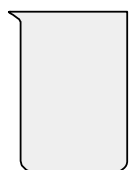


Zajęcia doształcające z języka angielskiego w chemii nr. 4

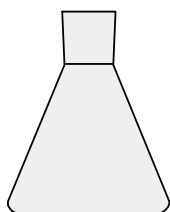
(opracował - P. Przybylski)

Część druga nazewnictwa szkła laboratoryjnego

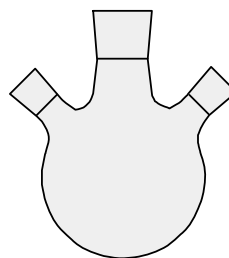
Laboratory glassware – basic glossary (on pictures):



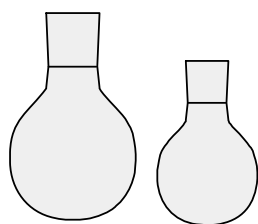
Beaker



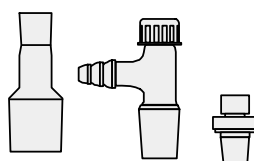
Erlenmeyer
Flask



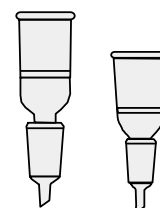
Three-Neck Round-Bottom Flask



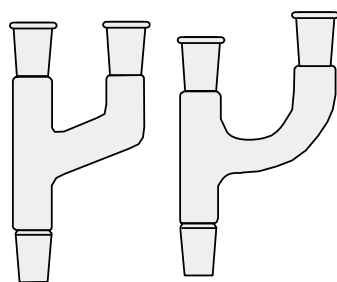
Round-Bottom Flasks



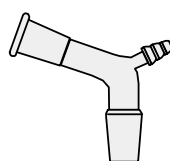
Reducing
Adapter



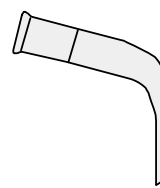
Buchner funnels



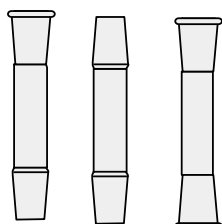
Claisen Adapters



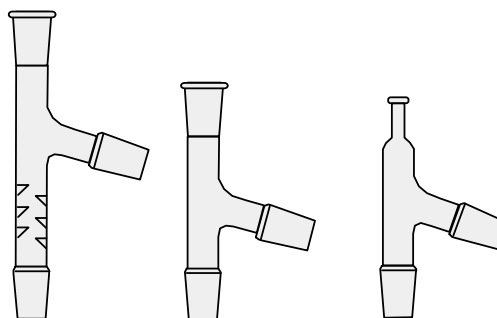
Vacuum-Distilling
Adapter



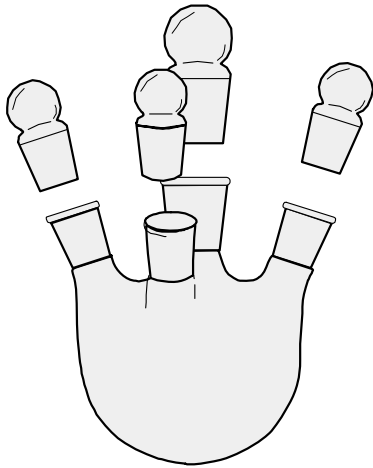
105 degree
bent adapter



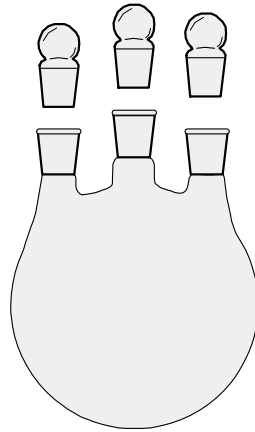
Straight Connecting
Adapters



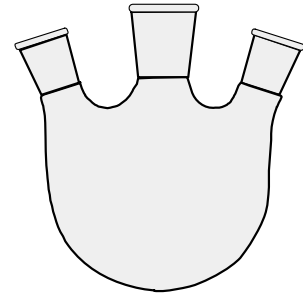
Three-Way Adapters



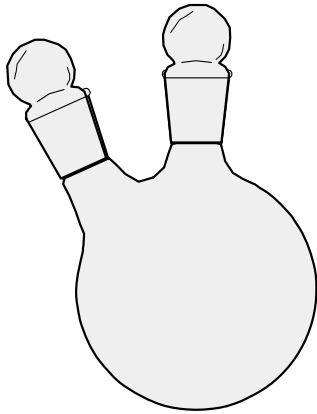
Four-Neck Angled
Round-Bottom Flask



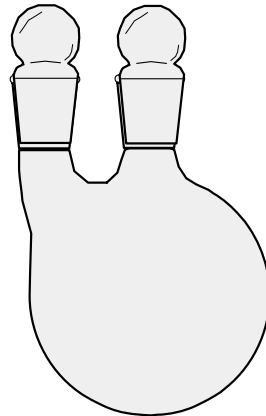
Three-Neck Vertical
Round-Bottom Flask



Three-Neck Angled
Round-Bottom Flask



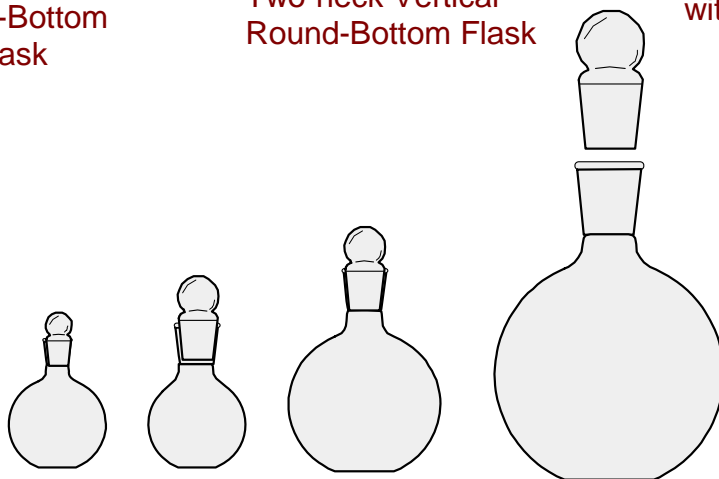
Two-neck Angled
Round-Bottom
Flask



Two-neck Vertical
Round-Bottom Flask

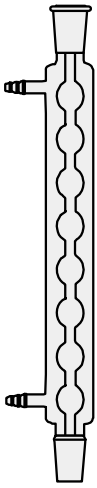


Round-Bottom Flask
with Septum Inlet

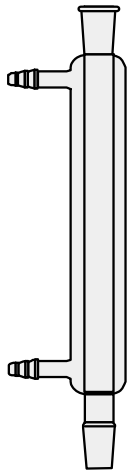


Round Flat-Bottom Flasks

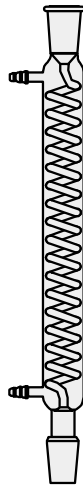
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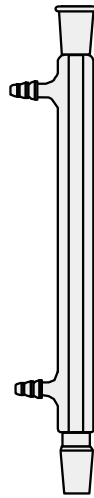
Allihn



Liebig



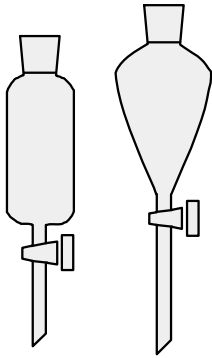
Grahams



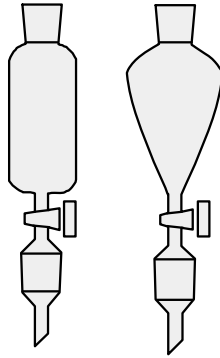
West



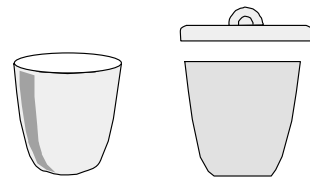
Thermometer



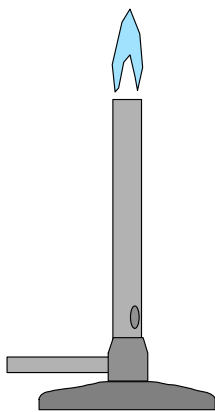
Separatory Funnels



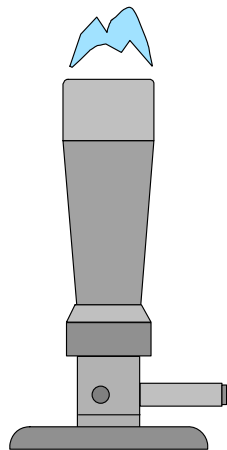
Dropping Funnels



Crucibles



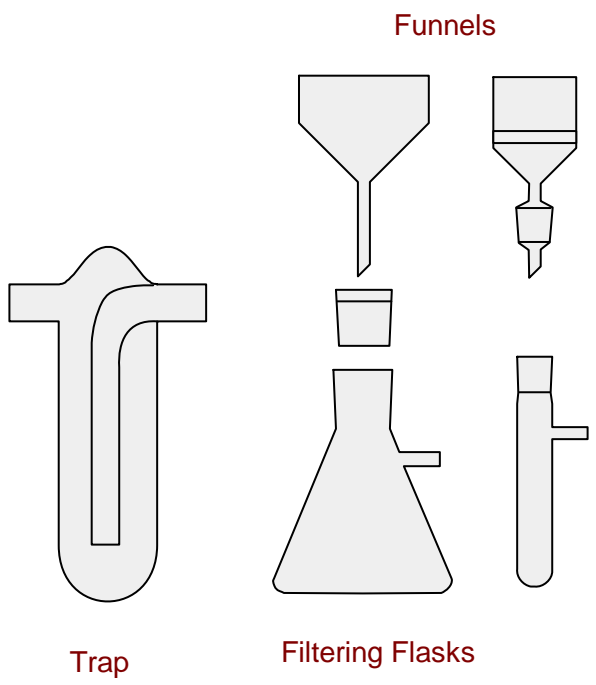
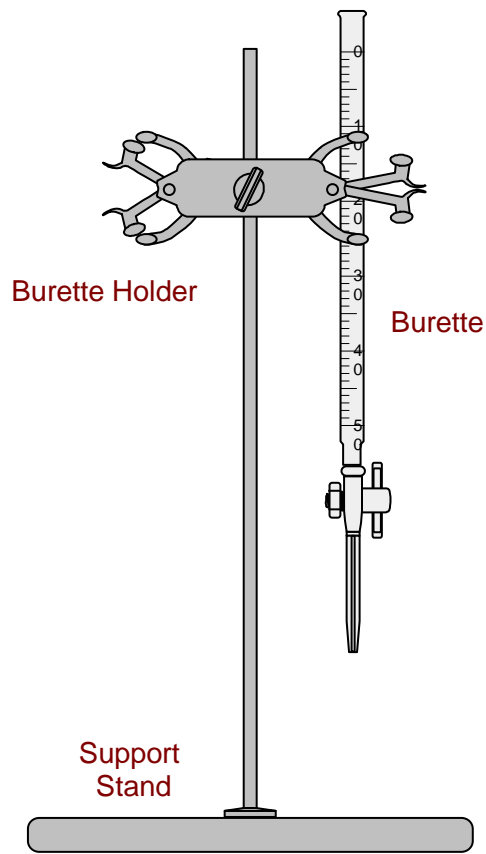
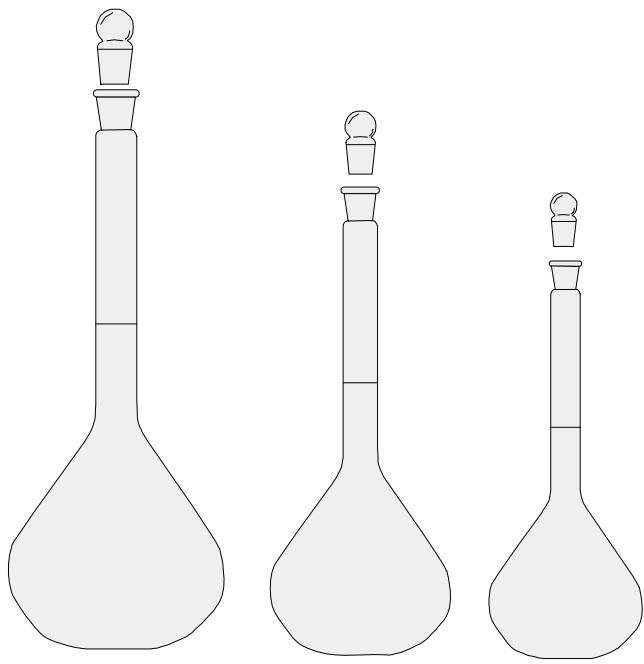
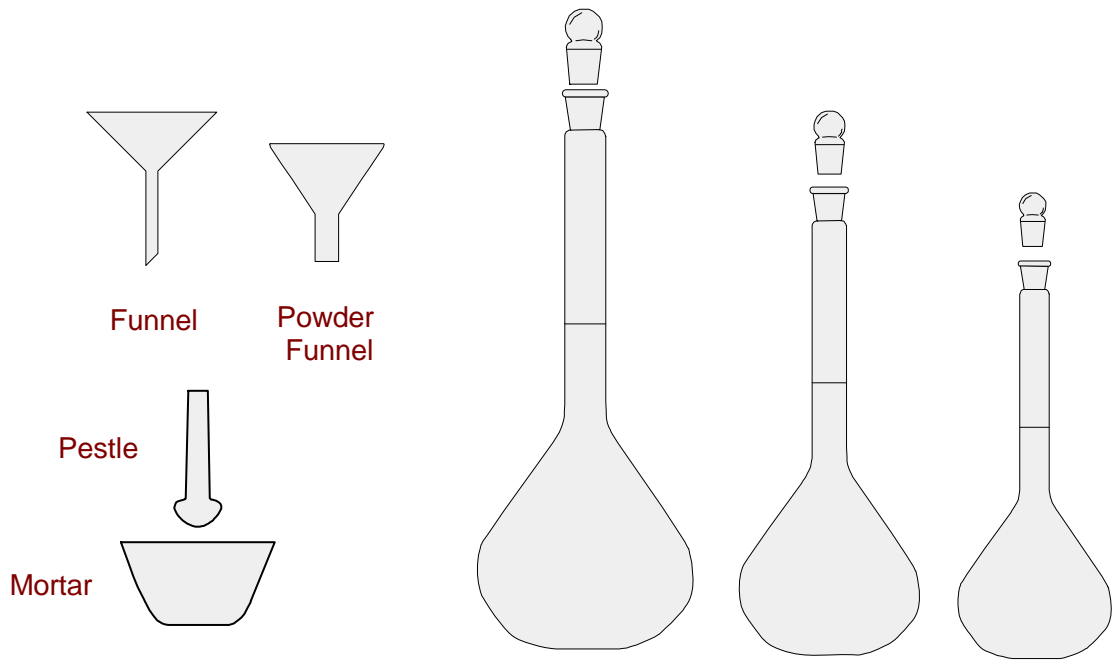
Bunsen
Burner

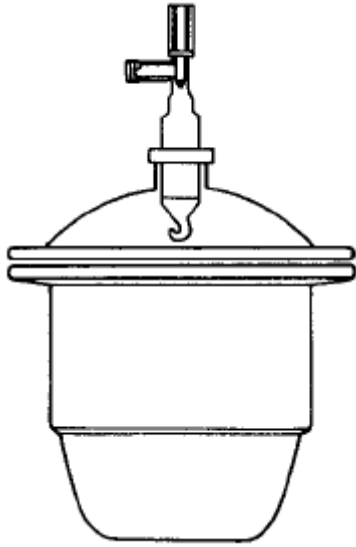


Meker Bunsen
Burner



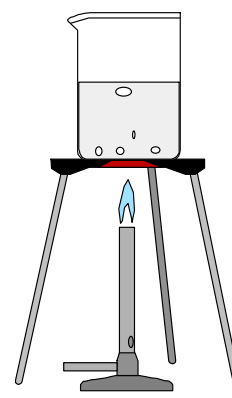
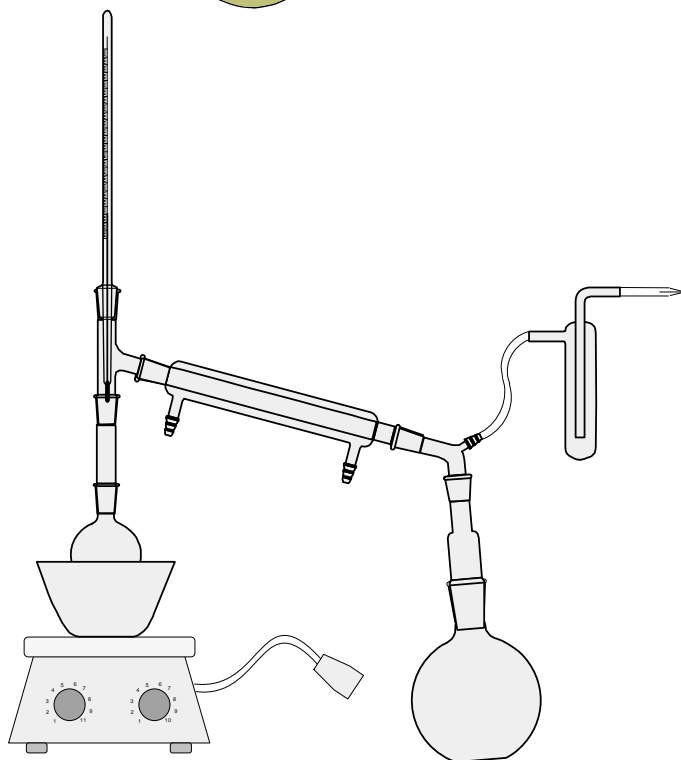
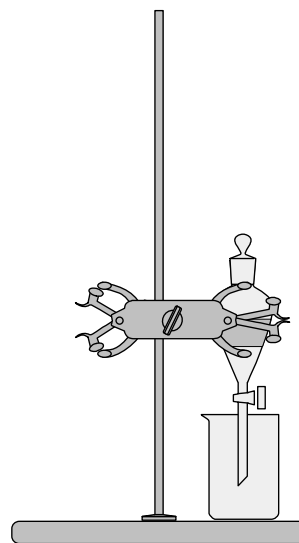
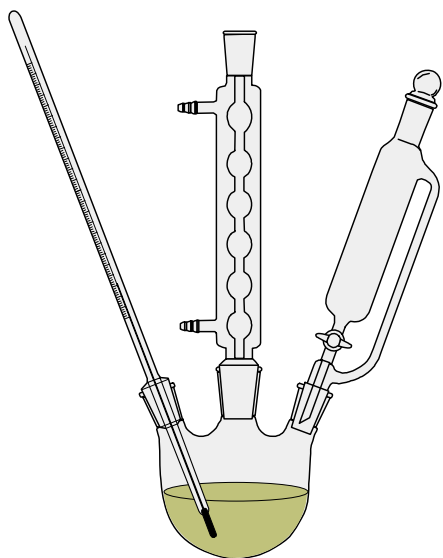
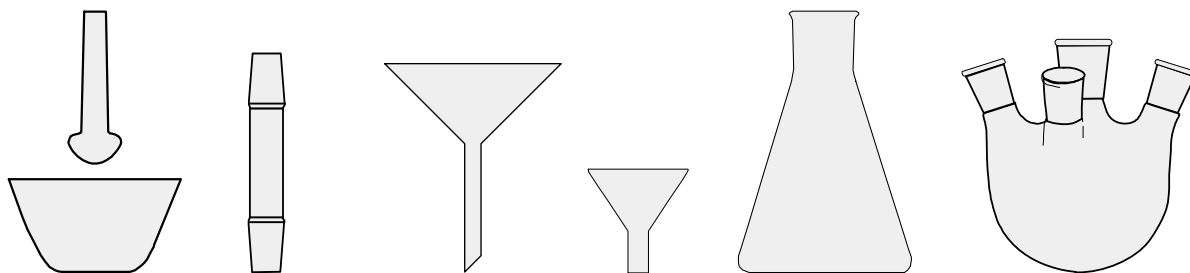
Tripod Stand





vacuum desiccator

Ćwiczenie. Nazwij poszczególne elementy wyposażenia laboratoryjnego:



Ta część zajęć ma na celu wprowadzenie słownictwa z zakresu technik laboratoryjnych (przykładowe teksty poniżej).

Thin layer Chromatography (TLC)

Extraction and Washing

Two-Solvent Recrystallization

Distillation

Reduced Pressure Distillation

Przykładowe teksty z części eksperymentalnych z czasopism naukowych

Thin layer Chromatography (TLC)

Thin Layer Chromatography (TLC) is an extremely useful technique for **monitoring reactions**. It is also used to determine the **proper solvent system** for performing **separations** using **column chromatography**. TLC uses a **stationary phase**, usually alumina or silica, that is **highly polar** (standard) or **non-polar (reverse phase)**. The **mobile phase** is a solvent whose polarity you will choose. In 5.301, and in most lab applications, you will use standard phase **silica plates**. You will apply your reaction mixture in solution to the plate and then "run" the plate by allowing a solvent (or combination of solvents) to move up the plate by **capillary action**. Depending on the polarity of the components of the mixture, different compounds will travel different distances up the plate. More polar compounds will "stick" to the polar silica gel and travel short distances on the plate. Non-polar substances will spend more time in the mobile solvent phase and travel larger distances on the plate. The measure of the distance a compound travels is called the R_f value. This number, between zero and one, is defined as the distance the compound moved from the **baseline** (where it was originally spotted) divided by the distance the solvent front moved from the baseline.

Steps for TLC:

1) Cut TLC plates. Usually silica plates are bought as square glass pieces that must be cut using a **diamond tipped glass cutter** and following a template. Before scoring the glass, use a ruler and a pencil to lightly mark baselines on the silica side of the plate (be careful not to remove any silica from the plate). Using a **sharp glass cutter** and a ruler as a guide, you should have no problem scoring the glass. Once the entire plate is **scored**, you can then break the glass into individual pieces. (In the beginning this may be frustrating, but after some practice, you should become comfortable with this technique.)

2) Determine an appropriate solvent system. Your compounds will travel different distances up the plate depending on the solvent you choose. In non-polar solvents like **pentane** and **hexane**, most polar compounds will not move, while non-polar compounds will travel some distance up the plate. In contrast, polar solvents will usually move non-polar compounds to the solvent front and push the polar compounds off of the baseline. A good solvent system is one that moves all components of your mixture off the baseline, but does not put anything on the solvent front - R_f values between 0.15 and 0.85. This is not always possible, but should be your goal when running a TLC. (For column chromatography the correct solvent system should give an R_f between 0.2 and 0.3.) Now, which solvents **to pick**? Here is a list of some standard solvents and their relative polarity (from LLP): Very polar additives: **Methanol** > **Ethanol** > **Isopropanol**. Moderately polar additives: **Acetonitrile** > **Ethyl Acetate** > **Chloroform** > **Dichloromethane** > **Diethyl Ether** > **Toluene**. Non-polar additives: **Cyclohexane**, **Petroleum Ether**, **Hexane**, **Pentane**. Common solvent combinations: Ethyl Acetate/Hexane: 0–30% most popular combination, sometimes tough to remove solvents completely on **rotary evaporator** Ether/Pentane: 0–40% very popular, easy to remove on the rotary evaporator Ethanol/Hexane or Pentane: 5–30% useful for very polar compounds Dichloromethane/Hexane or Pentane: 5–30% sometimes useful when other mixtures fail.

3) Fill **TLC chamber** with 1–2 mL of the desired solvent system. Place a large piece of cut filter paper in the chamber as well.

4) Spot the compound on the baseline of the TLC plate. We will use commercial spotters, but spotters can be pulled from hot Pasteur pipets. If you are monitoring a reaction, make sure **to spot** the starting material, the reaction mixture, and a co-spot of both.

5) Run the TLC. Let the solvent go about 90% of the way up the plate.

6) Remove the plate from the chamber and **mark** the solvent front immediately with a pencil. You will use this to calculate the R_f .

7) Let **the solvent dry off of the plate**.

8) Visualize the TLC using non-destructive technique(s). The best non-destructive method is the **UV lamp**. Place your plate under the UV lamp and circle any UV active spots with your pencil. Although we won't do this in 5.301, another popular non-destructive method is **staining with iodine**.

Glossary:

Thin Layer Chromatography – chromatografia cienkowarstwowa

monitoring reactions – monitorowanie przebiegu reakcji

proper solvent system – odpowiedni układ rozpuszczalników

separation – rozdział

column chromatography – chromatografia kolumnowa

stationary phase – faza stacjonarna

highly polar – wysoce polarny

non-polar (reverse phase) – niepolarny (odwrócona faza)

mobile phase – faza ruchoma

silica plates – płytki do TLC

capillary action – efekt kapilarny

baseline – linia bazowa

diamond tipped glass cutter – nóż diamentowy do cięcia szkła

sharp glass cutter – urządzenie do cięcia szkła

scored – zarysowany, nacięty

pentane – pentan

hexane - heksan

to pick – wybrać

Methanol – methanol

Ethanol – etanol

Isopropanol – izopropanol

Acetonitrile – acetonitryl

Ethyl Acetate – octan etylu

Chloroform – chloroform

Dichloromethane – dichlorometan

Diethyl Ether – eter dietylowy

Toluene – toluene

Cyclohexane – cykloheksan

Petroleum Ether – eter naftowy

Hexane – heksan

Pentane – pentan

rotary evaporator – wyparka obrotowa

TLC chamber – komora do TLC

to spot – nanieść w postaci plamki

to mark - zaznaczyć

the solvent dry off of the plate- rozpuszczalnik odparował z płytki TLC

UV lamp – lampa UV

staining with iodine – wybarwianie jodem

Extraction and Washing

1) Pick an organic solvent. Ether is the most popular because it can be removed easily on the rotary evaporator, ethyl acetate also works well but is harder to remove, dichloromethane is a poor choice and **should be avoided**, if possible, since it often forms **nasty emulsions** and complicates matters because it is **heavier than water**.

2) Pick the size of your separatory (sep.) funnel. You will usually use 125 or 250-mL, large scale reactions (1–10 g) can require 500-mL or 1-L sizes. Remember that your **sep. funnel** will contain the solvent and wash liquid which must be thoroughly mixed.

3) **Dilute** the crude reaction mixture with your solvent of choice and transfer to your chosen sep. funnel. Large amounts of material require large amounts of solvent. Normal reactions (50–500 mg of product) can be diluted with between 25–100 mL of solvent.

4) **Wash the organic layer** to remove impurities. The volume of a **wash phase** is typically one tenth to one half the volume of the organic phase. It is sometimes best to repeat a wash two or three times. An **acid wash** (usually 10% HCl) **is used to remove amines**, while a **basic wash** (usually sat. NaHCO₃ or 10% NaOH) is used to remove unwanted acids. In most cases, when neither acidic nor basic impurities are an issue, the solution is washed with distilled water to remove any non-organic compounds. (*Note: When shaking mixtures in a sep. funnel be sure to vent it regularly by holding it upside down, pointing it up and to the back of your hood, then opening the stopcock. This will release any pressure that has built up during mixing. Additionally, when draining liquids out of the sep. funnel, be sure to first remove the stopper.*)

5) **Back-extract** to recover lost product. If your compound is somewhat **water soluble** (has several **polar functional groups**), you may need to back-extract the water layers with ether or ethyl acetate to avoid significant loss of compound in the aqueous phase. TLC can be used to determine when all of your compound has been removed from the water.

6) Finish with a **brine** (saturated NaCl solution) wash. This helps disrupt any emulsions and will "dry" the organic layer by extracting water that may have dissolved in the organic phase.

7) **Dry the organic layer**. After removing your solution from the **aqueous phase**, a **drying agent** is added to remove all **traces of water**. This is usually MgSO₄, more effective and faster, but slightly acidic; or Na₂SO₄, less effective and slower, but neutral. These compounds bind to any water remaining in the organic solution, forming **clumps** when they react. A decent amount of drying agent should be added, but as long as some solid is not clumped, no more needs to be added. (This will make sense once you've done this a couple of times.)

8) While the compound is drying, it is time to flute the filter paper. Some chemists prefer to use a **Büchner funnel** and **unfluted filter paper** (or a fritted funnel) under mild vacuum as their standard **filtration method**. Their motive is a slightly **higher yield of product**.

9) **Filter the solution** into a large **round bottom flask** using your expertly fluted filter paper and a large funnel (or the Büchner method). To guard against bumping on the **rotavap**, do not fill the flask more than half full.

10) **Concentrate the solution** on the rotavap, then **dissolve** the compound in a small amount of solvent and transfer to a small pre-weighed (tared) flask.

11) Concentrate the solution on the rotavap again. **Higher boiling solvents** are more effectively removed by concentrating, adding dichloromethane then repeating once more.

12) Use the vacuum pump to remove residual solvent. For **non-volatile compounds**, residual solvent is most effectively removed by using the vacuum pump. One useful trick to speed up this process is the following: evacuate the flask and vent to N₂, repeat this again, then pump on the flask for 30 minutes. If your compound is volatile—low molecular weight and/or low boiling point—obtain a constant weight using the rotavap, not the vacuum pump.

13) Obtain a **constant weight**. Weigh the flask after leaving it on the vacuum pump (or rotavap), then return to the pump (or rotavap) for 15 to 30 minutes and weigh again. Once two weights in a row are the same, you're ready to take an NMR.

Glossary:

should be avoided – powinien być unikany

nasty emulsions – „nieprzyjemne” (w sensie do rozdziału) emulsje

heavier than water – cięższe niż woda

sep. funnel - rozdzielacz

Dilute - rozcieńczyć

Wash the organic layer – przemyć warstwę organiczną

wash phase – faza przemywająca

acid wash – przemycie kwasem

is used to remove amines – jest stosowane w celu usunięcia amin

basic wash – przemycie zasada
Back-extract – zawrócenie ekstraktu do rozdzielacza
water soluble – rozpuszczalny w wodzie
polar functional groups – polarne grupy funkcyjne
brine – solanka
Dry the organic layer – wysusz warstwę organiczną
aqueous phase – faza wodna
drying agent – środek suszący
traces of water – ślady wody
clumps – bryłki, zbitki
Büchner funnel – lejek Büchnera
Unfluted/fluted filter paper –
filtration method – metoda sączenia
higher yield of product – wyższa wydajność produktu
Filter the solution – przesącz roztwór
round bottom flask – kolba okrągłodenna
rotavap – wyparka obrotowa
Concentrate the solution – zagęść roztwór
Dissolve – rozpuszczać
Higher boiling solvents – wysokowrzące rozpuszczalniki
non-volatile compounds – małowolne związki
constant weight – stała masa

Two-Solvent Recrystallization

For a two-solvent recrystallization, you should have one solvent (solvent 1) in which your desired compound is **soluble** at the **boiling point**. The second solvent (solvent 2) should **induce crystallization** when added to a **saturated solution** of your compound in the primary solvent.

Recrystallization Steps:

1) The first step is **to remove insoluble material** from your compound by filtration.

2) Transfer the material to a 50-mL **Erlenmeyer flask**, equipped with a **stir bar**. Add an excess amount of solvent1 (about 20 mL in experiment 3.1) and **heat to boiling** on a **stir/hot plate**. The **excess solvent** is used to keep the compound from **precipitating** during the filtration.

3) Filter off any insoluble contaminants through fluted filter paper in a pre-warmed stemless funnel (pre-warm by adding some hot solvent just before you filter the solution, thus preventing loss of material on the filter paper.)

4) Wash the flask and filter paper with about 2 mL of hot solvent.

5) Reduce the volume of the solution (to about 15 mL) by boiling off the excess solvent.

6) **Cool to room temperature**. At this point, it is probably not a saturated solution, so **crystallization** will not occur.

7) **Add** solvent 2 **dropwise** until the solution just becomes **cloudy**. Again heat the solution to the boiling point (with stirring!) and continue addition of solvent 2. After each drop, you will notice a cloudiness that dissolves away. Continue dropwise addition of solvent 2 until the solution is saturated (i.e. if you were to add one more drop, the **cloudiness would persist**, and the solution would be super-saturated.) If this happens, add a drop of solvent1 to return to a clear solution.

8) Remove the flask from heat, fish out the stir bar with a magnet, allow to cool undisturbed to room temperature before placing in an **ice bath**.

9) **Chill** a mixture of the solvent system (in about the same ratio you used to obtain a saturated solution). This will be used to wash your **crystals**.

10) Collect the crystals on a small Büchner funnel by **vacuum filtration**, and rinse with the cold solvent mixture.

11) Pull air through the filter cake, then dry thoroughly in vacuo before obtaining a yield. One option to dry your product is to place it in a **pre-weighed vial**, and place the vial in a **vacuum desiccator**. You can cover the vial by fastening a Kimwipe on top with a rubber band.

Glossary:

Soluble – rozpuszczalny

boiling point – temperatura wrzenia

to induce crystallization – wywołać, zaindukować krystalizację

saturated solution – nasycony roztwór

to remove insoluble material – usunąć nierozpuszczalny materiał (związki)

Erlenmeyer flask – kolba Erlenmaeyera

stir bar- mieszadło magnetyczne

heat to boiling – ogrzać do wrzenia

hot plate – płyta grzejna

the excess solvent – nadmiar rozpuszczalnika

precipitating – strącanie

to cool to room temperature – schłodzić do temperatury pokojowej

crystallization – krystalizacja

add dropwise – dodawać kroplami

cloudy – zmętniony

cloudiness would persist – tak aby zmętnienie było utrzymane

ice bath – łaźnia lodowa

to chill – schłodzić

crystals – kryształy

vacuum filtration – sączenie pod próżnią

pre-weighed vial – uprzednio zważona fiołka

vacuum desiccator – eksykator

Distillation

Distillation is an extremely useful technique that is used **to purify** reagents and **separate crude product mixtures**. There are two varieties of distillation - **atmospheric pressure** and **reduced pressure**. The former is easier, while the latter involves some more complicated techniques.

Distillations require special glassware that is unique to this technique. There are several types of set-ups, but we will use only two. In both cases we will use a short path **distillation head**, varying only in the use of a **Vigreux column**.

Atmospheric Pressure Distillation:

1) Collect the necessary glassware: short path distillation head, thermometer and adapter, receiving flasks (at least two), Vigreux column.

2) Preheat **oil bath** or **heating mantle**. If the **boiling point** is unknown, this step should be omitted. Keep in mind that for most distillations the heating apparatus must be 20–30 °C higher than the boiling point of the **distillate**. Note: Due to thermal breakdown and possible ignition, oil baths are only useful for temperatures below 200 °C.

3) Record weight of labeled **receiving flasks**.

4) Put compound to be distilled in a **round-bottomed flask** with **stir bar** or **boiling chips**. (The stir bar or boiling chips will prevent **bumping**.) The size of the round bottom flask is very important. It should be roughly half to two-thirds full; any higher and it may boil over prematurely, any less and it may take too long to distill.

5) Assemble glassware, making sure all **joints** are **snug**. A large assembly of glassware should involve at least two **clamps** - when in doubt use more clamps! Also, no **joint grease** is necessary for atmospheric pressure distillations. (Note: for **air** or **water sensitive compounds** the apparatus should be flame dried and distilled under N₂ or Ar.

6) **Insulate** the column. When using a Vigreux column, it should be wrapped with **glass wool** and **aluminum foil**. Without insulation, these set-ups tend to take a very long time.

7) Connect the condenser to the water lines, turn on the water, and check for **leaks**.

8) Raise the stir plate and heating apparatus to the flask and begin heating. Note: Variac gauges do not correspond to temperature. Setting the dial at 70 will not heat your oil bath to 70 °C - it will actually go much higher. Also, different oil baths and heating mantles will heat to different temperatures at the same settings.

9) Lower the **hood sash**. This is always a good practice in case of accident, but it also keeps the distillation apparatus away from the **air conditioning** of the lab. This will cool your set-up and make your distillation take longer.

10) **DO NOT HEAT TOO QUICKLY!!!** Patience is the key to distillation.

11) Slowly increase the temperature of the heating apparatus until the solution is refluxing.

12) Wait to see the distillation thermometer respond. If nothing happens after about 10 minutes then raise the temperature slightly.

13) Repeat step 12 until you see the distillation thermometer respond. Once this happens, prepare to collect.

14) Try to keep the apparatus at a constant temperature - at least within 5 degrees of the temperature when the distillation thermometer registered.

15) Collect until a dramatic change in temperature occurs. Usually the temperature of the distillation thermometer will drop when one fraction is done distilling. At this point you should change receiver flasks or stop the distillation entirely.

16) When you have collected everything you want, drop the heating apparatus and let the entire apparatus cool.

17) Weigh the collection flask(s) and obtain the weight of your product(s).

Glossary:

to purify - oczyszczać

separate - rozdzielać

crude product mixtures – mieszaniny surowych produktów

atmospheric pressure distillation – destylacja pod ciśnieniem atmosferycznym

reduced pressure distillation – destylacja pod zmniejszonym ciśnieniem

distillation head – nasadka destylacyjna

Vigreux column – kolumna Vigreux

oil bath – łaźnia olejowa

heating mantle – płaszcz grzejny

boiling point – temperatura wrzenia

distillate - destylat

receiving flasks - odbieralniki

round-bottomed flask – kolba okrągłodenna

stir bar – mieszadło

boiling chips – kamyczki wrzenne /porcelanka/

bump – wyskoczyć (o cieczy z naczynia)

joints – połączenia (szlify)

snug – dobrze dopasowane

clamp – łapa

joint grease – smar do szlifów

water sensitive compounds – związki wrażliwe na działanie wody

air sensitive compounds – związki wrażliwe na działanie powietrza

insulate - izolować

glass wool – wełna szklana

aluminum foil – folia aluminiowa

leaks - nieszczelności

hood sash – szyba od wyciągu

air conditioning - klimatyzacja

Reduced Pressure Distillation:

- 1) Collect the glassware - the same as above except this time make sure to include a pig (3-neck) or cow (4-neck) adapter.
- 2) Perform steps 2–4 above.
- 3) Assemble the glassware, making sure to grease all of the joints. Be sparing with the vacuum grease - it's expensive and you don't want it getting into your compound.
- 4) Perform steps 6–7 above.
- 5) DO NOT START HEATING!!!
- 6) SLOWLY open the **distillation apparatus** to vacuum. You should see the liquid begin to bubble. Don't worry, this is normal. Excess solvent or low boiling impurities will often boil away **under vacuum** at **room temperature**. (This is a good example of why you need to keep your trap full of **liquid nitrogen**, otherwise these compounds will go directly into your **pump oil!**)
- 7) Once the bubbling subsides, or slows almost to a stop, then you can start heating the flask.
- 8) Perform steps 9–15 above.
- 9) Release the vacuum. When you are done collecting, it is not quite time to cool the apparatus. First, you must release the vacuum. Before you do this, however, make sure that all of your **collection flasks** are secured to the apparatus by clamps, joint clips, your hand, etc. Once everything is secure, **vent the apparatus to nitrogen** and then remove the heating apparatus and let the set-up cool to room temperature
- 10) Once everything has cooled, record the weight of your **tared** collection flask(s) and calculate the weight of your product(s).

Glossary:

distillation apparatus – zestaw destylacyjny

under vacuum – pod próżnią

room temperature – temperatura pokojowa

liquid nitrogen – ciekły azot

pump oil – pompa olejowa

collection flasks – odbieralniki

vent the apparatus to nitrogen – przepuszczenie azotu przez aparaturę

tared – wytarowane

Przykładowe teksty z części eksperymentalnych z czasopism naukowych:

Zobi et al. *Inorganic Chemistry* (2010) DOI: [10.1021/ic100458j](https://doi.org/10.1021/ic100458j)

Synthesis of $[\text{ReBr}_2(\text{CO})_2(\text{MeIm})_2]$ (**3**). 100mg of **2** (0.122 mmol) was suspended in 15mL of DME, and 32 mg of N-methylimidazole (MeIm, 3 equiv) was added. The mixture was heated to 60 °C for 3.5 h and stopped when the red suspension had become a yellow solution and a yellow precipitate had formed. The mixture was filtered while still hot. A bright-yellow solid of **3** was collected, dried in vacuo, and recrystallized from a CH_2Cl_2 /hexane mixture giving dark-red crystals. Yield: 49 mg, 71%. Anal. calcd for $\text{C}_{10}\text{H}_{12}\text{Br}_2 - \text{N}_4\text{O}_2\text{Re}$ (566.2): C, 21.21; H, 2.14; N, 9.89%. Found: C, 21.89; H, 2.32; N, 9.64%. IR (solid state, KBr, cm^{-1}): $\nu_{\text{C=O}}$ 1982, 1825. Single crystals suitable for X-ray diffraction were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the compound.

Synthesis of $[\text{ReBr}_2(\text{CO})_2(\text{BzIm})_2]$ (**4**). 100mg of **2** (0.122 mmol) was suspended in 15 mL of DME, and 46 mg of benzimidazole (BzIm, 3 equiv) was added. The mixture was heated to 60 °C for 3.5 h and stopped when the red suspension had become a yellow solution and a yellow precipitate had formed. The mixture was filtered while still hot. A bright-yellow solid of **4**

was collected and dried in vacuo. The crude product was purified by loading a CH₃OH solution of 4 onto a chromatofix C18 filter. This was washed with a 15% CH₃OH solution in water and then extracted with CH₃OH.

Yield: 39 mg, 50%. Anal. calcd for C₁₆H₁₂Br₂N₄O₂Re (638.3): C, 30.11; H, 1.89; N, 8.78%. Found: C, 29.99; H, 1.82; N, 8.47%. IR (solid state, KBr, cm⁻¹): νC=O 1992, 1833. Single crystals suitable for X-ray diffraction were grown by slow diffusion of hexane into a CH₂Cl₂ solution of the compound giving dark-red crystals.

Vougioukalakis et al. *Journal of Organic Chemistry* 2010, 75, 4124–4130

Experimental Section

Synthesis of Aza[60]fullerene (C₅₉N)₂ (1). **a.** 2-Methoxyethoxymethylazide (MEM-N₃). A mixture of NaN₃ (2.08 g, 32 mmol), MEM-Cl (1.82 mL, 16 mmol), and dry CH₃CN (50 mL) was placed in a dry, two-necked round-bottomed 150 mL flask, which was then heated to reflux under an Ar atmosphere for 3 h. The reaction mixture was subsequently cooled to room temperature and 50 mL of diethyl ether was added. This solution was transferred to a separating funnel and was extracted with saturated NaCl solution. The organic layer was dried over anhydrous MgSO₄ and then the solvent was removed with a rotary evaporator to give 1.66 g (79%) of MEM-N₃, as pale yellow oil. This product was subsequently used without further purification. ¹H NMR (500 MHz, CDCl₃) δ 4.70 (s, 2H), 3.76 (m, 2H), 3.58 (m, 2H), 3.39 (s, 3H).

b. [5,6]-N-MEM-azafulleroid. A solution of C₆₀ (1.44 g, 2 mmol) in ODCB (100 mL) was added in a dry, two-necked round-bottomed 250 mL flask, which was placed in an ultrasound bath for 15 min. To remove oxygen traces from the solvent, the solution was degassed through five vacuum-Ar cycles. Next, MEM-N₃ (0.656 g, 5 mmol) was added to the flask and the mixture was heated to reflux under an Ar atmosphere for 4 h. After cooling at ambient temperature, the product was purified by column chromatography, using silica gel and toluene. Separation of [5,6]-MEM-azafulleroid from [6,6]-MEMaziridinofullerene 23 was completely achieved in most of the cases. [5,6]-MEM-azafulleroid comes out from the column first and [6,6]-MEM-aziridinofullerene elutes second. After evaporation of the solvent with a rotary evaporator, the solid was washed several times with Et₂O and dried under vacuum for 12 h. [5,6]-N-MEM-azafulleroid (0.295 g, 18%) was isolated as a black powder. ¹H NMR (500 MHz, CDCl₃/CS₂) δ 5.36 (s, 2H), 4.25 (m, 2H), 3.79 (m, 2H), 3.50 (s, 3H).

c. N-MEM-ketolactam. [5,6]-N-MEM-azafulleroid (0.206 g, 0.25 mmol) was added in a round-bottomed 500 mL flask and dissolved, using a magnetic stirring rod, in ODCB (400 mL). After a homogeneous solution was obtained, toluene (100 mL) was added and the resulting solution was placed in an ultrasound bath for 15 min. Next, O₂ was passed through the mixture and the solution was irradiated with a Xe 300W lamp as the light source. A water cooling system, in order to maintain the reaction temperature close to room temperature, and a K₂Cr₂O₇ 1% (w/w) aqueous solution as a filter was placed between the lamp and the flask. Reaction progress was monitored by HPLC analysis and it was typically completed in 20 h. The desired product was purified by column chromatography, using silica gel and toluene/EtOAc 9:1. After evaporation of the solvent, using a rotary evaporator, the solid was washed several times with Et₂O and dried under vacuum for 12 h. N-MEM-ketolactam (0.150 g, 70%) was isolated as a black powder. ¹H NMR (500 MHz, CDCl₃/CS₂) δ 6.38 (d, J=10 Hz, 1H), 6.00 (d, J=10 Hz, 1H), 4.03 (m, 2H), 3.60 (m, 2H), 3.36 (s, 3H).