HumiPyc - Gas Pycnometer Quick Tutorial

<u>Note: The actual hardware may look differently then the items used below for graphical presentation only.</u>

The HumiPyc Gas pycnometer serves for determination of sample volume (density). Based on the amount of the sample to be used in the experiment, the user needs to select either small or large reference chamber, appropriate volume reducing adapters, and one of the two sample chamber closure adapters (see below). The best results are obtained when the volumes of the reference and sample chambers are comparable. The volume reducing adapters should be used to reduce dead volume of the sample chamber, especially when using small reference chamber and small amount of sample.

Normally, the adapter with the inner bore (on the right) should be used with large reference chamber. Only if additional, custom designed volume reducing adapters are used to handle thin and long samples, then this adapter can be used with small reference chamber. The picture below shows one of the adapters used for closure of the sample chamber and the locking mechanism in upward position. The knob needs to be tightened until it brings the adapter with the contact with the block. The squeezed O-ring makes air-tight seals between the block and the adapter. A small amount of vacuum grease can be put occasionally onto the O-ring to make better seal.

A volume determination experiment consists of pressurizing the sample chamber to some pressure and expanding the gas into additional chamber of known volume, called reference chamber. This sequence of events, called a step in further discussion, is carried out without the sample and it is repeated with the sample. Practically, to get some statistics, the measurement steps with and without the sample are repeated. If the sample chamber volume without sample(s) is known and the same sample holder is used, then the user may carry out experiments with the samples only.

Calibration of the selected reference chamber does not need to be carried out for each experiment. Upon receiving the instrument, the selected reference chamber must be calibrated by the user, as the configuration file is supplied for ease of installation only and does not necessarily contain the particular instrument data. When selecting a different chamber, changing the type of gas, if the ambient temperature, or the pressurization pressure change substantially, the reference chamber should be calibrated.

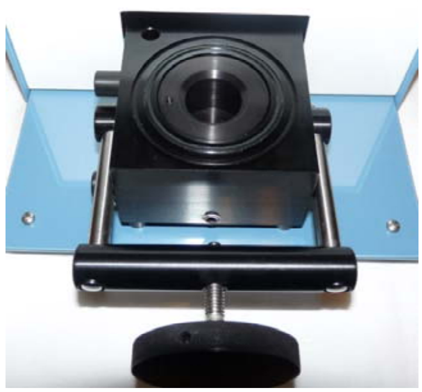
Recommendations for Reference Chamber Calibration

There are two reference volume chamber, the Small (about 10 – 11 cc) and Large (about 72 - 75 cc).

To calibrate the small reference chamber, the following hardware can be used:

1. The flat sample closure adapter (see above on the left)
2. The volume reducing adapter with the inner cylindrical bore of diameter just over 1” (25mm).
3. The metal ball of nominal diameter of 1“ (25.4 mm). The nominal volume is 8.580247 cc. The actual volume of the selected ball for calibration needs to be calculated.

The first picture below shows sample chamber after sufficiently unscrewing the knob, moving the locking mechanism forward until it rests, and removing the sample closure adapter. The large volume reducing adapter is inserted into the sample chamber.

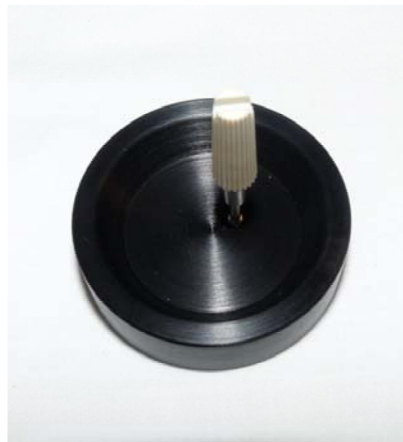


Using the smaller of the vacuum suction tool from the calibration kit, the 1” ball can be carefully transported to the sample chamber (picture on the right hand side. The picture on the left shows the ball inside the large volume reducing adapter.

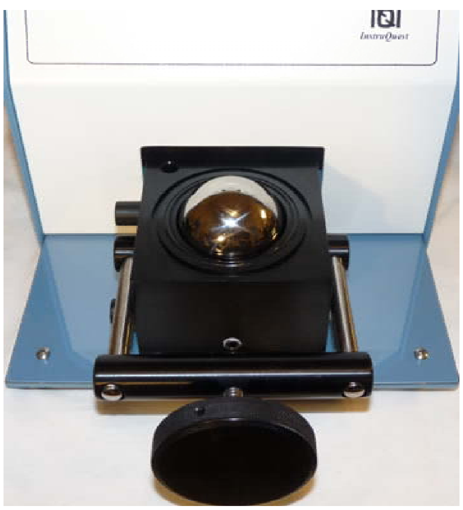
To calibrate the large reference chamber, the following hardware can be used:

1. The sample closure adapter with inner bore
2. The special volume reducing adapter (with conical wall)
3. The metal ball of nominal diameter of 2" (50.8 mm). The nominal volume is 68.641973 cc. The actual volume of the selected ball for calibration needs to be calculated.

The picture below on the right hand side shows the special volume-reducing adapter with the thumbscrew installed for easy transport into the sample chamber. The picture on the left hand side shows the adapter installed and the thumbscrew removed.



Using the larger of the vacuum suction tools, the large calibration ball can be carefully transported (see the photo on the right hand side) into the sample chamber . The photo below on the left hand side shows the ball already placed into the sample chamber.



The user is free to use any hardware and calibration ball(s) that can be suitable for the reference chamber volume determinations.

For volume determination experiments, different sample holders can be used. When using the small reference chamber, the large volume reducing adapter and one the small sample holders that fits into the bore can be used. When using the large calibration chamber, the volume reducing adapter used for calibration needs to be removed and one of the large volume sample holders can be used. The user can utilize other sample holders.

Using the Auto mode, the experiment can be defined by either downloading a previously saved template or creating a new one (and saving it for future use). Please see the screen snapshot below. The calibration procedure of reference chamber is essentially the same as for running a sample volume measurements with some exceptions:

1. The check box next to the word **Calibrate** in the **Calibration of reference volume** frame must be checked.
2. The volume of the selected metal ball must be entered in the **Vcal [cc]** text box.

The appropriate selection of the **Small** or **Large** in the **Reference Chamber** frame must be made.

Before running an experiment, the prepared template can be saved for future use.

The calibration of a selected reference chamber requires one measurement (or several repetitions of it) without the calibration ball and another measurement (or several repetitions of it) with the calibration ball. It does not really matter in which order. When one sequence of the measurements will be finished and a wait Tag = 0 will be detected, the user needs to either introduce the ball or remove it, close the chamber, and hit the OK button to allow the second sequence of measurements to take place.

Upon finishing the calibration, a message window appears with the results and a prompt for saving the calibration results. If the obtained data are close to previously calibrated results (for the same chamber) and have small statistical error, the results can be accepted. Otherwise, the results cam be rejected and the calibration needs to be repeated. The calibration ball should be equilibrated thermally with sample chamber as sequential data will show a trend rather than a usual statistical scatter. The room temperature should be relatively stable and the instrument warmed up for best results.

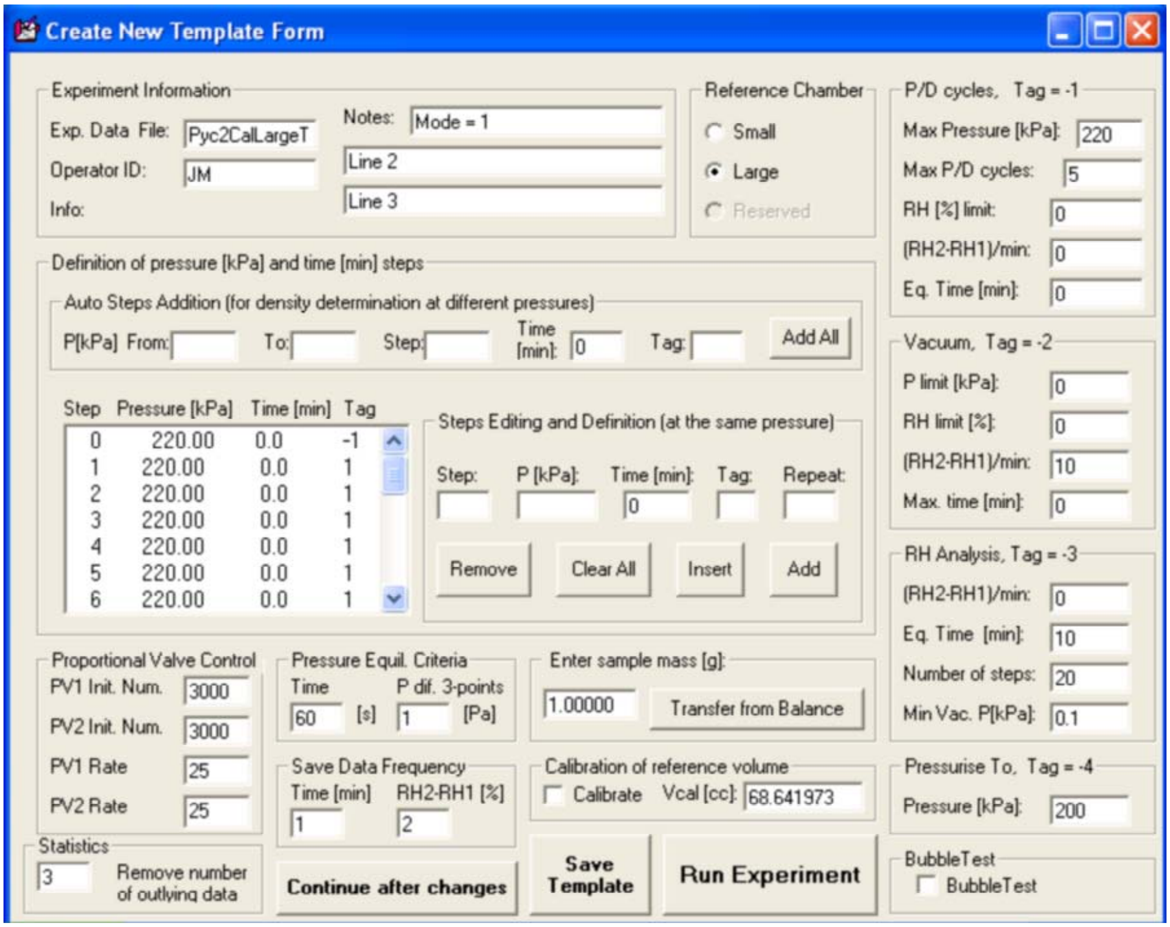
Additional difference between the calibration of the reference chamber and a regular experiment will be noticed when some partial data will be acquired. There will be rather Vc/Vr ratio than typical Vc values as the Vr values are not yet known during the calibration (please review the theoretical section of the user manual) .

Regular experiments for sample volume determinations

The same downloaded or prepared template can be used for regular experiments but the **Calibrate** check box in the **Calibration of reference volume** frame must be unchecked. That indicates, that a regular volume (density) determination experiment is to be carried out. The last calibrated reference chamber size (Small or Large) must be selected in the Reference Chamber frame to yield correct data as the value of the reference volume value will be used for the sample volume calculations.

The actual experimental activity that the instrument will carry out after hitting the **Run Experiment** command button should be declared in the list table located in the main frame **Definition of pressure [kPa] and time [min]** steps. The labels **Step Pressure [kPa] Time [min] Tag** help in identifying the experimental step parameters. If all the steps are done in the sequence as they appear in the list table (not in their step numbers) or if there were no steps in the table, the hardware is shut down to default values and the experiment is finished. Pressing the Print button on the chart form causes printing of the report.

Introducing the experimental steps into the list table and their meaning is described in the software manual. Some practicing with filling the list table is recommended. **The following discussion of a simple experiment is only for illustrative purposes. The user is free to use his/her own parameters that can be more suitable for specific application and speed of the experiment**.



For simple volume determination experiments, the Time [min] should be always zero. Non-zero values are reserved for future implementations of special applications.

Let say, that after calibration of the reference chamber, the sample volume determination is to be carried out and the first stage is to purge several times the sample chamber, 5 times in this case, with pressure build to 220 kPa and discharge to ambient pressure. The Tag number for this P/D Cycles procedure is -1. This is the first experimental step in the list table. This is an optional step, meaning, it does not have to be carried out for volume determination experiments. For all tags with negative values, the parameters in the respective frames for the negative tags will be used.

Next, ten repetitions of experimental steps (from 1 to 10) are to be carried out for volume determination of the sample chamber (without the sample) with the tag value of one. The actual number of repetitions is up to the user. It is assumed, that the appropriate volume reducing adapter(s) and empty sample holder are already in the sample chamber that is closed before starting the experiment. The table containing the Step/Pressure/Time/Tag data could be scrolled up and down to see the remaining steps. Most of the remaining steps are shown below.

After the ten steps, **there is one step with the tag value of zero**. If the program execution gets there, a Message with detecting the wait tag will appear and the software will wait for the user until the introduction of the sample into the sample chamber (or any other activity) is finished and the OK button is pressed. If the speaker volume is ON, the beep signal will sound three times to announce completion of this experimental stage. This special "wait tag" is especially useful when carrying multiple sample measurements using the same sample holder and the same reference chamber. There can be many sequences interrupted by the tag = 0, when the user will need to replace the sample. Having the first sequence without the sample with the tag = 1, and subsequent sequences with (consecutive) positive tag values (higher than 1), the usual step of determining the chamber volume without the sample can be determined only once and volumes additional samples can be measured more productively.

Step	Pressure [kPa]	Time [min]	Tag
7	220.00	0.0	1
8	220.00	0.0	1
9	220.00	0.0	1
10	220.00	0.0	1
1	220.00	0.0	0
1	220.00	0.0	-1
1	220.00	0.0	2

<== Wait Tag (Tag value of 0) Will wait for user activity until OK button is clicked to continue experiment

Step	Pressure [kPa]	Time [min]	Tag
2	220.00	0.0	2
3	220.00	0.0	2
4	220.00	0.0	2
5	220.00	0.0	2
6	220.00	0.0	2
7	220.00	0.0	2
8	220.00	0.0	2

After the sample was introduced and the OK button pressed, the software will continue with the next step, which is again the purge of 5 P/D cycles with the same build pressure.

Following the preparatory step, there are next ten steps with the Tag value of two (only 8 steps are shown), which supposed to be the repetitions of sample chamber volume measurements with the sample this time. If there are no more steps, the software will bring the instrument to a default state and shut down the hardware.

At that stage, the user can print the report with the default mass value of 1.0 gram or input the actual mass value in the appropriate text box and then print the report. In case the actual mass cannot be determined before or after the experiment and inputted into the text box in the **Enter sample mass [g] frame**, or if the report has not been printed, the density of the sample can be determined later using the recorded data. Subtracting the average volumes (at the end of each tag sequence) to get the sample volume from the recorded summary data file (*.SUM) and dividing the sample mass by the volume yields the density.

This simple example does not need to end there. Declaring additional sequences of steps with other tag values and with the "wait tags" in between, volumes of additional samples can be determined assuming using the same sample holder and the same reference chamber. Additional sample treatment stages, like using vacuum (Tag = -2) can be introduced to see the effect of outgassing on the density values. A report can be printed after each "wait tag" is detected and OK button pressed.

Beyond these simple volume measurements, more complex experiments can be designed and other experimental techniques can be implemented using this unique volumetric system.

Time of experiment duration

Another issue for discussion is the time spent for an experiment duration and there are several possibilities to manage the experiment time. One of them is equilibration time. Many other pycnometers have short fixed time for equilibration before measurements of pressures (pressurization, depressurization, ambient) are taken. In HumiPyc this time is programmable and since the highest resolution (24-bit) in the industry is used, very fine pressure changes can be tracked. Therefore, using one minute or longer equilibration time and strict equilibration criterion, like 1 or 0.5 Pa pressure change in the last three readings will certainly increase the overall time of experiment. The number of repetitions can be reduced to 3 or 5 if the user finds that the volume data do not change that much. The pressure equilibrium criterion can also be relaxed. Using for example 2-5 Pa window (zone) for 3 consecutive measurements should be more then enough as and it exceeds ability to resolve 7 Pa stipulated in some standard methods for a high quality pycnometer.

In cases that the elutriation problem is not an issue, the **Proportional Valve Control** parameters in the frame Proportional Valve control can be modified. Instead of using the rather small increments of 25 in PV1 and PV2 rate, much larger numbers like 250, 500, or so can be used. Also, the PV1 and PV2initial numbers (for initial voltage setting) can be increased from the minimum values determined for a given system at particular gas type and tank pressure regulator setting. Please be aware, that other pycnometers use only ON/OFF valves, and elutriation (removing fine powders upon pressure surge) is a problem for such designs.

Recorded Data Structure in the Summary File (*.SUM)

In addition to other files created during a run, the summary file contains data that are recorded for each step declared in the list table after the 10-line header. The header contains the name of the experiment, date of start, name of the template used, and other information about the experiment.

The recorded data are organized into 11 columns:

1. Time[min] – Time at which the data were recorded
2. Pp[kPa] – Pressurization pressure (to which the sample was pressurized)
3. Pd[kPa] – Depressurization pressure (when the path to the reference chamber was opened)
4. Pa[kPa] – Atmospheric pressure
5. TRTD1[C] – Temperature indicated by temperature sensor (RTD1)
6. RH[%] – Relative Humidity indicated by RH probe (if installed)
7. Tprobe[C] – temperature indicated by the RH probe (if installed)
8. Vcell[cc] – Sample cell volume
9. Tag - tag value used
10. AVG Vcell[cc] – Average value of Vcell
11. STD VCell[cc] – Standard deviation of V-cell

In case the report has not been printed or not available, the user can easily extract volume data from this file. In the following example only the last 4 columns are presented. There has been ten repetitive measurements for each Tag. For empty sample chamber the tag value of one was used and for measurements with sample (1” diameter ball) the value of two was selected. The Vcell volumes are recorded in the order as obtained and the AVG Vcell column averages the volumes for a given sequence (the same tag number). The volume of the sample can be easily calculating by subtracting the last averaged volume for tag = 2 from the last averaged volume fro the tag = 1. These values are shown in larger font size, bold and underlined. The last column is the standard deviation calculations and depending on the amount of rejected points, the value may be different. The user can easily recalculate the value from the Vcell column.

Vcell[cc]	Tag	AVG Vcell[cc]	STD VCell[cc]
22.1403	1	22.14034	.000000
22.1331	1	22.13674	.005094
22.1386	1	22.13738	.003767
22.1401	1	22.13807	.003373
22.1372	1	22.13794	.001007
22.1389	1	22.13825	.000899
22.1418	1	22.13873	.001197
22.1392	1	22.13882	.001057
22.1407	1	22.13907	.001131
22.1387	1	**22.13903**	.001040
13.5618	2	13.56180	.000000
13.5627	2	13.56224	.000621
13.5595	2	13.56134	.001622
13.5589	2	13.56072	.001804
13.5610	2	13.56139	.000574
13.5611	2	13.56128	.000448
13.5601	2	13.56098	.000698
13.5590	2	13.56069	.000887
13.5595	2	13.56002	.000854
13.5580	2	**13.55986**	.000890