Extraction of Flasks at the Graphitisation-Line

27.05.24

“Flask” stands for all kind of vessels like flasks, gas bottles or intermediate containers.
The amount of carbon in the text is that of a "normal" sample, i.e. 0.6 mg C, corresponding to a pressure of 165 to 210 mbar in the KF cold trap. For small samples the pressure values have to be divided by 2.4.

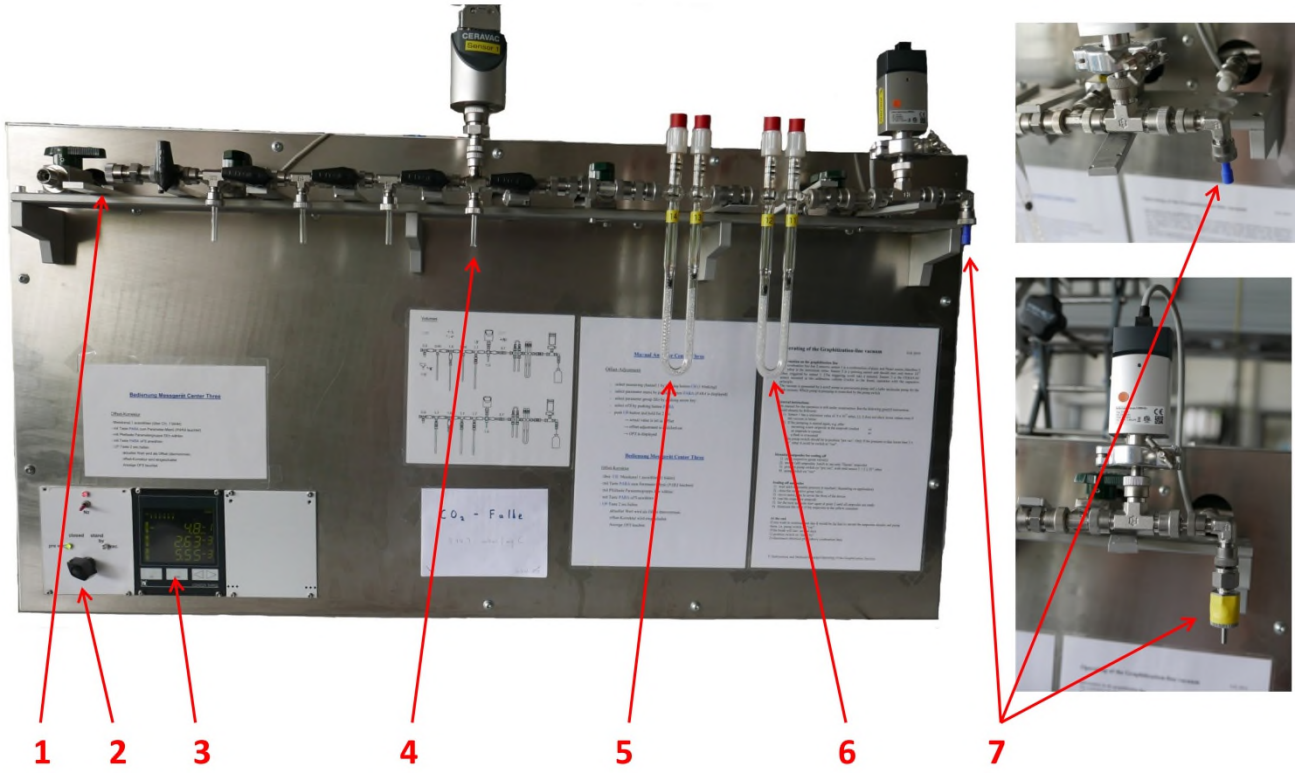

Fig. 1 Photo of the line: 1. port for the riglets (reaction container), 2. switch for vacuum pump, 3. pressure display for all 3 sensors, 4. cold trap KF, 5. trap WF2 (used as CO_2 trap), 6. water trap WF1, 7. port for the flask. The upper magnification of point 7 shows the flask port with plug, the lower with the Luer adapter.

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).

What makes the operation difficult is that glass balls in the traps WF1 and WF2 have to be cold during the operation. The main cooling mechanism is heat conductivity by a gas, and is therefore weak is the line is pumped. For this before every sample the two traps have to be filled with N2, the dewars have to be placed around the traps and then one has to wait 10 minutes. These steps are included in following procedure.

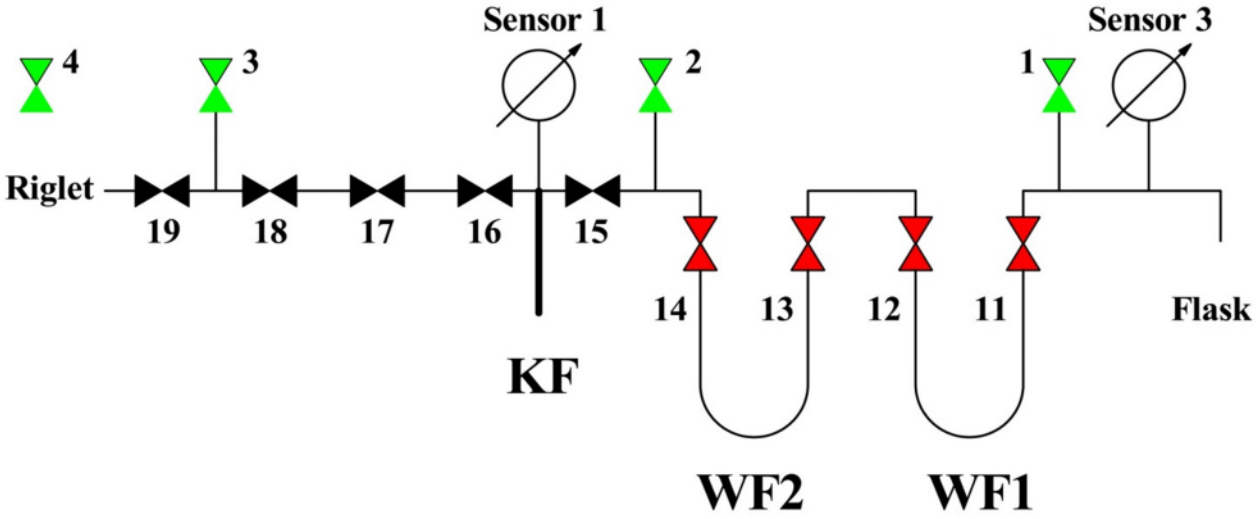

Fig. 2 Valve diagram with the valves the colors of the handles.

Valves are marked in fig. 2 by numbers *n*, in the text as V*n*.
The volumes are identified by "Vol(*n*-*m*)" with the valve numbers *n* (left) and *m* (right). Special volumes are: the water trap WF1 is Vol(11-12), the water trap WF2 (used as CO_2 trap) is Vol(13-14) and the CO_2 trap (KF) is Vol(15-16).

Sleep: plug in flash port, all valves open except V4 and V19
(V4 is always closed)
Remarks: V19 closed if no riglet is mounted,
Switch (bottom left) should be set to "prevac" and sensor 2 should be < 3 10-3 mbar
At the end of "pump out" this value should be reached by sensor 2.
(slightly higher for water in the system)
During operation, the water trap WF1 is cooled with a refrigeration mixture (isopropanol and dry ice) and the traps WF2 and KF are cooled with liquid nitrogen.

Preparation:
1) check if pressure sensor 2 < 3 * 10-3 mbar
2) 4 dewars are needed, the numbers are not written on them

No.	quantity	diameter opening	description
1	1	160	blue foam
2&3	2	70	glass dewar with a blue net
4	1	40	glass dewar, outside blue

Inside the dewar #1-#3 a refrigerant mixture of dry ice and isopropanol has to be prepared.
Dewar #4 will be filled with LN_2, for its filling use another 5^{th} dewar.
3) in dewar #1 are always the next *n* flasks, *n* depends on the size of the flasks
4) in dewar #2 is the flask which is actually extracted
5) dewar #3 is to cool the water trap WF1
6) dewar #4 is for the traps WF2, KF, and the riglet (only placed there when needed)

Extraction of flasks

0) for the start it is assumed that the whole line is pumped, i.e. with all valves open except V19. In this stage sensor 2 should be < 4 ·10^{-3} mbar.
1) Control the temperature of the dewars of the refrigerant mixture. It should have a temperature around -77°C with dry ice crystals in the solution.
2) Close the vacuum pump and fill in 100 – 300 mbar N_2, read on sensor 1. Put the respective dewars under the traps WF1 and WF2 and stop the time. The time to wait is 10 minutes. During the waiting time
   a) close valves 11 and 14, open the pump and pump the volume with V1 - V3 open
   b) Also the next flask can be connected, but with the extra valve in front of the flask closed. And the respective dewar can be lifted to cool the mounted flask (or the flask can be connected being already in the dewar.)
   c) A new riglet should be mounted and V19 be opened to pump the volume in front of the riglet valve (but the riglet valve should be kept closed until step 14)
3) After the waiting time of 10 min set the valves as in Fig. 3, i.e. pump the whole line trough V3

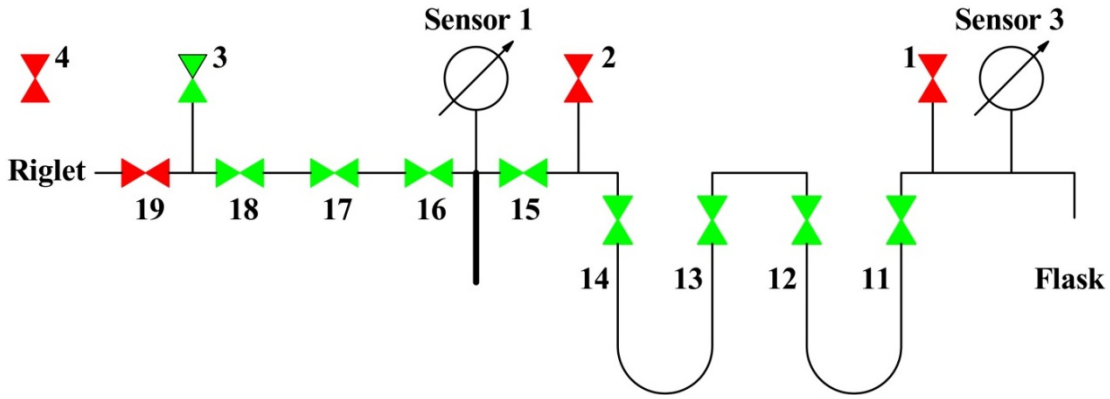

Fig. 3 Opening states of the valves in step 3, green = open, red = closed

4) Start pumping the flasks by opening its valve (not shown in the figures)
5) The pumping of the flask should be stopped if the sensor 3 shows 20 mbar, then close the valve in front of the flasks.
6) When sensor 1 is close to the offset value close valve 12. Pump until sensor 2 < 4 ·10^{-3} mbar, then close valve 16 and 13 (status of valves as given in Fig. 4)

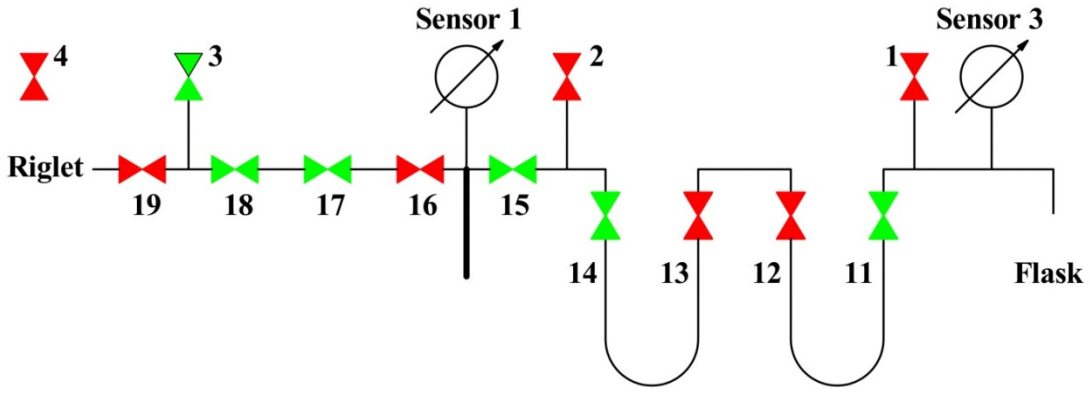

Fig. 4 Opening state of the valves in step 6, i.e. the first measurement of the CO_2, green = open, red = closed

7) lower the dewar of the trap WF1 (so that the liquid drops back into it)
8) lower the dewar of the trap WF2
9) defrosting the trap WF2 with the hot air pistol until the pressure in sensor 1 rise.
10) measuring the CO_2 quantity at sensor 1, i.e. in Vol(13-16)
    - if the pressure is > 260 mbar ➔ close valve 15 and go to step 11
    - if the pressure is > 95 mbar ➔ close valve 14 and go to step 11

    (a pressure betwen 35 - 45 mbar is expected for a normal sample, the half for a small sample)
11) Freeze the CO_2 in the trap KF by placing it in the dewar with LN_2
    Wait until the pressure at sensor 1 is stable (hopefully close to the offset) then open valve 16 to pump the remain away (for a few seconds), close 16 and V15 (if open) and defrost the trap.
12) If the value is higher than 260 mbar (or 130 mbar for a small sample) pump off CO_2 by
    a) close V17
    b) open V16 (for a second) and close it again
    c) open V17

    This way the amount of CO_2 is reduced by 22 % in each step. This has to be repeated until the pressure is within the limit, i.e. smaller than 260 / 130 mbar.
    If V18 instead of V17 is used, each step reduces the CO_2 by 35 %.
13) If the pressure is below/equal 260 mbar, it should be checked whether the gas contain no water. Therefore the CO_2- trap is placed in a dewar with refrigerant solution. If the pressure drops no more than 5 %, it is ok. In this case the pressure should be adjusted to 165 - 210 mbar (normal sample) or 68 – 85 mbar (small sample) (as exception > 50 mbar is accepted.)
    If the pressure drops more than the 5 %, i.e. if there is water in the sample, the sample should be purified during the transfer into the riglet (next step) due to stopping the transfer after 25-30 s. (Therefore the pressure should not be adjusted before the transfer.)
14) open V19 and the riglet valve (the pressure Ch2 should stay constant) and **close V3 !!!**. Transfer the CO_2 by freezing it into the riglet by opening V16. It should not take longer than 30 s. After 1 minute it should be stopped because there is too much water in the residual gas.
15) if the CO_2 is transferred into the riglet, seen on the pressure 1, close V19 and the (green) handle of the riglet and put it back into the stand. Then the dewar with refrigerant solution around the CO_2-trap can be taken away.
16) The line should be pumped with all valves open (except V19)
17) Then one can extract the next flask starting with step 0.

Together with the P number and pressure in the KF (step 15) must be noted on the sample form coming with the riglets. If the transfer into the riglet was stopped the residual pressure should be noted also.

At the end of the day or extraction, the apparatus should be pumped at least overnight. Close the flask port and set it to sleep mode (page 1).

Before returning the flasks to the ^{14}C analysis, hydrogen must now be added to the UGCS (see section “postprocessing at the UGCS”)

Other samples than incubation samples

The description up to now is mainly for incubation samples. These are characterized by (i) large fraction of air in the samples, and (ii) large humidity.

The large humidity requires the cooling of the vessel plus the water trap. Depending on the samples both measures or only one can be left away.

The large amount of air requires the use of the volume Vol(13-14) as first CO_2 trap. If e.g. ampoules with pure CO2 have to be refilled, then this can be done directly into the KF, Vol(15-16). For this

- the ampoule has to be mounted in an ampoule cracker,
- the whole system has to be pumped off,
- all valves V1, V2, V3 and V16 have to be closed,
- the ampoule be broken
- the KF has to be put in LN2 (equivalent to step 13)
- further treatment like the incubation samples.

The different possibilities to reduce the C amount (if necessary) are analog.

Postprocessing at the UGCS

Hydrogen is added to the samples at the end with the line called UGCS. The UGCS pump should be started 1 hour before use. The amount of H_2 is twice the pressure than the one of CO_2 in the trap of the other line. The pressure of H_2 at this line has to be measured with Ch. 2.

The UGCS (pump and the port valves) is controlled via the switch board. Since the cold trap is not required for the following applications, it should be disconnected, i.e. V24 and V34 should remain/be closed. In case the H_2 is pumped, that pressure sometimes don't decrease further, then open the O_2 valve for 5 s. (The final pressure should be below 10^{-1} mbar)

The steps for adding the hydrogen are
- mount the riglets on the ports (see below), the distances between the dewars don't matter, but with two neighboring ports the handling is more difficult.
- pump the manifold and the volumes between port and riglet valves (hand valves)
- riglets with the same required amount of H_2 can be filled parallel
- dip the riglets into LN_2, wait a moment, then to open the hand valves.
- the samples are filled hydrogen with 2-times the KF-trap pressure (-5 up to + 20 %). If much too much H2 was filled, it can be pumped away as long as riglets are inside the LN_2.
- close the riglet valves and the port valves of the filled riglets,
- remove the filled riglets

Fig. 5 Recommended arrangement of the dewars.