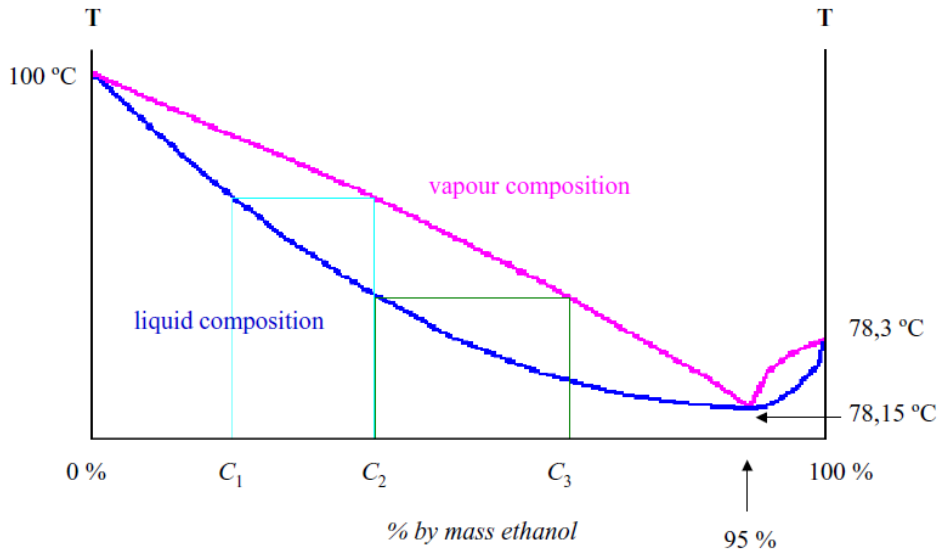
19. Determination of the alcohol content in beverages – distillation method

Accurate alcoholic beverages analysis ensures excellent beverages quality [1]. Therefore this analysis is an essential part of the daily work in the labs in the breweries, vineyards and distilleries. Knowledge of the alcohol content is necessary to ensure that the beverage conforms to the label declaration of alcohol content [2] and to establish the basis for the payment of tax [3].

Distillation. Distillation is the most important method of separation and purification of liquids. In the simplest case of distillation liquid is heated to boiling and produced vapor is condensed in a condenser and collected as a distillate. Distillation when only one phase is in the motion – vapor – is called simple distillation. Distillation when portion of condensed vapor still flow down into the distillation flask is called rectification. Rectification is performed using fractionating column [4].

Many substances form azeotrope mixtures, which at definite composition show maximal or minimal boiling temperature. Azeotrope mixture cannot be separated by distillation because vapor and liquid phase have the same composition. The example of azeotrope mixture is exactly water-ethanol mixture. The mixture containing 95 % by mass of ethanol boils at the lower temperature i.e. 78,15 °C, than pure water (100 °C) or pure ethanol (78,3 °C).

The following diagram shows the phase equilibrium between liquid and vapor in the function of concentration for water-ethanol mixtures [5].



Suppose, we are going to distill a mixture of water and ethanol with composition C_1. It will boil at a temperature given by a liquid curve and produce a vapor with composition C_2. When a vapor condenses it will still have the composition C_2. If we reboil this new mixture it will produce a new vapor with composition C_3. If we carried on with this boiling-condensing-reboiling procedure we end up with a vapor with a composition of 95 % by mass of ethanol. If we condense this vapor we gat a liquid with this same composition. Because of liquid and vapor curves meet at this point, each time when we boil the liquid with the composition of 95 % by mass of ethanol, the condensed vapor still has the same composition of 95 % by mass of ethanol. It means that it is impossible to get pure ethanol (100 %) by distilling any mixture of water-ethanol containing less than 95 % by mass of ethanol. This particular mixture of ethanol and water boils as if it were a pure liquid. It has a constant boiling point and the vapor composition is exactly the same as the liquid. This liquid is known as an azeotrope.

In the consequences of this for fractional distillation of dilute aqueous solutions of ethanol we cannot get pure ethanol, but only a product with a maximum concentration of 95 % of ethanol. What we can get it is a pure water, of course if we earlier ethanol rich vapor given off from the distillation flask.

Pure ethanol can be produce only by the fractional distillation of ethanol-water mixtures containing more than 95 % by mass of ethanol. In this case we get a distillate containing 95 % of ethanol in the collecting flask and pure ethanol in the boiling flask.

Determination of alcohol content in beverages – distillation method. The base of the method of the determination of alcohol content in beverages is a precise measurement of volume (or weight) of a degassed and filtered sample of beverage. The sample is quantitatively transferred to the distillation apparatus, then the distillation is performed and the obtained alcohol fraction is filled up to the original volume (or weight) with distilled water. In this way a liquid is obtained which has the same alcohol concentration as the original sample but no longer has extract. The alcohol concentration in % *by vol.* or in % *by mass* is determined highly accurately via density or refractive index measurements and an appropriate alcohol concentration tables [6-11].
The alcoholic strength by volume is the number of liters of ethanol contained in 100 liters of beverage, both volumes being measured at a temperature of 20 °C. It is expressed by the symbol '% *by vol*'.
Homologues of ethanol, together with the ethanol and ethanol homologues in ethyl esters, are included in the alcoholic strength since they occur in the distillate.

Methods of measurements of alcohol content in distillate. The alcohol content in a distillate can be determined using [8, 9, 12]:

- pycnometer – determination of density or specific gravity of distillate – method basing on a precise measurement of a mass of liquid,
- areometer (hydrometer), alcoholometer – determination of density, specific gravity or alcohol concentration of distillate – method basing on buoyancy,
- hydrostatic weighing – determination of density of distillate – method basing on buoyancy,
- digital density meter – determination of density of distillate – measurements of the frequency of oscillation of the U-shaped tube filled with a sample,
- refractometer – measurement of the refractive index of a distillate,
- spectrometer – measurement of the alcohol-specific range of the near infrared (NIR) spectrum.

<u>Aim of exercise</u> The aim of this activity is a distillation of a sample of a chosen beverage like beer, wine, sparkling wine, liqueur, tincture or mead and determination of alcohol content in received distillate.

Materials:

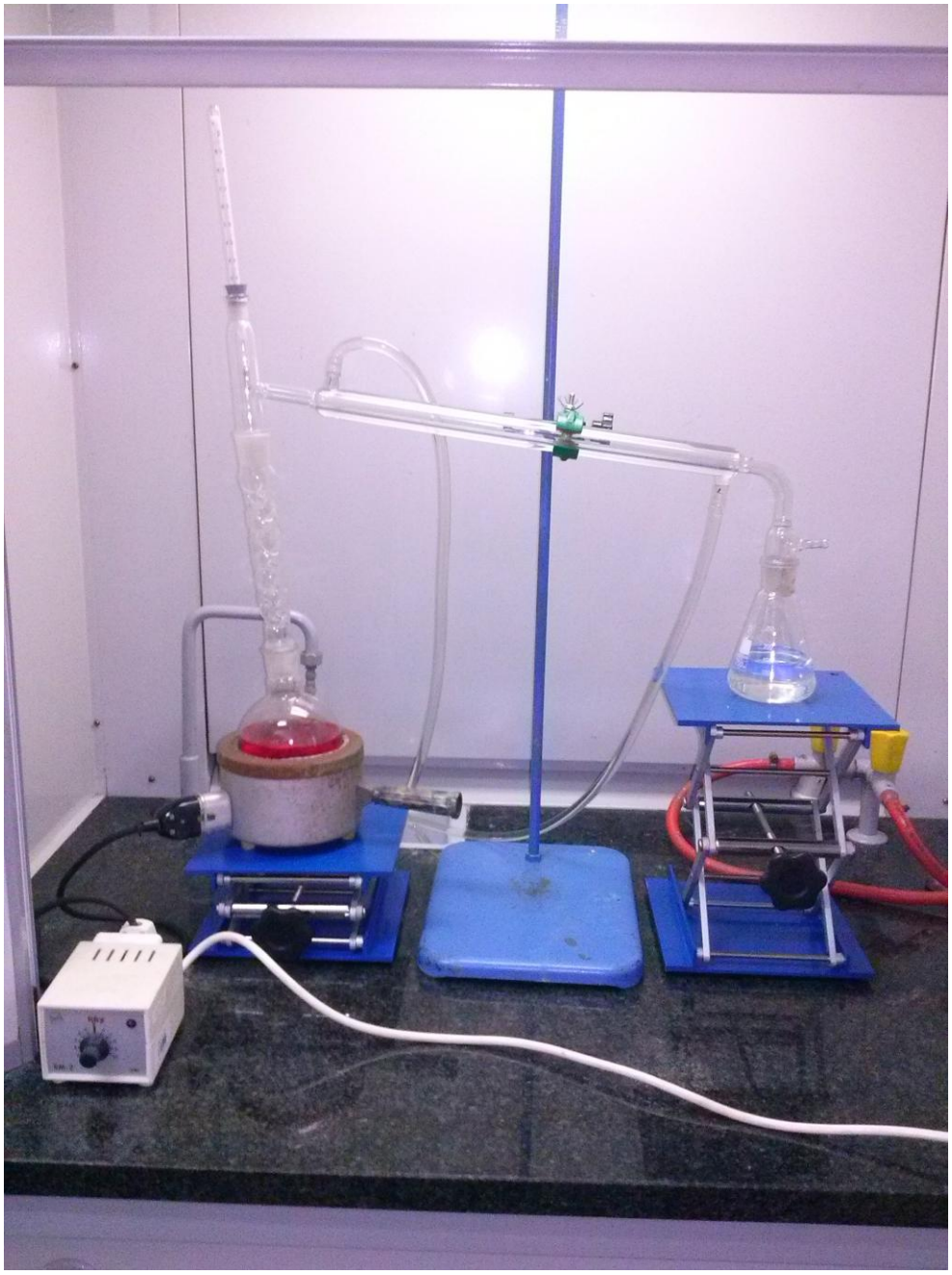
- round flat-bottomed flask with ground glass joint per 1000 cm^3,
- 2 round flat-bottomed flasks with ground glass joint per 500 cm^3,
- Erlenmeyer flask with ground glass joint per 250 cm^3,
- Liebig condenser,
- fractionating column,
- thermometer with ground glass joint,
- rubber tubing,
- heating mantle,
- laboratory support jack,
- laboratory stand,
- condenser clamp + clamps holder,
- glass beads or pumice pieces,
- Pasteur pipette with nipple,
- funnel,
- cellulose wool or filter paper,
- analytical balance Radwag WPS 600/C,
- graduated cylinder per 250 cm^3,
- graduated cylinder per 25 cm^3,
- hydrometer calibrated from 0,900 to 1,000 g/cm^3,
- thermometer,
- magnifying glass.

Chemicals:

- 2 M suspension of $Ca(OH)_2$,
- distilled water,
- indicator paper.

PROCEDURE

Sample preparation. If the analyzed sample is a beer or a sparkling wine – the sample should be degassed. In this purpose pour about 350 cm^3 of the sample to round flat-bottomed flask per 1000 cm^3 and stir it as long as the pressure of carbon dioxide in the flask is detectable by hand. Next filter the sample through the cellulose wool or filter paper to a round flat-bottomed flask per 500 cm^3.



Analysis. Weigh precisely 200 ±0,1 g of prepared sample in a clean and dry tared round flat-bottomed flask per 500 cm^3 on a balance (last drops of a sample should be added carefully with a Pasteur pipette). Next add about 30 cm^3 of distilled water. If the analyzed sample is a wine or a mead add additionally 10 cm^3 of 2 M $Ca(OH)_2$ in the presence of an indicator paper to neutralize the solution. Next add a few glass beads or pumice pieces.

Place the flask in the heating mantle and join it with a fractionating column and the Liebig condenser and tared Erlenmeyer flask with ground glass joint per 250 cm^3 (the mass of the clean, dry and empty!!! Erlenmeyer flask note down earlier in the lab-book). Join the rubber tubing with

the condenser – cooling water should enter through the lower fitting and exit through the upper fitting. Ask the assistant to check the correctness of the connections of apparatus.
Turn on the cooling water flow and begin heating the flask with a mantle. Adjust heat as necessary to achieve uniformly boiling of the liquid. Distill as long as you receive in the collecting flask about 180 cm^3 of a liquid. End up the distillation process – disconnect the electric power, turn off the water, cool down the apparatus and disconnect the condenser.
Place the collecting flask with the distillate in the analytical balance and fill up drop by drop with distilled water to 200,0 g of the liquid with ±0,1 g accuracy. Plug the flask and gently swirl the liquid.

Measurements of the distillate density, $\rho_{\text{sample}}^{t^\circ\text{C}}$.

a) Hydrometry. Pour the distillate into the measuring cylinder per 250 cm^3. Ensure that the cylinder is kept vertical. Insert carefully the thermometer and hydrometer. Read the temperature on the thermometer two minutes after stirring to equilibrate the temperature of the measuring cylinder, the thermometer, the hydrometer and the distillate. Write down the temperature in the lab-book. Remove the thermometer and read the apparent density after one minute. Take at least three readings using a magnifying glass and write down the measured density $\rho_{\text{sample}}^{t^\circ\text{C}}$ in the lab-book.

Calculations. In order to determine the alcohol strength expressed in % *by mass* refer to the international alcoholometric tables [13]. Find in the tables the smallest density greater than the measured density of sample, $\rho_{\text{sample}}^{t^\circ\text{C}}$ at the temperature *t* °C.

Alcohol strength expressed as % *by vol.* in the analyzed sample can be calculated from the following formulae:

$$\%\,by\,vol. = \frac{\rho_{\text{sample}}^{t^\circ\text{C}}}{\rho_{\text{CH}_3\text{CH}_2\text{OH}}^{t^\circ\text{C}}} \cdot \%\,by\,mass$$

where:

% *by mass* – is the ethanol strength by mass, $\rho_{\text{CH}_3\text{CH}_2\text{OH}}^{t^\circ\text{C}}$ – is the density of ethanol at *t* °C, it can be found in respective tables.

b) Densimetry using an automatic density meter Rudolph Research Analytical DDM 2911. Transfer about 3 cm^3 of the distillate to a clean and dry test-tube and cork it. To perform a measurement please contact with doctor Andrzej Burakowski. Office 401A, phone number 375 7235. The measurement could be performed during lab or in the other appointed time. Obtained data has to be included in the final report.

Report

The report should be composed of:

- first name and last name of the person conducting the analysis,
- analysis' date,
- all the necessary information enable to sample identification,
- short description of sample preparation and analysis,
- analysis' result (if possible, comparison of the analysis' result and the alcohol content provided by the producer from the beverage's label),
- comments.

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