Practical Problem I
(23 blue points, 23 red points)

DETERMINATION OF FATTY ACIDS

The starch and phenolphtalein indicator are shared between three students. They should be returned immediately after use, and should be handed to the referees to be exchanged if they become contaminated.

A mixture of an unsaturated monoprotic fatty acid and an ethyl ester of a saturated monoprotic fatty acid has been dissolved in ethanol (2.00 mL of this solution contain a total of 1.00 g acid plus ester). By titration the acid number[1], the saponification number[2] and the iodine number[3] of the mixture shall be determined. The acid number and the saponification number shall be used to calculate the number of moles of free fatty acid and ester present in 1.00 g of the sample. The iodine number shall be used to calculate the number of double bonds in the unsaturated fatty acid.

Note: The candidate must be able to carry out the whole exam by using the delivered amount of unknown sample (12 mL). There will be no supplementation.

   1)   Acid number: The mass of KOH in milligram that is required to neutralize *one* gram of the acid plus ester.

   2)   Saponification number: The mass of KOH in milligram that is required to saponify *one* gram of the acid plus ester.

   3)   Iodine number: The mass of iodine (I) in g that is consumed by 100 g of acid plus ester.

Atomic masses:

I = 126.90		O = 16.00
K = 39.10		H = 1.01

1) Determination of the acid number.

Reagents and Apparatus: Unknown sample, 0.1000 M KOH, indicator (phenolphthalein), ethanol/ether (1:1 mixture), buret (50 mL), erlenmeyer flasks (3 x 250 mL), measuring cylinder (100 mL), graduated pipette (2 mL), funnel.

Procedure: Pipet out aliquotes (2.00 mL) from the unknown mixture into erlenmeyer flasks (250 mL). Add first ca.100 mL of an ethanol/ether mixture (1:1) and then add the indicator (5 drops). Titrate the solutions with 0.1000 M KOH.

Calculate the acid number.

2) Determination of the saponification number.

Reagents and Apparatus: Unknown sample, 0.5000 M KOH in ethanol, 0.1000 M HCl, indicator (phenolphthalein), volumetric flask (50 mL), round bottom flask (250 mL), Liebig condenser, buret (50 mL), erlenmeyer flasks (3 x 250 mL), volumetric pipette (25 mL), volumetric pipette (10 mL), graduated pipette (2 mL), funnel, glass rod. The round bottom flask and Liebig condenser are to be found in the fume hoods.

Procedure: Pipet out a 2.00 mL aliquote of the unknown sample into a round bottom flask (250 mL) and add 25.0 mL 0.5000 M KOH/EtOH. Reflux the mixture with a heating mantle for <u>30 min</u> in the fume hood (start the heating with the mantle set to 10, then turn it down to 5 after 7 min.). Bring the flask back to the bench and cool it under tap water. Transfer quantitatively the solution to a 50 mL volumetric flask and dilute to the mark with a 1:1 mixture of ethanol/water. Take out aliquots of 10 mL and titrate with 0.1000 M HCl using phenolphtalein as indicator (5 drops).

Calculate the saponification number.

3) Determination of the iodine number.

In this experiment iodobromine adds to the double bond.

$$
\begin{array}{ccc}
 & & \overset{\text{I}}{\underset{|}{}} \quad \overset{\text{Br}}{\underset{|}{}} \\
C = C & + \text{ IBr} \oslash & C - C
\end{array}
$$

The Hanus solution (IBr in acetic acid) is added in excess. After the reaction is complete, excess iodobromine is reacted with iodide forming I_2, $IBr + I^- \oslash I_2 + Br^-$, which in turn is determined by standard thiosulphate titration.

Warning: Be careful when handling the iodobromine solution. Treat any spill immediately with thiosulphate solution.

Reagents and Apparatus: Unknown sample, 0.2000 M Hanus solution , dichloro-methane, 15% KI solution in distilled water, distilled water, 0.2000 M sodium thiosulfate, starch indicator, erlenmeyer flasks (3 x 500 mL), buret (50 mL), graduated pipette (2 mL), measuring cylinders (10 and 100 mL), volumetric pipette (25 mL), aluminium foil.

Procedure: Pipet out aliquotes (1.00 mL) of the unknown mixture into erlenmeyer flasks (500 mL) and add 10 mL of dichloromethane. With a pipet add 25.0 mL Hanus solution, cover the opening with aluminiumfoil and place your labelled flasks in the dark in the cupboard (under the fume hood) for 30 min. with occasionally shaking. Add 10 mL of the 15% KI solution, shake thoroughly and add 100 mL of dist. water. Titrate the solution with 0.2000 M sodium thiosulphate until the solution turns pale yellow. Add starch indicator (3 mL) and continue titration until the blue colour entirely disappears.
Calculate the iodine number.

4) Use the results from 1) 2) and 3) to:

i) Calculate the amount of ester (in mol) in 1 g of the acid plus ester

ii) Calculate the number of double bonds in the unsaturated acid

Practical Problem II
(17 blue points, 17 red points)

VOLUMETRIC DETERMINATION OF BROMIDE BY BACK-TITRATION WITH THIOCYANATE AFTER PRECIPITATION WITH SILVER IONS IN EXCESS

Moments worth considering:
- The candidates must consider the number of significant figures that will be reasonable in the results.
- The candidates must be able to carry out the whole analysis by using the delivered portions of silver nitrate and potassium thiocyanate. Supplementation of these two solutions will not be available.
- Only *one* 25 mL pipette will be at disposal for each candidate.

Principle

Bromide is precipitated as silver bromide after a known amount of silver ions has been added in excess.

$$Ag^+(aq) + Br^-(aq) \oslash AgBr(s) \qquad \text{(faint yellow-green)}$$
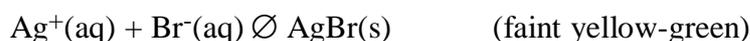
The excess of silver ions is titrated with thiocyanate with a known concentration, after a previous standardization of the thiocyanate solution.

During the titration of the following reaction takes place, resulting in the precipitation of silver thiocyanate:

$$Ag^+(aq) + SCN^-(aq) \oslash AgSCN(s) \qquad \text{(white)}$$

Fe(III) is added as indicator producing a red-coloured ion at the equivalence point:
$$Fe^{3+}(aq) + SCN^-(aq) \oslash FeSCN^{2+}(aq) \qquad \text{(red)}$$

a)

Procedures

Every candidate has got a 0.5 liter brown bottle with screw cap, containing about 0.08 M of a potassium thiocyanate solution , *and* also a 0.25 liter brown bottle with screw cap, containing the silver nitrate solution. The concentration of this solution is 0.1000 M. The exact concentration of the KSCN solution is to be determined by the candidates.

i) Determination of bromide in the unknown sample solution
Fill the 250 mL volumetric flask containing the bromide sample solution to the mark with water.

Transfer three 25.00 mL portions (pipette) of the sample solution to three erlenmeyer flasks. Add about 5 mL of 6 M nitric acid (measuring cylinder) to each flask.

Transfer 25.00 mL (pipette) of the accurately known silver solution and about 1 mL of iron(III) indicator (ind.) (measuring cylinder) to each solution.

Titrate the contents of the three aliquotes with the potassium thioscyanate solution. The end-point of the titration is detected when the solution (including the precipitate) becomes permanently *very faint* brownish. It is important to shake the contents vigorously near the end-point and rinse the walls of the flask with water. The colour should be stable for at least one minute.

ii) Standardization of the potassium thiocyanate solution:
Transfer 25.00 mL (pipette) of the silver nitrate solution to an erlenmeyer flask, add about 5 mL of 6 M nitric acid and about 1 mL of the iron(III) indicator solution and about 25 mL of water (use measuring cylinders for these solutions).

Titrate the contents with the thiocyannate solution and determine the end-point according to the instruction given in the "Determination" procedure.

Atomic mass: Br = 79.90

b)

Exercise

At the equivalent point the solution is saturated with respect to both AgBr and AgSCN. Find the molar consentration of free (unprecipitated) Br^- in this solution:

$$K_{sp(AgBr)} = 5.00 \cdot 10^{-13} \qquad K_{sp(AgSCN)} = 1.00 \cdot 10^{-12}$$

Ignore the effect of pH and Fe(III) species.

Note: On the answer sheet, not only the required final results shall be given, but also examplifications of how the calculations are carried out.