OFFICIAL COMMUNICATION

GLOVEBOX SAFETY GUIDELINES

MANDATORY ASPECTS AND BEST PRACTICES

EPFL VPO DSE-OHS

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For all questions: open a support ticket: https://go.epfl.ch/support-ohs**.**

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Distribution	Professors & COSECs (all units).

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Table of content

General Warning

DANGER OF ASPHYXIATION

WHEN WORKING WITH LARGE VOLUMES OF INERT GAS

✦

A GLOVEBOX IS NOT EXPLOSION-PROOF

✦

IF MISUSED, A GLOVEBOX DOES NOT GUARANTEE YOUR SAFETY

WHEN WORKING WITH TOXIC CHEMICALS

Your glovebox is the property of your research group,

It is your responsibility to maintain it!

These guidelines were developed by the Occupational Health and Safety and the Safety Intervention team in order to reduce the risks associated with the use of gloveboxes on the EPFL campuses and to help students and staff maintain their equipment.

The present document is available on the OHS Glovebox webpage.

Purchase of a new glovebox

Contact the OHS if you need assistance with purchasing a new glovebox. We have direct contact with the main manufacturers, and we can provide support in determining which system best suits your research needs.

The main brands of gloveboxes found on the EPFL campuses are:

- MBraun©
- INERT Technology© (previously: Innovative Technologies)
- Jacomex©
- LC Technologies©
- COY©

Pre-requisites for installing a glovebox in your laboratory:

Each new glovebox installation must be announced to the OHS to check the feasibility of the installation.

Room: must be well ventilated (6 to 8x room volume atmosphere change per hour); temperature between +15°C to +30°C; dry atmosphere (max 65 % relative humidity).

Room size: the glovebox should be in a room with a significantly larger volume than the glovebox interior volume (room volume approx. 10x larger than glovebox volume); clearance from back wall ≥ 60 cm plus sufficient working space where glove ports, antechambers, etc., require access.

Room ventilation: each room must be equipped with a trident connection to the building ventilation (see Fig. 3 and 5).

Floor: firmly structured floor; no oblique position; load capacity ≥ 100 kg/m^2.

Nitrogen vs. argon: most gloveboxes are operated with nitrogen (N_2) as the inert gas. If you would like to conduct work with lithium (Li), titanium (Ti) or magnesium (Mg), you should use argon (Ar) instead.

1. MAINTENANCE OVERVIEW

Time	Suggested maintenance tasks
Every 1 or 2 weeks	- Clean and tidy interior of glovebox, antechamber(s) & gloves. * - Inspect gloves for punctures and tears; replace if necessary.
Every month	- Check O-rings of gloves and antechamber doors; replace if necessary.
Every 3 to 6 months (Frequency depends on the workload **).	- Perform regeneration. - Change vacuum pump oil. - Replace activated carbon (if present). - Clean moisture sensor (MBraun© sensors only).
Every 1 to 2 years	- Calibrate oxygen & moisture sensors (all brands). - Change HEPA filters. - Check and clean the valves block. ***
Every ~ 5 to 8 years	- Replace catalyst and molecular sieve with new material.

* = See section: Tips for cleaning your glovebox.
** = See section: Technical aspects of the regeneration.
*** = Please contact the mechanical workshop of your faculty to check the valve block (see Fig.2).

2. MANDATORY GUIDELINES

The **five (5) items** listed below **must be implemented and respected in each laboratory using a glovebox**. These items will be verified by the OHS team during safety visits.

1. Every research unit must **appoint at least one person (Technician, COSEC, PhD student, etc.) as the person responsible for the glovebox maintenance**. Appointing two people reduces the workload and prevents delays in case of long-term absence. It is strongly advised that the person(s) responsible for the glovebox maintenance transfer their expertise to their successor(s) before leaving the research unit.

2. Every glovebox must have a **logbook to keep track of each maintenance item**. It is advisable to use the *Maintenance checklist* available on the OHS website. Write down as much information as possible (e.g. regeneration dates, replacement parts, supplier's contacts, etc.).

3. Use a regeneration gas containing **NO MORE THAN 5 % hydrogen**. Above this level, the regeneration gas is considered flammable.

4. It is **forbidden to conduct a regeneration overnight, during the weekends** (from 5pm on Fridays) or during **public holidays** (from 5 pm on the eve of the public holidays). The regeneration process increases the risk of leakage, so it's recommended to do it in pairs to be able to react quickly in the event of an incident.

5. If you use an **oil vacuum pump, it must be stored in a retention tray**, and **the oil must be changed regularly** (every 3 to 6 months or after each regeneration, whichever is most frequent).

3. BEST PRACTICES

3.1 Preparing a glovebox before fully opening it

Fully opening a glovebox for maintenance (e.g. if you remove the front window, open both the inner and outer doors of an antechamber or replace a glove without the glove port cover) will result in specific risks**.** These risks depend on the materials/processes used inside the glovebox:

- Acute and chronic health risks if toxic substances are handled inside the glovebox.
- Fire hazard if pyrophoric substances reach ambient air and react with oxygen.
- Risk of suffocation by inert gases if the glovebox is not properly prepared for opening.

1) If you recently worked with toxic substances, purge the box for approx. 15 to 20 min.
   CAUTION: if you do not have the *Purge* option on your glovebox, let the box atmosphere circulate for at least one day (24h) before fully opening the glovebox.
2) If you store pyrophoric substances in the glovebox, transfer them to another glovebox (if available) or temporarily store them in a secondary container filled with inert gas.
3) Switch off the inert gas inlet, turn off the blower and open both doors of the antechamber to allow for a slow equalization of the glovebox interior atmosphere with the room ambient air.

After maintenance is completed

The oxygen content inside the glovebox will be very high (> 1000 ppm). Thus, before restarting the circulation (turning the blower ON), you should purge the box for approx. 20 min to lower the $[O_2]$ below 100 ppm. If you do not lower the $[O_2]$ before restarting the blower, it will contaminate your Copper catalyst with oxygen and regeneration will be necessary.

3.2 Tips for cleaning your glovebox

- For liquid spills: use paper towels (unless you spilled HNO_3) to absorb the liquid and promptly move them out of the box.
- For dried liquid spills: use acetone or 70% isopropyl alcohol with paper towels.
- For powder spills or if you create a lot of powder/dust inside the glovebox: use tape and press on the particles to pick them up. Dispose of the tape in the bin for toxic solid waste.
- To clean the outside window: use a mild conventional detergent (NO caustic detergents) or a slightly watered tissue.
- Labwipes and paper towels hold a significant amount of water. For stringent water-free conditions, always vacuum dry your paper towels overnight before placing them inside the antechamber.
- You can cover the glovebox floor with aluminum foil or a disposable plastic mat to protect it.

3.3 Personal Protective Equipment (PPE)

- Always wear your Personal Protection Equipment (lab coat, safety glasses and chemically resistant disposable gloves).
- Wear cotton gloves under the glovebox gloves to reduce sweatiness.
- Wear disposable gloves over the glovebox gloves to protect them against aggressive chemicals and to prevent cross-contamination.
- Always remove your jewelry from your hands as it can damage the gloves.

3.4 Maintenance items

Vacuum pump:

- Check the vacuum pump oil level regularly – low oil level is the most common reason for poor vacuuming performances.
- Always attach an oil mist eliminator on the vacuum pump (Fig. 6).
- An oil vacuum pump can be replaced with a dry vacuum pump (dry vacuum pumps are more expensive, but maintenance is easier and less frequent).
- Edwards© vacuum pump: you can change the *Mode Selector* and the *Gas-ballast Control* to optimize the pump performances (Fig. 7). The *Mode Selector* and the *Gas-ballast Control* can be changed when the pump is OFF or when the pump is operating. Refer to the pump user manual for more information.
  - Select the *High Vacuum Mode* (position "small💧") when working with water vapor only.
  - Select the *High Throughput Mode* (position "larges💧") when working with solvent vapors.
  - Select *Low flow gas-ballast* (control position "I") when performing routine work inside the glovebox (= when pumping low concentrations of condensable vapors).
  - Select H*igh flow gas-ballast* (control position "II") when performing a regeneration (= when pumping high concentrations of condensable vapors).

Gloves:

- Several glove materials are available depending on the research application. Most gloveboxes use Butyl gloves. Butyl gloves with a hypalon© layer are available for working with higher temperatures.
- Ensure that the correct type of glove is chosen and installed (i.e. left, right or ambidextrous and of the correct size).
- Before replacing a glove ensure that the box atmosphere is safe to breathe. If you worked with toxic chemicals, purge the box before removing a glove from its port.
- Use a glove port cover when changing a glove (port covers are available for all type of gloveboxes; Fig. 10).
- Always immerse your hands and arms slowly into the gloves to avoid a sudden increase of pressure inside the box. If your glove box has a foot pedal to control the pressure, apply a gentle vacuum to balance the pressure increase associated with immersing the gloves inside the box.

Oxygen and moisture sensors:

- The blower must be ON for the sensors to accurately measure oxygen and moisture levels (glovebox atmosphere must circulate for a few minutes to get an accurate reading).
- Operating the oxygen sensor at $[O_2] > 1000$ ppm (e.g. in air) should be avoided. If exposed to air, it will take several hours until the sensor correctly reads low level of oxygen in inert gas.
- Step-by-step procedure to clean an MBraun© moisture sensor can be found here. MBraun© recommends a cleaning procedure every 3 months.
- MBraun© oxygen sensors must always be placed before the moisture sensor (in the direction of the gas flow).
- The MBraun© oxygen sensor cannot be calibrated by the user, it must be sent back to Mbraun© factory (calibration recommended once a year; Mbraun© Declaration of decontamination form).
- Other brands: sensors differ from one brand to another; please refer to your instrument USER MANUAL or contact the OHS.

Antechambers:

- Always leave the antechambers under a slight vacuum when not in use (default position).
- When transferring items inside the glovebox, repeat the vacuum/refill cycle at least 3 times.
- When transferring liquids with an enclosed gaseous volume, slightly open any seals (e.g. the lids of bottles) so that the enclosed gases will also be exchanged during the vacuum/refill cycles.
- Do not try to open the door of an antechamber under vacuum; the opening mechanism can be damaged.
- Do not force the doors when closing an antechamber. Closing the chambers too tightly will damage the O-ring, and thus reduce the leak-proof capability of the antechamber.

Miscellaneous:

- The glovebox should be free from clutter; only chemicals and tools currently in use as well as air-sensitive chemicals should be stored inside the glovebox.
- Be very cautious when handling sharp objects such as needles and razor blades to avoid puncturing the gloves. Do not try to recap used needles before disposing of them; dump them in a syringe waste bin (Sharp safe).
- It is strongly recommended not to work inside the glovebox during the regeneration (especially with flammable and/or toxic solvents) because the vacuum pump and the gas purification system cannot undergo the regeneration and maintain a clean and inert atmosphere at the same time. EXCEPTION: systems with two separated purifier canisters, the normal circulation mode can be running via one canister while the other purifier canister is undergoing regeneration. Ask the OHS if you are not sure about your system.
- All volatile liquids (reactants and waste) stored inside the box should be capped at all times.

- Any chemical that is taken inside the box should be dry (i.e. anhydrous) and deoxygenated. If available, use DriSolv solvents (DriSolv solvents are packed under Nitrogen and sealed with a septum). If not available, it would be preferable to use solvent bottles that have not been opened outside the glovebox.
- The dirtiness of a High Efficiency Particulate Filter (HEPA filter) is relatively hard to assess. Thus, it is easier to schedule regular replacements (recommended once a year). Simply unscrew the used filter and screw the new one in. MBraun© sells additional solvent filters combined with HEPA filters (Fig. 11).
- If multiple people use the glovebox: It is strongly advisable to have a properly labelled personnal plastic tray/box to store personnal items and samples. A working area in front of the gloves should be kept clear and cleaned after every manipulation.

4. TECHNICAL ASPECTS OF GLOVEBOX REGENERATION

See Annex 2 for a short overview of the regeneration process.

If you do not feel confident performing the regeneration on your own, please contact the OHS.

1. WHAT TYPE OF REGENERATION GAS SHOULD YOU USE?

The gas used to perform the regeneration is a mix of hydrogen (H_2) balanced with either nitrogen (N_2), argon (Ar) or helium (He) depending on the inert gas used in your glovebox. These gas mixes are named **FORMIER GAS**.

- Hydrogen/nitrogen mixture (max. 5 % H_2 with 95 % N_2)
- Hydrogen/argon mixture (max. 5 % H_2 with 95 % Ar)
- Hydrogen/helium mixture (max. 5 % H_2 with 95 % He)

!! IT IS FORBIDDEN TO USE A FORMING GAS CONTAINING MORE THAN 5 % H_2 !!

- Formier gas bottles can be purchased from CARBAGAS (95/5 only) or prepared using an in-house gas mixer.
- Gas purity: medium purity (4.8 or higher). CARBAGAS' forming gas purity is typically 5 or higher. Explanations on gas purity can be found here.
- Make sure you have sufficient forming gas available before starting the regeneration (a 50 L/200 bars gas cylinder lasts 5 to 6 regeneration cycles).

2. WHEN SHOULD YOU PERFORM A REGENERATION?

As mentioned before, regeneration takes place only **during the day (not overnight)** and one user should keep an eye on the regeneration process at least until the end of the 2nd regeneration step (formier gas injection step, see Annex 2). It corresponds to approximately 6h to 8h after the beginning of the regeneration.

Option #1: Regenerate on a regular basis. Every 3 to 6 months depending on the workload and the type of work performed inside the glovebox (i.e. the more solvent you use, the more frequent the regeneration should be).

Option #2: Regenerate based on O_2 and H_2O levels. Perform regeneration a few weeks before the [O_2] and [H_2O] reach a pre-defined level. For example, after the last regeneration, it took 5 months for the purifier canister to reach saturation (saturation is indicated by levels of O_2 and H_2O constantly staying high). Therefore, the next regeneration should be performed after approximately 4.5 months.

Caution:

- If your glovebox atmosphere showed high concentrations of oxygen and/or moisture before the regeneration was performed, then you should purge the glovebox for approx. 15 to 20 min. after the regeneration is completed (do not select the option: *auto-start of the circulation after regeneration*). This will prevent the glovebox atmosphere from contaminating the freshly regenerated materials.

- If, during the regeneration, you see condensation on the window inside the glovebox, you must stop the regeneration immediately (indication of a damaged valve).

3. WASTE PRODUCED DURING THE REGENERATION

The regeneration process can release water and solvents from the purifier canister (approx. 100-200 mL). **If present, this liquid must be collected and treated as chemical waste after each regeneration**.

- **Which waste label should you use?**

Use the waste label with the **OMoD code 16 05 06**.

Waste labels should always indicate: date, research unit acronym, name of the person, as well as the major solvents used in your glovebox.

For further information on waste management, please consult the OHS webpage on special waste.

Substances to avoid in the glovebox

The following substances should not be used inside a glovebox without precautions as they can damage the copper catalyst:

- Bleach (NaClO) and other chlorinated chemicals, incl. solvents: dichloromethane (DCM), Trichloroethylene (TCE).
- Amines
- Phosphines
- Thiols
- Volatile sulfides

If you still want/need to use these substances, follow the steps below to minimize catalyst poisoning:

(1) STOP the gas circulation (i.e. shut OFF the blower).
(2) Once you finish working with these substances, purge the glovebox for approx. 20 min.
(3) Restart the blower.

Remember that all solvent bottles should be capped at all times!

If you work with lithium (Li), titanium (Ti) or magnesium (Mg)

You should operate your glovebox with argon and not with nitrogen (Li, Ti and Mg react with N_2). In addition, remember that nitrogen (from the air) will constantly diffuse through the gloves (and nitrogen is not eliminated by the purifier system). Thus, it is recommended to purge your glovebox for approx. 15 to 20 min with argon prior to start working with these substances.

Advanced technical information

If you would like to perform one of the following tasks, please contact the OHS.

1. Modify your glovebox or add new equipment (e.g. add a freezer or a spin coater, add a secondary purifier canister, etc.).
2. If you would like to install a purge option on your glovebox.
3. Check, clean and replace the valves. There are two types of valves on a glovebox: electromagnetic and pneumatic valves. Since some of these valves open and close thousands of times per year and receive large amounts of solvent vapors, it is necessary to check them for mechanical and chemical damages. It is especially the case for the valves regulating the pressure inside the glovebox and for the valves connecting the purifier canister(s) to the enclosure and to the exhaust. (Fig. 2: valves encircled in red).

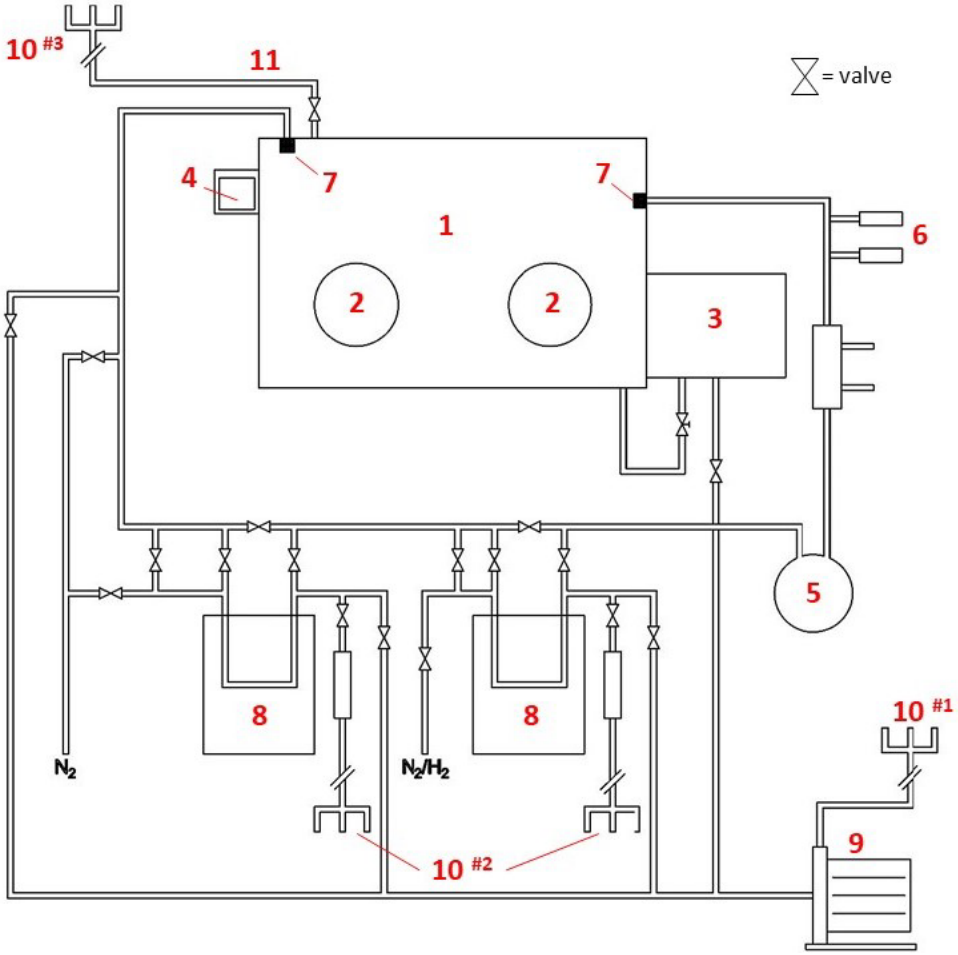
   Manufacturers recommend checking these valves at least once every two years.
4. Replacement of a used copper catalyst and/or a used molecular sieve with new materials (task frequency 5 to 8 years). This operation requires the dismantling of the purifier canister and numerous valves and internal tubing parts. It is imperative that these parts are reassembled correctly.

   Additionally, this procedure must be carried out in a high ventilated area and proper PPE (i.e. respiratory mask) must be worn. The used catalyst must be placed in a metallic recipient to cool down before being discarded (due to the heat, it will melt a plastic recipient). Note that after replacing the copper catalyst and/or the molecular sieve with new materials, users must perform two regenerations one after the other to “prepare” the new materials.
5. Replace molecular sieve with activated carbon OR add an additional purifier canister with activated carbon. Indeed, the molecular sieve can be replaced by activated carbon to absorb the water moisture and the solvent vapors. But remember that activated carbon cannot be regenerated and must be replaced with new material every couple of months. In addition, once an activated carbon canister is saturated, it will slowly release the solvent captured.

   OHS always recommends the use of molecular sieve in place of activated carbon.

ANNEX 1: Figures

Figure 1: Simplified schematic of a glovebox showing the main parts.



1) Enclosure (the “box”)
2) Gloves portholes
3) Antechamber(s); most gloveboxes have one big antechamber and one small antechamber
4) Digital control panel
5) Blower
6) Oxygen (O_2) and moisture (H_2O) sensors (the position of the sensors may vary; also see Fig. 9)
7) Dust filter - High Efficiency Particulate Air filters (HEPA 13X)
8) Purifier system: column-shaped reactor(s) containing filtering materials (i.e. copper catalyst and molecular sieve or activated carbon). Gloveboxes may have one or two separated canisters depending on the instrument design and applications (also see Fig. 8)
9) Vacuum pump
10) Connections to the building ventilation system (also see Fig. 3)
    $10^{\#1}$ = vacuum pump exhaust
    $10^{\#2}$ = regeneration exhaust
    $10^{\#3}$ = purge exhaust

Figure 2: Top: Simplified schematic of a glovebox showing the various valve's theoretical positions. The red circles indicate which valves should be checked regularly. **Bottom:** These valves are grouped in a valve block.

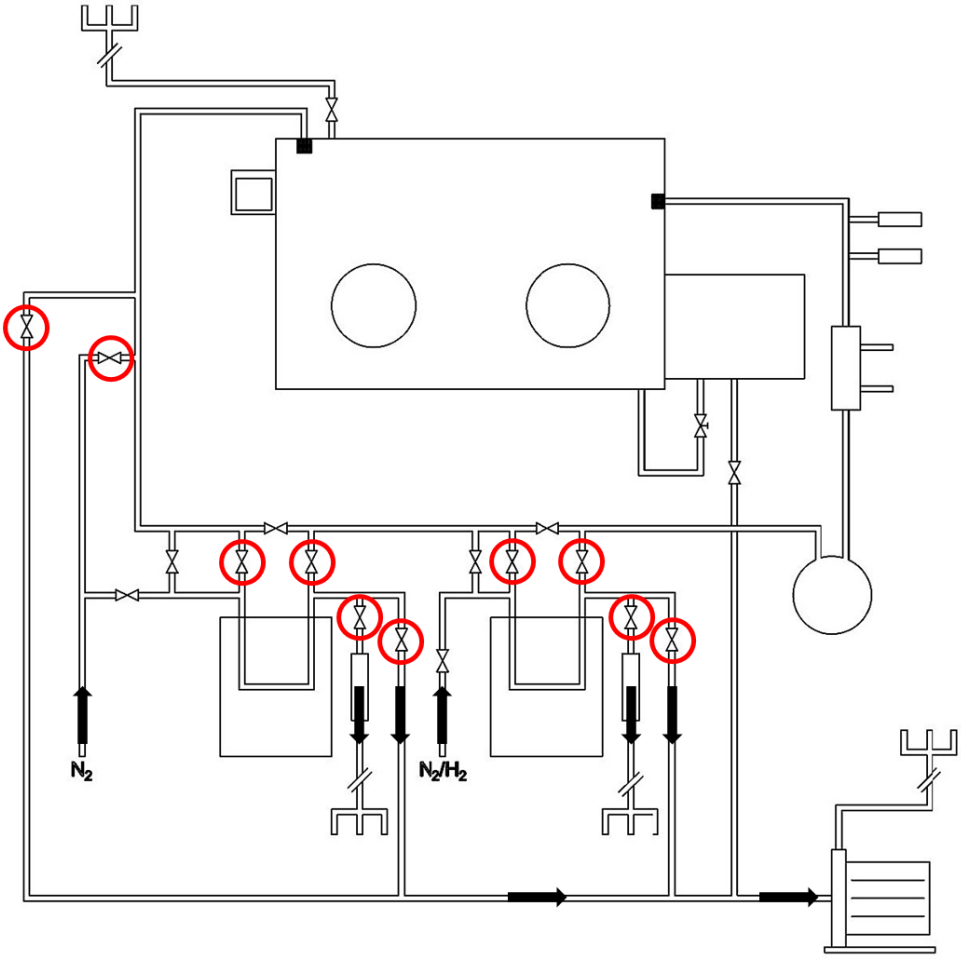


Figure 3: Example of a trident connection to the building ventilation system. Also see **Fig. 5** for the new Trident design.

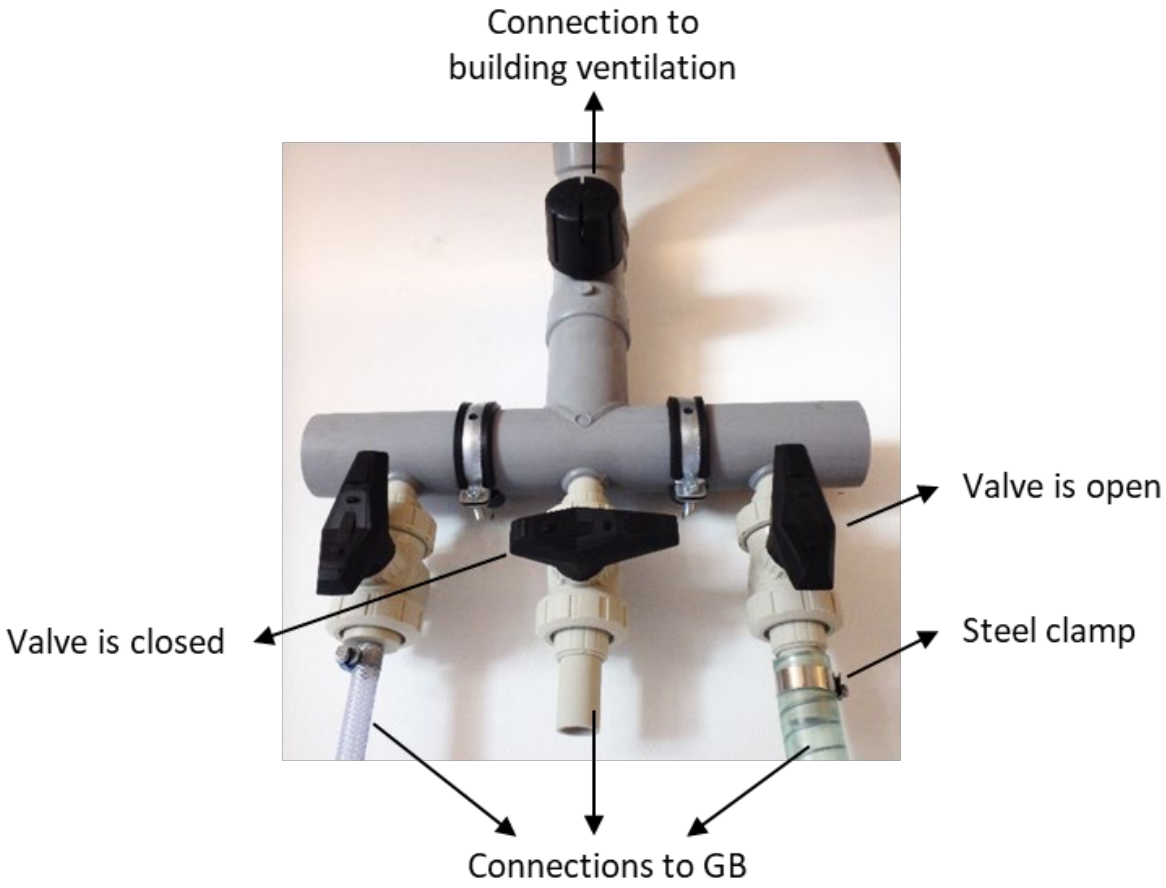


Figure 4: Flowmeter indicating the flow of forming gas during the regeneration process. Flow should be between 0.3 and 0.5 mbars (the ball should sit at approx. 20 Nl/min). Check the user manual.

By default, the flowmeter is placed after the purifier canister. Therefore, it may be damaged over time by the flow of hot solvent vapors. OHS recommends adding a secondary flowmeter directly on the gas bottle or on the gas line (contact the OHS to install a secondary flowmeter).

Figure 5: Example of new Trident design. The old Trident system (Fig. 3) will be replaced over time.

Vacuum pump exhaust connects on “Trident” network; all other exhausts (regeneration, purge, gas outlet, overpressure relief valve) connect on the “Fume hood” network. Note: not all gloveboxes have all these exhausts. Exact design may vary from one building to another.

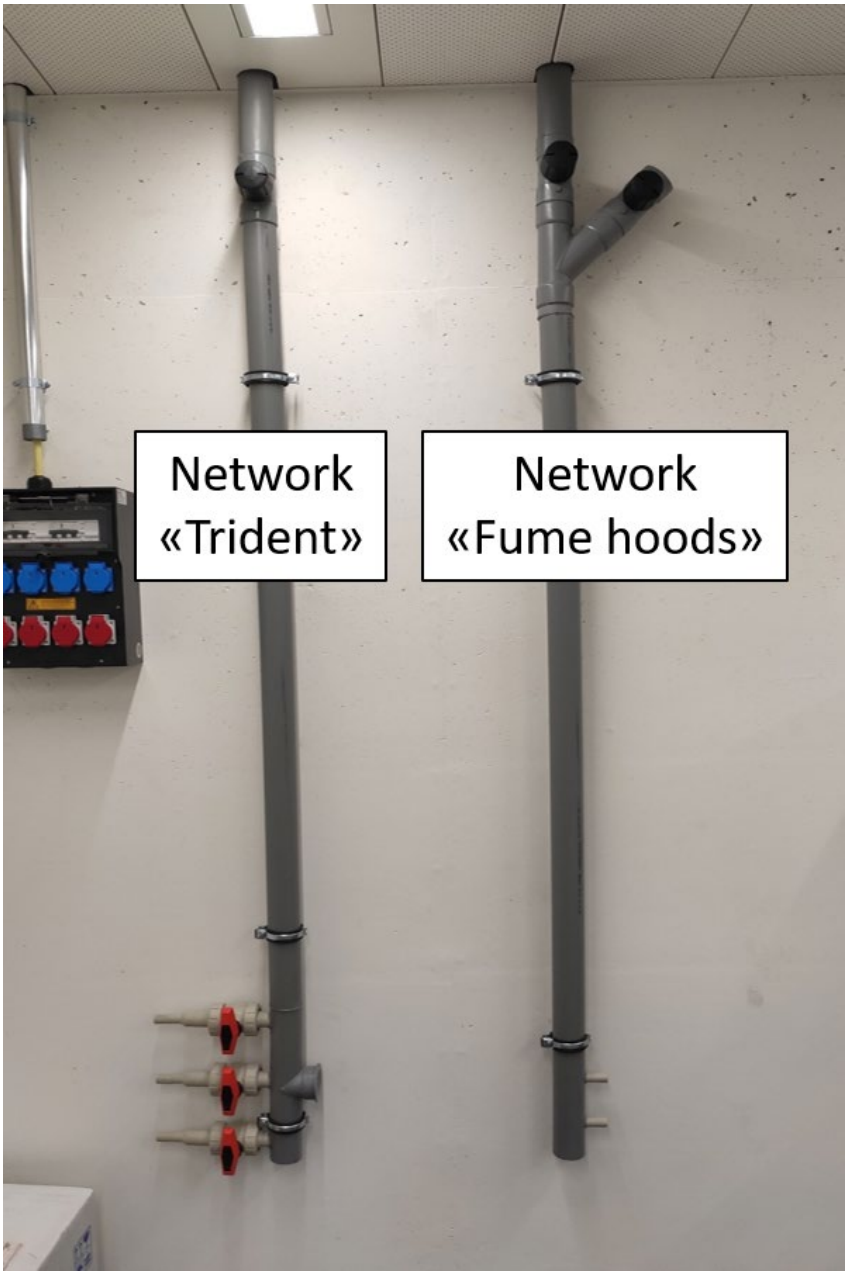


Figure 6: Example of an oil mist filter/eliminator for Edwards© vacuum pumps.

Figure 7: Left: Example of the gas ballast control knob. **Right:** Example of the mode selector knob on Edwards© vacuum pumps.

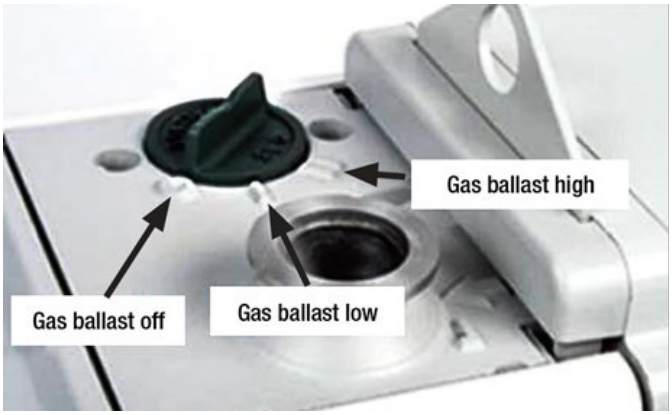


Figure 8: Left: Example of a purifier system with two separated canisters. These canisters can be duplicates, each containing a mixture of molecular sieve and copper catalyst OR the first canister contains the molecular sieve or the activated carbon and the second one contains the copper catalyst. **Right:** Example of a purifier system with only one canister containing a mix of molecular sieve and copper catalyst.

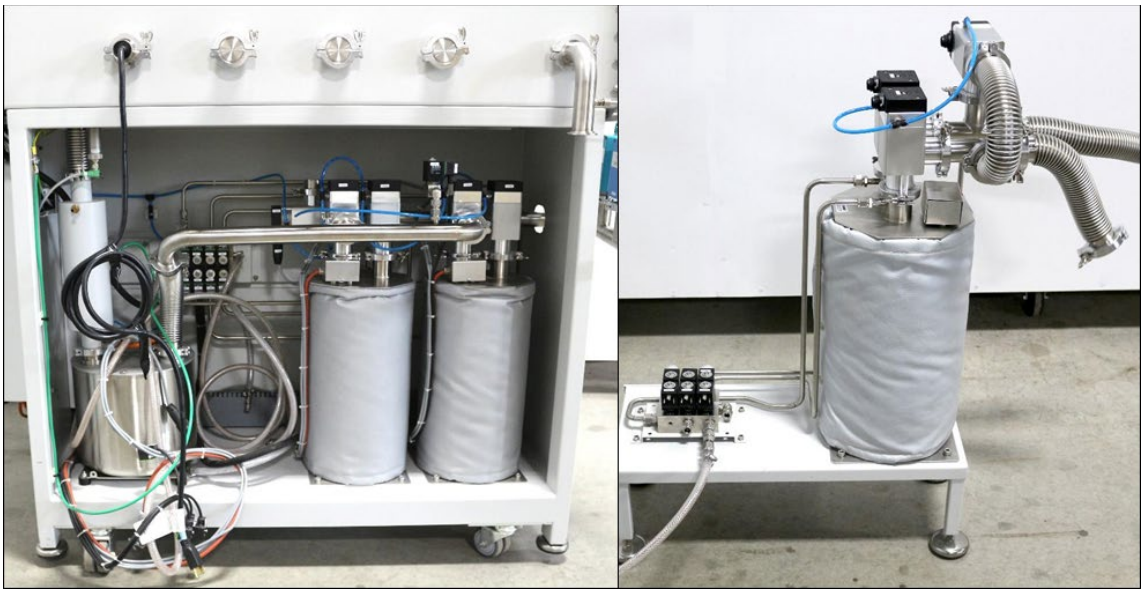
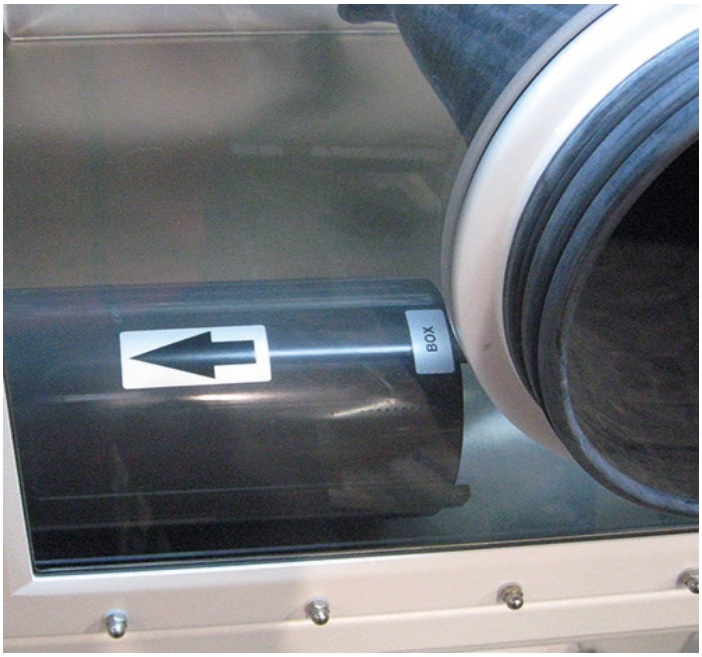


Figure 9: Example of MBraun© moisture sensor (left) and oxygen sensor (right).

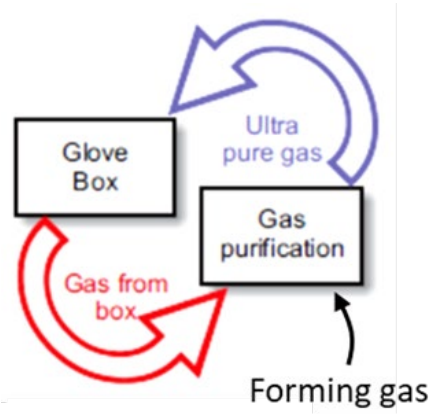
Figure 10: Glove port cover.

Figure 11: An additional activated carbon solvent trap can be installed in the box instead of the outlet dust filter. This cartridge integrates a small HEPA dust filter H13.



ANNEX 2: Regeneration overview

The purifier system of a glovebox consists of one (or more) purifier canister(s) containing materials which can remove oxygen, water moisture and solvent vapors (Fig. 8). Two main different materials exist: a copper (Cu) catalyst and a molecular sieve (typically 13X, pore size approx. 10Å). In some cases, activated carbon can replace the molecular sieve or come as an additional adsorbing material.



The Cu catalyst is used to remove the O_2 through the following reaction: $O_2 + 2Cu \rightarrow 2CuO$, and the molecular sieve (or the activated carbon) removes the H_2O moisture as well as the solvent vapors through adsorption. Over time these materials get saturated thus impeding the removal of the contaminants. The regeneration process aims to restore the purifying capacities of these materials. It is divided in four steps (these steps are carried automatically by the software and can be monitored through the digital control panel). Typically, a full regeneration cycle takes 12h to 15h.

Step 1 - Heat: The molecular sieve is heated at 250°C. This operation will "shrink" the sieve, setting free the water and the solvents that were previously trapped inside. Due to the heat, complex solvents will partially degrade into smaller organic chains and CO_2. The Cu catalyst is heated at 110°C to facilitate the chemical reduction of copper oxide (see step 2).

Step 2 - Gas injection: Hydrogen contained in the forming gas is used to regenerate the Cu catalyst according to the following reaction: $CuO + H_2 \rightarrow Cu + H_2O$.

Step 3 - Vacuum: A vacuum is applied on the purifier canister to help strip away the remaining water moisture and solvent vapors.

Step 4 - Re-equilibrium: The purifier canister cools down and re-equilibrate with the glovebox.

Notes:

1) Once the regeneration process has been carried out several times and it does not restore the absorbing capacity of the materials, the used molecular sieve and the Cu catalyst need to be replaced with new materials. Typically, if a glovebox is well maintained, replacement is only needed every 5 to 8 years. In order to activate a new Cu catalyst and/or a new molecular sieve, two regeneration cycles must be done.
2) If used, activated carbon cannot be regenerated and must be replaced with new material each time it gets saturated (typically every 3 to 6 months depending on the solvent load).