at 40–50 °C. Add 20% hydrogen peroxide solution (7-fold stoichiometric excess) under stirring (magnetic stirrer). Then, close the beaker with a watch glass and boil the solution for 30 minutes. Filter the hot solution over a filter paper and cool down at room temperature. Then overlayer the solution with ethanol (volume of the solution), cover the beaker with a watch glass and leave in dark overnight. To overlayer the solution, add ethanol slowly from a wash bottle on wall of the flask so that the liquids do not mix and two layers are formed. Filter the product on a fritt, wash with ethanol and air-dry in dark.

4.76. Cobalt(II) carbonate, $CoCO_3$

Theory: Cobalt(II) carbonate is prepared in a precipitation of cobalt(II) salts with sodium or potassium carbonate.

$CoSO_4 + Na_2CO_3 \rightarrow CoCO_3 + Na_2SO_4$

Properties: Water-insoluble ligh purple powder.

Preparation: Prepare a 20% sodim carbonate solution (30% stoichiometric excess) in a beaker. Boil the solution and add a 10% colbalt(II) sulfide solution dropwise under stirring (magnetic stirrer). Boil the resulting suspension for addition 15 minutes. Cool down the mixture. Filter the product on a Büchner funnel, wash with water and ethanol and air-dry by passing air through the fritt. Finish drying at 100 °C.

4.77. Sodim carbonate, Na_2CO_3

Theory: Sodium carbonate is prepared by calcination of sodium hydrogen carbonate.

$$2\,NaHCO_3 \rightarrow Na_2CO_3 + CO_2 + H_2O$$

Properties: Water-soluble white powder. Crystalization from aqueous solutions at different temperatures yields various hydrates. Unhydrous form is prepared by calcination of hydrates and it is used as drying agent.

Preparation: Pulverize sodium hydrogencarbonate, transfer to a crucible and heat in an owen at 500 °C for 1 hour. Cool down the product in a desiccator and store in a closed vessel.

5. Instrumental and analytical tasks

5.1. Analysis of metal sulfates

Task 1. Metal content determination

Theory: The abundance of metal ions is determined by complexometric titration with Complexone III – disodium ethylenediamminetetraacetate (Na_2EDTA). The equivalence point is determined with a metalochromic indicator. Xylenol orange and murexide (Figure 1) are used as indicators. The titrations are performed in the presence of ammonia or urotropine (Figure 1), which are the buffers maintaining constant pH which is necessary for the titration.

Determination of metal ions which show oxidation/reduction or slow complexation kinetics such as Cr(III) or Co(II) must be done by indirect titration. Metal ion is bound by an excess of Comlexone III. The Complexone III exces sis then determined by titration with other metal ion – e.g. Pb(II).

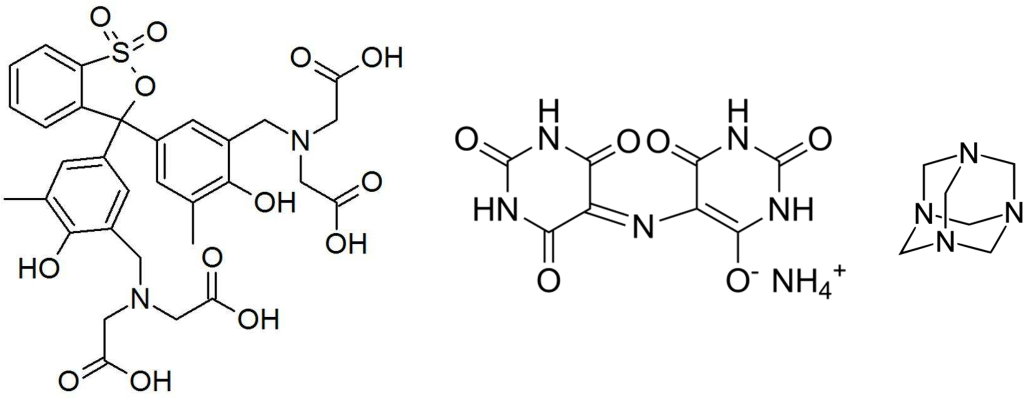


Figure 1. Xylenol orange (left), murexide (middle) and urotropine (right).

Procedures: **Repeat the analysis three times**. Calculate the average percentage of the metal content. Each value should deviate less than 3% from the average. When the deviation is higher than 3%, repeat the analysis. Calculate the metal content from each analysis, calculate the average and compare it with the theoretical value. Weighed accurately to four digits.

Determination of Zn(II)

Buffer solution preparation: Prepare a 0.3 M urotropine solution (50 ml) in a beaker.

Buffer is used in an excess and, thus, concentration must not be known precisely. Insert a stirring bar and pH electrode and adjust pH with 6M HCl until pH = 5.8.

Complexomatric titration: Dissolve the compound (0.1 g) in water (30 ml) in a titration flask. Add buffer solution (10 ml) and few crystals of xylenol orange. Perform the titration with the solution of Complexone III (*c* ~ 0.05 M) until the solution turns from purple to yellow.

Determination of Co(II) and Cd(II)

Buffer solution preparation: Prepare a 0.3 M urotropine solution (50 ml) in a beaker. Buffer is used in an excess and, thus, concentration must not be known precisely. Insert a stirring bar and pH electrode and adjust pH with 6M HCl until pH = 5.8.
Complexomatric titration: Dissolve the compound (0.03 g) in water (30 ml) in a titration flaks. Add a Complexone III solution (10 ml, c ~ 0,05M) from a burette. Then add buffer solution (10 ml) and few crystals of xylenol orange. Perform the titration with the solution of lead(II) nitrate (c ~ 0.05 M) until the solution turns from yellow to purple.

Determination of Cu(II)
Dissolve the compound (0.03 g of $CuSO_4{\cdot}5H_2O$ or 0,05 g $(NH_4)_2Cu(SO_4)_2{\cdot}6H_2O$) in water (30 mL) in a titration flask. Add ammonium chloride (0.1 g), concentrated ammonia (3 drops) and such amount of the provided Murexide/NaCl mixture (1:100) to obtain dark green solution (one small spatula). Perform the titration with the solution of Complexone III (c ~ 0.01 M) until the solution turns from green to violet.

Determination of Ni(II) ions
Dissolve the compound (0.03 g of $CuSO_4{\cdot}5H_2O$ or 0,05 g $(NH_4)_2Cu(SO_4)_2{\cdot}6H_2O$) in water (30 mL) in a titration flask. Add concentrated ammonia (5 ml) and few crystals of the provided Murexide/NaCl mixture (1:100). Perform the titration with the solution of Complexone III (c ~ 0.01 M) until the solution turns from yellow to violet.

Task 2: Water content determination

Theory: Water content is determined by thermogravimetry. A known amount of the compound is heated (calcinated) at a high temperature, and the water content is determined from the mass loss. The compounds undergoing decomposition at high temperatures must be calcinated at controlled temperature in an owen.

Procedure: Heat **three crucibles** in a flame or in an owen for 15 min. Coool down the crucibles in a desiccator and determine their mass accurately to three digits. Do not touch the crucibles with your hand. Repeat the process to constant crucible mass (mass change < 1 mg). Weigh 0.2 g of the compound (well powdered) accurately to three digits into each crucible. Heat the crucibles for 20 min in a flame or in an owen (**see Table 1**). After cooling in a desiccator, determine the masses. Repeat the process to constant mass (mass change < 1 mg).

Table 1. Calcination methods in thermogravimetry

Compound	**Calcination method**
$CuSO_4{\cdot}5H_2O$	burner or owen at 500 °C
$CoSO_4{\cdot}6H_2O$	burner or owen at 500 °C
$(NH_4)_2Cu(SO_4)_2{\cdot}6H_2O$	owen at 250 °C
$CdSO_4{\cdot}8/3H_2O$	burner or owen at 500 °C
$NiSO_4{\cdot}6H_2O$	burner or owen at 500 °C
$ZnSO_4{\cdot}7H_2O$	burner or owen at 500 °C

Lab report

Calculate the metal content or the water content from each analysis, calculate the averages and compare them with the theoretical values. The difference between the average and the theoretical value mostly results from the inconvenient drying of the compound. Using the averages, calculate the composition of the compound as e.g. $CuSO_4 \cdot xH_2O$ independently from the metal content or from the water content.

5.2. Separation of complexes by column chromatography

Theory: Chromatography is a method based on differences in the affinities of various compounds to a sorbent. The most common method is column chromatography. In column chromatography, a column is filled with a sorbent. The compounds are separated while passing through the column in a stream of a solvent mixture. Compounds with high affinity to the column are eluted later than compounds with low affinity. The sorbent is known as the stationary phase. The elution solvent is termed the mobile phase. The most common sorbent is silicagel (SiO_2), which is polar and, hence, has a higher retention than nonpolar compounds. On a polar sorbent, the analyte has a lower retention in a polar mobile phase than in a nonpolar mobile phase.

Another method is thin layer chromatography (TLC) using a thin layer of a sorbent anchored on a glass or metal support. The mixture is injected as a drop at the start, and the TLC plate is placed in a chamber with a small amount of the mobile phase. The solvent slowly rises through the plate, carrying the analytes. TLC is mostly used for analytical purposes.

The analyte is characterized by the Retardation factor (R_f). The retardation factor is expressed as the ratio of analyte velocity to the mobile phase velocity. In TLC, the retardation factor is defined as the ratio of the distance traveled by the center of an analyte spot to the distance traveled by the mobile phase front. The first step in the chromatography is to search for a suitable mobile phase composition in which the mobilities of the analytes are as different as possible. In column chromatography, mobile phase composition is mostly optimized using TLC as a surrogate.

In this task, the goal is to separate two cobalt(III) complexes $[Co(acac)_3]$ and K[Co(EDTA)]. The polarities of the complexes are considerably different and thus show different mobilities on silicagel column. The first step is to determine their retardation factors using different mobile phases on TLC. Subsequently, the complexes are separated on a silicagel column.

Task 1: Determine the retardation factors of the complexes on TLC

Procedure: Mark a start line on the TLC (1 cm above the plate bottom) using a soft pencil. Do not scratch the layer of the sorbent! Put a drop of each standard solution of the complex ($[Co(acac)_3]$ or K[Co(edta)]) side by side at the start line using a pipetting tip. Put the TLC plate in a chamber filled with mobile phase (3 mL) and close the chamber. Remove the TLC plate from the chamber when the mobile phase reaches the top of the plate. Dry the plate with a heat gun. Measure the distance of the spot from the start line (d_1) and the distance of the top from the start line (d_2). The retention factor is ratio of the two distances $R_f = d_1/d_2$. Perform TLC analysis using three mobile phases according to Table 1.

Table 1. Mobile phases used for TLC optimization

$[Co(acac)_3]$	K[Co(edta)]
ethylacetate	ethanol
ethanol:ethylacetate 50:50	water:ethanol 10:90
ethanol	water:ethanol 50:50

Taks 2: Separate two cobalt(III) complexes by column chromatography and determine their ratio in the starting material by UV-VIS spectroscopy

Procedure: Pour ethylacetate (50 mL) into a 250-mL beaker. Slowly add silicagel (15 g) under vigorous stirring on a magnetic stirrer. Fix the chromatographic column to a rack. Pour the suspension into the column and release the excess of the solvent. Caution: The mobile phase surface should never drop bellow the surface of the sorbent. Pour the powder sample (0.5 g) in the column using a funnel. Wash the column with ethylacetate (30 mL). Pipette the solution into the column with a Pauster pipette. Release the excess of the solvent. Then, wash the column with ethanol until the eluted solution becomes colorless. Consequently, wash the second complex quntitatively with an ethanol:water mixture (1:1 volume ratio). Collect each complex in a separate round bottom flask. Evaporate both solutions of the complexes using a rotavap. Dissolve the solid remaining in the $[Co(acac)_3]$ fraction in the minimum amount of ethanol, transfer the solution into a 100-ml volumetric flask and fill the flask with ethanol. Dissolve the solid remaining in the K[Co(edta)] fraction in the minimum amount of water, transfer the solution into a 100-ml volumetric flask and fill the flask with water. Measure UV-VIS spectra of both solutions at the wavelength range of 400–700 nm. Plot both spectra in one figure. Calculate the concentrations of the complexes in the solutions and the ratio of the complexes in the starting mixture using the corresponding molar absorption coefficients (Table 2).

Cleaning:

- Turn the column and fix it above a large beaker. Push out the sorbent using pressured nitrogen. Keep the beaker in a fume hood overnight to evaporate the solvent. Store the silicagel in a chemical-waste barrel (red).
- Wash the flasks with ethanol or acetone.
- Store the waste solvents in solvent-waste bottles.

Table 2. Extinction coefficients of Co(III) complexes

complex	λ_{max} [nm]	ε [$dm^3cm^{-1}mol^{-1}$]
$[Co(acac)_3]$	595	140
K[Co(edta)]	540	142

5.3. Complexation kinetics[*]

Task: Determine the rate constant of the reaction of chromium(III) ions with ethylenediaminetetraacetic acid (H_4EDTA).

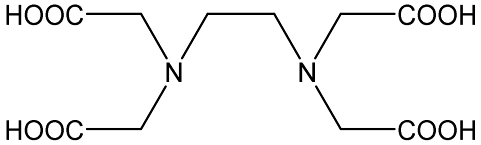


Figure 1. Ethylenediaminetetraacetic acid (H_4EDTA)

Ethylenediaminetetraacetic acid (H_4EDTA) is a strong complexing agent. EDTA reacts with transition metal ions in a 1:1 ratio. Complexes are formed immediately, except those containing a kinetically inert metal ion. A typical example of a kinetically inert metal ion is chromium(III). The reaction of chromium(III) ions with EDTA is described by the following equation:

$H_xEDTA^{(4-x)-} + Cr^{3+} \rightarrow [Cr(EDTA)]^- + xH^+$

This is a bimolecular reaction. The reaction rate is proportional to the concentrations of both reactants:

$v = k.[EDTA].[Cr]$

To simplify the data evaluation, one of the reactants is usually used in a large excess. The concentration of this reactant is considered constant. Such conditions are termed "pseudofirst" because the equation that describes the reaction rate resembles that of a first-order reaction:

$v = k.[EDTA].[Cr] = k_{obs}.[Cr]$,

where k_{obs} is termed the "observed" rate constant, which includes the concentration of the reactant in excess. The concentration of free cromium(III) ions is described by the following equation:

$[Cr] = [Cr_0].e^{-kt}$,

where $[Cr_0]$ is initial concentration of cromium(III) ions.

Most organic ligands are protonated in solution over a broad pH range. EDTA is protonated in six steps. Every protonated form shows a different complexation rate, and thus the reaction rate strongly depends on the pH of the solution. However, protons bound to EDTA are released during the reaction. For this reason, the reactions are mostly performed in

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[*] Modified experiment published by C. E. Hedrick in *J. Chem. Edu.* **1965**, *42*, 9, 479–480.

buffered solutions to keep the pH constant. In the following experiment, EDTA is used in a large excess and hence is also the buffer.

Many transition metal ions show strong absorption in the visible region. The position and intensity of the absorption bands differes between complexes with different ligands. The reaction is followed at the wavelength with the highest difference between reactants and products. Usually, this is the wavelength of the maximum intensity.

Procedure:

Absorption spectra of $[Cr(H_2O)_6]^{3+}$ *and* $[Cr(EDTA)]^-$

Add a stock solution of $CrCl_3$ (5 mL, c = 0.010 M) and water (5 mL) into a vial using a micropipette. Wash a cuvette with the solution. Fill the cuvette with the same solution and measure absorption spectra in the range of 300–700 nm. Wash the cuvette with water and with a stock solution of $[Cr(EDTA)]^-$ (c = 0.005 M). Fill the cuvette with the same solution and measure absorption spectra in the same range.

The cuvettes must not come into contact with acetone or other organic solvents!

Determination of the optimal wavelength

For kinetic measurements, choose the wavelength of the maximum $[Cr(EDTA)]^-$ absorption band between 500 and 600 nm.

Preparation of the EDTA solution

Add a solution of Na_2EDTA (10 mL, c = 0,5 M) and waster (10 mL) into a small beaker using a micropipette. Add a stirring bar. Insert the electrode of the pH-meter. Adjust the pH of the solution with 6 M HCl to pH = 5.7. Remove the electrode, transfer the solution to a 25-mL volumetric flask and fill the flask with water. Shake the flask. Transfer part of the solution to a small beaker and measure the pH with a freshly calibrated electrode (for calibration, use fresh buffer solutions). The pH is determined accurately to two decimals.

Determination of the rate constant

Add the solution of EDTA (5 mL) and the stock solution of $CrCl_3$ (5 mL, c = 0.010 M). Shake the vial swiftly, fill a clean and dry cuvette with the solution and measure kinetics at the optimal wavelength for 40 min in 1-min increments. Evaluate the data using the software.

Discus the results with a teacher immediately after finishing the experiments!!!

Lab report

The protocol should contain:

1) A plot of absorption spectra of $[Cr(H_2O)_6]^{3+}$ and $[Cr(EDTA)]^-$. Both spectra will be plotted in a single plot. Determine the wavelengths of all absorption bands in both spectra. For each maximum calculate the molar absorption coefficient.
2) A plot the kinetic measurement – variation of absorbance as a function of time. Show experimental points and the fitted curve in one plot (see the section Data treatment).

3) The rate constant and the corresponding error. Calculate the half-time of the reaction.

Spectrometer operation and data treatment

Spectral measurements

Switch on the spectrometer

1) Start the program PVC
2) On the spectrometer, press 1 (Applications)
3) Press 3 (Wavescan)
4) Adjust the range (Mode = Absorbance) and confirm with the green button
5) Insert the cuvette with water and press the button OA/100% (baseline measurement)
6) Insert the cuvette with the studied solution and press the green button
7) To record the next spectra, repeat point 6

Warning: The cuvette must be in the correct position. Only two walls of the cuvette are fully transparent. The measuring beam must go through the transparent walls.

Kinetics measurements

1) Press the red button to return to the main menu
2) Press: 4 (Kinetics)
3) Adjust the wavelength; Delay time = 0; Duration = 40 min; Interval = 60 s and confirm with the green button
4) Press the green button again
5) Insert the cuvette with water and press the button OA/100% (baseline measurement)
6) Insert the cuvette with the studied solution and press the green button

The spectral and kinetics results are saved in the directory **DATA** on the desktop. The **.pvc** files are used for visualization. The data are saved in **.csv** file. The file names are generated automatically.

Data treatment

1) Open the **.csv** file with the results from the kinetics measurements.
2) Open the program **Notepad** and copy the experimental data from the **.csv** file. There must be only two columns of numbers in the file – time and absorbance. Save the file as **data.txt**.
3) Open the file **1.gp.** A window with the sign **paused** appears on the screen. Confirm by clicking **OK**. The graphical output is saved in the file **graf.eps**. Results are saved in the file **fit.log** in the table entitled **Final set of parameters**. The table contains

the calculated values of the initial and final absorbances, the rate constant and the corresponding errors.

4) After finishing the data treatment, save the files on your memory stick. Lastly, delete all files except the file **1.gp**.

The data are treated using the software GNUPLOT 4.6 and the method of least squares. The curve is fitted to the equation describing the exponential function:

$A = A_1 - (A_1 - A_0) \cdot e^{(-k \cdot t)}$,

where t is time, A is absorbance in time t, A_0 is initial absorbance, A_1 is final absorbance, and k is the rate constant of the studied reaction.

5.4. Separation of complexes by HPLC

Task: Separation of complexes with preparative HPLC.
Theory: High-Performance Liquid Chromatography (HPLC) is an analytic separation method. As the solution of analytes in a suitable solvent mixture (**mobile phase**) passes through a sorbent (**stationary phase**), analyte movement slows down due to interactions with the stationary phase. Thus, the analytes are separated according to their affinities to the stationary phase.

Chromatographic column

The core of the HPLC system consists of a pump and a **chromatographic column**. The column (Figure 1) is a cylinder (mostly metallic) packed with the sorbent. The most common sorbent is silica bonded with a layer of long aliphatic chains (C8 or C18). C8/C18 columns are suitable for separating many organic compounds and complexes (except for the most polar molecules). Thus, they are commonly used for routine analyses of reaction products. C8/C18 modified silica **(reversed phase**) shows the reverse analyte retention order of "naked" silica (**normal phase**). Interactions of analytes with a normal phase are based on polar or ionic interactions. As such, more polar compounds show higher retention. Interactions of analytes with a reverse phase are based on hydrophobic interactions. Hence, retention decreases with analyte polarity. Several other sorbents are also available – silica modified with polar or ionic groups, and sorbents based on different inorganic materials or on organic polymers. However, they are used only for special analytic applications due to specific properties.

Figure 1. Analytic (top) and preparative (bottom) HPLC columns

HPLC columns are characterized by their length, inner diameter, sorbent type and particle size. For analytical applications, the typical column length is 30–150 mm, and the inner diameter is 1.0–4.6 mm. Column size for preparative applications is given by the amount of the separated compounds. For small-scale laboratory separations, columns are usually 50–250 mm in length, with an inner diameter of 5–50 mm.

Separations in analytical columns run with a minimum amount of the compounds (1 µg – 1 mg), whereas preparative columns with the aforementioned dimensions allow the separation of tens to hundreds of milligrams. The columns that exceed these dimensions are very expensive and suitable only for industrial use.

Generally, separation effectiveness increases with the decrease in sorbent particle size. However, small particles allow dense packing. Under these conditions, a higher pressure is required to pass the mobile phase through the column.

An HPLC apparatus usually runs at pressures of up to 200 bars. Nevertheless, new systems (labeled as UHPLC) run at pressures of up to 1000 bars. Higher pressures make it possible to use smaller sorbent particles and, consequently, smaller columns by improving the separation efficiency, accelerating analyses and decreasing solvent consumption.

Mobile phase

Several solvents are available for HPLC separations. High-purity solvents are required because many common impurities give rise to a signal and, thus, decreases the detection sensitivity. These solvents are labeled as HPLC or HPLC-MS. The most common solvents are water, methanol and acetonitrile, and routine analyses in synthetic laboratory are only rarely performed with other solvents. The analysis runs with a mobile phase of constant composition (**isocratic mode**) or with a changing ratio of solvents (**gradient mode**). Modern HPLC systems typically allow mixing up to four different solvents according to a computer-controlled procedure (**method**).

Various modifiers are often added to the mobile phase to improve separation. The separation of analytes with protic groups is affected by their ionic state. For this reason, an acid (trifluoroacetic, acetic and formic acid) or a buffer (formate, acetate and phosphate buffers) is typically added to the mobile phase, but the mobile phase must be compatible with the stationary phase and detection. The small silica particles and their coverage are sensitive to a strongly acidic or alkaline pH. The typical pH window for C8/C18 columns is 2–8. However, special, shielded (protected) C18 columns can be used over a wider pH range of 1–11. Furthermore, some column types require a minimal content of organic solvent in the mobile phase of 10% due to particle degradation in purely aqueous solutions. To minimize degradation, the column should be washed with a pure organic solvent after each run. The sample solution must be filtered before injection to avoid the deposition of solid particles on the column. To further reduce column contamination, a short, separate, exchangeable column (**precolumn**) is placed at the inlet of the column. Sample solubility in the mobile phase (mainly for gradient methods) must be checked before the separation to avoid sample precipitation on the column.

HPLC system

The HPLC system consists of many parts, which are often modular. Analysts can thus choose an optimal configuration when purchasing the instrument. Figures 2 and 3 show a scheme and photograph of the HPLC system, respectively. During its path through the system, the solvent stored in the reservoir is pumped through a filter to the **degassing unit**. The degassing unit decreases the concentration of dissolved gasses in the mobile phase, thereby preventing the formation of bubbles in the high-pressure section of the system. Then, the mobile phase enters the **pumps** that generate the high pressure in the ongoing sections of the system. Before entering the column, the mixture must be dosed to the mobile phase, either manually with the **injector** equipped with a dosing loop or automatically with the **autosampler**. The autosampler is an arm with a needle which sacks the sample solution from vials in a rack. The autosampler is often thermostated to keep the samples under defined conditions. The mobile phase with analytes enters the **chromatographic column**. In modern systems, the column is closed in a thermostated **column chamber** to control the separation conditions. After passing through the column, the mobile phase enters the **detector/s**. The signal of the **detector/s** is transmitted to the **computer**. In the final stage, the mobile phase passes to **waste** or to the **fraction collector** in preparative applications. The individual sections of the system are connected to tubings. The tubing diameter and void volumes must be kept as low as possible to reduce diffusion in the system and peak broadening.

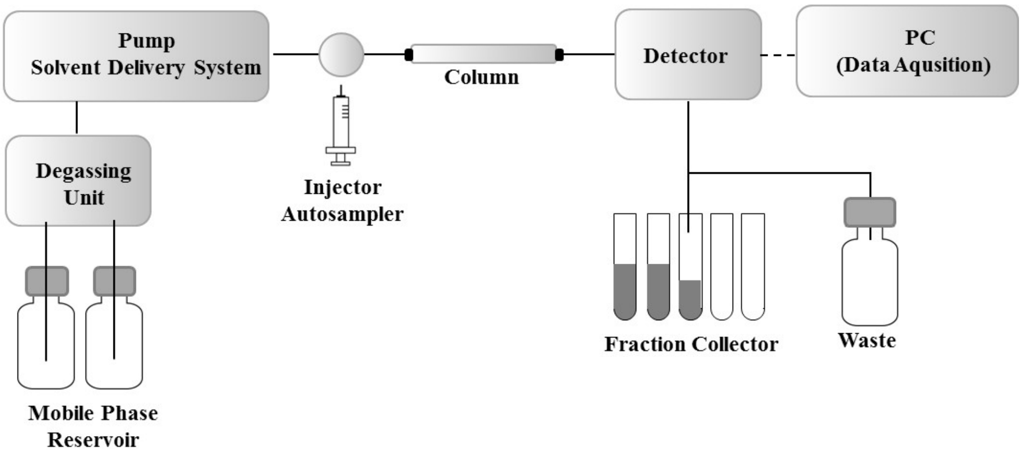

Figure 2. Scheme of a typical HPLC system

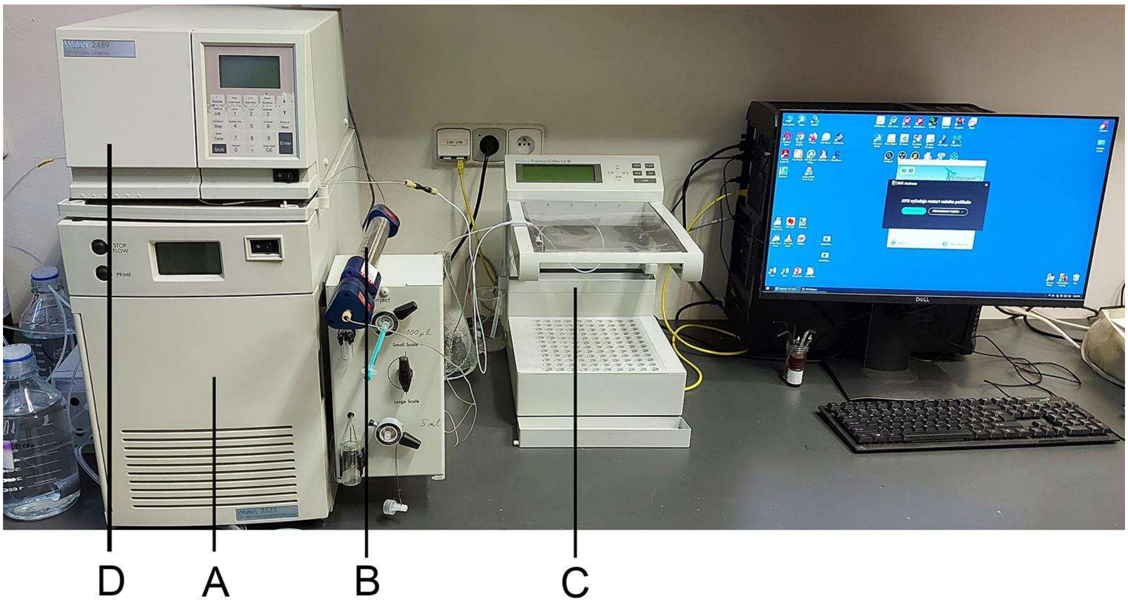

Figure 3. Analytical HPLC system used in our course: A – pumps, B – column, C – fraction collector, D –UV-VIS detector

Detection

The HPLC system used in our course is equipped with spectrophotometric (UV-VIS) detector, which is the most common detector. Less common include mass-spectrometric detectors or detectors based on conductivity, refractive index or amperometric measurements.

UV-VIS detectors can be used for a broad range of organic molecules and metal complexes, showing very good sensitivity for compounds with intensively absorbing groups, such as aromatic groups, or for complexes with d-d or CT electron transitions. UV-VIS detection can also be used for other organic molecules because most of them absorb near 200 nm. However, such experiments require solvents and buffers that do not absorb in this region. UV-VIS detectors usually allow running measurements at two or more different wavelengths in parallel. The best UV-VIS detectors are equipped with a diode array, which allows acquisition in the whole spectra.

Analysis, chromatograms and data evaluation

The output of analysis is a chromatogram – the detector response as a function of time. For UV-VIS detection, the chromatogram displays absorbance at particular wavelength. The signal of the mobile phase is the baseline, which is constant in isocratic mode and can drift in gradient mode. Each compound passing through the detector forms a peak characterized by the apex retention time, area, width (halfwidth or width at baseline) and shape. All these parameters are characteristic of the method.

Compound identity is given by the retention time. The “fastest” analyte shows the shortest retention time (Figure 4). The methods are mostly developed to reach short retention times, thereby accelerating the analysis. However, compounds often show insufficient separation at short retention times. Thus, a reasonable compromise between separation and analysis time is sought. In the reversed phase, retention time decreases with the abundance of the less polar component of the mobile phase and increases with water abundance. The mobile phase composition has the opposite effect on the normal phase.

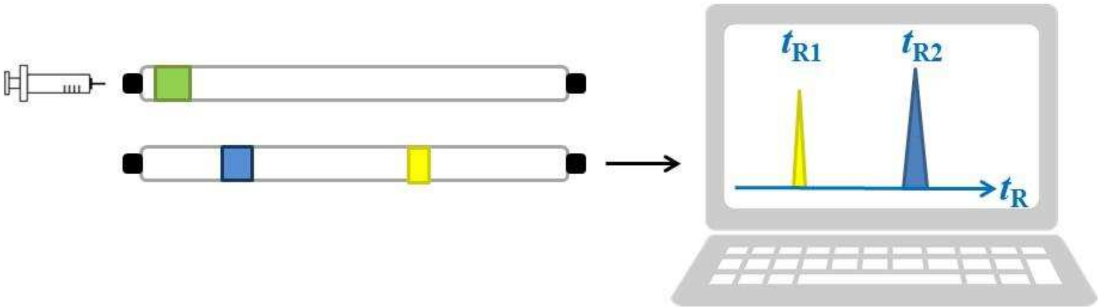

Figure 4. Schematic representation of HPLC analysis and chromatogram

Procedure:

Run separation of the selected mixture obtained in preparation of the Co^{III} complexes under supervision of the teacher.

1. Develop a method using analytical column.
2. Separate complexes on preparative column using fraction collector.
3. Combine fractions containing each complex.

4. Measure UV-VIS spectra of the complexes and identify the complexes with help of their standards.
5. Evaporate the solutions and determine yiled of the reaction.

Lab report

The protocol should contain:

1) Detailed description of separation condition – column type and size, mobile phase composition and flow, temperature etc.
2) Chromatogram.
3) Absorption spectra of the initial mixture and separated complexes. Comparison with spectra of standards and identification of products.
4) Yileds.

6. Solubility data

Name	Formula	Solubility [g/100 ml H_2O]	
		20 °C	100 °C
Ammonium acetate	NH_4CH_3COO	148	-
Ammonium dichromate	$(NH_4)_2Cr_2O_7$	47,1	-
Ammonium sulfate	$(NH_4)_2SO_4$	75,4	103
Ammonium vanadate	NH_4VO_3	0,5	7
Ammonium-copper(II) sulfate	$(NH_4)_2Cu(SO_4)_2\cdot 6H_2O$	17,9	51,7
Boric acid	H_3BO_3	5,0	40,3
Cadmium(II) sulfate	$CdSO_4\cdot 8/3H_2O$	115	87
Cobalt(II) sulfate	$CoSO_4\cdot 7H_2O$	93	464
Copper(I) chloride	$CuCl$	0,006	-
Copper(II) acetate	$Cu(CH_3COO)_2\cdot H_2O$	7,2	20
Copper(II) sulfate	$CuSO_4\cdot 5H_2O$	36,6	205
Ethylenediaminetetraacetic acid	$C_{10}H_{16}N_2O_8$	0,2	0,6
Glycine	$C_2H_5NO_2$	25	-
Hexaamminnickel(II) chloride	$[Ni(NH_3)_6]Cl_2$	0,8	-
Hydrogenchloride	HCl	210	
Iron(II) sulfate	$FeSO_4\cdot 7H_2O$	62,1	100
Lead(II) chloride	$PbCl_2$	1,0	3,3
Lead(II) iodide	PbI_2	0,08	0,44
Lead(II) nitrate	$Pb(NO_3)_2$	56,5	139
Manganese(II) sulfate	$MnSO_4\cdot 4H_2O$	133	60
Mercury(II) chloride	$HgCl_2$	6,5	61,3
Mercury(II) iodide	HgI_2	0,006	-
Nickel(II) formate	$Ni(HCOO)_2\cdot 2H_2O$	3,4	4,9
Nickel(II) chloride	$NiCl_2\cdot 6H_2O$	253	596
Nickel(II) sulfate	$NiSO_4\cdot 7H_2O$	102	371
Oxalic acid	$H_2C_2O_4\cdot 2H_2O$	13,9	345

Name	Formula	Solubility [g/100 ml H_2O]	
		20 °C	100 °C
Potassium acetate	KCH_3COO	1100	-
Potassium dichromate	$K_2Cr_2O_7$	12	80
Potassium hydroxide	KOH	112	178
Potassium chromate	K_2CrO_4	62	76
Potassium iodide	KI	144	208
Potassium nitrate	KNO_3	31,6	246
Potassium sulfate	K_2SO_4	12	24
Potassium tartarate	$K_2C_4H_4O_6\cdot 0{,}5H_2O$	150	278
Potassium-chromium(III) sulfate	$KCr(SO_4)_2\cdot 12H_2O$	24	50
Potassium-manganese(II) sulfate	$KMn(SO_4)_2\cdot 6H_2O$	18	12
Sodium acetate	$NaCH_3COO\cdot 3H_2O$	111	-
Sodium carbonate	$Na_2CO_3\cdot 10H_2O$	91,4	542
Sodium hydrogencarbonate	$NaHCO_3$	9,6	-
Sodium hydroxide	$NaOH$	109	347
Sodium chloride	$NaCl$	36,0	39,8
Sodium tetraborate	$Na_2B_4O_7\cdot 10H_2O$	5,2	188
Tetraammincopper(II) sulfate	$[Cu(NH_3)_4]SO_4\cdot H_2O$	18,5	-
Zinc(II) sulfate	$ZnSO_4\cdot 7H_2O$	168	390

7. Literature sources

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- V. Kubíček, J. Kotek, L. Míka: Anorganické praktikum; education text, Charles University, Prague 2020