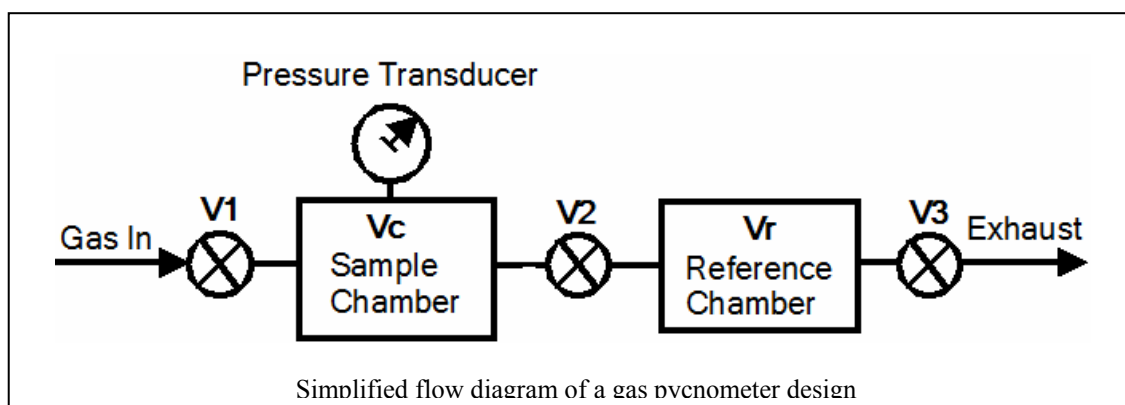# Gas (Helium) Pycnometer Theory and Practice
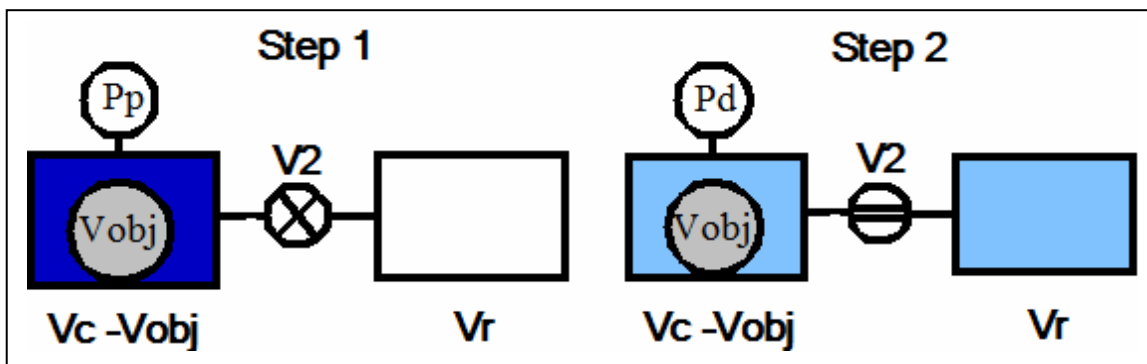
By Jan Malczyk

Gas (helium) pycnometer is a laboratory or field instrument that measures volume (density) of materials using gas displacement method by employing the ideal gas law, **pV = nRT**. The basic operation relies on having a user accessible sample chamber, and an added volume (reference chamber), often more then one. There are usually at least three valves used: the first (**V1**) to provide gas to the sample chamber, the second (**V2**) to allow expansion of the gas from sample to reference chamber, and the third (**V3**) to release the gas to atmosphere to establish atmospheric pressure **Pa** value.

Simplified flow diagram of a gas pycnometer design

The typical pycnometer operation consists of three steps:

1. Opening the V1 valve, pressurization of sample chamber to the pressure **Pp**, and closing V1 valve.
2. Expansion of the gas to the reference chamber by opening valve V2 (V3 and V1 stay closed). After the depressurization, the same pressure **Pd** will be in both chambers, Vc and Vr.
3. Release of gas to the atmosphere by opening valves V3 and V2. The transducer will read the atmospheric pressure, **Pa**.

The underlying theory will be easier to understand by placing an object into the sample chamber and writing the mass balance equations, as the amount of gas in the first step must be equal to the amount of gas in step 2, obviously assuming no additional sources or leaks.

$$\frac{Pp(Vc - Vobj)}{RT} + \frac{PaVr}{RT} = \frac{Pd(Vc - Vobj + Vr)}{RT} \qquad (1)$$

The equation 1 states, that the amount of gas (number of moles) in the reduced sample chamber volume by the object volume at the pressure Pp and the amount of gas at atmospheric pressure in the Vr volume must be equal to the amount of gas in both chambers after expansion to the pressure Pd.

Assuming further constancy of temperature during the experiment, the sought Vobj volume, after trivial manipulations, can be calculated as follows:

$$Vobj = Vc - \frac{Vr(Pd - Pa)}{Pp - Pd} \qquad (2)$$

The equation (2) is the working equation employed by the gas expansion pycnometer. When using an absolute pressure transducer, the Pa pressure is around the standard atmospheric pressure value of 101.325 kPa. When a pycnometer uses a gauge type pressure transducer (referenced to zero at atmospheric pressure), then the Pa value is set to zero. It is important to remember, that the pressure values from absolute pressure transducers are higher then the pressure values of gauge pressure transducers or pressure gauges by 101.325 kPa.

In order to obtain the Vobj from eq. 2, the Vc and Vr must be known and need to be determined first. Since there are two unknowns, two independent experiments are needed. Typically, one experiment is conducted with empty Vc. Since the Vobj = 0 in this case, the above equation yields relationship of Vc vs Vr:

$$Vc = Vr \frac{P_1 d - P_1 a}{P_1 p - P_1 d} \qquad (3)$$

In the second experiment, an object of known volume, typically a calibrated sphere of volume **Vsphere**, is used. The equation (2) for the second experiment becomes:

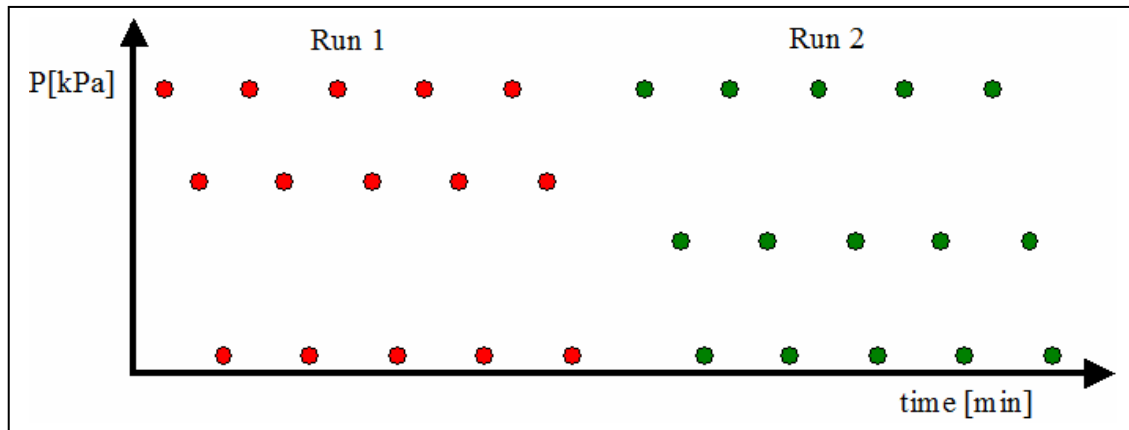$$Vsphere = Vc - Vr \frac{P_2 d - P_2 a}{P_2 p - P_2 d} \qquad (4)$$

Solving the system of two equations (3) and (4) allows calculation of Vr:

$$Vr = \frac{Vsphere}{\dfrac{P_1 d - P_1 a}{P_1 p - P_1 d} - \dfrac{P_2 d - P_2 a}{P_2 p - P_2 d}} \qquad (5)$$

Substituting the found Vr value into equation (3) yields the Vc value. Plugging the Vc and Vr values into the working equation (2) allows calculation of the sought object volume Vobj.

Knowing the object mass, m, its density, d, can be easily calculated using the density definition d = m/Vobj [mass/volume].

In case you think that you have understood this simple theory, here is an easy problem to solve. The diagram below shows two hypothetical runs, where each consists of several repetitions of the basic cycles (pressurization, expansion, and releasing gas to atmosphere). The measured pressure values are presented as red and green circles. Can you tell (with explanation) which run is done with the sample and which is without the sample in the sample chamber, assuming everything else remains the same?

Practical considerations

The obtained volume Vr is the primary result of the calibration procedure. Typically the reference chamber is most often not accessible to the user or at least not changed during experiment and in this sense it can be considered as an invariant. However, that does not mean that a calibration done one time is good forever. The Vr volume is not directly measured like a ball diameter with a micrometer, but is measured indirectly by gas and the whole electronics is involved. Due to many factors involved, even consecutive calibrations of Vr will produce close but not exactly the same numbers. Calibration of Vr should be carried out when experimental conditions change, like a change of pressurization pressure, change of gas, ambient temperature, hardware, etc.. It does not mean though that it has to be carried out in every sample volume measurement. The periodic calibration results should be recorded and kept on file for reference, as unusually large discrepancies would indicate a developing problem. It is often a good idea to carry out a "dummy" experiment just to exercise the valves and transducer before actual calibration of Vr. When an instrument has not been used for a while and especially if equipped with a capacitive type pressure transducer, it can take more then just one "dummy" experiment needed to bring the functionality back to normal.

Although the Vc volume is also obtained during calibration procedure, it is not of much of value, as depending on what is inserted to the Vc, its volume changes. Any experiment of sample volume measurement involves some additional hardware, like a sample holder and perhaps a volume reducing adapter. Then the Vc volume with sample holder and any volume of reducing adapters placed there has to be determined anyway (often referred to as Vc without sample). Once the sample is added and the Vc measured again, the difference between the both Vc volumes yields the sample volume. Carrying out experiment with all the hardware included in the Vc but without sample and next one with the sample has the benefit of canceling out all current small errors (at least to a large extend). The sample can be nothing (to see the baseline noise), a calibration ball (to recheck), or the actual material under study.

The mentioned above three steps of operation form a basic cycle. Practically, such cycles are often repeated several times to obtain statistics. The standard deviation from several cycles is a measure of repeatability and it is sometimes wrongly used for accuracy, as it often looks great on paper. To determine actual measure of accuracy, use one of available metal balls of precisely known volume and allow some time to equilibrate thermally with the pycnometer chamber.

A complete (full) sample volume measurement by pycnometer consists of two separate runs (experiments):

1. Calibration procedure, where several cycles are carried out with and without the calibration ball.
2. Actual sample volume measurements, where several cycles are carried out with and without the sample.

If regulatory stipulations or internal procedures do not require submission of full experimental results, and to reduce the overall analysis time, the calibration can be done one time and many samples measurements can utilize the same calibration results. Therefore, the analysis time can be reduced by half.

 If the same sample holder is used and everything else remains the same, then the experiment time can be further reduced by skipping the determination of the Vc value without the sample each time, if it was previously determined and the same value is being used. Once the Vc value is entered into the software and such option is selected, only the consecutive sample volumes can be measured, and it takes about 25% of the full experiment time for each determination.

Additionally, if the same Pa value can be used instead of tracking Pa changes during experiment, then even shorter experiment time would result. If the volumes Vr and Vc without sample are known, the shortest experiment is just the one cycle. However it is rather used just for quick test. Although minimizing the experiment time is understandable, using long equilibration times can provide additional information about samples.

To operate a pycnometer is quite simple as often everything is automated, ready experiment definition templates are provided, and just a few mouse clicks are needed to run an experiment. To comprehend the results and troubleshoot problems requires a basic understanding of the technique.   There are many assumptions that one should be aware of. In addition to the ideal gas behavior and perfect mechanical integrity of the instrument (no leaks, linearity of transducer), it is assumed that the sample is not easily deforming, the gas absorbed during pressurization is given off during expansion, no net chemical reaction with the gas used, no sample removal (elutriating) during pressure changes. Pressure cycles of dry gas remove moisture from samples and that can affect the sample state. Real samples rarely fulfill all the assumptions, so to alleviate some effects, selection of different experimental conditions need to be considered, e.g. different setting of pressurization pressure.

In early-automated pycnometers using keypads and simple displays, most parameters were of fixed values, but additional capabilities are provided when newer generations of pycnometers are controlled using PC capabilities. One of them is programmable equilibration time and the process of equilibration can be graphically presented. Comparing the equilibration time profiles without sample and with the sample and varying the equilibration time to see if that can substantially affect the volume results, can be very useful in developing the best strategy for particular type of samples. When comparing the volume (density) results to literature data, be sure to review the experimental conditions if they are provided. Using different gases, pressurization pressures, equilibration times, sample amount, preparation, and its history, etc., may affect the results.

Gas pycnometers can provide good results if they are used in their optimal range of operation. Typically the pressurization pressure used is somewhere between 200-240 kPa absolute pressure (100-120 kPa gage pressure). This region is a compromise between using high pressures and ability of low power solenoid valves to withstand it without excessive leakages. For many samples, like easily deformable foams, the actual pressure used is much lower, which increases errors. Typically, there is always some error of volume generated for a given hardware configuration, and the larger the sample amount is used, the lower the relative error will be. Certain pycnometers are designed specifically to handle low sample amounts. Reduction of dead volume in the sample chamber can help up to a certain point. If inaccessible dead volume of the internal construction is high, then in addition to other design factors, the measured volume error will be high as well. The best way to determine the amount of such error is to use several different sizes of small diameter balls, like 1, 1.5, 2, 3, 4 mm diameter balls and see at what point a volume of such ball can be determined reasonably well. Repeating such experimentation in later time can give an idea as to what the actual volume errors are in a given setup, not the highly optimistic paper specifications obtained at optimal conditions.

Keep in mind that a gas pycnometer measures only volume of samples and it should be calibrated for volume only. Be aware of efforts by some creative sellers who try selling unnecessary hardware or "standard samples" that are calibrated for density. Density involves measurement of volume (e.g. by pycnometer) and mass (by balance). The overall error of density calculation is a combination of errors

from volume measurement and from mass measurement, and two completely independent pieces of equipment are involved. There is absolutely no need for any samples of "standard density".

In addition to measurements of volume of various materials, like powders or irregular objects, there can be some additional information obtained by subsequent sample processing. For example, a foam sample can be cut into smaller pieces to expose additional surface area of cut closed cell and re-measured again. This is used in standard methods for foam characterization to obtain correction for cutting cells when preparing the sample. Crushing larger pieces of solid state material containing closed pores and re-measuring again allows evaluation of pores volumes that are initially not accessible to the gas used. Knowing the powder sample density, the sample can be placed into a suitable container, pressed with a plunger, (and even vibrated to achieve the best packing), and the porosity of the formed bed can be obtained. There can be many chemical or thermal sample treatment techniques involved and the results of subsequent volume measurements by pycnometer that can yield additional information.

There are many samples that have characteristics between solids and liquids, e.g. glues, pastes, slurries, etc. Density meters that are designed for liquids only cannot measure such substances and it can be too difficult to fill specialized glassware pycnometers designed for volumetric determination of density. Using gas pycnometers seems to be the last resort, but it can be also problematic considering some of the assumptions listed before. The practical problem with cleaning can be easily solved by using disposable plastic bags that fit into the special design sample holders with covers containing metal filters to reduce pressure changes and practically eliminate sample escape.

From the instrumentation design point of view, a gas pycnometer can be considered as a simple volumetric analyzer. In practice it is a dedicated one to only volume measurements of samples. It does not have to be that way as additional analytical capabilities can be achieved with usage of auxiliary hardware, assuming that some design features allow for that. Using open architecture design of hardware and software, many other analytical measurements can be made with little expense and some ingenuity, as the hardware and software resources are available to the user. A gas pycnometer can be easily used as a bubble point tester or permeation analyzer for studying gas transport rates through membranes (plastic films) or gas sorption/evolution from geological samples. Using dry gas cycles and vacuum can provide an effective treatment of sample that can be prepared for other analysis.

One of the attractive applications is usage of pycnometers for studying of gas flow resistance through packed beds, essentially as a gas (air) permeameter. Connecting an external cell holding the packed bed to the pycnometer, and using bubble meter and stopwatch, flow rates through packed beds of various materials can be obtained. Having the data of density, porosity, packed bed dimensions, and flow rates versus pressure settings used, the specific surface area by the gas permeability method can be calculated. Determining cement fineness that way is an alternative to ASTM C204 method and no Blaine or similar apparatus is necessary.

While additional capabilities and specialized pycnometers are continuously being developed, more detailed information can be found in applications notes and materials presented in our websites.