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Extraction of Flasks at the Graphitisation-Line

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"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.

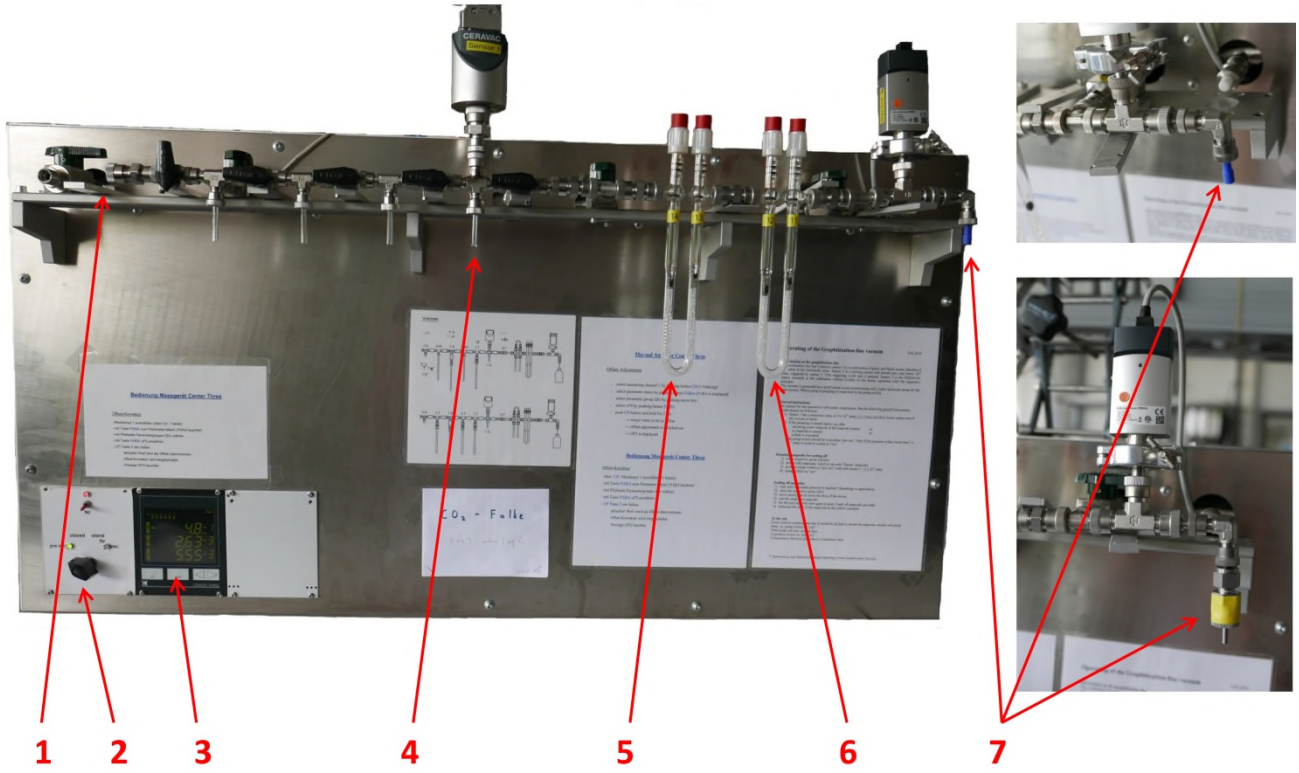

Fig. 1 Photo of the line: 1. port for the riglets (reaction container), 2. switch for vacuum pump, 3. pressure display for all 3 sensors, 4. cold trap KF, 5. trap WF2 (used as CO_2 trap), 6. water trap WF1, 7. port for the flask. The upper magnification of point 7 shows the flask port with plug, the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

Remark: The ultra-torr connector are based on a O-ring sealing. These should not become colder than -15°C. So always keep a distance to the cooling liquids of at least 10 mm.

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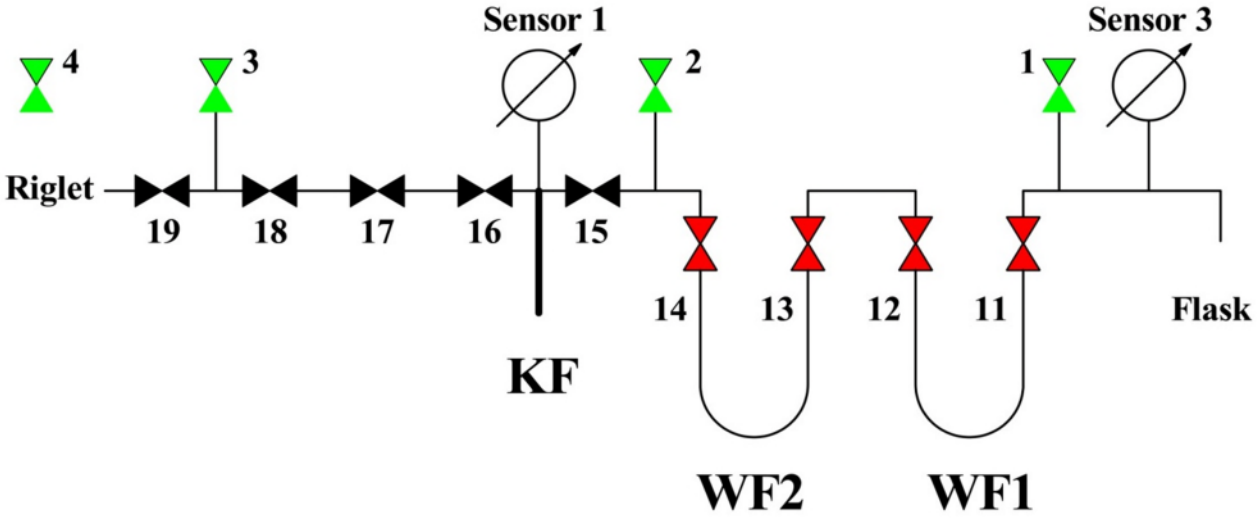

Fig. 2 Valve diagram with the valves the colors of the handles. This figure is mounted also at the line.

Valves are marked in fig. 2 by numbers *n*, in the text as V*n*.
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).

Measures written in blue are recommended and not necessary.

Preparation:

1) check if the line is switched on (plug into socket). The vacuum pump is operated with the switch No. 2 in Fig. 1, it is open in the position “prevac”
   2) as minimum 2 dewars are needed:
   a) one for LN_2 used for the traps WF2, KF and the riglet. For this the opening of 40 mm is sufficient.
   b) As second one, used for trap WF1, filled with refrigerant mixture of dry ice and isopropanol. This dewar should be one with a larger opening (70mm).
   (“Dry Ice” is used always in a refrigerant mixture in the instruction.)
   c) But with samples containing water, e.g. from incubation set-ups, the vessels of the sample (jars, flasks, or bottles) should be additionally cooled with dry ice. It is recommended to work with two dewars for the vessel-cooling: one with the sample actually extracted and the other with the next sample as precooling. The respective dewar have to fit to the vessel size, in most cases the foam dewars are appropriate.
d) It is worth to write down all three the pressures, they are the offset / background values. If the pump was started on the previous day, sensor 2 should be around $4 \cdot 10^{-3}$ mbar. Even if this was forgotten, one can work with the line, but the background value is higher. The offset value of sensor 1 is not constant, but should be below 1 mbar.

Extraction of flasks

0) for the start the whole line has to be pumped, i.e. with all valves open except V19.
1) Control the temperature of the dewars of the refrigerant mixture. It should have a temperature around -77°C. This is guaranteed if there are dry ice crystals in the solution.
2) Close the vacuum pump and fill in 100 – 200 mbar N_2, read on sensor 1. Put the respective dewars under the traps WF1 and WF2 and stop the time. The waiting time is 10 minutes. During the waiting time
   a) close valves V11, V13 and V14, open the pump and pump the volume with V1 - V3 open
   b) Also the next flask should be connected, but with the extra valve in front of the flask closed. If the flask was not connected being already in the dewar, the respective dewar can be lifted to cool the mounted flask.
   c) A new riglet should be mounted and V19 be opened to pump the volume in front of the riglet the valve.
   d) If the sensor 2 has reached its offset value, the riglet valve can be opened, it can be controlled that sensor 2 is constant and the riglet can be closed again.
3) After the 10 min start the pump (switch "prevacuum") and set the valves as in Fig. 3, i.e. close V1, V2 and V19 and open V11, V13, and V14. Thereby the whole line is pumped with V3

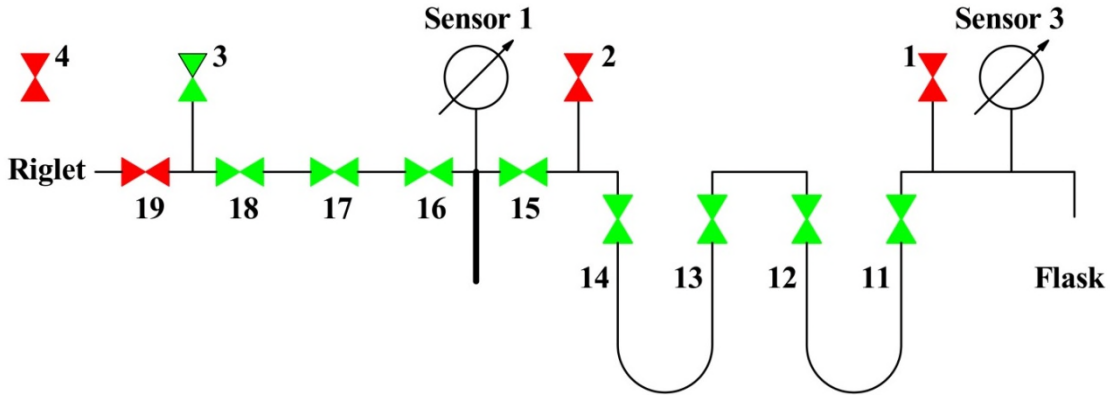

Fig. 3 Opening states of the valves in step 3, green = open, red = closed

4) If the filling pressure of the sample vessel is wanted by the user, close V11, open the flask valve (not shown in the figures), read sensor 1 and open V11 again.
5) Start pumping the flasks by opening its valve. This starts the extraction of the flasks.
6) If the sensor 3 shows 50 mbar, then close the valve in front of the flasks.
7) When sensor 1 is close to the offset value, close valve 12. Continue until sensor 2 is at its offset value, then close valve V16 and V13 (status of valves as given in Fig. 4)

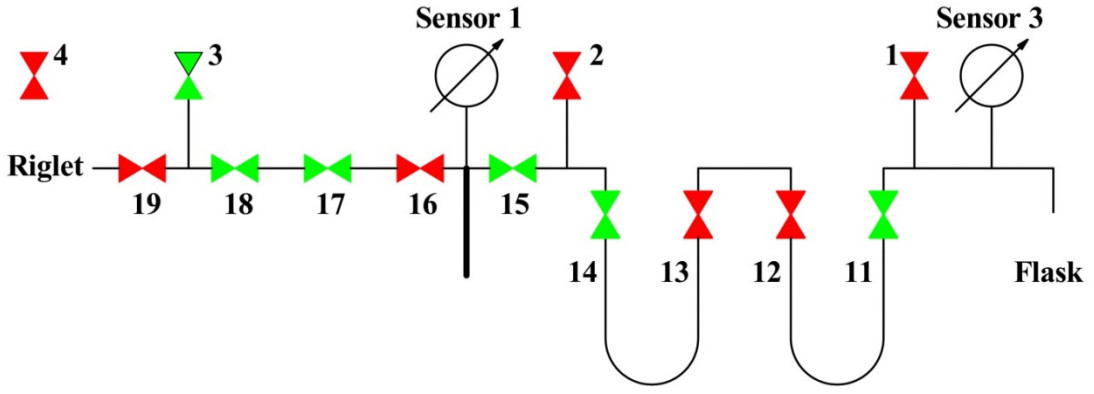

Fig. 4 Opening state of the valves in step 6, i.e. the first measurement of the CO_2, green = open, red = closed

8) lower the dewar of the trap WF1 (and let the liquid drop back into it)
9) take away the dewar of the trap WF2 and defrost the trap WF2 with the hot air pistol until the pressure in sensor 1 rise (can take several minutes).
10) measuring the CO_2 quantity at sensor 1 with Vol(13-16), if the pressure is > 260 mbar then close V15. (Between 35 - 45 mbar are expected for a normal sample, the half for a small sample.)
Write down the value of sensor 1.
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.
Write down the value of sensor 1.
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 %.
Write down the value of sensor 1.
13) If the pressure is below/equal 260 mbar, it should be checked whether the gas contain no water. Therefore the trap KF with the CO_2 is placed in the dewar from WF1 with the dry ice.
Write down the value of sensor 1 after 3 minutes.
14) open V19 and the riglet valve (sensor 2 should stay constant) and **close V3 !!!**. Only then open V16. The pressure should be lower than the one of step 13 by a factor 3.74. If it is significantly more go back to step 11. (In this case, one has to open V3 if sensor 1 is stable.)
15) Transfer the CO_2 into the riglet by putting the tube of the riglet in the LN_2-Dewar and start a clock. Stop the transfer by closing V19 either after a pressure reduction of 45 – 56 mbar (or the 15 – 24 mbar for small samples) or after 30 – 40 s. If the pressure is higher (than 100 mbar) it can take longer to transfer the CO_2. In this case one should start with low LN2 level, so that one can increase this during the transfer and one should close V19 as soon as the decrease of the pressure becomes slowly, even if it becomes only a small sample.
Write down the pressure difference in the riglet form.
16) close the (green) handle of the riglet valve and put it back into the stand. Now the dewar with refrigerant solution around the CO_2-trap KF can be taken away.
17) The line should be pumped with all valves open (except V19)
18) Then one can extract the next flask starting with step 0.

In the form with the riglets number has to be written the value of the pressure drop in step 15 and, if large than the offset value, the values in step 15. But also the P number should not be forgotten.

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 riglets 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 2 * 3.74 = 7.5 the pressure than the one of CO_2 in step 15. 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 7.5-times the CO_2 pressure of step 15(-5 up to + 20 %). If 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, pump of the hydrogen and continue with the next riglets

Fig. 5 Recommended arrangement of the dewars.