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# Explanation to the instruction „Extractions of Flasks at the Graphitisation-Line"

The line is called "Graphitisation line" because it was for seen for the step Irvine method in which the $CO_2$ is transferred in special ampules to become graphitized.

The principle of the line is simple: a vessel with the sample is mounted on the right side, the $CO_2$ of the sample passes on its way to the riglets (reaction containers) a water trap and it is first stored in a second trap (WF2). In this stage the other gases of the sample (mainly air) is pumped away. Then the $CO_2$ is released from the trap WF2 and transferred to the cold trap KF, where it is measured and finally it is transferred into the riglets, mounted on the left side. The transfer of the $CO_2$ is reached by cooling the destination volume with liquid nitrogen ($LN_2$). But

der Teufel steckt im Detail / the devil is in the details/ el diablo está en los detalles / 细节决定成败

Therefore here are explanations to the details. In the following the step numbers refer to page 3 and 4 of the instruction.

**Remark to the temperatures**

The temperatures to freeze out $H_2O$ and $CO_2$ are not the respective freezing temperatures of 0°C and -78°C (in case of $CO_2$ sublimation). Freezing temperatures define when a substance freeze at 1 bar pressure. The relevant parameter is the vapor pressure as function of the temperatures, (if the processes are not too fast.)

Look at the trap WF1: Due to the dry ice it is cooled down to -78°C. At this temperature the vapor pressures for $H_2O$ and $CO_2$ are $10^{-3}$ and 1 mbar, respectively. So both substances are freezing on the surfaces. But as soon as the partial pressures are lower than the vapor pressures the respective substance went back in the gas phase. And the gas mixture leaving the trap WF1 transport both gases according to respective vapor pressures.

The second trap WF2 has the temperature of $LN_2$, i.e. -196°C. At this temperature the vapor pressures of $CO_2$, $N_2$, and $O_2$ are $< 10^{-2}$, 1000, and 100 mbar, respectively. So only very little $CO_2$ is leaving this trap, but the partial pressures of $O_2$ should be watched.

**Capillary**

The capillary in front of valve V11 reduces the flow and therefore pressures inside the traps. This avoids the danger of $O_2$ condensing. Furthermore the freezing of $H_2O$ and $CO_2$ is supported by lower pressures (larger mean free path, lower gas flux). While the flow reduction is wanted at the high pressures in the full flask, it is slowing down the extraction of the nearly empty flask. In case of a septum/needle set-up a double reduction should be avoided by using larger and shorter needles. Long extraction can be reduced by increasing the threshold at which the extraction is stopped. If the initial pressure is 1000 mbar and if it is stopped at 50 mbar the loss is only 5 % and much less water is introduced into the line. If a long, thin needle is used, one can keep the threshold of 20 mbar.

**Step 2:** To act in the expected way the glass balls in the traps have to have to respective temperatures. But first the heat conductivity of glass is not very high. Second the heat has to be transferred over several boundaries of the different bodies. And the gas inside the trap does not help much as the pressure is very low. Therefore 100 – 200 mbar N2 should be introduced into the traps.

In the step 2 d it is recommended to open the riglet for a short time. The reason is that sometimes in step 14 a high pressure in the line was observed. This step is to exclude that this gas came out of the riglet. (In case of strange effects also strange explanations have to be considered/excluded.)

**Step 4:** This measure is only for seen if the user is not sure about the pressure in the flask.

**Step 5:** The gas inside the flask is driven by its own pressure through the line, so it is not really pumped. As long as gas flows, there are different pressures along the line.

**Step 6:** See the comments to capillary

**Step 7:** A value of sensor 1 close to the offset value means that the line up to this position is nearly pumped off. Then the water trap is closed as the frozen water evaporate again until the vapor pressure is reached. Sensor 2 reach its background value nearly at the same time. After this all the $CO_2$ should be closed up in the volume Vol(13-16) including the traps KF and WF2

**Step 8:** if the trap WF1 cool is kept cool one can't be sure that first it stays cool enough and second that the capacity for storing water is large enough for several samples. The 10-minutes waiting time are needed anyhow for the trap WF2. Therefore it is for seen to let it warm up and pump part of the water away (during step 17).

**Step 10:** the real measuring of the $CO_2$ happen in step 11. In step 10 is only a first looking whether the amount of $CO_2$ is much too much and if this is the case, too avoid many reduction steps as in step 12. The blue recommendation to write down the pressure value would help to identify a problem (as the following similar proposals.)

**Step 11:** This is a first purification step. If there is a fraction of the gas not condensing, it is no $CO_2$.

**Step 12:** The value of 260 mbar is still larger than the wanted value. But as there could be a fraction of water and/or oxygen, a puffer is needed.

**Step 13:** The pressure decrease even with pure $CO_2$, as can be seen from the gas equation. But if the gas contain water, it freezes and reduce the pressure much more. The given time of 3 minutes is only, because the pressure never stay constant, it always varies a little bit.

Step 14: On older versions was the amount of $CO_2$ after step 13 reduced to the desired values and transferred into the riglet. But very often problems occurred during the transfer. Therefore step 14 was introduced, again without reducing the amount of $CO_2$ to have a puffer.

**Step 15:** Assuming we have after step 13 no water in the gas anymore. But it could be still some oxygen in the sample, frozen as the pressure was high enough and covered by frozen $CO_2$, so that it stayed frozen in step 11. Step 15 is a trial and I'm not sure how good one can stop the transfer. The alternative is also no easy solution. If it went completely wrong one could freeze back the CO2 into the KF trap and transfer it again.