InstruQuest, Inc.
January, 2020

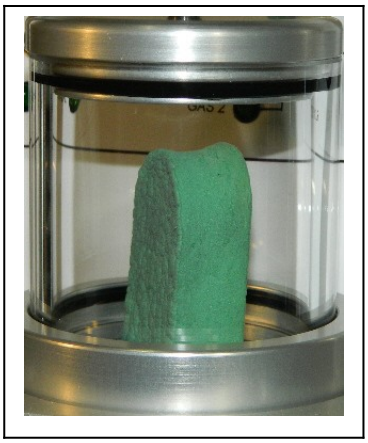
Volume changes of compressible materials versus pressure intervals and foam characterization by a density profile instead of a single value using pV/T Master, a versatile volumetric analyzer

By Jan Malczyk

Since compressible (cellular) materials do not fulfill some assumptions stipulated in gas (helium) pycnometry, their density cannot be described by a single number but rather by a range of values. This technical note presents a new instrumental and methodological approach for studying materials that can change their volume versus pressure, like the easily compressible foams with closed cells.

Density of solid state samples is most often determined using gas (helium) pycnometers. Out of several types, the pycnometers employing the gas expansion method are commonly used as they provide the best repeatability, full automation, ease of use, etc. In their basic functionality, the sample is inserted to the sample chamber of known volume, pressurized to some pressure **Pp**, and the gas is expanded to previously calibrated reference volume yielding the same pressure **Pd** in both chambers after depressurization. There are several tacit assumptions made about the sample behavior, which are rarely fulfilled by many materials. Therefore, the density value obtained by gas (helium) pycnometer is not some absolute value but dependent on particular experimental conditions, like pressure values, gas type, equilibration time, temperature, etc.

One of the assumptions made is lack of sample distortion during experiment. While many samples may exhibit only negligible compressibility versus pressure, other samples like foams with large number of complex closed-cell structure are notable exceptions. To illustrate visually compression and expansion of such materials, a special sample chamber using a borosilicate glass tube (pressure rated) was constructed. Presented below are three photos of the same sample but at different pressure.



P = 220 kPa

P = 101 kPa

P = 7 kPa

The photo on the left hand side shows the foam sample compressed when the chamber was pressurized to 220 kPa (absolute pressure). The photo in the center shows the same sample at atmospheric pressure, about

101 kPa. The photo on the right hand side shows the foam sample expanded at vacuum conditions, at about 7kPa.

Considering such dramatic change in volume, and assuming constancy of mass, the density of such sample will strongly depend on the experimental conditions used. Although standard test methods stipulate using small overpressures, like 20 kPa over atmospheric pressures to reduce the compressibility problem, such materials still get distorted. Using small over-pressures has adverse effect on accuracy of measurements as such conditions are out of optimal pressure region and performance of gas pycnometers. Generally much less accurate results are obtained then for incompressible materials at much higher pressurization pressures.

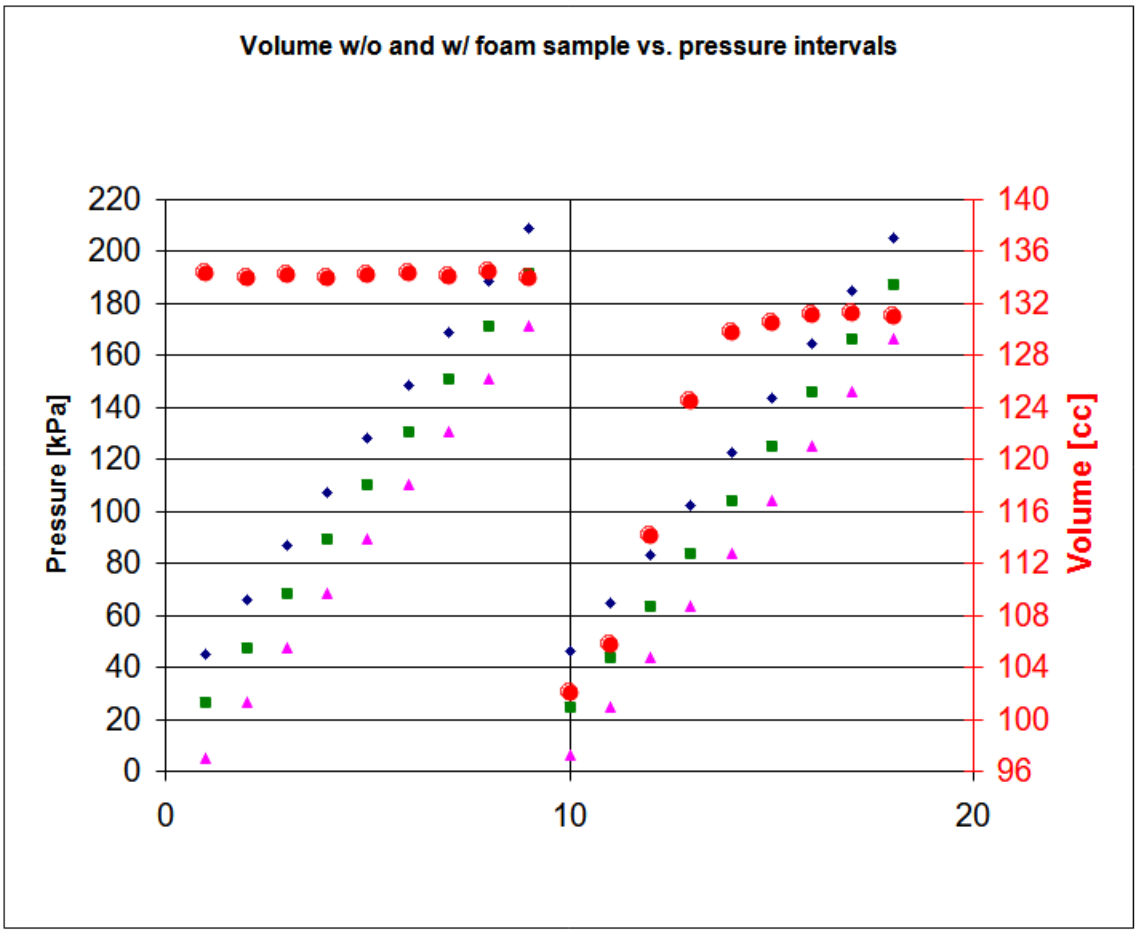
Commonly available gas (helium) pycnometers use atmospheric pressure value as the universal reference. The volume (density) values are therefore valid for the pressure intervals, from the selected pressurization pressure to the atmospheric pressure. If a different reference pressure value is selected, the volume (density) can be different if the sample is compressible. Generally, along with the density values provided in literature, the experimental conditions at which they were obtained should also be specified.

To study compressibility of materials, a more sophisticated design of a gas pycnometer and software was undertaken. The availability of miniature diaphragm vacuum pumps that can be embedded into the instrument and easily controlled from software allows for generating sufficiently low vacuum levels (about 7 kPa). Another major design improvement was addition of high performance mass flow controller (MFC) instead of relying on metering valves or proportional valves. This allows for much more precise pressure buildup values, from the vacuum level to the maximum available pressures. Incorporation of MFC resulted also in achieving new capabilities. The sample chamber, or any other volume connected to the instrument, can be precisely pressurized to any required level in a linear way. The linear pressure buildup versus time allows for introduction of a dynamic technique of sample volume measurements, namely time-domain pycnometry. Using auxiliary hardware, additional analytical techniques, like liquid expulsion porometry, permeability of gases through membranes, surface area analyzers, can be materialized.

The classical automatic gas expansion pycnometer can be considered as a static method in a sense that the gas after reaching pressurization and depressurization states gets equilibrated for some time according to applied criteria of pressure stability. It also features a fixed reference pressure level, which is the atmospheric pressure Pa. In most simple pycnometers the Pa is not monitored during experiment and only read out initially to create zero value for gauge type pressure transducers. When absolute pressure transducers are used, the additional range from vacuum to atmospheric pressure becomes available for volume (density) measurements.

Let us assume that instead of using the single Pa reference state, the reference state can be extended to vacuum and to higher pressures well above atmospheric. Having the reference state anywhere in the pycnometer pressure transducer range, and being able to build pressures just above and below it with subsequent expansion to the previously achieved reference level, the sample volume can be theoretically determined in any pressure interval. For incompressible (ideal) samples, like metal balls, this should be ideally a single number. For compressible samples, which volumes can change in a complex way from vacuum to high pressures, the density cannot be described by a single number, but rather by a density profile with range of values often quite differing from the literature cited numbers.

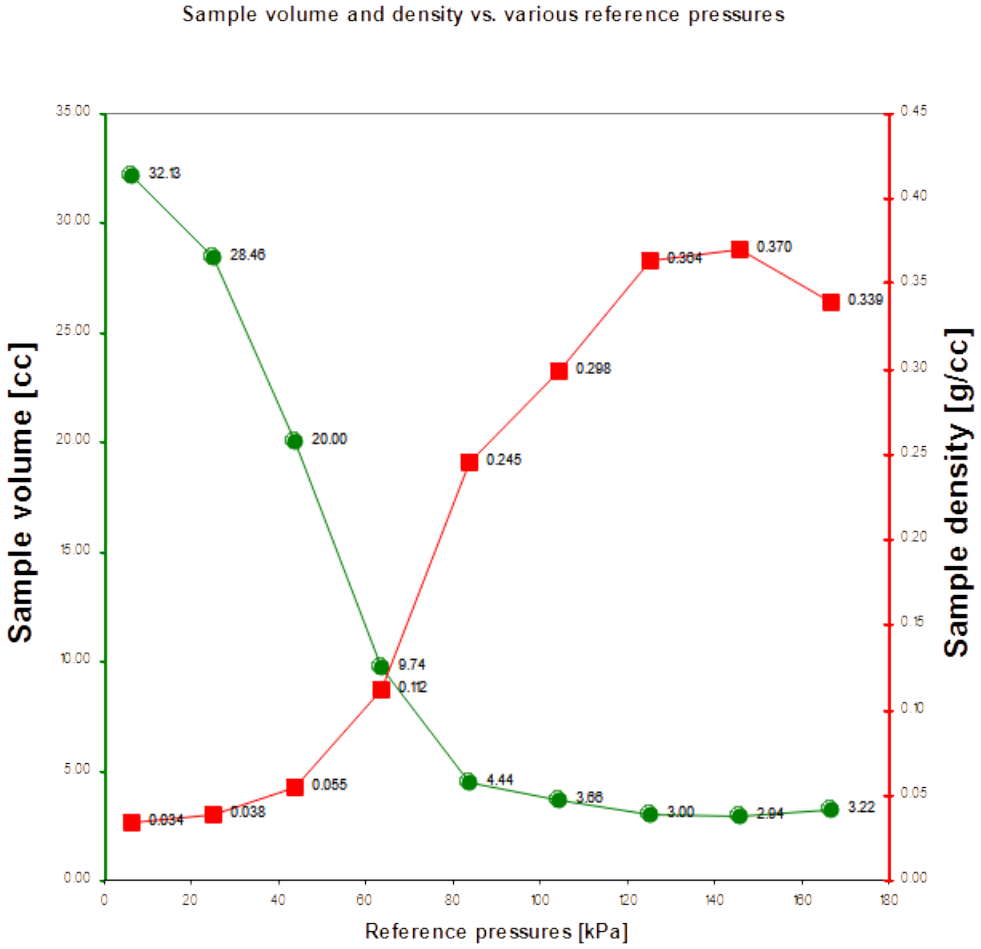
Practically, the selected interval of pressures should not be of very narrow range as the experimental results will not be as accurate. Using let say 20 or 40 kPa intervals, from vacuum to high pressures, the trend of volume (density) changes can be obtained. The software allows for declaring a set of values of Pp above the previously achieved Pd values, which act as reference pressure for the next measurement. The same foam sample was used for measurements of its volume in the 40 kPa pressure intervals from vacuum to just over 200 kPa and the results are presented in the graph below.



The graph above presents experimental results of measuring empty sample chamber from vacuum to just over 200 kPa using 40 kPa increases over previous Pd and the same conditions were used for the shown foam sample. The large red color circles represent the sample chamber volume and the values are referenced on the secondary y-axis on the right hand side. The first nine data for empty sample chamber are more or less having the same value of the chamber volume (with an experimental scatter). The next nine measurements are for the sample chamber with the foam sample in it. It is quite an interesting result as the volume changes are far more dramatic in the vacuum region then well above the atmospheric pressure.

The series of blue color diamonds represent pressure values for the pressurization pressure (40 kPa above the reference chamber pressures (violet color triangles) in this example). The series of green squares represents the values of depressurization pressures when both, the sample and reference chambers are connected. After equilibration, these depressurization pressure values become the new references for the next cycle. The sample volumes are thus determined in the partially overlapping pressure intervals. Each interval can be visualized as the vertical distance between the blue diamond and violet triangle. The pressure values are referenced on the primary y-axis.

The sample volume, which is the difference between the volume of empty sample chamber and sample chamber with the sample, changes from about 32 cc at lowest vacuum range (6.27 to 46.04) kPa to about 3.2 cc at pressure range (166.61 to 205.26) kPa. The density, defined as mass over volume, will exhibit lowest value using the 32 cc and the highest for the 3.2 cc sample volume. The mass of the foam sample used for the experimentation is 1.0905 gram. The graph below provides summary results for the sample volume and density changes as the pressure interval gets sequentially shifted to higher pressures.



Both, the sample volume and density show rather a complex trend and about tenfold change of values in the range of pressures used. From the visual observation of compression/expansion it is easy to conclude that the sample shape undergoes anisotropic changes and rather not so much visually change in size then the volume changes determined by gas pycnometer. The internal closed cells, perhaps of various size and complex structure, seem to be responsible for such large volume changes. Since most of the changes occur near and below the atmospheric pressure, this unique volumetric analyzer allows for obtaining such additional experimental data where other pycnometers are not able to. The experimental results of density determined in specific pressure intervals can serve as a "fingerprint" for the specific material and it provides more characterization information then a single value of density that is obtained between the atmospheric pressure and some arbitrary pressure value. The obtained density values per given pressure intervals plotted versus pressure can be called differential density profile or reference dependent density profile. Although results of compressing samples above atmospheric pressure using a series of increasing pressures can be found in literature, it is believed that the presented above approach is unique and offers a more meaningful characterization of cellular materials then the ASTM 6226 or the ISO 4590 standard methods. These methods may yield similar values for different materials but the materials can exhibit much different characteristics at other conditions.

9091 SW 21st Street, Ste. A, Boca Raton, FL 33428, USA · Ph: (561) 271-1958
Websites: www.instruquest.com, www.thermopycnometer.com
E-mail: info@instruquest.com