

Using the In-situ XPS

A not short anymore guide to using the In-situ XPS

In case of emergency notify the on-call duty under 8413-4423 and/or the Bessy-support (number listed on the beam status screen)

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Introduction

A. Beam Line

For being able to use the synchrotron light source at all, you'll have to open all valves between the storage ring and the experiment (**Fig. 1**). The control panel is inside the hutch next to the big window. It's the one with the lot of switches and green and red lights. All in all there are 11 valves including to the beam shutter which have to be opened/closed one after the other (marked "beamshutter" and valve 3 to 13).



Figure 1: beam valve control panel with "roline" control box (to switch between XPS and NEXAFS); in the upper right corner you see the pressure reading of the beamline part just behind valve 13 on the beamline side.

Only valve 13 just in front of the reaction cell can be opened separately. If the X-Ray window between reaction cell and valve 13 is leaking in the 10^{-8} mbar range or if the reaction cell

pressure is higher than 20 mbars (if you want to go higher than 2mbars please ask in advance!!!), valve 13 won't open or is automatically closed. To open the others always start to switch valve 12 and wait until the "status" light as well as the "Freigabe" light of valve 11 turn green. Do the same for valve 10 and so forth up to the beam shutter. The switch for the shutter has to be hold a short time until the "Freigabe" light is blinking. Finally, you can open valve 13 connected to the reaction cell.

For closing the valves proceed exactly in reversed order. During operation it is always useful just to close valve 13, e.g. when changing samples. Thereby the beam keeps the mirror warm.

Figure 2 gives you an overview of all computers you'll need to control and perform experiments. Mainly there is a computer to control each of the experiments, i.e. XPS, NEXAFS and MS. The latter also controls the MFCs. Details about what they do and how to use them you'll find in the following.

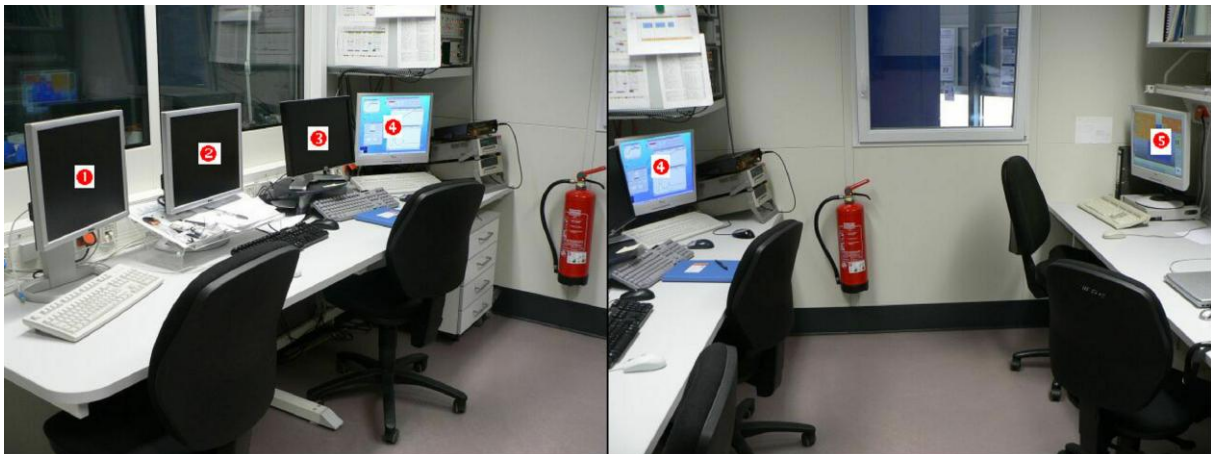
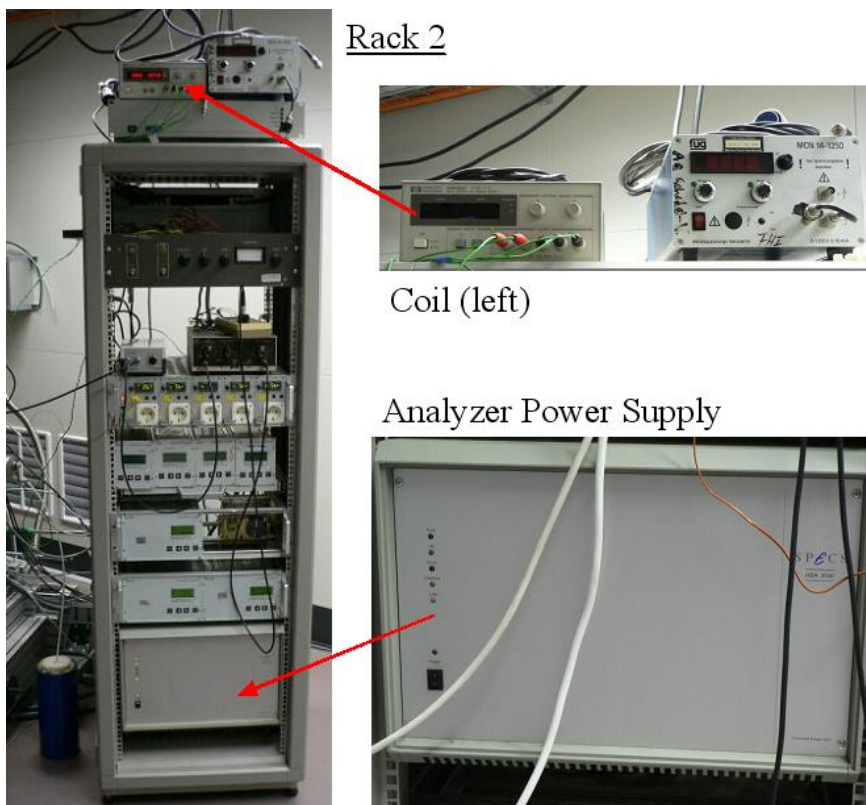
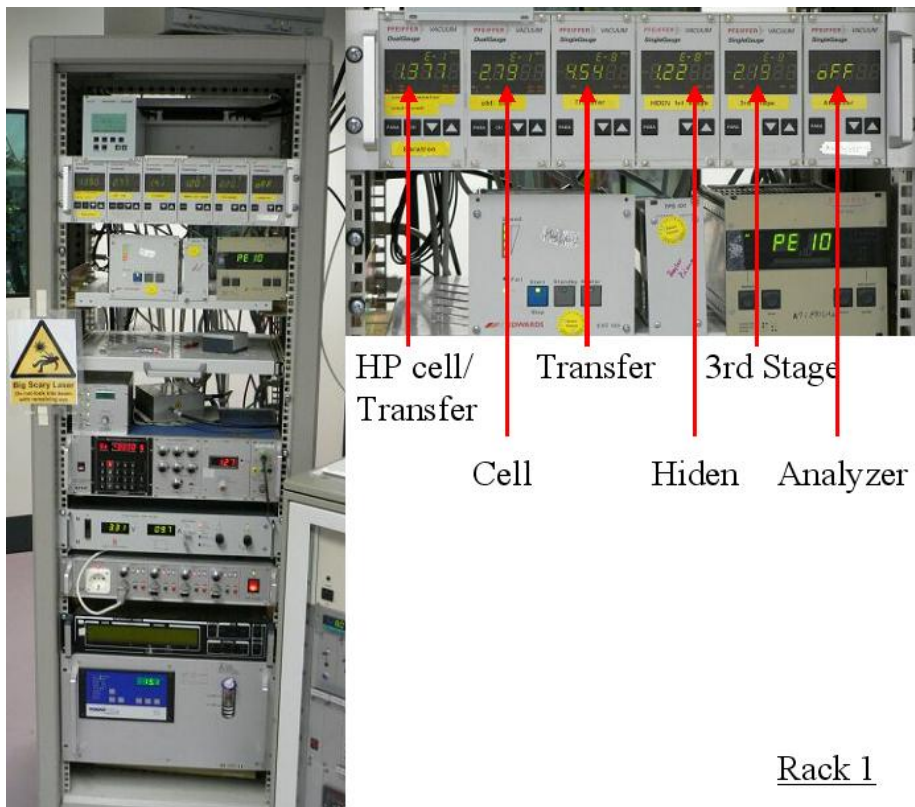


Figure 2: Lab computers; ❶ Mass spec and MFCs, ❷ work station, ❸ XPS control, ❹ NEXAFS control, ❺ Beam line control and Lab Status.



Figures 3a and b: Rack 1 (top) with controls of laser heating, laser cooling device, pressure readings and electronics for controllable valve. Rack 2 (bottom) with Coil- and Analyzer Power Supply.

B. Preparing for XPS experiments

For using the XPS you need computer 3 (**Fig. 2**). There you'll find the SPECS2 icon on the desk top. Open the program by double clicking. Then proceed as follows:

1. Check the pressure in the analyzer (**see Fig. 3a**; pressure readings in Rack 1; far right), then switch off the pressure its pressure gauge.
2. Switch on analyzer power supply (**Fig. 3b**; rack 2, bottom, front panel) and wait until self test is finished (green light is blinking).
3. Switch on power supply for coils (on top of rack 2); make sure coil is attached to window (the blue extra window on top of the UHV window of the reaction cell with the green cable around it (**Fig. 6**, lower right). This window not only serves as a compensation for stray fields but is the **safety window for the IR-Laser!!!**
4. Goto analyzer/settings in the SPECSLab program.
5. Set the topmost "server" button in the analyzer part to "Phoibos Hsa 3500" (top); if you see "XPS" and "AMC-Monochromator" appears in "Sources" and "none" in the "remote" part of the window click the ok-button.
6. Make sure that the switch of the "roline" control box (just above the valve control panel, **Fig. 1**) is switched to "XPS".
7. Finally, the sample has to be put into the focus of the beam in front of the analyzer nozzle (**Fig. 7**, bottom). For that go into a region window set **a**) a photon energy (e.g. 1010 eV), **b**) the analyzer mode to fixed energies, **c**) the pass energy to 10 eV, **d**) a proper background energy (under energy), e.g. 150 eV and finally **e**) 1000 in "values". Now turn the screen towards the lab window so you can see it when you are standing next to the machine and move the sample via the manipulator back and forth until you see the maximum counts.

Now you can measure with XPS. With a short intro you can easily program the desired scan regions.

C. NEXAFS

For NEXAFS experiments make sure that the "roline" control box is switched to "EMP" and the analyzer is working, if you want to measure the Auger Yield as well.

You'll need the two beamline computers in our office section (④ and ⑤, Fig. 2).

1. The following windows are needed on ④: "EMP/2" and by pressing the channel buttons "EMP-Dis/Ch[3]", "EMP-Dis/Ch[4]", "EMP-Dis/Ch[5]".
2. The following windows are needed on ⑤: "ISISS.adl" and from there by clicking the "continuous" button the "continuous" window.
3. On computer ④: Goto "measure" in the "EMP/2" window and "TCM". Set the "monochromatorControl" to "none" and choose your "PointsperScan". It may be necessary to recheck the needed points per scan after taking the first spectrum.
4. On computer ⑤: Put the cursor in the "start" field of the "continuous" window and type your start energy and confirm with "return" key. Do the same with "end" and "Vel.(ev/s)". Press the "sweepInit" button.
5. Return to ④ and goto "run", then "run" and "ok".
6. Wait a few seconds and return to ⑤. Press the "SweepRun" button.

Now the NEXAFS experiment should run. After a spectrum is taken the computer will ask for saving. Click "ok".

If you want to measure the **Auger Yield** simultaneously, you can do this via the SPECS program:

1. Prepare a region window with the same photon energy you use for the EMP (only for your orientation; this is not really necessary). Set the analysis mode to "fixed energies". Choose a start kinetic energy e.g. 50 eV below this value. Actually, you have to try this out as well as the number of data points by running the EMP and SPECS simultaneously (see below). Set the pass energy to 50 eV and the dwell time to 0.05s.
2. Goto "Analyzer" and "settings". Set "sources"/"server" to none and "Remote" to "remote input". Check if in "remote settings" the TEY and "mirror current" are activated. If not do this.
3. Now start the EMP (point 4. and 5. above), start the sweep in the SPECS and finally press "sweep run" (point 6 above).
4. When you want to return to XPS reverse point 2. for the analyzer settings and switch the roline box back to XPS.

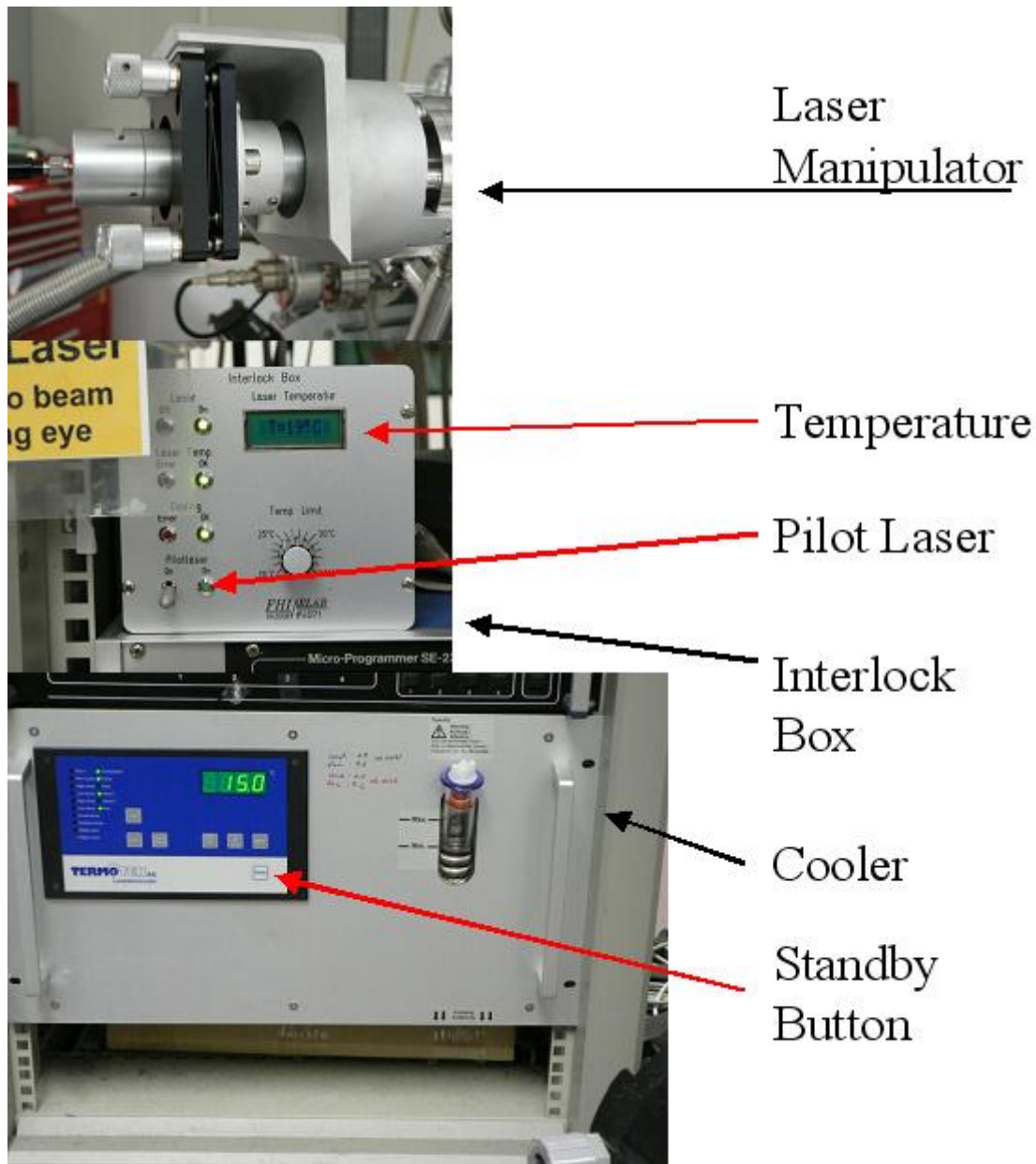


Figure 4: Power supplies for laser cooling.

D. Temperature control

1. Switch on laser cooling (**Fig. 3 and 4**; rack 1 bottom: “standby”-button; rack 1 interlock box: switch on the backside); the system will give unpleasant noises until the proper temperature is reached
2. Wait until 15°C are reached. You’ll notice that by the reading of the cooler and the fading noise. Switch on power supply (rack 1, middle; please leave the temperature control always “on”.)

3. Switch key “laser emission” of power supply to “on”

Now Heating is ready to use.

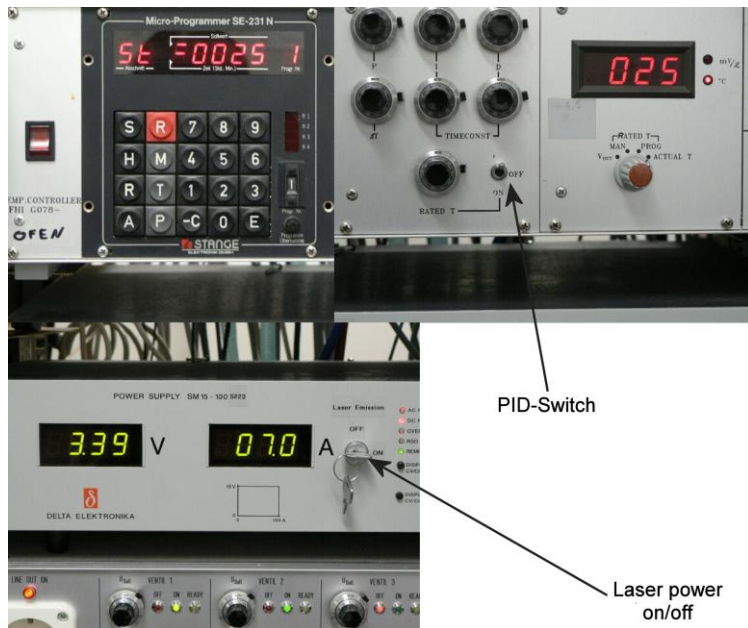


Figure 5: Temperature control.

You have two possibilities: heating a ramp or control manually (see Fig. 5)

Manually:

1. Switch of the PID-controller to “on” (lower position).
2. Use the poti to the left to increase or decrease the power. The temperature can be controlled via the TC-reading.

Ramp:

Switch of the PID-controller to “up” (where no reading visible anymore, but it’s not the “off”-position). Several routines can be programmed. If you have a special routine, please ask in advance. We can program a new one. For Ramping use program 1 (usually set) as follows:

1. For test press “T” four times. You’ll see the starting temperature.
2. For change press “-C” and type a new value. Confirm with “E”.
3. Press “T” two more times; this is the end temperature. Change again by “-C”, typing desired value and “E”.
4. Press “T” one more time. The LED shows the time for heating from start to end value. Change by “-C” and typing the value (**careful:** first two digits are in h, second two in min). Confirm with “E”. Press the red “R”.

Now you can start with pressing “S”. (For further tricks ask us.)

When the ramp is finished the temperature will be hold at the end value unless you press the red “R” again. For stops in between heating: press “H”, continue with “S”.

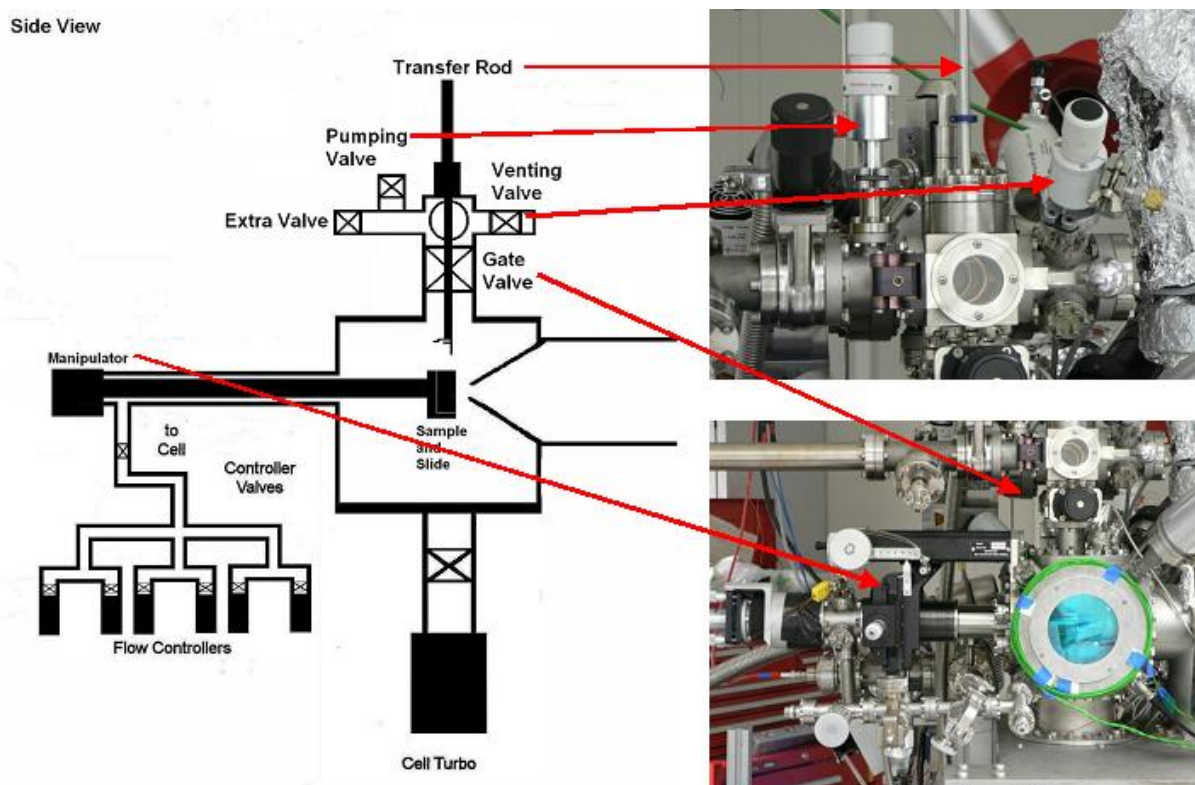


Figure 6: Sample transfer (side view).

E. Sample transfer

Take a look at the sketch first (Fig. 6)! Let’s start with a sample prepared for analysis:

Take the blue Dewar to one of the big dewars in front of the hutch and fill it up with liquid nitrogen. Place the rubber tube attached to the venting valve next to the fast entry into the dewar. Close the valve to fast entry turbo (backside of fast entry; it is marked in **Fig. 12**). Make sure that the gate valve between the reaction cell and the transfer part is closed. Open the venting valve between rubber tubes and fast entry. Check the pressure changes on the transfer as well as the HP-Transfer gauge (Fig. 3a, rack 1). The gauge reading of the latter has to be switched to **Ch. 1**! When atmospheric pressure is reached, you can open the load lock

door and close the venting valve. Do not close too tight so be aware of the two blue markings which indicate the proper position.



Insertion Tool



Sapphire with sample



Sample and Slide

Figure 7: Insertion tool (top) for the sapphire with sample (middle); bottom: sapphire in the slide of the manipulator in the reaction cell.

1. Insert the sapphire with the sample facing to away from you using the insertion tool. Fix it by inserting the two pins on the transfer rod in the holes of the sapphire and make sure that the metal spring above the pins is really holding the sapphire. Start the roughing pump (which should be attached to the pumping line). Close the door and open the pumping valve. Wait until the HP-gauge reading reaches $1\text{e-}2\text{mbars}$, then close the pumping valve and slowly open transfer turbo valve. Wait until pressure reading shows at least $1\text{e-}5\text{mbars}$.

2. Open gate valve to reaction cell. Move the transfer rod (without bending it, it's not like pulling a pint!!!) downwards until you can see it through the cell window. Now approach the manipulator slide and sample holder until backside of sample holder meets the slide. X-Y-manipulation should be in the marked positions (look at the manipulator; black felt pen marks). When the sapphire has hit home, move the slide with help of Z-manipulation until you see the spring of the transfer rod bending upwards. Now you can slowly try to move the rod upwards. If the pins still stick, move the slide further. Carefully retract the rod fork until the sapphire is released (maybe you have to turn the transfer rod a **little (!!!)** to get the pins out). Retract the transfer rod **fully (!!!)** to the transfer part and close the gate valve.
3. For measuring with XPS you have to optimize the sample position again (see XPS chapter above).

For taking out the sample do everything in reversed order except of course venting the transfer. We will show you at the beginning how to do this without losing the sample.

F. Handling pressure

Low pressures:

For pressures ranging from UHV to $\sim 10^{-3}$ mbars the cell pressure can be controlled by the cell turbo. Usually, for low pressure experiments gases are introduced by using leak valves directly attached to the reaction cell. Hence, the pressure will be controlled by the opening/closing these valves. (If you need a controlled temperature when using liquids, we have a cryostat available.) When reaching 10^{-3} mbars the valve of the cell turbo can be partly closed to reach a little higher pressures. This method is not very accurate concerning the absolute pressure and the gas flow.

High pressures:

Between 10^{-3} and 1mbar the best way to control the pressure is the use of the controllable valve in the process line (**Fig. 8, red box**).

1. **First step:** open the valve between cell and process line.
2. **Second step:** close the valve to the cell turbo.

3. **Third step:** To set the proper ratio for a gas mixture or a single gas the mass flow controllers have to be preset (see Setting the gas flow). Then you can set the desired pressure with the electronics of the controllable valve in rack 1 (top left, just above the pressure readings; see also **inset in Fig. 8**):

- Usually the reading says “flow” (top left) and “open” (second from left). Press the black “command” button; you will see the configuration menu. Press edit; an arrow indicates which item can be reconfigured, starting with “mode”. Press one of the arrow keys until the mode changes to “pressure”. The bottom reading will show the preset pressure for this mode. Confirm with “command”. The reading will change to pressure mode showing the actual and the preset pressure.
- To change the presettings press the black button just below the reading “param” (top row, far left). The reading will change to the range menu. Then press “edit”; an arrow next to the reading “nom” will show up. You can change the presetted pressure with the arrow keys. Confirm your changes with pressing the black button just below the reading “save”. You will return to the reading “pressure” which now shows the new presettings.
- For returning to flow mode just press “command”, “edit” and one arrow key until “flow” is indicated and confirm with “command”.

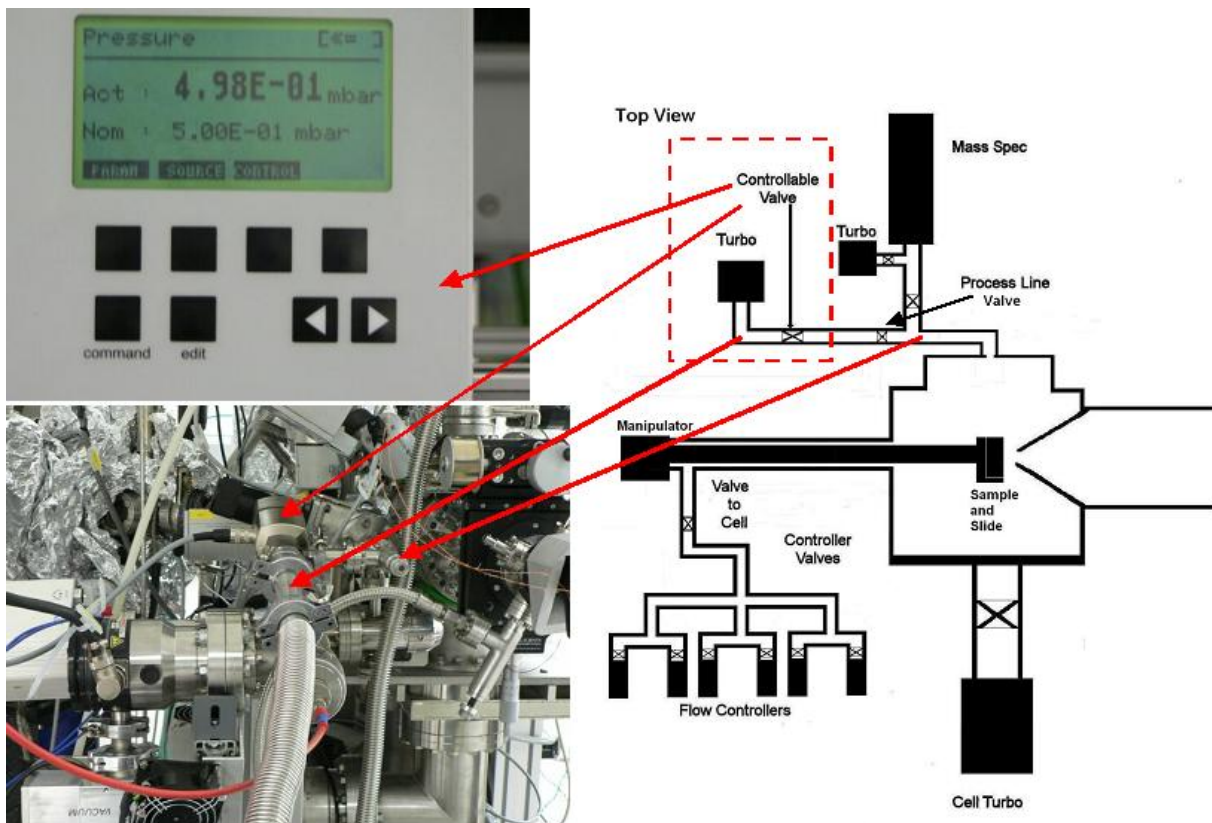


Figure 8: Process line (top view, red box)

G. Setting the gas flow

First see Fig. 9 (red box).

Together with controlling the high pressures the correct setting of gas flow is a prerequisite to most experiments. We have several mass flow controller available. You should choose the most suitable by consulting us before the experiments. We've performed calibrations for several gases and suitable controllers to ensure a proper flow.

General:

Start with taking a close look to Fig. 9. For operation first open the valves just in front of the mass flow controllers you want to use to an upward position. Then open the valve to the reaction cell **slowly** to pump the gas line clean. Wait until the cell pressure reading doesn't drop further. (This step can be skipped when done at the beginning by us.) Perform the steps described in "**handling high pressures**". Use the calibration tables for choosing the best MFC settings for your desired gas ratio. To use the MFCs do as follows:

1. The MFC software you'll find on PC 1 in a folder called "BronkhorstMFC". In it are several subfolders. Open the one called "Flowdde32". There you'll find a "Flowdde.exe" (NOT flowdde2.exe) which you'll start by doubleclicking. A window will pop open. To actually open the connection to the MFCs click on "communication" and then "open communication". A self test procedure will run until the reading "server active and ready for client". The window must be kept open!
2. Goto the "BronkhorstMFC" folder again and open "flowview". There, double click "flowview.exe". A window will pop up, which, after a time will show a reading "serial tag" (this is the respective MFC) and below that a serial number of the MFC and a reading for the different channels. The latter correspond to the different MFCs as well. Below that are two switches, one of which is movable. With that one you can set the desired percentage of gas flow. The other one shows the actual flow measured at a detector within the MFC. For more information click the button "advanced". The window will expand and show more readings. E.g. the maximum ml/s of the respective MFC are displayed under "capacity". You'll only need the "setpoint" and "

Fluid” reading. Both can be changed. The former should always be kept on “0. bus/RS232”, the latter can be set to different gases. The program has an internal calibration library based on theoretical calculations which change the “capacity reading according to the used gas. It is always better to rely on the calibrations provided by us but if none is available the theoretical values are okay to use.

3. If you’ll need more controllers click the “flowview.exe” or “new” in the first pop up window until the required number of windows is open. To reach the different MFCs you click through the “channels” switches until you find the respective MFCs.
4. To shut down everything at the end of your experiments, just close the “flowview” windows by pressing the “exit” button in each window, then goto “communication” in the “floedde” window. There click “close communication”. A message “communication forced to stop” will emerge. Now you can close “Flowdde” as well.

You can operate up to four controllers simultaneously.

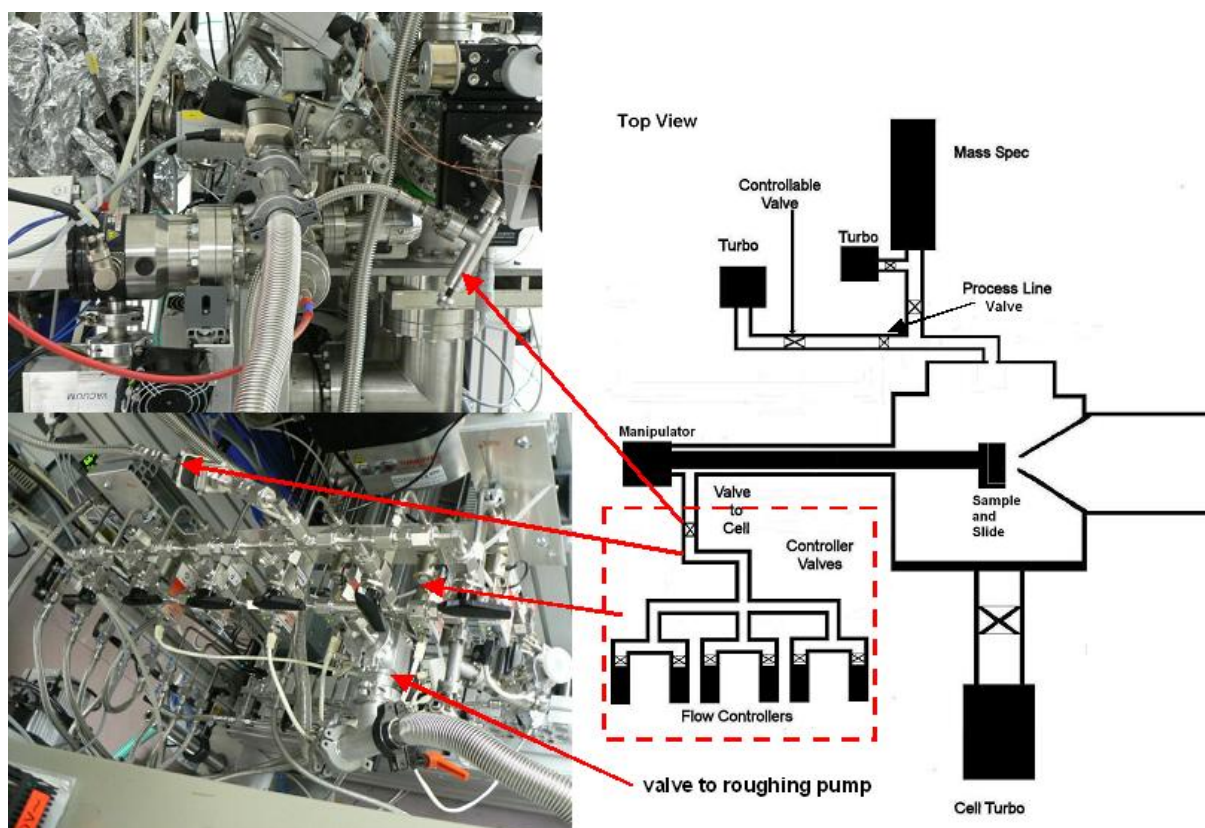


Figure 9: Flow controllers and valves (red box)

H. Setting the Mass Spec

Two different MS are available. Usually, we only use the so called Prisma which is directly connected to the reaction cell via a leak valve. The second one is a Hiden connected to the 1st pumping stage via a valve with a small aperture. Both MS are differentially pumped.

The Prisma:

For monitoring products and educts, TDS etc. a balzers mass spec is attached to the reaction cell via the process line (**Fig. 10, red box**) and controlled by Lab computer **1** (**Fig. 1**).

Detecting gases:

1. Before measuring under pressures, make sure that the leak valve is closed.
2. Proceed with the necessary steps for introducing gases into the reaction cell (see above).
3. When the desired conditions are reached open the leak valve. The pressure reading (Pfeiffer, next to the mass flow controller electronics in Rack 1) shouldn't exceed 5×10^{-7} mbars.
4. To have an undisturbed mass reading, switch of the pressure reading by pressing both buttons on the left simultaneously.

Switching on the mass spec:

1. Open the MS Program by double clicking the "Measure" icon on the MS computer's desktop (far left in the office section). A window will open.
2. Goto "setup" and "SEM/EmissionControl". Make sure that the emission and the SEM are active.
3. Goto "MID". You have several possibilities to measure. Usually "versustime" is chosen. A window will open with several parameter file prepared for different types of reactions. Click on the desired file and confirm with "open" (If you need one with new settings we can prepare one in advance.). The MS now starts to measure.

4. To save the data goto “file” and “savecycledata” and give a file name. We always use the date followed by the experiment’s number. Make sure the file is saved under the path “R:\prisma\data\”year”\”month”\”yourgroupname”.
5. For an interactive display during or after the experiment open the Display program by double clicking the DispSav” icon on the MS computer’s desktop. A window will open.
6. Goto “process” and “cycle”. Open the file you want to view.

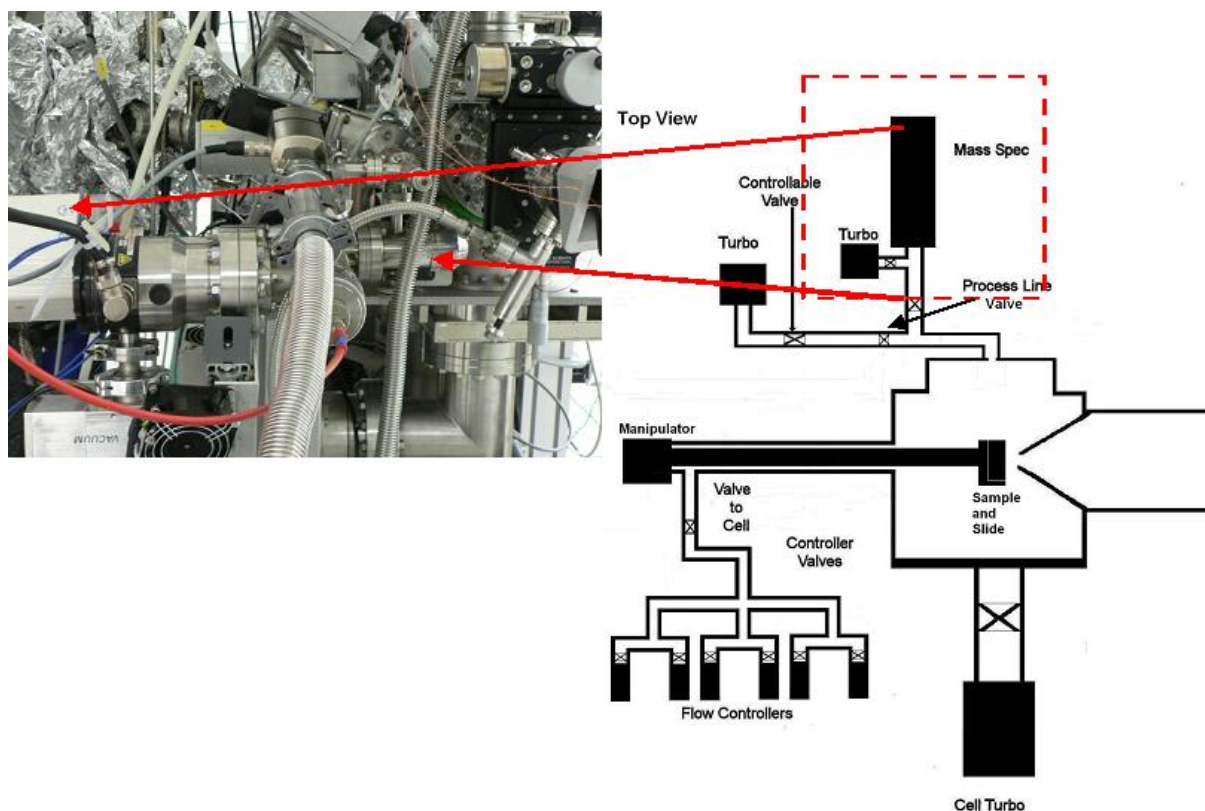


Figure 10: Mass Spec (top, view, red box)

The Hiden:

For the Hiden you have to ask us because the control PC has to be set up (it is usually not in use.). When this is done switch on the power supply of the Hiden (Figure. has to be described as well). Then proceed as follows:

1. Open the MS program by double clicking the “Massoft_old” icon on the Hiden desktop.

2. Goto “file” and “open” and select a file. There are several templates for the usual “MID” mode. If you want to measure in the other modes just click “gallery” and select a mode in the pop up window.
3. In MID click on the “flash” button to prepare the Hiden for measuring the click the “green light” button. The emission and the multiplier will switch on and you are asked for a file name. Then goto “view” and “trend view setup”. Here, you can set the masses display.
4. To stop the experiment press the “yellow” or “red light” for “hold” and “stop“, respectively. To stop the emission and the switch of the multiplier press the “no flash” button. You will be asked to save the data.

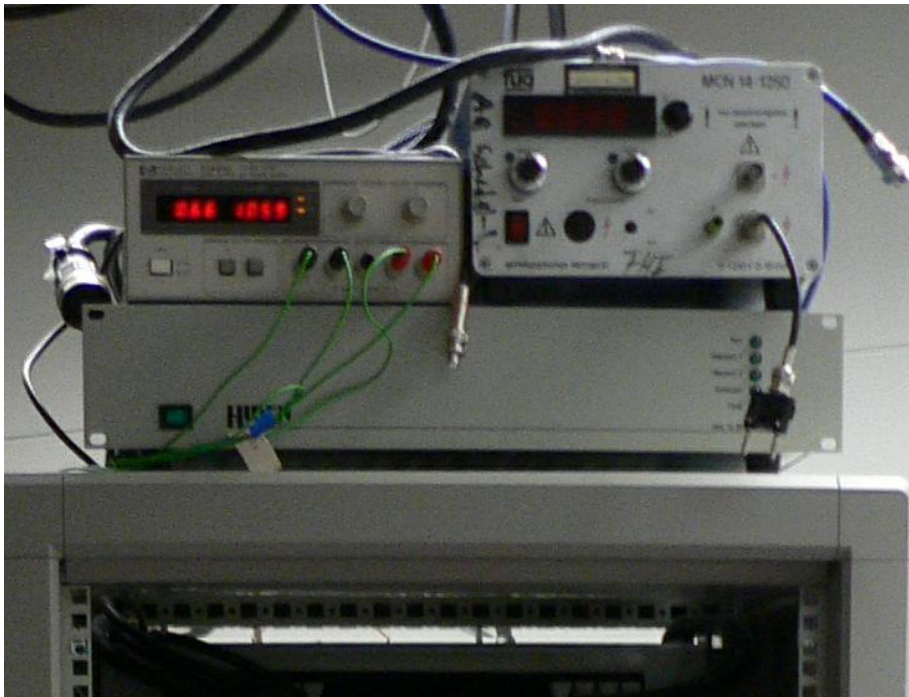


Figure 11: Power supply of the Hiden in Rack 2 just beneath the coil supply (see Fig. 3b).

I. Sputtering

Look at Figure 12 first. For sputtering the sample has to be inside of the transfer chamber facing away from the transfer port. The sputter gun is located just on the opposite side. Make sure that the gate valve to the reaction cell is closed. Goto Rack 2 and turn the power switch of the sputter electronics to “on”. Then increase the emission current to 20 mAmps by rotating the “emission” switch clockwise. Now, open the valve of the Ar bottle and subsequently the

Ar leak valve until the transfer pressure reading is showing 2×10^{-4} mbars. Now set the acceleration voltage (usually 1.5kV) and switch on the voltage. The sample will be sputtered.

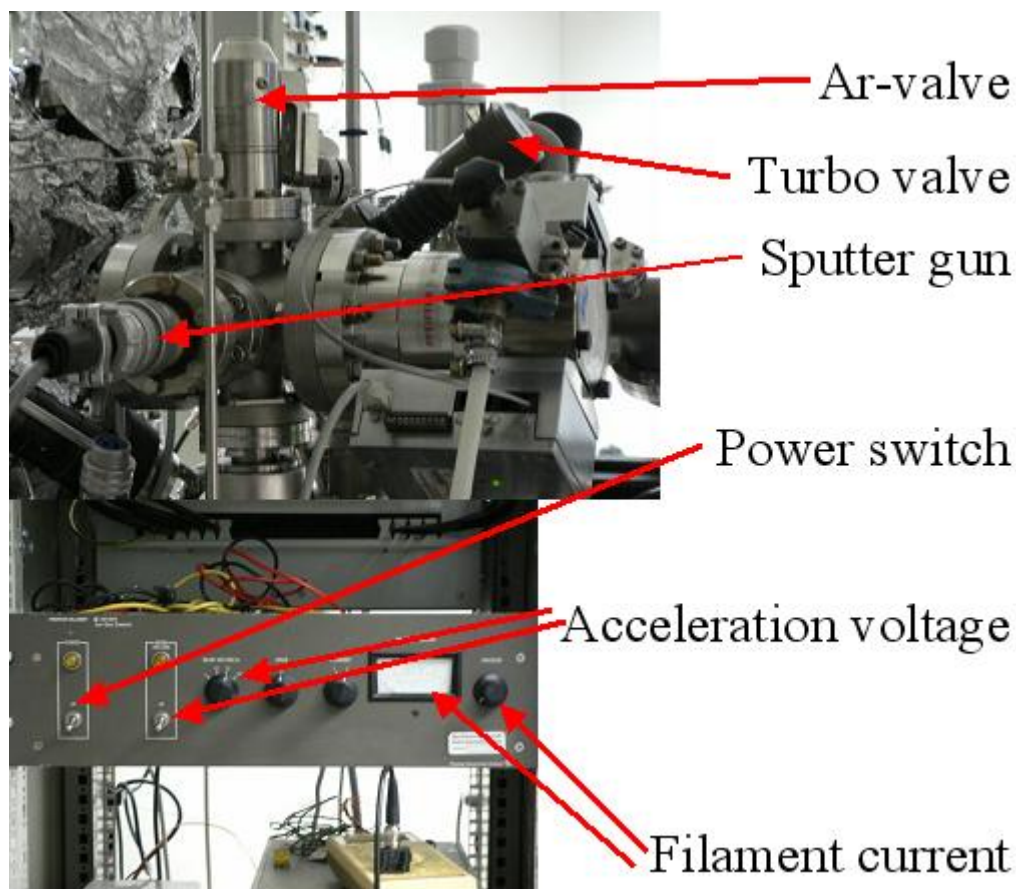


Figure 12: Sputter gun with Ar-valve (top) and sputter electronics located in Rack 2 (bottom; see fig. 3b).

J. Using the GC

I. Introduction to Gas Chromatography

Gas chromatography is a chemical analysis for separating chemicals in a complex sample. A gas chromatograph uses a flow-through narrow tube known as the column, through which different chemical constituents of a sample pass in a gas stream (carrier gas). The column is filled with a stationary phase to separate these constituents. The rate at which the molecules progress along the column depends on the strength of adsorption, which in turn depends on the type of molecule and on the stationary phase materials. Since each type of molecule has a different rate of progression, the various components are separated as they progress along the column and reach the end of the column at different times (retention time). A detector

monitors the outlet stream from the column; thus, the time at which each component reaches the outlet and the amount of that component can be determined.

Since the movement of the molecules depends on the strength of adsorption, retention time is a strong function of temperature and pressure (carrier gas). Higher temperature and higher pressure will decrease the time needed to elute the components, and hence their separation might be not satisfactory.

Gas chromatography is quantitative (the area under a certain peak is proportional to the amount), and thus suitable to quantify and calculate catalytic performance. Its drawbacks are that *i*) sampling requires atmospheric conditions (mbar cannot be fed in) and *ii*) GC might be damaged by vapors with low vapor pressures (condensation).

Please keep in mind that if you dose for example 0.2 mbar methanol with 0.2 mbar oxygen into the chamber, and you want to analyze it by GC, this will obviously not work! The gas mixture will be compressed to 1 bar (500 mbar methanol, 500 mbar O₂), but the vapor pressure of methanol at 20°C is 130 mbar! Therefore methanol will condense in the pump used to compress the gas mixture, and there might be a condensation in the GC, as well. If you want to quantify vapors, always check whether it will or not condense after compression! Condensation might be avoided by diluting your feed by inert gas, e.g. He (weak electron scatterer).

II. Our micro-GC

II/1. Hardware

Our gas chromatograph is a 4 channel CP-4900 micro-GC from Varian. Micro-GC only means that the GC is small, and all the major components (inlet/injector, column, and detector) are integrated into one small box. A 4 channel micro-GC can be considered as 4 such small boxes put together.

Our 4 channels are:

1. CP-Molsieve 5Å PLOT, 10m
2. CP-Molsieve 5Å PLOT, 20m
3. PPQ 10m
4. AL2 (alumina) 10m

The Molsieve (molecular sieve) channels can be used to separate simple non-polar molecules like O₂, N₂, H₂, CH₄, noble gases (He, Ne, Ar), CO. The 20m long column (10m not!) can separate Ar from O₂.

Channel 3-4 should be used for separating typically bigger or more polar molecules (CO₂, H₂O, NH₃, hydrocarbons, hydrocarbons with different polar functional groups: alcohols, ketones, acids, organohalogens, etc.) These channels will not separate e.g. air, but will give you an air peak at low retention times.

On the SUN: office1/user/Detre/Gc_appl_notes/, you will find a folder with application notes for the individual channels. These will give you some information about the chemicals separated by our channels and their retention time orders. Please keep in mind that the actual retention time will be a function of the carrier gas, T, p, but these application notes can tell you the order of retention and at least give you a hint about retention time.

Since we have to compress our gas to feed in into the micro-GC, we use a membrane pump to do so. Until now, we had a system (an automated valve switching) that operated as follows:

Phase1: purge the membrane pump by pumping N₂ from LN₂ to remove residual contaminants from the pump may be there from previous sampling.

Phase2: switch (no more pumping N₂), and let the pump establish vacuum.

Phase3: switch, and pump our gas that has to be analyzed through the membrane pump.

Phase4: switch, and let the GC take a sample from the volume behind the exhaust of the pump.

After some tests evaluating the effect of time spent at these stages, we will modify this system in a way that we permanently pump our gas through the membrane pump, that is, without N₂ purging. However you will have still the possibility to purge the membrane pump in case you feel it necessary.

Please use this membrane pump only if you want to use the GC! Its lifetime is relatively short.

With this modification the gas analyzed by the GC contains ~98% of the gas coming from the XPS cell and only 2% air leaked into the membrane pump. (Of course, this might slightly depend on the flow rate you use, and the pump should work as effectively as now.) One of the reasons to use the micro GC is to quantify, for example, CO₂. Assuming the air contains 0.04% CO₂, CO₂ leaked in will have a proportion of 8×10^{-6} of the whole gas analyzed. Take a feed in the XPS cell containing 0.2 mbar C₂H₄ and 0.1 mbar O₂, you would need as low as 2×10^{-3} % ethylene conversion to CO₂ to double the CO₂ signal in the GC. Hence you will be able to quantify low CO₂ yields.

To be able to scale your GC peaks in a way that you are independent of the amount of air leaked in, you should use a tiny but constant flow of inert (I advise you to use Ne!).

Since neon will be not consumed you can always normalize your peaks to the same Ne signal, and you can remove artifacts from different air leakage.

Add basics on the operation (carrier gas pressure, max. T, etc.)

II/2. Software

“CP-Maitre Elite” is the GC software you will find installed on the micro-GC computer. This program controls the micro-GC, sets all the parameters of your GC routine, acquires your GC trace, calculates concentration and export your results for further data handling.

There is a dossier about the software manual; unfortunately this describes not exactly our version! Although you will find some differences, however, the main ideas how to operate the software is identical. Therefore if you have any question concerning the software, you may find the answer in that manual.

The main idea behind the software is that you develop a (set of) *method(s)* according to your need. A method is used whenever you acquire and/or reprocess a data file. It contains instructions for data acquisition (column T, p, run time, sampling rate, etc.), integration, calibration and peak information, and reports, as well as optional functions such as data export. Each method is capable of acquiring multiple independent channels of data from a micro-GC. Each channel can have its own complete independent parameters, including sampling rate, run time, integration events, external events, calibration, and reporting.

Although the method file is a separate file, the information contained in the method is saved in the raw data file at time of acquisition. This way, the original method can be reproduced, even if the method file was subsequently modified.

CP-Maitre Elite is a Windows based software, so you will find the same kind of menu when using the right bottom of your mouse. By starting the program you will get first a window with an icon “micro GC” inside. You have now the possibility (right click) to *Open*, *Open Offline* (without controlling the hardware) or *Configure* the program. Offline, you can set up a complete method, including instrument configuration, which can be opened at a later time and used for data acquisition. By clicking Open or Open Offline, you will get to the main window of the software.

The menu structure you see is: *File*, *Edit*, *View*, *Method*, *Data*, *Sequence*, *Analysis*, *Control*, *Reports*, *Window* and *Help*. The most important commands are:

1. *File*: Open previously created data, method, and sequence; save (as) method or sequence; get a new method or sequence.
2. *Edit*: Copy/Paste

3. *View*: Preferences (to show toolbars and status bars, and to display the chromatogram in minutes/seconds)
4. *Method*: Instruments Setup (to set the parameters of the individual channels); Integration Events (to set the parameters used for the Integration; take care: you have to select the channel of your interest in the toolbar!); Peak/Group Table (here you will define your components, their retention time, etc.); Review Calibration (to see your calibration, of course only after you performed it); Advanced (here you can define what results you want to export into ASCII files); Properties (for example to set when your chromatogram should be analyzed).
5. *Data*: Manual Integration Fixes (Special integration parameters used only for your actual file; not included into the method)
6. *Sequence*: Edit a previously created sequence; Process (to run a sequence), Properties (to set file path used for your sequence)
7. *Analysis*: Analyze (to analyze your chromatogram); Analysis / Single Level Calibration (to analyze your data, or analyze and use it as a single level calibration)
8. *Control*: Run a Single experiment, a sequence, queue experiments, upload/download method from/to the GC (if you modify your method and you want that the GC runs accordingly, you have to press *Download Method*, that is, the method will be sent to the GC!)
9. *Reports*: View/Print reports
10. *Window*: arrange your windows
11. *Help*: to display Help.

In your data window (Channel 1-4) the actual chromatogram is displayed. You can use the right bottom click of your mouse to add a single or multiple chromatogram(s) or clear this overlay; to set the axis, appearance, legends; to perform operations or graphical programming of the integration events. You will find the same integration event commands as toolbar (and tool tips) in the bottom part of the window as icons.

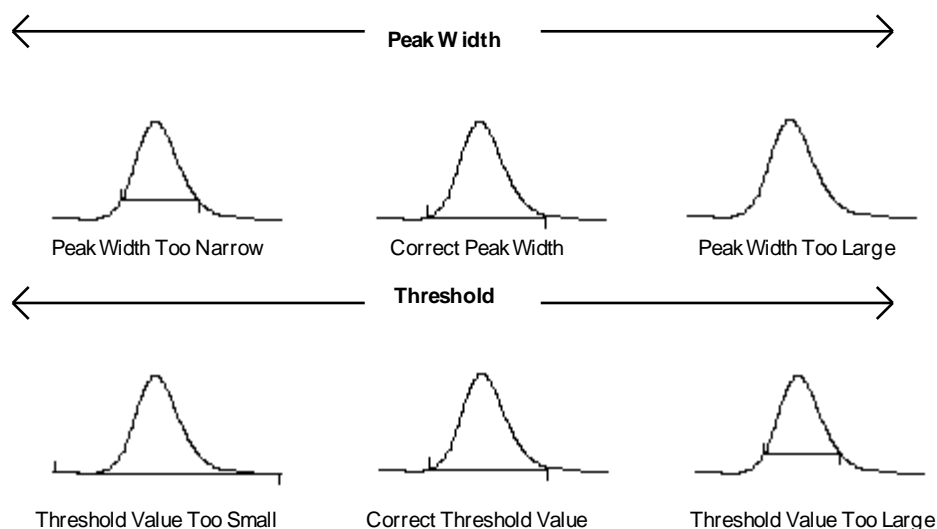
III. How to use the micro-GC for your problems (from method development to data evaluation)

Some of the following points are included in chapter 7 of the software manual in much greater details. Please consult the manual if you have question concerning these.

1. Make a list of chemical components you want to identify in the GC. Consult the application notes to identify the channels you need, the retention order, to get an idea about the temperature and pressure of the columns you should set.

2. Consider the concentration range of the constituents you want to use. Carefully check whether you run into any condensation issues after the membrane pump compresses your gas to atmospheric pressure.
3. Find out the temperature and pressure conditions of the individual channels to get the best compromise between time resolution of your reaction data (if it is a concern for you) and capability to separate all your components of interest. This you can do by dosing your component(s) into the GC (directly or through the XPS cell) and study the effect of T&p on the retention time. You open a previously created method or ask for a new (default), set parameters in the Instrument Setup according to previous experiments (application notes), save the method to the hard disk and make a single data acquisition run. (Before the acquisition you will specify the method to be used for the analysis, the file name and the data path.) Acquire data for all your components of interest until you confidently identify all your peaks. If you do not find one of your peaks, it is very likely not eluting within the time frame of your experiment. In such case increase the length of the run, increase T or p of the actual channel. However if you identified all your components, and they elute in separate peaks, you may want to decrease their retention time. Until your components elute in separate peaks you can decrease retention time by increasing T and carrier gas pressure.
4. Once you optimized the parameters in the Instrument Setup you can optimize the integration parameters. The best you do this when you feed most of your components together. The aim is here to integrate the component peaks as good as possible, that is, the program should find the baseline best describing your experiment. Two integration events (*Method/Integration Events*) are required for each run: **Width** and **Threshold**. These events are used to detect peak start, stop, and apex, and to distinguish true peaks from noise. The system uses default values of Width = 0.2 minute and Threshold = 50. Although these values work well for many cases, you can graphically optimize these. The **Width** event is used to calculate a value for bunching, or smoothing, the data points before the integration algorithm is applied. From the graphical programming list (right click of mouse), click **Width**. (Or click the **Width** button on the Toolbar.) Follow the instructions in the status bar at the bottom of the window to optimize the width integration parameter. Click once at the beginning of your narrowest peak, then once again at the end of the narrowest peak. CP-Maitre *Elite* will suggest a width value and you can update with this the

integration event table. Second, set the **Threshold** in a similar way following the instructions. This parameter is the first derivative, used to allow the integration algorithm to distinguish the start and stop of peaks from baseline noise and drift. The effect of **Width** and **Threshold** on the peak integration is shown on Figure 1. For simple chromatograms these two parameters might be enough to get the proper area of your peaks. However, you may have certain peaks that require special integration treatment. The following integration events are available for this case: shoulder sensitivity, integration off, valley to valley, horizontal baseline, backward horizontal baseline, back tangent skim, front tangent skim, minimum area, negative peak, manual peak, manual baseline, split peak, force peak start/stop, reassign peaks, disable end of peak detection, move baseline start/stop. These are described in the Software Manual (chapter 10), in great details. These events should be inserted into the Integration Events table, that is, it will be a part of the method you use. However, you may want to add one of these events into the Manual Integration Fixes table when you want to apply this only for to your actual chromatogram. When applying these events you should be able to adequately integrate your peaks.



Figure

1: The effect of **Width** and **Threshold** on the peak integration.

- Now you know at which time your components elute, the integration parameters are set correctly, but you still do not know how the detector is responding to your components. To tackle this you have to **calibrate** the GC to your components. Setting up a calibration for a method involves the following steps for a multi-level calibration: *i*) using your data acquisition method, run calibration standards and save them on the hard disk. Use here simple gas streams (your component of interest and a

diluting gas with known flow rate) at well defined concentrations. (You will get this only if the MFC's are calibrated!) Use gas flow directly from the mass flow controller, that is, the gas stream should not go through the membrane pump! Make at each concentration replicas and check the areas for stability. *ii*) Use your stored standard data files to graphically create your calibration peak table using the **Define Peaks** (or **Define Single Peak**) command (follow the instruction in the status bar). All the parameters for each compound are entered now in the Peak Table. *iii*) Complete your peak table by typing the peak names and other necessary parameters for your samples. *iv*) Save your method! *v*) Calibrate your method. This you can do in many ways (see software manual), but I will describe one that seems to be easy. Go to File/Sequence/Sequence Wizard. Choose your method and set "from existing data files"; click next and choose your data files; and Finish. Now you should see a yet untitled sequence table. Rename the "0" in the "Level" column to 1, 2, 3 etc, respectively to the different concentration levels. (For example, you calibrate C₂H₄ and you have 5 concentration levels 0.1, 1, 5, 20, 100% in 5 files stored. You will enter 1 into the Level cells row 1, 2 for row 2, etc. if your files are ordered accordingly.) Run type will change to calibration. In the "Conc. Override" cells you have to enter the corresponding concentration (0.1, 1, 5, etc.). Then save your sequence! Now you can go to Sequence/Process to start this sequence. If everything worked well, you can go now to Method/Review Calibration and you will find your calibration curves there. Using the right click of your mouse you can change fit types. If you want to extend your calibration by adding new point or new compounds, you can go back to sequence table and you can add new rows with new data points to the sequence. You can even add replicates of certain concentration level to the table or calibration data of new components. (If you want to use replicates and want that the program averages them, please go to Method/Properties/Calibration and click the averaging box. Furthermore in the Peak Tables "Calib. Flag" column set "Wt Average".) Save your method after you carried out the calibration.

6. Right now you are ready to perform real experiments to quantify any reaction of your interest. However before you do so, you may want to set which of the results should be exported automatically for you in ASCII files. Go to Method/Advanced and click the "Export Enabled" box. (A filled Peak Table is necessary here, otherwise the program cannot assign a certain peak to your compound of interest. Please keep in mind that if your peak shifts, i.e. its retention time changes, it might even shift outside

the range you set in the Peak Table. If it happens, the peak will not be exported!) After you carried out the calibration, exporting “ESTD concentration” (external standard concentration) should be enough, but you can choose many others, like peak area, retention time, etc. You can even export the chromatogram itself. Set the export options (export path, field separator), as well. Save the method! Now any time you acquire a chromatogram and the program analyzes it, concentrations will be calculated according to your calibration curves and the concentrations will be exported in a file. These will appear as new rows in your ASCII file.

7. You can open the ASCII file with the program of your choice to further manipulate the results. If you followed my advice to use a small constant stream of Ne, you can scan all data to get to the same Ne level when there was no air peaks in the GC trace. After this you subtract any impurity related to the air leakage in the membrane pump, and calculate conversion and selectivities.

On the side note, if you consider these 7 points, you can easily realize if you compare them to the menu *Method* that after some “preparation” (checking application notes) we went through the under menu of *Method* practically step by step.