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Technical Note
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Isothermal and non-isothermal approach to true volume measurements using the gas (helium) micro thermo pycnometer

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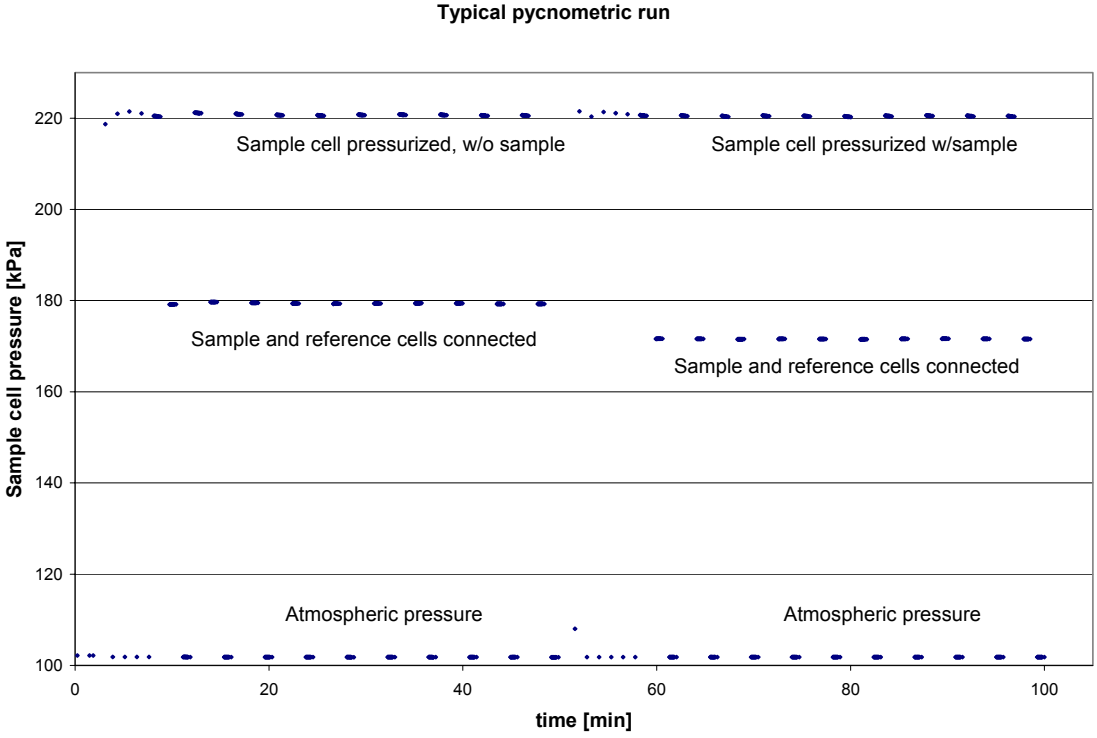
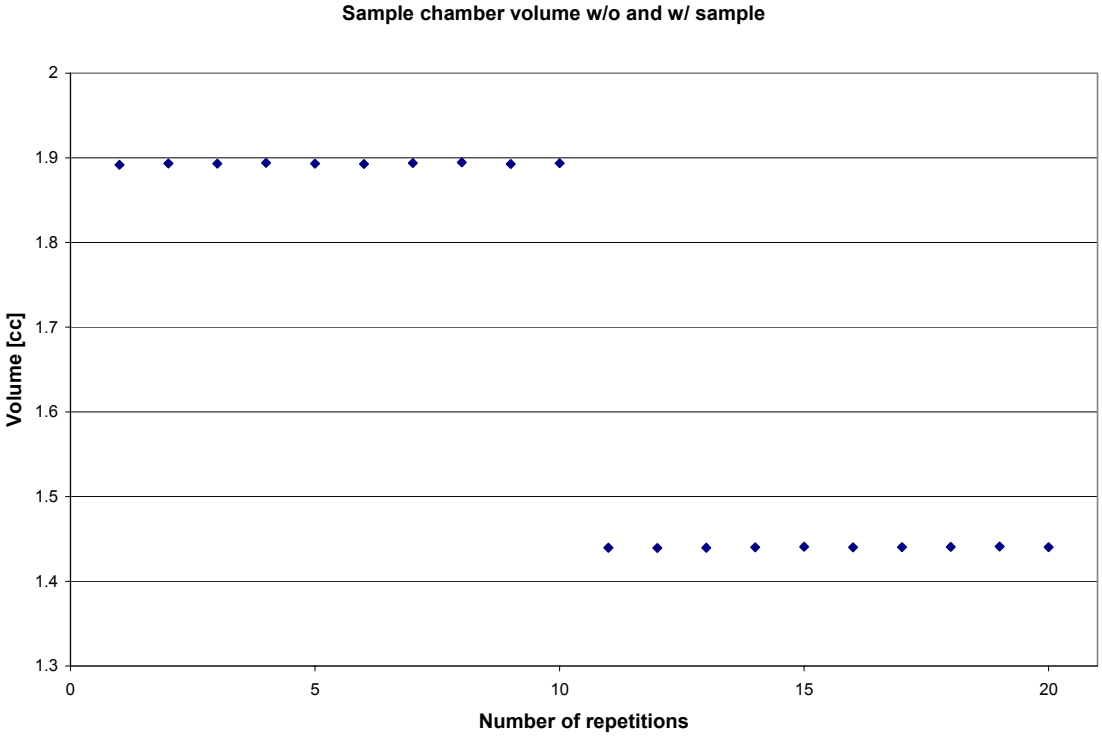
Gas (helium) pycnometers employing gas displacement principle are commonly used nowadays to measure true volume (density) of solid-state samples (powders, foams, etc). In addition to applicability of ideal gas law and many other assumptions, the constancy of temperature is assumed during the experiment. Although there are some models with temperature control, mainly to improve the performance, the basic premise is the isothermal operation. Although the principle of operation is very simple, technologically things are a bit more complex as a gas pycnometer requires some optimal conditions to provide the most exacting results. There are designs with more then a single reference chamber to measure large range of sample volumes or more specific design for a narrow volume range. To measure small amount of samples, usually well below 1 cc, the term micropycnometer was coined for such specialized gas pycnometer.

Automated or computer controlled models are far more accurate as many factors introduced by operator in manual only models are removed. The advantage of repeatable operation and recording of data for further processing are invaluable for everyday operation. For example, the user can view the experiment progress and spot any problem as various graphs with measured or calculated quantities can be presented on the computer screen in real time.



The above graph shows a typical isothermal run after the pycnometer has been calibrated. Initially, after placing the empty sample holder and closing the sample chamber, some preparatory steps like five pressure cycles (pressurization to some high value and depressurization to atmospheric pressure) take place to remove air/moisture from the sample chamber. Next, the actual process of measurement begins and in this

example, there are ten consecutive repetitions of pressurization, depressurization, and reaching the atmospheric pressure. Actually one such cycle is enough but usually several of them are used to see the performance and obtain a reasonable statistics. After the determination of the sample chamber volume without the sample, the sample chamber is opened, the sample is placed in the sample holder, and the chamber is closed. Usually the same experimental steps with the sample loaded are repeated. After the five pressure cycles, the ten repetition of pressurization of the sample chamber, depressurization to the reference chamber that was maintained at atmospheric pressure, and measuring the atmospheric pressure are carried out. After completion of the run, the results of the sample volume and other calculations are obtained.



The above graph presents the calculated sample chamber volume after each measurement cycle. The difference between the two sets of repetitions is the sample volume. Knowing the sample mass, the true density is easily calculated and presented in the report for such experiment.

If the same sample holder is used and no other hardware or experimental conditions changes from experiment to experiment, then the same sample chamber volume can be used for successive samples and the first half of experiment can be omitted. That obviously reduces the experiment time. The measurement of the atmospheric pressure after each cycle can also be eliminated to save time as only one-time measurement at the beginning of experiment can be done. Using let say 20 seconds or so of equilibration time instead of the 60 seconds used in this experiment, it can further reduce the time of experiment.

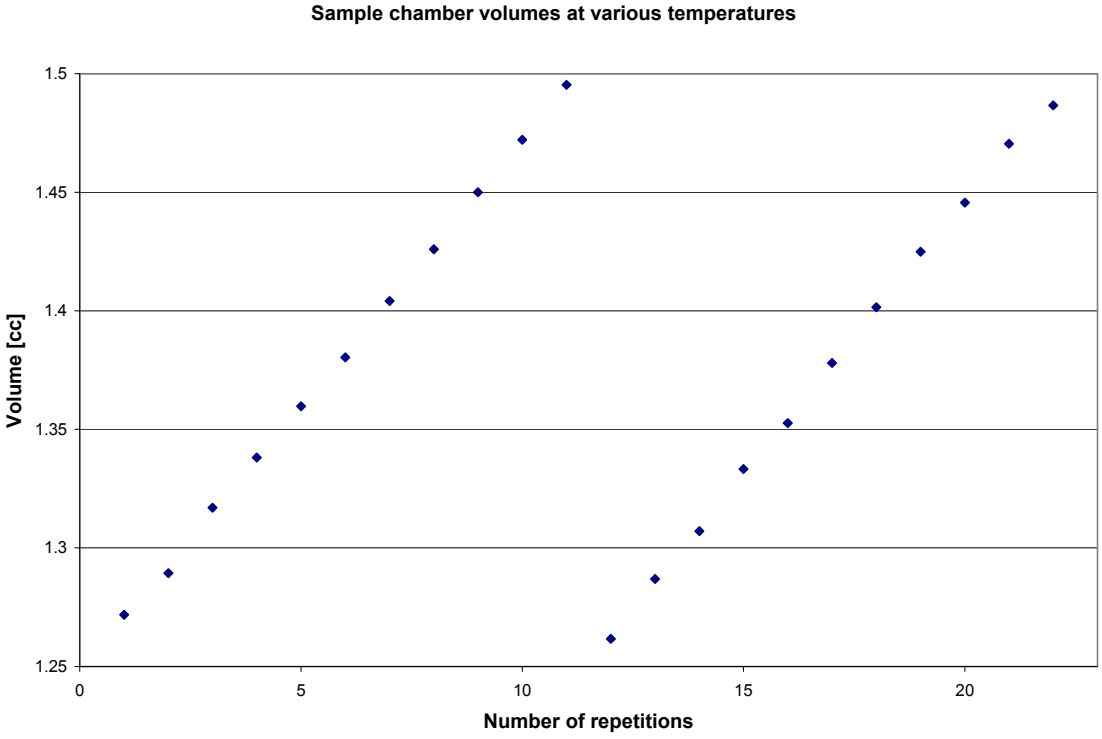
The density of a various materials obtained by using a gas (helium) pycnometer is frequently stated in data sheets, often without specifying the experimental conditions used. It is tacitly assumed that results were obtained at room temperature. Since temperature in many industrial laboratories can very, especially during winter-summer seasons, knowledge of influence of temperature and other factors, like type of gas or pressure used, are important. In case of compressible materials, like foams, the length of equilibration time is also relevant as the amount of sample distortion is time dependent.

A pycnometer that can carry out measurements of sample volumes in a wide temperature range seems to be a natural extension of isothermal pycnometers for characterization of solid-state samples. The pycnometer operating in a large temperature range can be called a thermo pycnometer or thermopycnometer. Since a

dedicated pycnometer for measuring small amount of sample is called a micro pycnometer or micropycnometer, the term micro thermo pycnometer refers to a pycnometer dedicated to measurements of samples volumes in a relatively wide-temperature range. The name μThermoPyc™ was given to such a new and unique pycnometer developed at InstruQuest Inc. for R&D purposes. It is able to measure true volumes (density) of samples in the temperature range from 0 to 150 ˚C and up to 2 cc of sample volume in standard configuration. One of the main advantages of this design is a very low dead volume (well under 1 cc) and therefore, high sensitivity of measurements. Additionally, a sharp thermal transition of minimal volume between the sample chamber temperature and the reference chamber temperature practically eliminates the problem with dead zone temperature profile that is encountered in many other volumetric analyzers. Surface area analyzers have much larger size of dead-volume of sample chamber and larger size of dosing manifold (reference chamber) and the upper pressure limit is usually the atmospheric pressure.

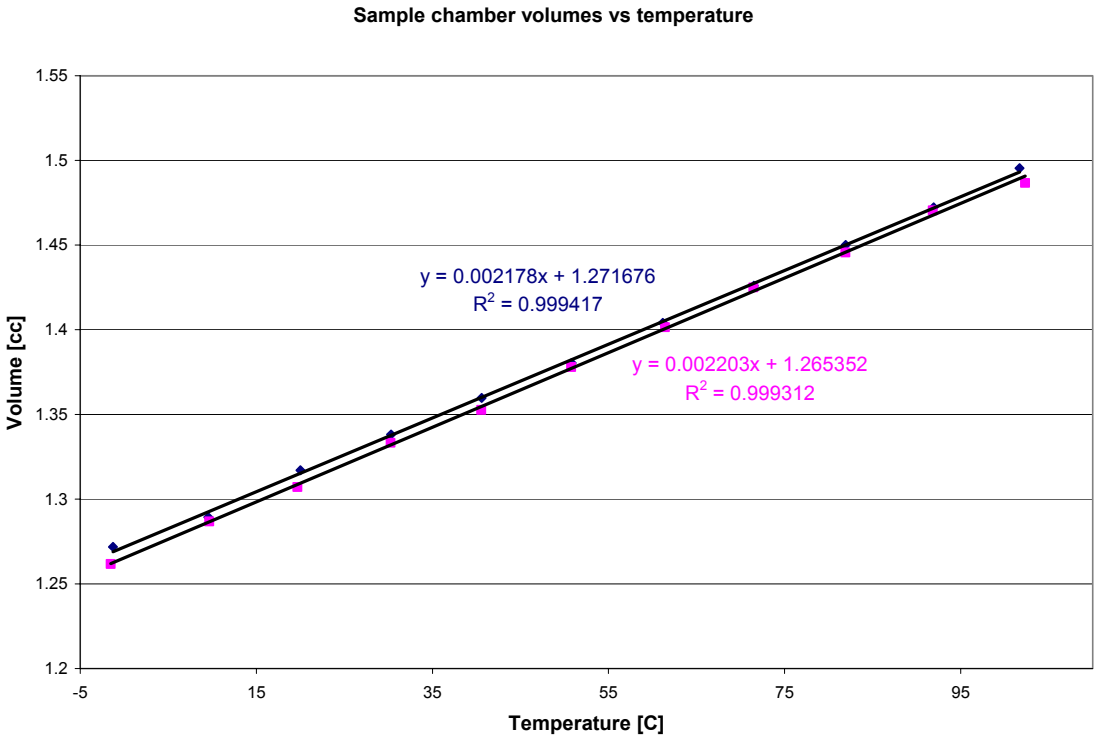
Using the μThermoPyc™, the non-isothermal measurements of the sample volume can be carried out in few different ways. In the basic mode, the sample chamber temperature can be set to any user selected value and the measurements without and with the sample can be carried our out, similar to the isothermal measurements, where the temperatures of sample and reference chambers are matched. Carrying out such measurements at many different temperatures, the density profile versus temperature can be obtained. This approach will become problematic when the high temperature values become a problem for the sample chamber handling operation (opening, sample loading, closure). Although the software allows for bringing the temperature to a safe value, it can consume too much time, especially if multiple samples are to be measured.

Another mode employs carrying out measurements at a series of temperatures for the empty sample chamber, bringing the temperature down to a safe value, and carrying out measurements for the sample at possibly the same set of temperatures.



The above graph presents results of single measurement cycles in the temperature range from 0 to 100 ˚C. The first set shows results for empty sample chamber (no sample) and the second set shows results when a 2mm metal ball was used as a sample. It is quite different outcome from the previous chart where the data were arranged in horizontal lines for the isothermal measurements. If multiple repetitions of the measurements cycles at the same temperature were added, then additional results would be clustered

around the above dots corresponding to the temperature. Instead of spacing measurements at equal temperature intervals, single measurements at a region of interest can be made denser. Since it is difficult to predict what the strategy will be undertaken by the user and what other special operations will be carried out, the recorded data for the non-isothermal scans need to processed later using spreadsheets. The obtained volume results should to be presented versus temperature to see if there is any sample behavior that could be worth to investigate further. The graph below presents the same results as in the previous graph but this time the sample chamber volumes are depicted versus temperature.



The upper straight line corresponds to volume results without sample and the lower line corresponds to volume results for the 2 mm ball as a sample. Obviously, the metal ball is not expected to show any phase changes or decomposition products, so the straight line is obtained. The difference between the lines at a given temperature provides measure of the sample volume. In a more realistic case of a sample that exhibit temperature driven phase changes and associated with them volume changes or a sample with onset of decomposition in the temperature range, the lower line would be rather a more complex curve.

The third mode of non-isothermal measurements can be implemented by using continuous temperature profiles. The software procedure devised for this purpose has four linear segments, each with start and stop temperatures, rate value, dwell time after the end of the segment, and the choice of bringing the sample chamber to atmospheric pressure before the segment starts. Not all segments need to be used, but it was envisioned, that getting to the region of interest can be achieved at higher rate while passing through the region can be done at much lower rate to achieve as good equilibration of the sample temperature with the sample chamber as possible. Since the linear profile in the temperature ramp is expected to generate linear response in the pressure values when the sample chamber is closed, any non-linearity in the pressure line versus temperature can determine the temperature or temperature range at which the sample exhibit some instability. Since the sample chamber volume is known and the sample volume can be measured, the non-linearity of pressure changes can serve to quantitatively describe the sample behavior. The linear temperature ramping can be repeated as many times as needed and combined with other procedures, like establishing vacuum or a selected gas atmosphere in the sample chamber. Considering the unique software and hardware design, the µThermoPyc™ can be used for extensive sample characterization beyond the typical volume (density) measurements. Combined with other custom features, it is inexpensive and effective tool for researchers involved in development of new materials and their characterization.