KEK209 Organic Chemistry Labworks 1
Identification Reactions and Qualitative Analysis

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Introduction

The laboratory work includes four experiments, the identification reactions of organic compounds as well as a three component qualitative analysis. In the analytic part of the laboratory course, the student gets to separate the three components of an analytical mixture by active extraction and to identify them with the help of their physical properties and on basis of spectroscopical methods. After the completion of the analytical work, a work report has to be composed. The identification reactions can be done alongside with the syntheses. The analytical work can be started once the syntheses and the identification reactions have been approved by the assistant.
Identification Reactions

The Lassaigne test

The identification of nitrogen, sulfur and halogens

Study the handling of sodium before starting the work (http://reagenssi.kemia.helsinki.fi/nettilabra/turvallisuus-natrium.shtml). Place 25-30 mg of fresh sodium metal into a dry Pyrex test tube (make sure that the test tube is undamaged). Add approximately 10 mg of the (anhydrous) compound to be analyzed. Let the mixture rest for a few minutes. Heat the test tube over a small flame, just enough to melt the sodium. Then heat more strongly so that the test tube becomes glowing red. Keep it glowing for 1-2 minutes and then let it cool down to room temperature. Carefully add 1 mL of methanol and heat the test tube softly. When all of the sodium has reacted, add 6-7 mL of water, heat the mixture until it boils and filter it. The filtrate possibly contains sodium cyanide (originates from the elements of the sample), sulfide and halogens as an alkaline solution. Use the filtrate (A) in the following tests.

Detection of nitrogen in the form of cyanide ions

To 1 mL of filtrate A, add a few drops of iron(II)sulfate (ferrosulfate) solution, and boil the mixture (to oxidize a part of the Fe$^{2+}$ions to Fe$^{3+}$ions by oxygen in air). Acidify the solution by adding 2 M sulfuric acid. A blue-green colour or blue precipitate (Berlin blue, Fe$_4$[Fe(CN)$_6$]$_3$) confirms the presence of cyanide ions.

\[
\begin{align*}
\text{FeSO}_4 + 6 \text{NaCN} & \rightarrow \text{Na}_4[\text{Fe(CN)}_6] + \text{Na}_2\text{SO}_4 \\
3 \text{Na}_4[\text{Fe(CN)}_6] + 2 \text{Fe}_2(\text{SO}_4)_3 & \rightarrow \text{Fe}_4[\text{Fe(CN)}_6]_3 + 6 \text{Na}_2\text{SO}_4
\end{align*}
\]

Detection of sulfur (sulfide) as sodium nitroprusside

Add one drop of a fresh, aqueous solution of sodium nitroprusside Na$_2$[Fe(CN)$_5$NO] to about 1 mL of the filtrate A. A pink or purple colour verifies the presence of sulfide ion.

Determination of halogens

Place 2-3 mL of the filtrate A into a test tube and acidify the liquid by adding 2 M sulfuric acid. Boil the solution in a fume cupboard (for example in a beaker) for five minutes to remove HCN and H$_2$S. Boiling is unnecessary if there is no nitrogen or sulfur in the sample. Take a sample of the cool acidic solution and add one drop of a silver nitrate solution. The appearance of a white or yellowish precipitate which is insoluble in nitric acid confirms the presence of halogen. If this test is positive, the halogens present are identified according to the following tests. Place a second sample of the sulfuric acid containing solution into a test tube, add chloroform (1 mL) and chlorine water or 1% sodium hypochlorite solution (2 drops). Mix well and let the chloroform phase separate. The colour of the chloroform solution gives a hint on the identity of the halogen present. Brown means that there is bromine, a violet colour points at iodine while chlorine is present if the colour of the solution does not change at all. If the iodine or the bromine test is positive, chlorine can be detected as follows: Boil a third sample of the original sulfuric acid solution with the same amount of concentrated nitric acid for 5 minutes, then add silver nitrate solution (this way Br$_2$ and I$_2$ are removed from the solution by distillation). An AgCl precipitate shows that the sample also contains chlorine.
Alkenes

Alkenes are easily identified through addition reactions to their double bonds.

a) Reaction with concentrated sulfuric acid
Place one drop of an alkene (eg. cyclohexene) into a test tube and add 5-10 drops of cold, concentrated sulfuric acid. Note that the mixture gets warm, the alkene dissolves and the colour of the solution darkens. This reaction is not specific to alkenes, as for example oxygen containing compounds form soluble oxonium salts.

\[
\begin{align*}
\text{C} &= \text{C} \quad \text{H}_2\text{SO}_4 \\
\text{C} &= \text{C} \quad \text{H} \quad \text{OSO}_3\text{H}
\end{align*}
\]

b) Bayer test
The reaction is based on the ability of potassium permanganate to oxidize double bonds whereby diols are formed. Depending on the structure of the diols, they can be oxidized further either to carbon dioxide, ketones or carboxylic acids.

\[
\begin{align*}
\text{C} &= \text{C} \quad \text{MnO}_4^- \\
\text{H}_2\text{O} &\quad \text{HO} \quad \text{OH} \quad + \quad \text{MnO}_2
\end{align*}
\]

Procedure: Place a few drops of cyclohexene into a test tube and dissolve it into a small amount of acetone. Add dilute (ca 0.5 %) aqueous potassium permanganate solution, drop by drop. Observe the quickly fading violet colour of the permanganate ion. For comparison, perform the test on cyclohexane. It cannot be oxidized. Besides the disappearance of the permanganate colour, evidence that the reaction occurs can be obtained also from the formation of a brown MnO₂ precipitate. Also other compounds such as alkynes, aldehydes, hydroxy and keto acids and various alcohols react with potassium permanganate. With the exception of alkynes, the reaction is slower with these.

c) Reaction with bromine in dichloromethane
Alkenes react rapidly with bromine in an addition reaction. The dibromo derivatives of most hydrocarbons are colourless which facilitates the observation of the progress of the addition reaction as the red-brown colour of bromine disappears.

\[
\begin{align*}
\text{C} &= \text{C} \quad + \quad \text{Br}_2 \\
\text{CH}_2\text{Cl}_2 &\quad \xrightarrow{} \quad \text{C} \quad \text{Br} \quad \text{Br}
\end{align*}
\]

Place a few drops of cyclohexene (or 0.1 g of a solid material) into a test tube and dissolve it into 1-2 mL of dichloromethane. Add a few drops of 10 % bromine solution in dichloromethane and mix well. If the colour of bromine disappears, continue with a drop by drop addition of bromine solution until the colour persists. Bromine does not add to all double bonds. If electronegative groups are bound to the double bond (eg. COOH) the reaction will be slower or will not occur at all.
Aromatic hydrocarbons

a) Flame test
Aliphatic compounds burn in air with a yellow, nearly smokeless flame, while aromatic compounds show a yellow, strongly sooting flame. In general one can say that the larger the degree of unsaturation of a certain compound, the sootier its flame. The test is carried out by burning a small amount of the examined compound on the tip of a glass rod. The test is not suitable for highly volatile compounds.

b) Substitution by halogens
In contrast to alkenes, aromatic hydrocarbons do not react with bromine in an addition reaction. If iron powder is used as a catalyst, though, they react by substitution whereby the colour of bromine vanishes. Very strongly activated benzene rings react by substitution, even without the use of a catalyst.

procedure: Place about three drops of an aromatic hydrocarbon compound (e.g., toluene) into a test tube and add two drops of bromine in dichloromethane (10 %). Notice that the colour of bromine persists. Add some iron powder and a drop of water. Observe that the colour of bromine now vanishes.

c) Friedel-Crafts reaction
The Friedel-Crafts reaction is an electrophilic aromatic substitution reaction where a hydrogen atom on the aromatic ring (monocyclic or condensed) is substituted by an alkyl or acyl group in the presence of anhydrous aluminium chloride. The progress of the reaction can be observed through the formation of a coloured complex. Simple aromatic compounds such as benzene and its homologs show an orange-yellow or red colouring, those with several rings a blue (naphthalene) or purple (biphenyl, phenanthrene), sometimes even a green hue (anthracene). The reaction does not take place if the ring contains substituents that strongly deactivate the ring towards electrophilic substitution (i.e., meta directing substituents). In addition, the reaction does not work with polysubstituted derivatives.
The triarylmethane that forms in the reaction can react with carbocations that are present as intermediates. As a result a stable and strongly coloured triarylmethyl cation forms.

**Procedure:** Place 2 mL of chloroform (=trichloromethane) and three drops of toluene (or 0.1 g of a solid compound) into a test tube. Add 0.5 g of anhydrous aluminium chloride. The latter forms a coloured complex when it comes into contact with the solution.

**Exercise:** Three test tubes hold a colourless liquid each. One holds heptane, the second cyclohexene and the third benzene. By which simple chemical reaction can you show which text tube contains which of the above mentioned compound? Write the reaction equations.

**Halogenated hydrocarbons**

Halogenated hydrocarbons are usually unreactive and are therefore widely used as solvents in organic chemistry.

**a) Reaction with silver nitrate at room temperature**

Add a drop (= 0.03 mL) (or 30 mg) of the compound to 0.5 mL of a saturated solution of AgNO₃ in ethanol. If the test is positive, a precipitate forms within two minutes. Compounds that react positively are alkyl iodides and bromides, tertiary alkyl chlorides, alicyclic iodides and bromides, allylic halides and 1,2-dibromoalkanes.
b) Reaction with silver nitrate under boiling
If no precipitate forms in the previous test after two minutes, the sample is boiled for half a minute. A positive reaction (the formation of a precipitate) now occurs in case the sample contains a primary or secondary alkyl chloride. Aryl and vinyl halides as well as polyhalogenated compounds (e.g., chloroform) give a negative result.

c) Hydrolysis
Mix 100 mg of the compound to be examined with 5 mL of a 5% solution of KOH in alcohol and boil the mixture for 5 min. Add 10 mL of water to the cool mixture, acidify with HNO₃ and filter if necessary until the solution is clear. Add two drops of a 5% silver nitrate solution. A positive reaction (precipitate) is obtained with all alkyl and cycloalkyl iodides, bromides and chlorides. Fluorides and aryl halides give a negative result (with the latter a cloudy solution might appear).

\[
R-\text{Cl} \xrightarrow{\text{KOH/EtOH}} R-\text{OH}
\]

Alcohols

a) Reaction with hydrochloric acid and zinc chloride (Lucas test)
This test can be used to find out if a compound is a primary, secondary or tertiary alcohol. The test is based on the reaction of alcohols with hydrochloric acid in the presence of anhydrous zinc chloride whereby alkyl chlorides are formed.

\[
\text{C-OH} + \text{HCl} \xrightarrow{\text{ZnCl}_2} \text{C-Cl} + \text{H}_2\text{O}
\]

The alcohols which are soluble in Lucas reagent are changed into insoluble alkyl chlorides. The nature of the alcohol can be determined from the relative speed of the reaction:
Procedure: Place 1 mL of n-butanol, sec-butanol and tert-butanol, each in a different test tube. To each test tube add 6 mL of Lucas reagent. Mix the solutions well and leave them to rest. In the test tube containing the tertiary alcohol, an emulsion or two separate layers form almost immediately. The secondary alcohol reacts more slowly. An emulsion or different layers appear after 5-10 minutes. The solution containing the primary alcohol stays clear for at least 15 minutes. Alcohols with a carbon skeleton of 7 or more carbon atoms are not soluble in the Lucas reagent. The test is therefore unsuitable for such alcohols. As the test is dependent on the formation of alkyl chlorides and the development of a new liquid phase, the compound under investigation has to be soluble in the reagent.

b) Esterification and the hydroxamic acid test
The test is based on the reactions shown below. An ester is prepared from the examined alcohol. When the ester reacts with hydroxylamine, a hydroxamic acid is formed. The latter reacts in its turn with ferric ion to produce a brown-red hydroxamate.
Procedure: To a mixture of 0.1 mL of acetyl chloride and 0.2 mL of alcohol, add 0.1 mL of dimethylaniline (to bind the HCl). Stir the mixture for approximately 5 min. Add 1 mL of cold water dropwise in order to hydrolyze excess acetyl chloride. With the help of a clean Pasteur pipette collect a few drops of the separated ester layer (if no layer has formed, collect from the solution). Add 0.5 mL of a 5 % solution of hydroxylamine hydrochloride in methanol. Make the mixture basic by adding 2 M NaOH solution. Warm the mixture until it boils and then cool it immediately. Acidify the cool solution with the help of dilute (2 M) HCl and then add a drop of 10 % iron(III)chloride solution. Observe a wine-red colour, which indicates the (initial) presence of alcohol.

c) The iodoform reaction
The presence of secondary alcohols of the type \( \text{CH}_3\text{CH(OH)}R \) that can be oxidized to the corresponding methyl ketones \( \text{CH}_3\text{C(=O)}R \) can be established through the iodoform test. Also ethanol and acetaldehyde give positive results in this reaction. The test uses an alkaline solution of iodine (sodium hypoiodite) as reagent.

\[
\text{I}_2 + \text{NaOH} \rightarrow \text{NaI} + \text{NaI}
\]

\[
\text{H}_3\text{C}-\text{C}-\text{OH} + \text{NaI} \rightarrow \text{H}_3\text{C}-\text{C} = \text{O} + \text{NaI} + \text{H}_2\text{O}
\]

\[
\text{H}_3\text{C}-\text{C}=\text{O} + 3\text{NaI} \rightarrow \text{I}_3\text{C}-\text{C}=\text{O} + 3\text{NaOH}
\]

\[
\text{I}_3\text{C}-\text{C}=\text{O} + \text{NaOH} \rightarrow \text{CH}_3 + \text{Na}^+\text{O} = \text{O}^-
\]

Procedure: Place 2 drops of the examined alcohol into a test tube, add 5 mL of water and 1 mL of a 10 % NaOH solution. Add a potassium iodide-iodine solution (contains KI, I\(_2\) and H\(_2\)O in the ratio 2:1:8) dropwise to the obtained solution while shaking it continuously, until the colour of the solution turns to light yellow. If a precipitate does not form after a few minutes, warm the mixture in a water bath (60°C) for about 5 minutes. If necessary, add iodine solution dropwise in such a way that the colour of the solution stays light yellow. In a
positive reaction, a yellow iodoform precipitate forms. The reaction is also positive for amongst others the following compounds:

\[
\begin{align*}
\text{OH} & \quad \text{OH} \\
\text{R} & \quad \text{R}
\end{align*}
\]

On the other hand, the test is negative for compounds of the type CH$_3$COCH$_2$X, if X=CN, NO$_2$ or COOR. Especially easily hydrolyzable ethyl and isopropyl esters also give a positive result (why?)

d) Reaction with chromotropic acid

The identification of methanol through the chromotropic acid test: To a test tube containing a drop of a 10 % aqueous solution of methanol add a drop of 5 % phosphoric acid and a drop of 5 % potassium permanganate solution. After a minute, while shaking add a saturated NaHSO$_3$ solution until the colour disappears. If a brown MnO$_2$ precipitate forms, add an additional 7 drops of phosphoric acid and a very small amount of NaHSO$_3$ solution. While shaking, add 4 mL of concentrated sulfuric acid and 4 drops of a 2 % aqueous solution of chromotropic acid (stored in a dark bottle) to the colourless solution. The violet colour, which deepens while the solution cools down, indicates the presence of formaldehyde which was formed from methanol when oxidized by KMnO$_4$ in a phosphoric acid solution.

**Exercises:**
1. Give an example of a primary, secondary and tertiary alcohol.
2. Which of these is not oxidized by potassium chromate?

**Ethers**

Ethers are unreactive like alkanes but form easily explosive peroxides as impurities.

**The solubility of ether**

Mix 1 mL of ether and 2 mL of conc. HCl in a test tube. A homogeneous, viscous solution forms. Add water so that the ether separates from the solution. The solvation of ether is caused by the formation of oxonium ions:

\[
\begin{align*}
\text{C}_2\text{H}_5\text{O}^-\text{C}_2\text{H}_5 \quad + \quad \text{HCl} & \quad \rightarrow \quad \text{C}_2\text{H}_5\text{O}^+\text{C}_2\text{H}_5 \quad + \quad \text{Cl}^- \\
\text{diethyl ether} & \quad \text{hydrochloric acid} & \quad \text{Diethylxonium chloride}
\end{align*}
\]

Alcohols are protonated to oxonium ions in the same way but usually react further (by substitution or elimination reactions).

**Aldehydes and ketones**

Aldehydes and ketones, functional group: carbonyl group C=O.
Aldehydes and ketones share the same functional group. Therefore they usually react with the same reagents resulting in similar reaction products.

a) The reaction with 2,4-dinitrophenylhydrazine

2,4-Dinitrophenylhydrazine is a common reagent used to indicate the presence of carbonyl compounds. Both aldehydes and ketones react with it to produce 2,4-dinitrophenylhydrazones.

\[
\text{H}_2\text{N}-\text{N}-\text{H}_2\text{NO}_2 + \text{C}=\text{N} \quad \text{NO}_2 + \text{H}_2\text{O}
\]

Procedure: Place 2 drops of a ketone (for example acetone) in a test tube and add 3 mL of the 2,4-Dinitrophenylhydrazine solution to it. Warm the mixture for 1 minute. While cooling, the 2,4-dinitrophenylhydrazone of the carbonyl compound precipitates. The precipitate is usually yellow if the carbonyl group is not conjugated. The conjugation with a carbon-carbon double bond or an aromatic ring causes the colour to change to orange-red. Strongly sterically hindered compounds do not react.

b) The iodoform test

This test can be used for the detection of a certain type of carbonyl compound (see the reactions of alcohols, part c).

c) The silver mirror test

Silver ion oxidizes the aldehyde group to a carboxyl group in alkaline solution, and is itself reduced at the same time to metallic silver. The reagent used is the diamine silver(I)ion (Tollens' reagent).

\[
\text{H}_3\text{C} - \text{O} + 2\text{Ag(NH}_3\text{)}_2^+ + \text{H}_2\text{O} \quad \text{H}_3\text{C} - \text{O} + 2\text{Ag} + \text{NH}_4^+ + \text{NH}_3
\]

The finely divided metallic silver formed adheres to the wall of the test tube as a silver mirror or precipitates as a black silver deposit.

Procedure: Place 1 mL of a 5 % AgNO\textsubscript{3} solution and one drop of 2 M sodium hydroxide into a clean, unscratched test tube (the silver mirror only forms on a clean and smooth surface). While shaking the test tube, add dropwise just enough concentrated ammonia to the solution that the precipitate formed in the previous step (grey silver oxide) dissolves. Be careful not to add ammonia in excess. Add a drop of aldehyde to the mixture and dip the test tube into a 60°C water bath. Within half an hour a silver mirror or a silver precipitate should appear. Avoid direct daylight as light easily leads to the decomposition of silver compounds. Formic acid also gives a positive result for this reaction.

Exercises: The examined sample is
a) pentanal or 3-pentanone
b) 2-pentanone or 2-pentanol
c) cyclopentanone or 2-cyclopentenone
Which simple analytical reaction can be used to identify each of the compounds of the above mentioned compound pairs? Write the reaction equations.
Esters

Esters are derivatives of carboxylic acids where the hydroxyl group of the acid has been replaced by a RO- or ArO-group.

The hydroxamic acid test
Esters react with hydroxylamines to yield hydroxamic acids which in their turn form a wine red ferric hydroxamate with ferric ions. Hydrochloric acid and acid anhydrides also form hydroxamic acids under the described conditions. They can be converted into salts, though, by the action of NaOH and slight warming. As salts they cannot react to hydroxamic acids.

\[
R\-O\-C\=O + H_2N-OH \rightarrow R\-O\-C\=O\-HN-OH + R'\-OH
\]

hydroxamic acid

\[
3\ R\-O\-C\=O + FeCl_3 \rightarrow \left[ R\-O\-C\=O\-HN-O \right]_{Fe}_3 + 3HCl
\]

ferric hydroxamate

Procedure: Place a drop of an ester to be examined into a test tube. Add 0.5 mL of a 1 M solution of hydroxylamine hydrochloride in methanol and a 5 M solution of potassium hydroxide in a 80 % mixture of methanol and water. Add enough of the latter so that the solution turns alkaline. Heat the mixture until it boils, then cool it down rapidly and add 2 M HCl until the solution becomes acidic. With the addition of one drop of 10 % iron(III)chloride solution, brown-red iron(III)hydroxamate should form.

Carboxylic acids

a) Reaction with sodium bicarbonate
Carboxylic acids are weak acids. Their protolysis in water is far from complete.

\[
R\-O\-C\=O + H_2O \leftrightarrow R\-O\-C\-O^- + H_3O^+ \quad pK_a = 5
\]

The degree of protolysis depends on the structure of the acid. Carboxylic acids are nevertheless stronger acids than carbonic acid H2CO3 (pKa = 6.35). The former will therefore cause the release of the latter from bicarbonate or carbonate solutions. Being unstable, carbonic acid is instantly decomposed into carbon dioxide and water.

\[
R\-O\-C\=O + HCO_3^- \rightarrow R\-O\-C\-O^- + CO_2 \uparrow + H_2O
\]
Procedure: Place 4-5 drops (or about 0.2 g of a solid eg. benzoic acid) of a carboxylic acid into a test tube and dissolve it into water. In case the acid is insoluble in water, dissolve it first into a few milliliters of ethanol and then into the same amount of water. Add several drops of saturated NaHCO₃ solution. Notice the development of carbon dioxide (bubbling). No bubbles can be observed if the solvent used (eg. acetone) can dissolve large amounts of carbon dioxide.

b) Esterification of carboxylic acids and the hydroxamate test
Place one drop of carboxylic acid into a dry test tube and add 2-3 drops of thionyl chloride. Heat the mixture in a boiling water bath for half a minute. Then add a few drops of butanol or pentanol and continue with heating for one minute. In a fume cupboard, add 0.5 mL of water in order to hydrolyze excess thionyl chloride. Continue with the addition of 0.5 mL of a 1 M solution of hydroxylamine hydrochloride in methanol and enough of a 5 M solution of potassium hydroxide in an 80 % mixture of methanol and water that the mixture becomes basic. Heat the mixture to boil, cool it immediately and add enough 2 M HCl so that the solution turns acid. Finally add one drop of a 10 % iron(III)chloride solution whereupon wine-red iron(III)hydroxamate appears.

\[
R\text{-CO-OH} + \text{SOCl}_2 \rightarrow R\text{-CO-Cl} + \text{SO}_2 + \text{HCl}
\]

\[
R\text{-CO-Cl} + R'-\text{OH} \rightarrow R\text{-CO-OR'} + \text{HCl}
\]

\[
R\text{-CO-OR'} + \text{H}_2\text{N-}OH \rightarrow R\text{-CO-} + \text{R'OH}
\]

\[
R\text{-CO-} + \text{FeCl}_3 \rightarrow \left[\begin{array}{c}
R\text{-CO-}\text{HN-}OH \\
\text{HN-}OH
\end{array}\right]_\text{Fe} + 3\text{HCl}
\]

Exercises: 1. Given two test tubes, one containing propanoic acid and the other cyclopentanone, choose simple chemical tests to distinguish the acids. Write an equation for the reaction.
2. In the reaction between an acid A and an alcohol B, the ester C₆H₁₂O₂ is produced. On the other hand, oxidation of the alcohol B gives the acid A. Draw the structure of the ester.
Phenols

Phenols are weaker acids than carbonic acid ($pK_a 11$) which means that they do not react with $\text{NaHCO}_3$, but do so with $\text{NaOH}$.

\[
\text{OH} + \text{NaOH} \rightarrow \text{O}^- + \text{Na}^+ + \text{H}_2\text{O}
\]

**phenol**  \hspace{1cm}  **sodium phenoxyde**

**a) Reaction with ferric chloride**

To a 1 % aqueous solution of phenol (or a 10 % ethanol solution) add a drop of a 5 % ferric chloride solution. The colour that arises originates from a three-valent complex anion:

\[
6 \text{OH} + \text{FeCl}_3 \rightarrow H_3\left[\begin{array}{c}
\text{Fe} \quad \text{O} \\
\text{O}
\end{array}\right]_{\text{6}} + 3 \text{HCl}
\]

The reaction is typical for most phenols and enolizable (over 5 % of enol) compounds. Hydroquinone does not give a colour reaction as it is oxidized to quinone when it comes into contact with ferric ions. The colour of the Fe3+ complex depends on the phenol in question: violet, blue, purple or green.

**b) Reaction with bromine water** (reaction of the aromatic ring)

A hydroxyl group connected to an aromatic ring activates the ring towards electrophilic aromatic substitution and is ortho/para-directing. Phenol reacts rapidly with bromine water whereby 2,4,6-tribromophenol precipitates. It is a white compound that is only slightly soluble in water.

\[
\text{OH} + 3 \text{Br}_2 \rightarrow \text{Br} \quad \text{Br} \quad \text{Br} \\
\text{OH} + 3 \text{HBr}
\]

The reaction is not specific for phenols. Also other compounds, such as aniline and a few enols, can form similar precipitates.

Procedure: Add bromine water to a dilute aqueous phenol solution. A yellowish-white precipitate appears almost immediately.
c) Reaction with diazonium salt

\[
\text{phenylamine} + \text{H}_2\text{SO}_4 \rightarrow \text{phenyldiazonium sulfate} \rightarrow \text{azo dye}
\]

The reaction can be used for the detection of several kinds of phenols (another phenol in place of β-naphthol in the scheme above).

Procedure: In a test tube mix 1 mL of water, 5 drops of concentrated sulfuric acid and 100 mg of a primary arylamine. Cool the test tube in an ice bath. Little by little, add 1 mL of a cold 10% sodium nitrite solution (the temperature of the mixture should be about 0-5°C) while at the same time shaking the test tube. Finally add 200 mg of β-naphthol that has been dissolved in 2 mL of 10 % NaOH. An azo dye forms (usually red).

Amines

Amines are basic by nature and dissolve in acids under the formation of ammonium salts. Eg.:

\[
\text{aniline} + \text{HCl} \rightarrow \text{anilinium hydrochloride}
\]

a) Colour reaction with copper ion
Mix a 3 % aqueous solution of an amine with the corresponding amount of 10 % copper sulfate solution. A blue or green colour or precipitate appears.

b) The diazo reaction of primary aryl amines
See the diazo reaction in Phenols section.
Qualitative analysis of three unknown compounds

Preexamination of the analysis mixture

The information obtained from the preexamination of a mixture can be used to determine which separation techniques should be used. The testing can include an infrared (IR) spectrum of the mixture and solubility tests.

Solubility test

Test the solubility of the mixture to determine which types of compounds are present

- aqueous NaHCO₃ solution identification of acids
- aqueous NaOH solution identification of phenols
- aqueous HCl solution identification of amines
- ether

In addition to solubility test, more evidence has to be collected to prove that a unknown component belongs to a certain group of compounds. This information can be obtained by IR spectrometry.

IR spectrum of the mixture

Try to identify the following:

- functional groups (COOH, OH, C=O, CHO, NH₂)
- aliphatic/aromatic nature of compounds
Mixture of compounds in ether → compounds which are insoluble in ether

**Carboxylic acids**

- Extract with 2M NaHCO₃
- Acidify with HCl
- Check the acidity with pH paper
- Extract with ether
- Dry the ether phase with MgSO₄
- Filter off the drying agent
- Distill the ether away

**Phenols**

- Extract with 4M HCl
- Acidify with HCl
- Check the acidity with pH paper
- Extract with ether
- Dry the ether phase with MgSO₄
- Filter off the drying agent
- Evaporate the ether away

**Amines**

- Dry the ether phase with MgSO₄
- Filter off the drying agent
- Distill the ether away

After separation the compounds must be purified either by distillation or recrystallization.

To identify the unknown compounds record mp, bp, refractive index, IR.
The separation of the compounds

The components are separated by extracting them with solvents which react with acid and basic components of the analysis mixture. The mixture is dissolved in ether (ca. 50 mL) (original ether solution). Any undissolved material is filtered off and examined separately (physical constants, solubility tests, IR spectrum). Note that this compound may be partly dissolved in ether. A suitable extraction solution chosen on the basis of the preexamination results.

**Carboxylic acids** are extracted from the ether solution using 2M aqueous NaHCO₃ (3x50 mL or more, until the generation of carbon dioxide has ended). The basic solution is extracted with ether (1x30 mL) and the ether phase obtained is combined with the original ether solution. This so called reextraction with ether assures the complete removal of the other components which might be soluble in water to a certain degree. The alkaline water solution that contains the sodium salt of the carboxylic acid is acidified (pH 2-3) with concentrated aqueous hydrochloric acid (the vessel has to be cooled in an ice bath), which leads to the release of the carboxylic acid from its salt. If the carboxylic acid forms a precipitate, it is filtered off by suction filtration. If no precipitate forms, the acidic aqueous solution is saturated with NaCl (salting out procedure) and is then extracted with ether (4x30 mL). The ether solution is dried with MgSO₄, the drying agent is filtered off and the ether removed by distillation.

**Phenols** are extracted from the ether solution with 2 M aqueous NaOH (2x50 mL). The basic water solution which contains the sodium salt of the phenol is treated the same way as was described for carboxylic acids: reextraction followed by the release of the phenol from its salt. In this case ether can be removed in a rotavapor of by distillation.

**Amines** are extracted from the ether solution with 4 M aqueous HCl (3x40 mL). The acidic aqueous solution is extracted with ether (1x30 mL) and the ether solution obtained is combined with the original ether solution (reextraction). The acidic aqueous solution which contains the hydrochloride of the amine is made basic (pH ca. 11) with concentrated (40%) NaOH, whereby the amine is liberated from its salt. If the amine forms a precipitate, it is filtered by suction filtration. If no precipitate forms, the solution is saturated with NaCl and then extracted with ether (4x30 mL). The solution is dried with MgSO₄, the drying agent is filtered off and the ether removed by distillation.

**Neutral compounds**: The original ether solution may contain neutral compounds after it has been extracted with NaHCO₃, NaOH and HCl. It is dried, drying agent is filtered off and the ether is removed by distillation.

**Purification of the separated compounds**

Liquid compound are purified by distillation either under atmospheric pressure or under reduced pressure. Determine the boiling point! (temperature and pressure)

Solids are recrystallized. Examples for suitable recrystallization solvents can be found in the table below.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>bp. °C</th>
<th>Added solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>carboxylic acid</td>
<td>water</td>
<td>100</td>
<td>ethanol</td>
</tr>
<tr>
<td>dicarboxylic acid</td>
<td>ether-toluene</td>
<td>35-110</td>
<td></td>
</tr>
<tr>
<td>phenol</td>
<td>water</td>
<td>100</td>
<td>ethanol, acetone</td>
</tr>
<tr>
<td>amine</td>
<td>water</td>
<td>100</td>
<td>ethanol</td>
</tr>
<tr>
<td>unipolar compound</td>
<td>chloroform</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>polar compound</td>
<td>propanol-water</td>
<td>97-100</td>
<td></td>
</tr>
</tbody>
</table>

In search for suitable solvent, a small amount of the solid is first tested. The compound to be recrystallized should dissolve well in the boiling solvent but poorly when the solvent is cold. If a suitable solvent cannot be found, a second solvent can be added to it in a certain stage.

**The identification of the separated compounds**

Once the functional groups of an unknown compound has been determined, the compound is identified by its physical properties (melting point/boiling point, refractive index). With help of these, search for suitable candidates from the list available in the assistant room.

Besides the identification mentioned above you also can use the comparison of IR spectra (The Aldrich Library of Infrared spectra in assistant room) or SDBS database [http://sdb.db.aist.go.jp/sdbss/cgi-bin/cre_index.cgi?lang=eng](http://sdb.db.aist.go.jp/sdbss/cgi-bin/cre_index.cgi?lang=eng)

**Reporting the analysis**

Fill in the analysis forms and show them to one of the assistants. Assistant will check your results and if all compounds are correctly identified you can write a report how the analysis was carried out. Points to consider are the separation of the components (with a help of the scheme) and the purification and identification of the components (calculated physical properties and corresponding values from the literature). Interpreted IR spectra are to be attached to the report.