Supplement Section 1: Detailed Build-Out description

This supplement describes how to build a SWISS as we have built ours. There are many places where the system could be modified or adjusted based on a user's needs.

Step 1: Prepare the storage case

To prep the case for the build out the two main tasks are:

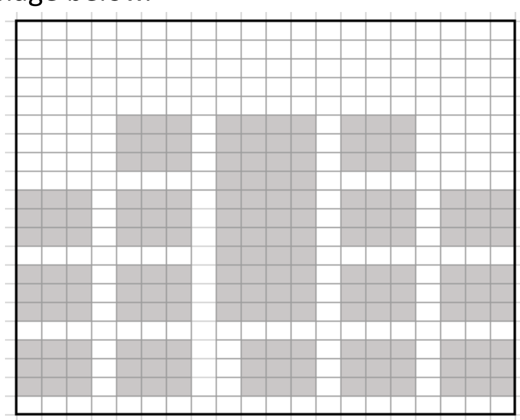
1. Pluck the foam so you can place the Valco stands & flasks
2. Drill the holes that you'll put the air and power cords through. I like to put the holes in the back (the one side without latches) so its easiest to route cords without having to go over the flasks later on.

Materials and tools needed for step 1:

- Pelican 0370 Protector Cube Case with Pluck n' Peel foam
- ¼" Push-to-fit Bulkhead Fittings (e.g. **5779K677**) (2 per sampling depth + 1 for the dry air inlet)
- Cordless drill

Plucking foam:
Inside your pelican case there are 7 pieces of foam: one base piece, 4 layers of Pluck N' Peel (we'll work with the top three) & two lid pieces. Each pluckable piece is 1" x 1" x 4" (l x w x h). For each flask we need to pull out a zone that is 3" x 3" X 12".

Working from the top piece of pluckable foam, pull out 15 3x3 holes for the flasks and one section that is 4" wide and 11" long. My preferred layout is to have the Valco valve hole in the center of the box, a row of 5 flask holes along the front, and 5 flasks arranged on either side of the valco valve, like in the image below.



Pull out the same pattern from the second and third pieces of foam. Note: the pieces are not all the exact same size and so they won't align perfectly.

Holes:

While there aren't breakable glass flasks in the box it can be nice to drill the holes you'll eventually feed power and sample air through. Drill one hole for each push to fit bulkhead fitting you will need, making the hole as small as allowable. I prefer to drill these holes on the back of the box so that my tubing can efficiently run out the box, and won't interfere with the valco at all. You will also want to eventually drill one hole for the power cords, but that one can be done later once power is all worked out. I tend to drill this hole on the side of the box to make cord management easier.

Step 2: Mount Valco valve vertically

Materials and tools:

- Wood
- Wood screws
- 6 X 1/8" diameter, 2" long machine with nuts and washers
- Valco valve and associated cords
- Hand drill

We used scrap 2x4's to build stands to mount the valco valve so that the head of the valco valve is positioned up. We used a 12" vertical piece, attached to an 11" horizontal piece of wood with screws. The Valco valve was then mounted onto the wood with 1/8" diameter, 2" long machine screws so that there was a 4" gap below the back of the valco valve so that cords can be plugged in/unplugged as needed.

** Note: it is very advantageous to attach all of the necessary cords (RS-232, power, display) at this step - it is very tricky once it is placed inside the box.

Step 3: Prep stainless steel tubing

Materials and tools:

- 316 Stainless Steel 1/8” OD tubing
- Tube cutter
- De-burring tool
- Optional: aluminum ⅛” OD tubing for mocking up tubes and string
- Valco valve fittings
- ⅜” wrench
- Valco valve

With a flask placed in each spot in the case, and the valco valve mounted and placed in the correct location, use aluminum tubing to create a mock-up tube that goes from the correct Valco valve port to the desired flask location. As you mock the tubing up make sure to have the tubing that attaches to the valco valve be completely vertical for 1 - 1.5” so that as you tighten the swagelok fittings there is no angular force. Don’t forget to make a jumper loop on port 1 of the valco valve, as well as an inlet and outlet tube!

Then use string to measure the length of each mock-up. Cut the ⅛” stainless steel tubing to the correct length. Be sure to thoroughly de-bur and clean the tubing after cutting. Any small pieces of stainless steel tubing that make its way into the Valco valve can scratch and wear down the valco valve, making it leaky.

Then, once all of the tubing has been cut and de-burred, use the mounted Valco valve to attach the fittings to one side. Make sure that the ferrule is clamped down and can no longer slide around.

Step 4: Prep glass flasks

I find it easiest to put the Swagelok fittings onto the glass flasks prior to putting them into the box.

Materials and tools:

- Glass flasks
- ¼” to ⅛” reducing union fittings from Swagelok
- PTFE ferrules
- ½” and 9/16” wrenches

I like to take a piece from the lid and the topmost plucked foam piece and to put all the flasks out into their spots. I then take all of the ¼”-1/8” (32) reducing unions from the box, and remove the stainless steel ferrule from the ¼” side. I take a spare piece of bev-a-line or other flexible ¼” tubing, and put the stainless steel ferrules onto the flexible tubing to save for other uses. They’re good to save because each ferrule set is about $2.50. I then put the ¼” caps on all the flasks, followed by a ¼” teflon ferrule from ohio valley. I typically buy about 20 extra teflon ferrules per SWISS box because you will inevitably break a few flasks as you go through the building process, and they’re nice to just have on hand. Then tighten the rest of the union fitting onto the glass flask.

Step 5: Bend the stainless steel tubing

<u>Materials and tools:</u>

- Tube bender
- Mounted valco valve
- Prepped stainless steel tubing
- Prepped flasks placed in case
- Patience.

Bend the stainless steel tubes attached to the valco valve so that they easily slide in and out of the swagelok fittings.

Pro-tips:

1. I position all of the flasks to start so that the center tube (the long one that goes to the bottom) is on the left side – and I attach the bottom Valco fitting to the center tube. I've done this so that is my inlet side and so air gets pushed down to the bottom and then you flush out the top.
2. While I'm tube bending, sometimes I flip the position of the flask – but still make sure the bottom goes to the center tube. Particularly for the flasks on the far right side of the box, it can be helpful to twist them around so you have a lot more room to fit wrenches in.
3. You should aim to have the portion of the tube that attaches to the flask to be completely vertical for 1 - 1.5" because the Swagelok fitting has to perfectly line up, otherwise you'll snap the tube in the tightening process.
4. As much as possible don't have tubes crossed – it makes your life a pain later if you need to replace something.

Step 6: Tighten Swagelok fittings

Materials and tools:

- Wrenches
- Infinite patience.

Use an extra union fitting to tighten the swagelok ferrules onto the stainless steel tubing. Then, attach and tight the stainless steel tubing to the union fittings. This is the most common step where flasks break. Go slowly and patiently through this step.

Supplement Section 2: Detailed Protocols for QA/QC

Terminology:

- Dry air fill: Flush flasks with dry air for a period of time such that the air in the flask is fully turned over 10 times.
- Water vapor fill: Flash flasks with water vapor of either known or unknown composition such that the gas in the flask is fully turned over at least 5 times.
- Dry air test: A short (e.g. 7 day) test where dry air is put into the flasks, allowed to sit for a period of time, and then the water vapor molar fraction is measured at the end of the test. The goal is for flasks to maintain a low water vapor mole fraction.
- Dead end pull measurement: There is no input of dry-air into the flasks during a measurement period. A cap is placed over the inlet tube on the Valco valve. During the dead-end pull method, there is no supply of a carrier gas and the picarro intakes gas at a rate of approximately 29 - 31 ml/min.
- Carrier gas measurement: Dry-air or dry-N_2 is supplied to the inlet of the Valco valve at a rate of 30 ml/min during the measurement phase. It is expected that fractionation would occur as pressure decreases, and so using a carrier gas prevents large pressure changes that might induce fractionation.

Dry Air Test Protocol:

Fill: We used air filtered through drierite (100 - 300 ppm), flowing at a rate of 2 L/min to flush each flask for 5 minutes. At this rate, the air in each 650 ml flask turned over 15 times. At the time of filling the flasks, we noted the molar fraction of water vapor in both the ambient atmosphere and the dry-air.

Hold period: We recommend at least 7 days, however, shorter timescales could be used

Measure: Use a *dead end pull measurement* style to measure flasks for 5 minutes. Do not use a carrier gas, because it will dilute the signal.

Data Processing: To determine the water concentration in each flask, we marked the time the flask opened using the ‘outlet valve’ value from the Picarro. For each new flask we saw the pressure wave as a peak in the Outlet Valve value. The advantage of using this method is that it is also easy to identify flasks that are likely leaking based on an outlet valve value that is lower and more similar to an ambient pressure value. After marking the start of each flask, we then removed the first 90 seconds of that measurement to discard any memory effects in either the tubing from the swiss to the picarro or the picarro itself. We then averaged the concentration across the subsequent 180 seconds. The code for this process is available via github.

How to ‘pass’ this protocol: Maintain a water vapor mixing ratio of less than 500 ppm.

Water Vapor Test Protocol:

Fill: Flush flasks with water vapor of known composition produced using the vapor permeable probes at a rate of 150 ml / min for 30 minutes. For a 650 ml flask, this is approximately 6 full turnovers of the water vapor in the flask. We found that 5 full turnovers was the minimum number required to get water vapor molar fraction values that were stable within ± 100 ppm for the final three minutes of the measurement period.

Hold period: We recommend at least 14 days. If the desired storage time is longer than one month, we recommend testing your system with a longer storage period.

Measure: Prior to the start of measuring each flask, we ran dry air via the flask bypass loop for 5 minutes to sufficiently dry and remove memory effects in the impermeable tubing that runs between the SWISS. During that five minute period, lightly warm the flasks and tubing. The goal is to make sure that everything is uniformly warmed to just at or above room temperature so that there is no condensation. This is especially important for the valco valve and stainless steel tubing. Using the *carrier gas measurement* method, measure each flask for 10 minutes. Closely monitor each flask for signs of condensation (i.e. increasing water vapor mole fraction through the measurement, associated with increasing isotope values). Also closely monitor the water concentration right after switching back to the bypass loop, if the water concentration stays the same or increases with a marked increase in isotope values, mark that flask as problematic.

Data Processing: To mark the start of each flask, we used the rapid increase in water vapor mole fraction as the start time. We then discarded the first three minutes of measurement, and averaged the next 3 minutes (see supplemental figure).

How to 'pass' this protocol: After applying an offset correction, flasks should be evenly distributed about 0, and ideally within the uncertainty of the vapor permeable probes ± 0.5 ‰ and ± 2.4‰ for $\delta^{18}O$ and $\delta^{2}H$, respectively (Oerter et al., 2017).