



FINALS : Laboratory

Dear students,

We congratulate you on your excellent results in the semi-finals of the Chemistry Olympiad, which allow you today to tackle the “Laboratory” test. **Before beginning this test, read the following carefully.**

Attached to this letter, you will find a document containing relevant information regarding three practical problems, as well as a questionnaire. You have **four hours** to perform all the necessary experiments and to answer all questions from the second document. For the entire duration of this final exam, the **safety guidelines** are to be followed scrupulously!

Indicate your name and your high school at the beginning of the questionnaire. Answer each problem solely on the sheet (front and back, if necessary) where the statement appears. You can use a non-programmable calculator, but you must not be in possession of any other documentation. The two last sheets are draft sheets that will not be considered for the evaluation.

You will be graded based on the following criteria:

- The **accuracy of the results** of your experiments.
- The **correctness of your answers** to the theoretical questions and the calculations.
- Your **behaviour at the laboratory** (respecting the safety guidelines, correct usage of lab equipment, scientific approach, ...).

As already stated at the beginning of the semi-finals, the score of this final exam as well as the score of the semi-finals will be considered to determine your final rank. The winners will be announced at an **official award ceremony on May 16th, 2019 at 17h00 at the Chamber of Commerce (Kirchberg)**. Every participant of this final exam is invited to partake in this ceremony, together with his or her parents! The 4 winners will be honoured with a prize and they will also make up the team, that will represent Luxembourg at the 51st IChO in Paris, from July 21st to 30th 2019!

Wishing you good luck, please believe in our best feelings.
The organizers of the Chemistry Olympiad



LE GOUVERNEMENT
DU GRAND-DUCHÉ DE LUXEMBOURG
Ministère de l'Éducation nationale,
de l'Enfance et de la Jeunesse



UNIVERSITÉ DU
LUXEMBOURG



Fonds National de la
Recherche Luxembourg



FVEMT
FONDATION VEUVE
EMILE METZ-TESCH



andré & henriette losch
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Haupt -

gruppen

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2	6,9 3Li	9,0 4Be																	27,0 13Al	28,1 14Si	31,0 15P	32,1 16S	35,5 17Cl	39,9 18Ar	
3	23,0 11Na	24,3 12Mg	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8 VIIIB	9 VIIIB	10 VIIIB	11 IB	12 IIB													
4	39,1 19K	40,1 20Ca	45,0 21Sc	47,9 22Ti	50,9 23V	52,0 24Cr	54,9 25Mn	55,8 26Fe	58,9 27Co	58,7 28Ni	63,5 29Cu	65,4 30Zn	69,7 31Ga	72,6 32Ge	74,9 33As	79,0 34Se	79,9 35Br	83,8 36Kr							
5	85,5 37Rb	87,6 38Sr	88,9 39Y	91,2 40Zr	92,9 41Nb	95,9 42Mo	99 43Tc	101,1 44Ru	102,9 45Rh	106,4 46Pd	107,9 47Ag	112,4 48Cd	114,8 49In	118,7 50Sn	121,8 51Sb	127,6 52Te	126,9 53I	131,3 54Xe							
6	132,9 55Cs	137,3 56Ba	57 bis 71 La-Lu	178,5 72Hf	180,9 73Ta	183,8 74W	186,2 75Re	190,2 76Os	192,2 77Ir	195,1 78Pt	197,0 79Au	200,6 80Hg	204,4 81Tl	207,2 82Pb	209,0 83Bi	209 84Po	210 85At	222 86Rn							
7	223 87Fr	226 88Ra	89 bis 103 Ac-Lr	261 104Rf	262 105Db	263 106Sg	262 107Bh	265 108Hs	268 109Mt	269 110Uun	272 111Uuu	277 112Uub	289 114Uuq	289		289 116Uuh	293 118Uuo								
	Lanthanoide			138,9 57La	140,1 58Ce	140,9 59Pr	144,2 60Nd	147 61Pm	150,4 62Sm	152,0 63Eu	157,3 64Gd	158,9 65Tb	162,5 66Dy	164,9 67Ho	167,3 68Er	168,9 69Tm	173,0 70Yb	175,0 71Lu							
	Actinoide			227 89Ac	232 90Th	231 91Pa	238 92U	237 93Np	244 94Pu	243 95Am	247 96Cm	247 97Bk	251 98Cf	252 99Es	257 100Fm	258 101Md	259 102No	260 103Lr							

Safety guidelines for a chemistry laboratory

Order and cleanliness are indispensable conditions, if you want to be able to work correctly. This will not only help you to limit your risks while performing your experiments, but it will also increase safety and help you avoid wasting time, efforts and chemical substances.

Most organic compounds are flammable. The higher their volatility, the more flammable they are (ether, acetone, ...). Some of those substances can even explode if their vapor is mixed with the right quantities of air.

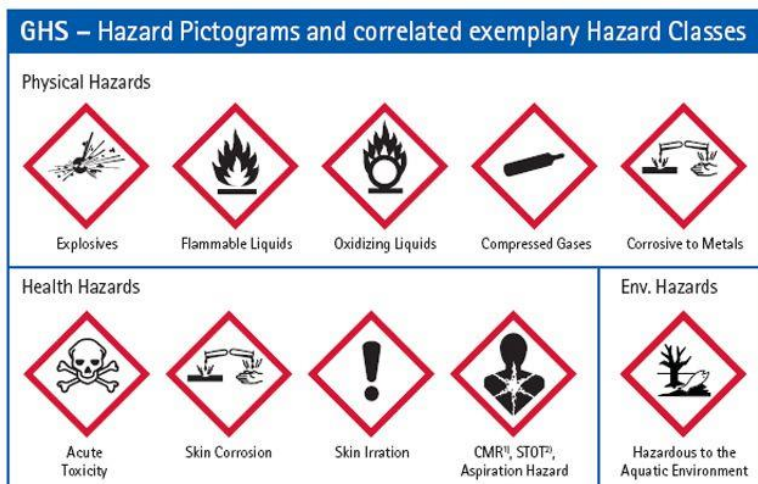
You are obliged to follow the following rules:

- Know the procedural details of the experiments you're conducting.
- Always wear your safety goggles.
- Always wear your lab coat (cotton).
- Wear closed shoes (no sandals).
- Attach your long hair.
- Keep pathways and doors clear.
- Work in a stable position.
- Wash your hands after each experiment.
- Report any problem to the supervising staff.
- Handle substances that produce vapors only under a fume hood.

It is forbidden:

- to smoke, drink, eat, or to taste samples.
- to run.
- to handle flammable or explosive substances next to an open flame.
- to abandon your work station or leave your reaction unsupervised.
- to pipet with the mouth

Note the pictogrammes used on the etiquettes of chemical substances :



Problem I : Iodometry

This oxidation-reduction lab is divided into two parts.

- Part 1: Titration of an iodine solution.
- Part 2: Application: titration of ascorbic acid in pharmaceutical products.

I. General information on redox reactions

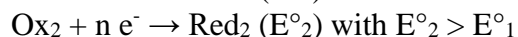
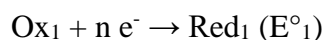
We can consider an oxidation reduction reaction as a transfer of electrons from one chemical species to another. An OXIDATION is a loss of electrons. An OXIDISING AGENT takes electrons. A REDUCTION is a gain of electrons. A REDUCING AGENT gives electrons.

This means that to each oxidising agent corresponds a specific reducing agent and vice-versa. Together, they form a redox couple, generally represented in the following manner:



E° is the normal potential of oxidation and reduction of the pair. The more E° is negative, the higher the reducing power of the species couple, and therefore, the more it will tend to supply electrons. Inversely, the greater E° , the higher the oxidising power of that couple, thus, the greater the tendency to fix electrons.

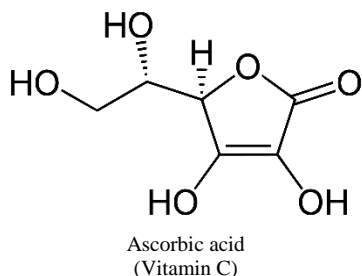
Electrons do not exist in a free state. For an oxidising agent to fix electrons, it must be in proximity of a reducing agent capable of providing those electrons. We can therefore consider the following two oxidation-reduction systems:



This gives, in total:



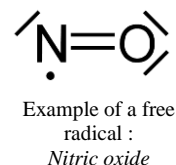
II. General information on ascorbic acid



Enantiopure ascorbic acid (L-ascorbic acid, "Vitamin C") can be found in lemons, in fruit juices and fresh vegetables. The recommended daily dose is 60 – 70 mg.

Its primary function is that of an anti-oxidant. It is used globally by the food industry to prevent the proliferation of bacteria which could degrade the products.

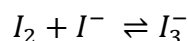
In the human body, it also plays an important role as a *scavenger* of free radicals. Free radicals are chemical species which possess one or more unpaired electrons on their outer shell (they are noted by a “point”). In most cases, the presence of an unpaired electron makes those molecules highly reactive.



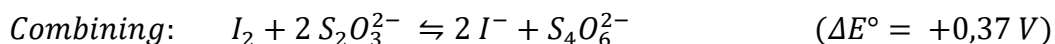
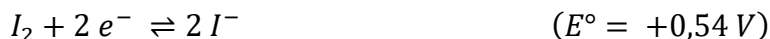
The superoxide ion $\cdot O_2^-$ is an example of such a free radical. This highly toxic species is metabolic waste, produced naturally by the cells of all living beings, which breathe oxygen. Even though unstable in aqueous solution, its stationary concentration would be way too high for cell viability, if it wasn't for a decent safeguard – one of which, ascorbic acid.

III. General information on iodometry

Iodine I_2 is very useful in analytical chemistry for the determination of the concentration of various substances. Iodine is only slightly soluble in pure water. Therefore, to increase its solubility in water, we create a solution called “Lugol”, a mixture of iodine and an excess of potassium iodide KI. In contact with the molecules of iodine and iodide ions, it forms triiodide ions I_3^- according to the following quantitative reaction:



It is the formation of the potassium triiodide, which allows for an explanation of the strong solubility of iodine in aqueous solution. The term iodometry is a collective term for all volumetric methods based on the following redox system:



The oxidising agent I_2 will be reduced to the iodide state I^- by the sodium thiosulphate $Na_2S_2O_3$ (fixing salt) in aqueous solution. This determination allows for the calculation of the concentrations sought.

The end point of the titration is revealed by the appearance or the disappearance of the iodine (brown colour). One could, in principle, do the titration without the use of an indicator. However, during the addition of the solutions, starch can be added to give the solution a dark blue colour, which is more easily discernible. The colour is due to the formation of an iodine-starch complex. As this complex does not completely release the iodine which participates in its formation, it is preferable to add the starch towards the end of the titration, when the brown colour of the iodine has started to disappear.

IV. Experimental part

Preliminary remark: you may choose to repeat your titrations any number of times, if you think it may be necessary to do so.

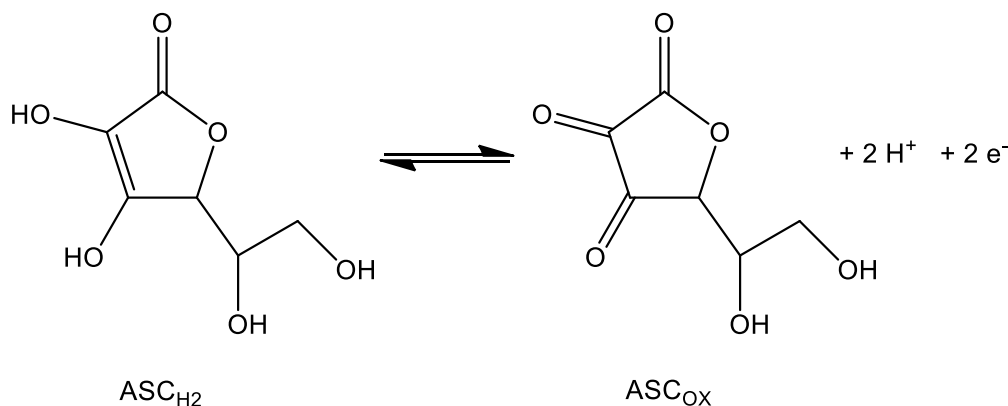
1) Titration of an aqueous solution of iodine with a solution of sodium thiosulphate.

Fill up the burette with an aqueous solution of 0,05M sodium thiosulphate $\text{Na}_2\text{S}_2\text{O}_3$.

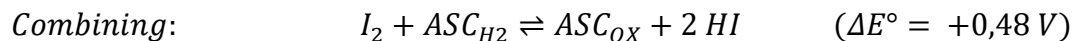
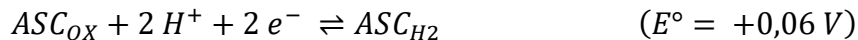
With the aid of a pipette, place 10 mL of an aqueous solution of "Lugol" in an Erlenmeyer flask and add 20 mL of distilled water (using a measuring cylinder). Add the starch towards the end of the titration.

2) Titration of ascorbic acid in pharmaceutical preparations.

The oxidised form of ascorbic acid is dehydroascorbic acid.



The redox potential of this system is smaller than that of iodine systems. This gives the following reaction :



For the titration of ascorbic acid, a precisely measured volume of 0,05M iodine solution is added in excess to a solution of vitamin C. All of the vitamin C reacts with the iodine as shown in the equations above. The iodine in excess is then titrated with a 0,05M solution of sodium thiosulphate. By combining the results of the redox reaction between the iodine and the thiosulphate, and the

results of the redox reaction between the iodine and the ascorbic acid, the proportions between the thiosulphate and the vitamin C can be determined.

Procedure:

Weigh the tablet and write down its mass. Crush the tablet using a mortar and pestle. Transfer as much of the powder as possible into a 100 mL volumetric flask and reweigh. Write down its mass.

Dissolve with a minimum amount of distilled water. Shake for at least 5 minutes until the sample is completely dissolved. Fill the volumetric flask to the mark.

Filter approximately 10 mL into a test tube and throw away this solution. Continue the filtration with a second test tube (at least 2 x 10 mL). Take 10 mL of the filtrated solution with a volumetric pipette and transfer into a 200 mL conical flask. Add 25 mL of 0,05M iodine solution (titrisol!).

Titrate the excess of iodine with a 0,05M thiosulphate solution. Add the starch towards the end of the titration.

Problem 2 : Analysis of organic functional groups

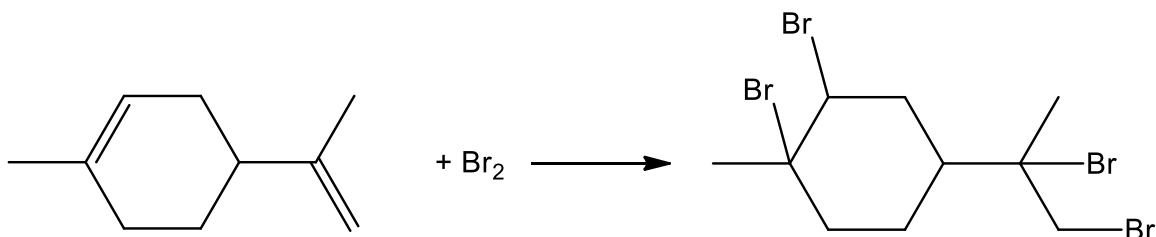
There is a great variety of tests that can be used to identify certain organic functional groups in the laboratory. As you won't have enough time to do all those tests yourselves, you are given all the results, as well as the appertaining infrared spectra – all of which you must use to identify two substances from the list of 16 substances provided in the questionnaire.

I. Brief description of the tests, for which you are provided the results:

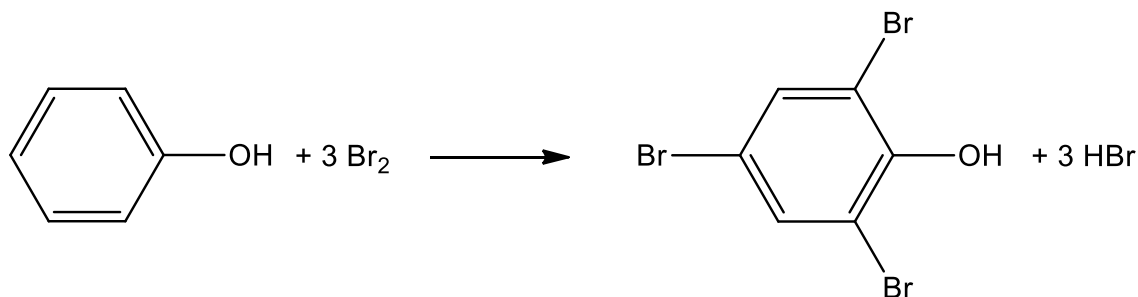
Test 1 : The presence of multiple bonds: reaction with a bromine solution

The decoloration of a solution of bromine in chloroform can indicate the presence of a multiple bond. The decoloration can also result from addition reactions or substitution reactions on phenols.

Example: Addition reaction of Br₂ on limonene:



Example: Substitution reaction of Br₂ on phenol

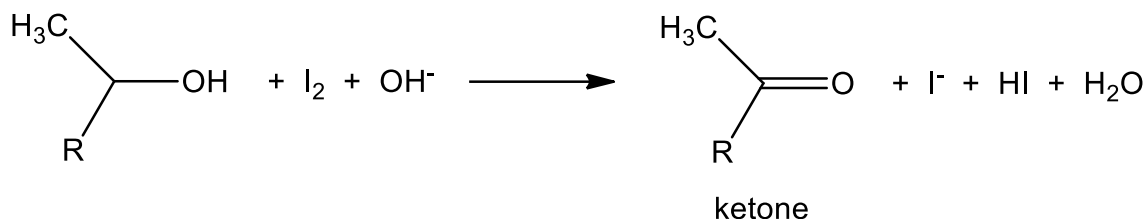


Test 2 : Reactions of aldehydes and ketones: action of iodine in basic conditions (iodoform test)

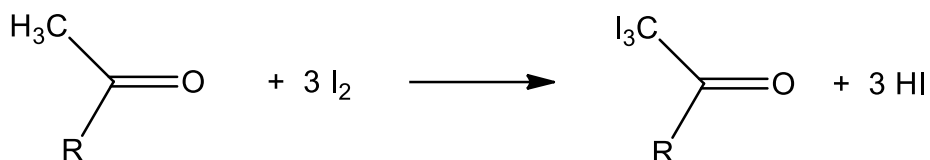
The formation of iodoform shows the substitution of a methyl group adjacent to a carbonyl group. But: secondary alcohols also give a positive test, under the condition that they can be oxidised to a methyl ketone. The following substances give a positive test :

- Substances with a carbonyl functional group of the type CH₃-CO-R or R-CO-CH₂-CO-R.
- Substances with a hydroxyl functional group of the type CH₃-CHOH-R or R-CHOH-CH₂-CHOH-R.

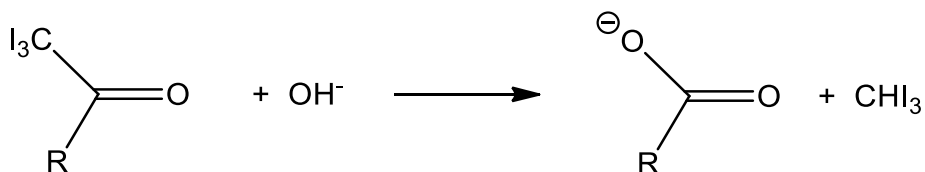
Oxidation of a secondary alcohol by iodine in basic conditions :



Substitution on a carbonylated substance :



Formation of iodoform CHI_3 :

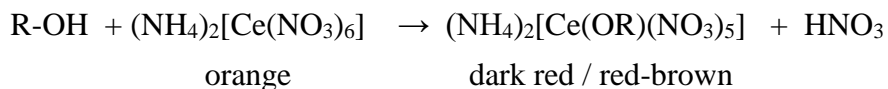


The iodoform test is positive if one observes the formation of a yellow precipitate of CHI_3 .

The test does not work on methyl groups adjacent to a carbonyl group pertaining to a carboxylic acid, an ester or an amide.

Test 3 : Reaction of alcohols and phenols with cerium salt

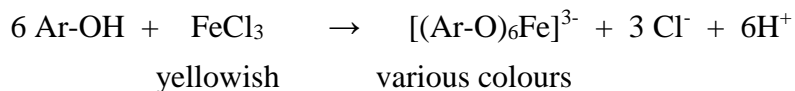
The presence of alcohols can be shown by their red coloration in the presence of cerium (IV) nitrate in ammoniacal conditions. During this reaction, a nitro functional group of the cerium complex is exchanged for an RO functional group, which yields the red complex $(\text{NH}_4)_2[\text{Ce}(\text{OR})(\text{NO}_3)_5]$.



Phenols give a similar reaction. In aqueous solution, they form a brown precipitate.

Test 4 : Detection of phenols with FeCl₃:

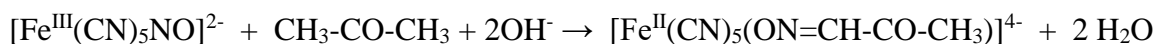
Phenols show an intense colouration in an aqueous solution of ferric chloride. This colour is due to the formation of an anionic complex where the electrons are delocalised either on the iron ion or in the unsaturated system.



(Ar = aryl functional group, meaning a functional group derived from an aromatic hydrocarbon structure, e.g. phenyl)

Test 5 : LEGAL reagent for the detection of aldehydes and ketones

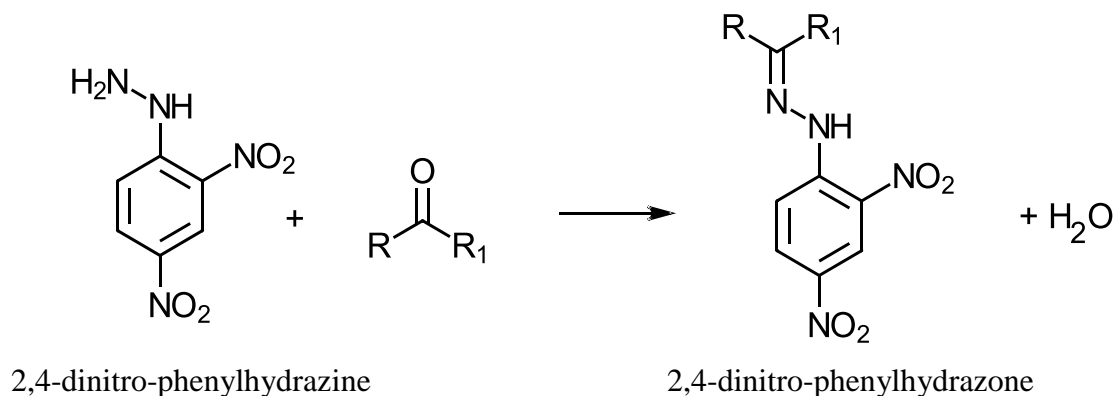
The reaction of acetone with sodium nitroprussiate in basic conditions (Legal reagent) produces isonitroacetone, which is fixed within the anionic complex. In the meantime, Fe³⁺ is reduced to the Fe²⁺ state.



The test is positive if one observes a red colouration.

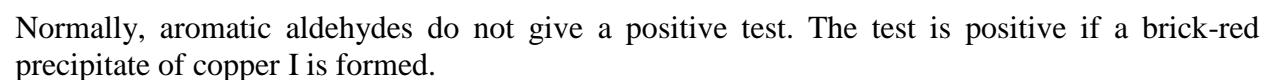
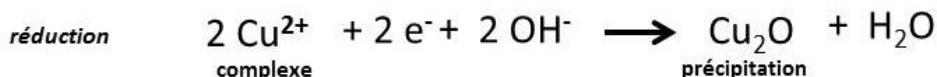
Test 6 : Detection of aldehydes and ketones with the BRADY reagent

Between the carbonyl group and the 2,4-dinitrophenylhydrazine (Brady reagent), there is formation of a 2,4-dinitrophenylhydrazone. Carboxylic acids, esters and amides do not react.

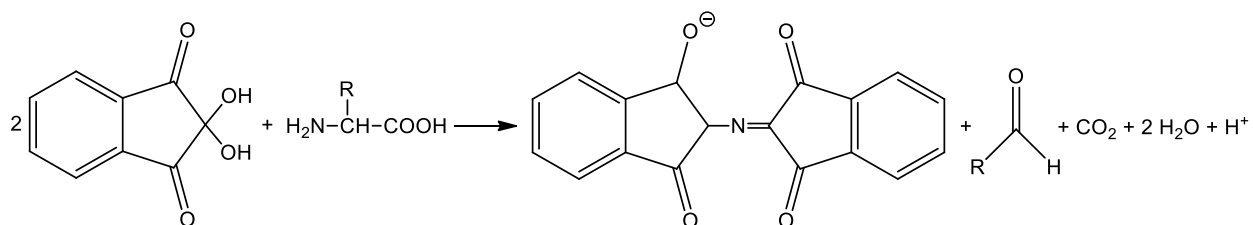


Phenylhydrazones form yellow, orange or red precipitates and thus colourful opaque solutions.

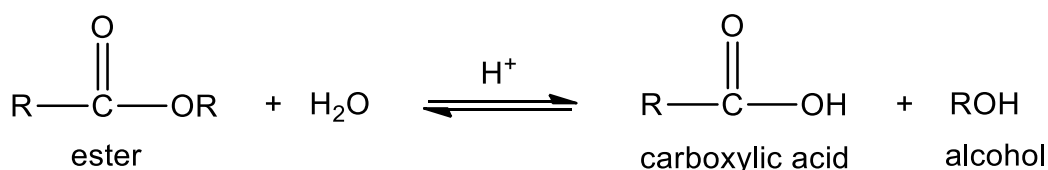
This reaction allows to differentiate between ketones and aldehydes, because the latter are better reducing agents. Potassium sodium tartrate is used as a complexation reagent and yields a deep blue Cu^{2+} complex.



α -amino acids and primary amines $R-NH_2$ react with ninhydrin to give a complex of a violet-blue (sometimes brown-red) colour. At high concentrations, the solutions can become very dark, almost black.



This test uses the hydrolysis of esters when heated. After adding NaOH until a slight pink colouration (slightly basic conditions) of the phenolphthalein indicator appears, the sample is heated for several minutes. Under those conditions, the esters will react to yield a carboxylic acid and the corresponding alcohol. The formation of acid is shown by the decoloration of the indicator phenolphthalein.



II. Infrared spectroscopy

To obtain complementary information, we use Fourier transformed infrared spectroscopy (FT-IR). To that end, a sample is irradiated by infrared light and the proportion of radiation that passes through the sample is measured. If the sample contains IR-active groups, they will be identified in the obtained spectra, by the areas of lower transmission intensity (absorption bands).

Infrared spectroscopy exploits the fact that molecules have specific resonance frequencies, at which they turn, twist or vibrate in correspondence with their discrete energy state. Those resonance frequencies are determined by the shape of the surface of their potential energy, by their atomic masses and by the associated vibronic coupling. For a vibrational mode in a molecule to be active in the infrared domain, it must undergo a modification of its permanent dipole moment. The analysis of those characteristics indicates details about the molecular structure of the sample.

The technique works almost exclusively on samples with covalent bonds. Simple spectra are obtained from very pure samples with only few bonds that are active in the infrared domain. More complex molecular structures give a lot more absorption bands and thus way more complex spectra.

You will ignore the area of the digital fingerprints and only evaluate the signals in the regions above 1500 cm^{-1} . Use the information from the figures 1,2 and 3 to help you identify the functional groups present in your unknown substance.

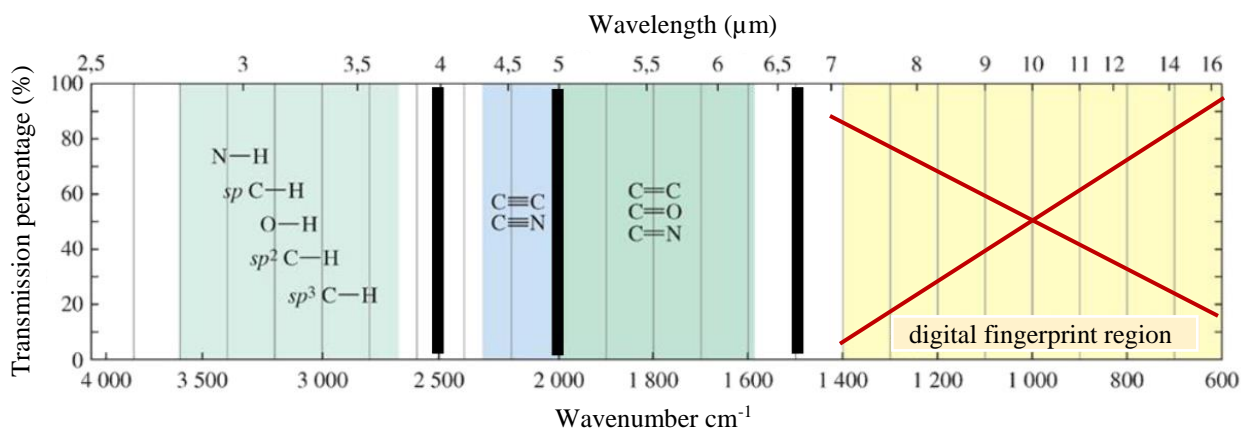


Figure 1: Main areas of the infrared spectrum, indicating the localisation of signals of double bonds ($1500\text{--}2000\text{ cm}^{-1}$), triple bonds ($2000\text{--}2500\text{ cm}^{-1}$) and of bonds between the atoms C, N, O and hydrogen atoms (above 2500 cm^{-1})

Also note the localisation of different C-H signals for carbon atoms of a different hybridisation sp^3 , sp^2 , sp^1 (figure 2).

Stretching (elongation) vibrations for C-H bonds	Wave number (cm ⁻¹)
$\text{C}\equiv\text{C}-\text{H}$	~ 3 300
$\text{C}=\text{C}-\text{H}$	3 100-3 020
$\text{C}-\text{C}-\text{H}$	2 960-2 850

Figure 2: Wavenumber of C-H bonds for atoms in the hybridisation states sp^1 , sp^2 and sp^3 .

Important elongating frequencies in IR:


Type of bond	Wave number (cm ⁻¹)	Intensity
$\text{C}\equiv\text{N}$	2 260-2 220	moyenne
$\text{C}\equiv\text{C}$	2 260-2 100	moyenne à faible
$\text{C}=\text{C}$	1 680-1 600	moyenne
$\text{C}=\text{N}$	1 650-1 550	moyenne
	~1 600 et ~1 500-1 430	forte à faible
$\text{C}=\text{O}$	1 780-1 650	forte
$\text{C}-\text{O}$	1 250-1 050	forte
$\text{C}-\text{N}$	1 230-1 020	moyenne
$\text{O}-\text{H}$ (alcool)	3 650-3 200	forte et large
$\text{O}-\text{H}$ (acide carboxylique)	3 300-2 500	forte et très large
$\text{N}-\text{H}$	3 500-3 300	moyenne et large
$\text{C}-\text{H}$	3 300-2 700	moyenne

Figure 3: Wave number for the elongating vibrations in IR. You are strongly recommended not to consider the signals that appear under 1500 cm^{-1} , as those areas are very complex, which can drive you to wrong conclusions.

Problem 3 : Identification of substances

You are provided with five vials (labelled A, B, C, D or E) that could contain 0,5M solutions of calcium chloride, sodium carbonate, sodium chloride, sodium hydroxide, or sulfuric acid.

Determine which solution is in which vial. Use only the material provided for this problem.